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Onset of severe nitrification in mildly nitrifying chloraminated bulk waters and its relation to biostability

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ABSTRACT

Triggers of severe nitrification in distribution systems are still not clearly understood. Recently, the biostability concept was proposed to explain the chloramine residual below which signs of nitrification would be seen. To improve understanding, mildly nitrifying bulk water samples (nitrite less than 0.010 mg-N/L) from Sydney Water distribution systems were incubated at constant temperatures and periodically analysed for nitrogenous compounds and total chlorine. Total ammoniacal nitrogen in the sample was between 0.25 and 0.35 mg-N/L. Severe nitrification was triggered when chloramine residuals dropped below about 0.4 mg/L – the critical threshold residual. In 45 such samples, the critical threshold residual was 0.2–0.65 mg/L. The biostability concept was found to be useful in explaining the residual below which net growth of microorganisms begins. However, this alone could not predict the critical threshold residual. Different means of overcoming this problem are discussed. One of these is the use of the microbial decay factor method, since microbiologically assisted chloramine decay in the samples studied was found to be mostly the result of ammonia-oxidising bacterial activity. Nitrite levels in winter were found to be poor indicators of nitrifying status. Overall the results were found to be useful in controlling nitrification and to obtain early warning of severe nitrification.

1. Introduction

Increased concern over disinfection by-products has prompted many water utilities to choose chloramine over chlorine as a disinfectant in drinking water distribution systems. Additionally, chloramine offers the advantage of greater stability than chlorine. However, the use of chloramine presents some additional challenges for water utilities. In addition to auto-decomposition of chloramine, and its direct chemical reaction with waterborne constituents, nitrification accelerates chloramine decay and promotes bacterial regrowth. A survey of US water utilities (Wilczak et al., 1996) indicated that nitrification may occur in the systems of 63% of those utilities that use chloramine.

Nitrification is a two-step microbial process. Ammonia is initially converted by ammonia-oxidising bacteria (AOB) to nitrite and then nitrite is converted to nitrate by nitrite-oxidising bacteria (NOB). Before the extensive use of molecular microbiological techniques, conclusions were made using *Nitrosomonas europea* as a representative organism (Wolfe et al., 1990). Recent use of a molecular microbiological approach has indicated *N. europea* is not the major species controlling the nitrification process in chloraminated systems where ammonium concentration is low (Regan et al., 2003; Lipponen et al., 2004; Hoefel et al., 2005). In Finland and US distribution systems, *Nitrosomonas oligotropha* was found to be the most abundant ammonia oxidiser. In distribution systems, it

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is generally believed that mostly partial nitrification (ammonia oxidation) takes place (Wolfe et al., 1990). Therefore, nitrite is generally used as the indicator of nitrification status (Wolfe et al., 1988) despite the fact that nitrite concentration measured in bulk water does not necessarily correlate well with AOB concentration measured by the most probable number (MPN) method in that water. The recent work of Regan et al. (2003) and Hoefel et al. (2005) indicated that nitrite-oxidising bacteria (NOB) are present in distribution system bulk waters.

Nitrification can accelerate chloramine loss in distribution systems (Cunliffe, 1991). The mechanism of chloramine decay by nitrification is not well established, although chloramine can be consumed in oxidation of nitrite to nitrate (Vikseland et al., 2001). Although any presence of nitrite in the water phase may suggest nitrifier activity, low levels of nitrite are regarded as unimportant and actions are usually not taken to eliminate it. However, once nitrification is severe, ammonia and total chlorine can reach zero levels and nitrite can reach very high concentrations. From a severely nitrifying status, it is very difficult to re-establish an adequate chloramine residual or preserve ammonia. For purposes of this paper, severe nitrification is defined as the situation in which a water sample immediately starts to show ammonia levels decreasing towards zero after collection and incubation at 20–30 °C, rather than just having a high initial nitrite level.

On many occasions, it has not been established whether bacterial nitrification was the primary cause of the accelerated decay or whether growth of the nitrifying bacteria was the consequence of the chloramine decay. Data presented by Liu et al. (2005) showed that nitrite concentration was dependent upon the chloramine concentration. Other authors (Fleming et al., 2005; Pintar et al., 2005) have also suggested dependence of nitrifier activity on chloramine concentration. Wolfe et al. (1988) reported that AOB can be present in concentrations as high as 1.5 mg/L. Wilczak et al. (1996) reported that nitrification was present even when chloramine residual was as high as 2 mg/L. It was not clear whether severe nitrification was present before this residual was reached in those samples that exhibited nitrification.

Various means of identifying the time of onset of severe nitrification have been proposed in the literature. In a study to detect broad-based trends in nitrification occurrence, Kirmeyer et al. (2004) proposed 0.05 mg/L NO_2^--N as an arbitrary critical threshold level. Pintar et al. (2005) suggested chloramine drop as a better indicator. They did not suggest a specific residual that provides an early warning or how this could be used in practice. Cunliffe (1991) proposed residual drop along with increased nitrite production as a means of rapid diagnosis for severe nitrification. Molecular microbiological analysis is being attempted by researchers (Regan et al., 2003; Hoefel et al., 2005) to obtain an early indication of its onset.

Woolschlager et al. (2001) and Harrington et al. (2002) proposed a simple formula to determine the point of biostability. Fleming et al. (2005) applied this concept to determine the residual below which potential for nitrification exists. This was done by balancing growth and disinfection by disinfectant. The model is valid for batch culture conditions since only growth and disinfection are considered. In their model, ammonia was used as food for AOB growth and dichloramine was used as the disinfectant. The resulting equation is:

$$\frac{\mu_m(\text{free ammonia})}{(K_s + \text{free ammonia})} = k_d \times \text{TCl} \quad (1)$$

where μ_m is the maximum specific growth rate of AOB (day 1); free ammonia is the sum of ammonia (NH_3) and ammonium (NH_4^+) concentrations (mg-N/L); K_s is the half saturation constant for AOB; k_d is the rate constant for inactivation of AOB by disinfectant (L day^{-1} mg Cl_2^{-1}); TCl is the total chlorine concentration (mg-Cl_2/L). As initial estimates, they used 2.0 mg/L for μ_m/k_d and 0.5 mg-N/L for K_s.

If chloramine residual or its decay rate could be used as one of the controlling parameters for determining onset of severe nitrification, tools such as the microbial decay factor method (Sathasivan et al., 2005), which showed promise in predicting chloramine residuals in Sydney distribution systems (Fisher et al., 2006), could be useful more generally. In this method, chemical and microbial components of total decay of chloramine (measured as total chlorine) are separated by simple decay measurements at a controlled temperature. The rate of chloramine drop due to microorganisms could therefore be determined by the microbial decay factor method.

Despite all these findings, most utilities are still struggling to cope with the uncertainty of the time of onset of severe nitrification. It would be particularly useful to understand what triggers it. Before the triggers of severe nitrification in a distribution system can be identified, it is necessary to understand the triggers in bulk water alone. In this paper, such an understanding is developed by comparing profiles of nitrogenous compounds and chloramine residuals in many different bulk water samples from three sub-systems of Sydney Water distribution systems. The implications for management of distribution system residuals are considered subsequently.

2. Materials and methods

Samples were collected from three different sub-supply systems of Sydney Water Corporation within a period ranging from January 2003 to December 2005. General characteristics of these samples are outlined in Table 1. These distribution systems typically have chloramine residuals less than 1.7 mg/L total chlorine and deliver water over medium distances. These systems contain about 200 service reservoirs (tanks). The farthest reservoir is about 50 km downstream from the treatment plant except one arm which is much longer. Retention time in the systems varies between 5 and 8 days except the longer arm which had a retention time up to 15 days. Altogether, 70 samples were collected from reservoirs and pipelines within the first 50 km. Results from 55 samples that had nitrite less than 0.010 mg-N/L are reported in this paper. Of these, 20 samples had nitrite less than 0.002 mg-N/L (the detection limit).

2.1. *Prospect, Macarthur and Woronora (Sydney Water) systems*

Sydney Water Corporation supplies water to about 5 million customers living in the Sydney metropolitan area. On average,