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Modelling combined effect of chloramine and copper on ammonia-oxidizing microbial activity using a biostability approach

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ABSTRACT

Continuous and batch laboratory experiments were used to evaluate the combined effects of copper and chloramine on ammonia oxidizing microbes present in otherwise high nitrifying water samples. The experimental data were analyzed using a biostability concept and quantified with the biostable residual concentratrion (*BRC*) of monochloramine, or the concentration that prevents the onset of nitrification. In the batch experiments, copper dosing $\geq$0.25 mg-Cu L^{-1} resulted in complete inhibition of nitrification, and a lower copper dosing (0.1 mg-Cu L^{-1}) delayed nitrification. The BRC was systematically lowered with the addition of copper. For example, a free-ammonium concentration of 0.1 mg-N L^{-1} had a *BRC* of 0.73 mg-Cl_2 L^{-1} with no Cu, but addition of 0.1 mg-Cu L^{-1} lowered the BRC to 0.16 mg-Cl_2 L^{-1}, while addition of 0.25 mg-Cu L^{-1} eliminated the need to add chloramine (*BRC* = 0). A non-competitive inhibition model fit the experimental data well with a copper threshold of 0.044 mg-Cu L^{-1} and can be used to estimate Cu doses needed to prevent nitrification based on the chloramine concentration. Full scale systems applications need further study.

1. Introduction

In order to meet the stringent regulations regarding formation of disinfection by-products (DBPs), chloramine is popular as a secondary disinfectant, particularly in Australia and the USA. Compared to free chlorine, chloramine is considered beneficial because it has a lower decay rate and is less reactive with natural organic matter (NOM), producing smaller amounts of regulated DBPs, such as trihalomethanes and haloacetic acids (Goslan et al., 2009; Vikesland et al., 2001; Jafvert and Valentine, 1992). Nonetheless, it still can be difficult to achieve target residuals at the ends of the system and to prevent nitrification, especially in the summer (Cunliffe, 1991).

Chloramine decays by microbial and chemical means (Sathasivan et al., 2005). The chemical decay of monochloramine in drinking water is due to auto-decomposition and reactions with organic or inorganic constituents. Jafvert and Valentine (1987) reported that auto-decomposition of monochloramine to form NH_4^+, N_2, and Cl^- (Equation (1)) is accelerated by acid-catalysis. Auto-decomposition also can produce small quantities of nitrate (Equation (2)) (Valentine and Wilber, 1987). The direct reactions between monochloramine and nitrite (Equation (3)) or between nitrite and hypochlorous acid (Equation (4)) also produces nitrate.

$$3NH_2Cl \rightarrow N_2 + NH_4^+ + 3Cl^- + 2H^+ \quad (1)$$

$$4NH_2Cl + 3H_2O \rightarrow 3NH_4^+ + NO_3^- + 4Cl^- + 4H^+ \quad (2)$$

$$NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^- \quad (3)$$

$$HOCl + NO_2^- \rightarrow NO_3^- + H^+ + Cl^- \quad (4)$$

It is commonly believed that nitrification accelerates chloramine decay in distribution systems (Cunliffe, 1991; Valentine and Jafvert, 1988; Wolfe et al., 1988). Nitrification involves two groups of bacteria: ammonia-oxidizing bacteria (AOB), which oxidize ammonia to nitrite, and nitrite-oxidizing bacteria (NOB), which oxidize nitrite to nitrate. In a chloraminated distribution system, partial nitrification, i.e., only the activity of AOB, produces nitrite that can react

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with chloramine (Equation (3)). Experimental evidence also suggests the soluble microbial products (SMPs), produced after the onset of nitrification, could accelerate chloramine decay beyond that could be explained by nitrite and pH changes usually observed in nitrified chloraminated systems (Sathasivan et al., 2008; Sathasivan and Bal Krishna, 2012; Bal Krishna et al., 2012). Thus, the presence of AOB is a factor in the loss of chloramine residual.

Recent advances show a number of nitrifying microbes can be present in chloraminated water-supply systems. Early studies isolated and studied *Nitrosomonas europea* as the representative AOB species of chloraminated systems (Wolfe et al., 1990). However, recent findings have shown that other species – e.g., *Nitrosomonas oligotropha* (Regan et al., 2003), nitrifying Archaea (Hoefel et al., 2005) , and heterotrophic nitrifiers (Daum et al., 1998) – can be present and contribute to nitrification. A common function of all ammonia-oxidizing microbes (AOM) is that they oxidize ammonium to nitrite (NO_2^-). Nitrite thus produced can increase the pool of NO_x ($NO_2^- + NO_3^-$); since contributions to the pool from other reactions such as Equation (2) are insignificant, a change in NO_x concentrations can be used as the indicator of an AOM activity.

The chloramine residual plays a significant role in controlling the onset of severe nitrification in distribution systems. Woolschlager et al. (2001), Harrington et al. (2002), and Fleming et al. (2005) proposed a simple formula to determine the point of biostability. This occurs when the net growth rate of AOM (r_g, d^{-1}) is just balanced by the disinfection rate (r_d, d^{-1}):

$$r_g = \frac{\mu_m(free\ \ ammonium\ \ as\ \ N)}{(K_S + free\ \ ammonium\ \ as\ \ N)} - k_b \tag{5}$$

$$r_d = -k_d \cdot CA \tag{6}$$

where μ_m is the maximum specific growth rate of AOB (d^{-1}), K_s is the half saturation concentration for AOB (mg-N L^{-1}), k_b is the rate of endogenous bacterial decay (d^{-1}), k_d is the rate constant for inactivation of AOB by disinfectant (L d^{-1} mg-Cl_2^{-1}), and *CA* is the chloramine concentration (mg-Cl_2 L^{-1}). μ_m, k_b, and k_d, depend on temperature, although not necessarily in the same way (Sarker et al., 2013). When r_g and r_d balance each other, the chloramine concentration is referred to as *biostable residual concentration* (*BRC*). Mathematically, *BRC* is defined as

$$BRC = \left(\frac{\mu_m}{k_d}\right) \cdot \frac{(free\ \ ammonium\ \ as\ \ N)}{(K_S + free\ \ ammonium\ \ as\ \ N)} - \frac{k_b}{k_d} \tag{7}$$

The potential for nitrification exists when *CA* is lower than *BRC*. As we show in Figure SI-1 of Supplementary Information (SI), Equation (7) can simulate the data of Sathasivan et al. (2008) for pairs of k_b/k_d and K_s values.

Several nitrification-control measures, including additions of metals like copper and silver, have been reported in the literature (Sathasivan et al., 2005; Laszlo, 2008; Fisher et al., 2009). Copper is bacteriostatic or toxic to bacteria, viruses, or cysts in general, and it has been shown specifically to inhibit AOB activity (Laszlo, 2008; Zhang et al., 2009). Toxic effects of metals such as copper include substitution of essential ions from cellular sites and blocking of functional groups of important molecules, e.g., enzymes (Martin and Richard, 1982), polynucleotides, and essential nutrient transport systems (Nies, 1999). This results in inactivation of enzymes and disruption of membrane integrity (Ochiai, 1987).

Copper is an essential nutrient for human, but excess copper intake is reported to cause gastrointestinal effects in healthy adults (WHO, 2004). Copper has a maximum contaminant level goal (MCLG) of 1.3 mg-Cu L^{-1} in USA (USEPA, 2015) and a health guideline value of 2 mg-Cu L^{-1} in Australia (ADWG, 2004; WHO, 2004). Copper on average costs US$6 per Kg. Therefore addition of copper below regulatory and guideline values is economically feasible.

Trials were conducted in the Goldfields and Agricultural Water Supply System (G&AWSS) in Western Australia using copper (as cupric sulfate) in the pipelines to inhibit nitrification. Following the Australian Drinking Water Quality Guidelines (ADWG, 2004) and authorized by the Department of Public Health, Western Australia, copper doses of 0.25–0.40 mg-Cu L^{-1} were applied in a part of the distribution system. The results showed that nitrification could be controlled by dosing copper into service reservoirs and pipelines, although an impediment was the significant loss of copper during transport through the corroded iron pipeline (Zhan et al., 2012). Several processes can significantly affect the copper concentration in the pipelines compared to the reservoir. Copper could be bound as cations into the biofilm matrix, and sulphide produced in anaerobic pockets can lead to CuS (Kristiana et al., 2010) or by other iron corrosion products of the pipelines (Zhan et al., 2012). Therefore, the success of the copper dosing depends on short time dosing into service reservoirs rather than into the pipelines where biofilm or corrosion is significantly present.

Copper in dissolved form, mainly Cu(II), is persistent and frequently detected in drinking water (Boulay and Edwards, 2000; Zhang et al., 2002). Zhan et al. (2012) noted that the majority of the inorganic copper added as copper sulfate (up to a concentration of 0.4 mg-Cu L^{-1}) existed as Cu-NOM complexes in Mundaring weir water in Western Australia at pH 8. Sarathy and Allen (2005) had similar findings for surface water. Copper speciation is highly affected by the pH, but most chloraminated systems are operated within a narrow range of pH, often around 8. Hence, most chloraminated systems can be expected to contain Cu-NOM complexes as the major species.

Most past studies on the effects of Cu on AOM were carried out with pure cultures of nitrifying bacteria or in the absence of a disinfectant. The combined effects of copper and chloramine on AOM, especially on indigenous microbes in chloraminated distribution system, are unexplored. The purpose of this study is to investigate how Cu inhibits AOM in the presence of chloramine. We evaluated water samples collected from a laboratory-scale chloraminated system with otherwise high nitrifying activity (i.e., exhibiting a high ammonium-oxidation rate). We also developed a model to represent the combined effects of Cu and chloramine.

2. Materials and methods

To evaluate the combined effects of copper and chloramine, we operated laboratory-scale reactors to simulate various nitrifying conditions. The feed water was collected from Mundaring weir, the only source for G&AWWS. Samples collected from the reactor for batch experiments had high nitrification activity, giving a strong test for the impacts of copper and chloramine dosed together. Details of the analytical procedures, operation of the laboratory scale reactor, and the experimental design are given below.

2.1. Preparation of stock chemical solutions

Standard stock solutions were prepared by mixing analytical-grade chemicals with Milli-Q ultra-pure water (18 MΩ cm^{-1}, <100 ppb-C L^{-1}). Stock solutions of free chlorine (1000 mg-Cl_2 L^{-1}), *NH_4-N* (500 mg L^{-1}), *NO_2–N* (500 mg L^{-1}), and *NO_3-N* (500 mg L^{-1}) were prepared using sodium hypochlorite, ammonium chloride, sodium nitrite, and sodium nitrate, respectively. Stock solutions of 1 mg-N L^{-1} were prepared using ammonium chloride, sodium nitrite, and sodium nitrate to calibrate the assays for *TAN*, *NO_2-N*, and *NOx-N* respectively. *TAN* (total ammoniacal nitrogen) is the sum of