Water Research 95 (2016) 280–288

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Copper deficiency can limit nitrification in biological rapid sand filters for drinking water production

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ARTICLE INFO

Article history:
Received 12 November 2015
Received in revised form
8 March 2016
Accepted 9 March 2016
Available online 14 March 2016

Keywords:
Ammonium
Biological filtration
Copper
Drinking water
Nitrification
Nutrient limitations

ABSTRACT

Incomplete nitrification in biological filters during drinking water treatment is problematic, as it compromises drinking water quality. Nitrification problems can be caused by a lack of nutrients for the nitrifying microorganisms. Since copper is an important element in one of the essential enzymes in nitrification, we investigated the effect of copper dosing on nitrification in different biological rapid sand filters treating groundwater. A lab-scale column assay with filter material from a water works demonstrated that addition of a trace metal mixture, including copper, increased ammonium removal compared to a control without addition. Subsequently, another water works was investigated in full-scale, where copper influent concentrations were below 0.05 μg Cu L^{-1} and nitrification was incomplete. Copper dosing of less than 5 μg Cu L^{-1} to a full-scale filter stimulated ammonium removal within one day, and doubled the filter's removal from 0.22 to 0.46 g NH_4-N m^{-3} filter material h^{-1} within 20 days. The location of ammonium and nitrite oxidation shifted upwards in the filter, with an almost 14-fold increase in ammonium removal rate in the filter's top 10 cm, within 57 days of dosing. To study the persistence of the stimulation, copper was dosed to another filter at the water works for 42 days. After dosing was stopped, nitrification remained complete for at least 238 days. Filter effluent concentrations of up to 1.3 μg Cu L^{-1} confirmed that copper fully penetrated the filters, and determination of copper content on filter media revealed a buildup of copper during dosing. The amount of copper stored on filter material gradually decreased after dosing stopped; however at a slower rate than it accumulated. Continuous detection of copper in the filter effluent confirmed a release of copper to the bulk phase. Overall, copper dosing to poorly performing biological rapid sand filters increased ammonium removal rates significantly, achieving effluent concentrations of below 0.01 mg NH_4-N L^{-1}, and had a long-term effect on nitrification performance.

1. Introduction

During treatment of groundwater for drinking water production, ammonium is commonly removed through nitrification in biological rapid sand filters. Nitrification is a two-step process: ammonia oxidizing archaea (Martens-Habbena and Stahl, 2011) and bacteria oxidize ammonia to nitrite, which is further oxidized to nitrate by nitrite oxidizing bacteria (Prosser, 1989). The presence of nitrifying organisms in biological groundwater filters is well established (de Vet et al., 2011; Gülay et al., 2014; Lee et al., 2014).

Even though biological filters are commonly used to remove ammonium, nitrification is sometimes incomplete (Lee et al., 2014), leaving ammonium residues in the finished water. This is problematic for the drinking water quality, since incomplete nitrification can lead to biological aftergrowth in non-disinfected distribution systems (Rittmann et al., 2012), which can involve oxygen depletion, taste and odor problems, material corrosion, and accumulation of the toxic intermediate nitrite (Lytle et al., 2007). In chloraminated distribution systems, nitrification may decrease the disinfectant residual, thereby increasing bacterial regrowth potential and the risk of violating disinfectant residual standards (Zhang et al., 2009). In systems without disinfection during drinking water distribution, biologically stable drinking water is achieved by maintaining low nutrient levels in the finished water. For

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http://dx.doi.org/10.1016/j.watres.2016.03.025
0043-1354/

example, the EU drinking water directive specifies a guideline for ammonium of 0.5 mg NH_4 L^{-1}. The EU member states are allowed to establish stricter values; as for instance Denmark, where water works effluent guidelines for ammonium and nitrite are 0.05 mg NH_4 L^{-1} (0.039 mg NH_4-N L^{-1}) and 0.01 mg NO_2 L^{-1} (0.003 mg NO_2-N L^{-1}), respectively (Miljøministeriet, 2014).

To achieve low effluent concentrations of ammonium and nitrite, nitrifying microorganisms need an adequate amount of nutrients for growth and activity, to be available during water treatment in biological filters. Otherwise, nitrification can be incomplete. For example lack of phosphorus can limit nitrification in groundwater treatment (de Vet et al., 2012). Besides phosphorus, nitrifiers also need trace metals for growth and activity, albeit required in comparably low concentrations. Earlier studies (Ensign et al., 1993; Pedroni et al., 1997) indicated the particular importance of copper for nitrification. The activity of the enzyme ammonia monooxygenase, which catalyzes the first step in the oxidation of ammonia to nitrite, was greatly increased *in vitro* under addition of copper (Ensign et al., 1993). Additionally, the loss of enzyme activity *in vivo* under addition of copper-selective chelators (e.g. allylthiourea), emphasizes the requirement of copper for ammonia monooxygenase (Sayavedra-Soto and Arp, 2011). Both ammonia oxidizing bacteria (Arp et al., 2007) and archaea (Leininger et al., 2006) have the genetic inventory to express this enzyme.

Processes such as copper complexation and adsorption in soil, copper sulfide formation under reducing conditions in anoxic groundwater, or low copper content in aquifer material (Adriano, 1986) can lead to decreased concentrations of copper in groundwater for drinking water production. During treatment in biological rapid sand filters, water phase concentrations can be further reduced due to copper sorption to iron-oxide (Benjamin et al., 1996) and manganese-oxide coated sand (Han et al., 2006), which may decrease the availability of copper for nitrifying microorganisms in the filters. Complexation with organic and/or inorganic ligands (Sylva, 1976), substrate diffusion limitations, and competition for nutrients by other microorganisms in the filter (de Vet et al., 2011) can further decrease copper availability.

At present, only little is known about copper deficiency in biological rapid sand filters for groundwater treatment and its importance for limitations of nitrification activity. Therefore, we investigated the effect of copper dosing on nitrification activity in potentially copper limited biological rapid sand filters. Specific questions were:

- Can dosing of copper to the influent water of biological filters, subject to incomplete nitrification, stimulate the removal of ammonium and nitrite?
- How fast does ammonium removal increase, and what is the corresponding magnitude of dosed copper? How persistent is the effect of copper dosing after it has been stopped?
- How are ammonium and nitrite removal patterns over filter depth affected by the dosing? What is the increase in removal capacity for ammonium at certain depths of a filter?

Two approaches were used in the study: (1) the potential of a trace metal mixture containing copper to stimulate ammonium removal was investigated employing a lab-scale column assay, and (2) the effect of controlled copper dosing on nitrification was examined with water and sand depth-sampling of two full-scale filters, in a 280 day comprehensive study at a groundwater treatment plant.

2. Materials and methods

2.1. Lab-scale study with trace metals

Potential stimulation of ammonium removal by addition of a broad mixture of trace metals was investigated in a lab-scale column assay (Tatari et al., 2013), under controlled conditions. The assay uses lab-scale columns, packed with full-scale filter media, and operated inside a refrigerator, in order to match the temperature at the water treatment plant. Complete mixing in the assay prevents stratification of nitrification activity in the columns (Tatari et al., 2013), which makes it possible to reproduce depth-specific nitrification kinetics of a full-scale filter media sample.

Filter media from a secondary biological rapid sand filter (filter number 4) at Langerød full-scale groundwater treatment plant (GWTP), Denmark, was used. Anoxic groundwater with high alkalinity (Table 1) is treated at this plant with simple stairs aeration and a de-ironing primary sand filter, followed by two secondary biological filters in parallel. The secondary filters have been suffering from incomplete nitrification for several years. With effluent concentrations of 0.32 mg NH_4-N L^{-1}, the filters remove only approx. 50% of the influent ammonium (Table 1).

Two lab-scale columns were packed with sand from 30 cm depth of the secondary filter (0.8–1.4 mm quartz) and filter effluent water was used as influent substrate, enriched with ammonium (stock solution was prepared from NH_4Cl; analytical grade). In one of the columns, extra trace metals were added. Trace metals stock solution (adapted from Verhagen and Laanbroek, 1991) was prepared from $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, H_3BO_3, and Na_2EDTA (all analytical grade). Concentrations of the extra trace metals added to the substrate of the column were: 6 μg Ni L^{-1}, 6 μg Co L^{-1}, 6 μg Cu L^{-1}, 33 μg Zn L^{-1}, 10 μg Mo L^{-1}, 18 μg W L^{-1}, and 11 μg B L^{-1}. The other column was a control without addition of metals.

The lab-scale columns were first operated for 54 h at the volumetric ammonium loading rate (ALR) of the full-scale system of 2.0 g NH_4-N m^{-3} filter material h^{-1}. When ammonium concentrations in the effluent of the columns became lower than approx. 0.2 mg NH_4-N L^{-1}, loading was increased simultaneously for both columns, to avoid primary substrate limitations. After 54 h of operation, ALR was increased to 5.4 g NH_4-N m^{-3} h^{-1}, and after 236 h, furthermore increased to 8.0 g NH_4-N m^{-3} h^{-1}, until the experiment was stopped after 289 h. Ammonium influent concentrations were 1.2 mg NH_4-N L^{-1} for the lowest ALR and 2.1 mg NH_4-N L^{-1} for the two higher ALRs. Effluent water was sampled and ammonium concentrations were analyzed. The effect of trace metals addition was quantified by comparing the volumetric ammonium removal rates (ARRs) of both columns, at the different ALRs. ALRs and ARRs for the lab-scale study were calculated as described in Tatari et al. (2013), and have the units [g NH_4-N m^{-3} h^{-1}], where m^{-3} refers to the volume of filter material in the column. During the experiment, effluent pH, concentration of dissolved oxygen and temperature were monitored.

2.2. Long-term full-scale study of copper dosing

Subsequent to the lab-scale study, we carried out a full-scale investigation. Here only copper was dosed as trace metal, because of its specific importance for nitrification (Ensign et al., 1993; Sayavedra-Soto and Arp, 2011). The study lasted for 280 days and was conducted at Nærum GWTP, Denmark.

2.2.1. Characteristics of the groundwater treatment plant

Nærum GWTP treats anoxic groundwater, abstracted from a limestone aquifer, also relatively high in alkalinity (Table 1), with