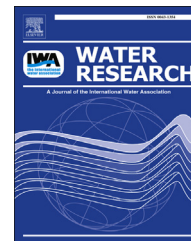


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A proposed abiotic reaction scheme for hydroxylamine and monochloramine under chloramination relevant drinking water conditions

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ABSTRACT

Drinking water monochloramine (NH₂Cl) use may promote ammonia-oxidizing bacteria (AOB). AOB use (i) ammonia monooxygenase for biological ammonia (NH₃) oxidation to hydroxylamine (NH₂OH) and (ii) hydroxylamine oxidoreductase for NH₂OH oxidation to nitrite. NH₂Cl and NH₂OH may react, providing AOB potential benefits and detriments. The NH₂Cl/NH₂OH reaction would benefit AOB by removing the disinfectant (NH₂Cl) and releasing their growth substrate (NH₃), but the NH₂Cl/NH₂OH reaction would also provide a possible additional inactivation mechanism besides direct NH₂Cl reaction with cells. Because biological NH₂OH oxidation supplies the electrons required for biological NH₃ oxidation, the NH₂Cl/NH₂OH reaction provides a direct mechanism for NH₂Cl to inhibit NH₃ oxidation, starving the cell of reductant by preventing biological NH₂OH oxidation. To investigate possible NH₂Cl/NH₂OH reaction implications on AOB, an understanding of the underlying abiotic reaction is first required. The present study conducted a detailed literature review and proposed an abiotic NH₂Cl/NH₂OH reaction scheme (RS) for chloramination relevant drinking water conditions (μM concentrations, air saturation, and pH 7–9). Next, RS literature based kinetics and end-products were evaluated experimentally between pHs 7.7 and 8.3, representing (i) the pH range for future experiments with AOB and (ii) mid-range pHs typically found in chloraminated drinking water. In addition, a ¹⁵N stable isotope experiment was conducted to verify nitrous oxide and nitrogen gas production and their nitrogen source. Finally, the RS was slightly refined using the experimental data and an AQUASIM implemented kinetic model. A chloraminated drinking water relevant RS is proposed and provides the abiotic reaction foundation for future AOB biotic experiments.

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1. Introduction

Upon final implementation (i.e., ~2015) of the Stage 2 Disinfectants and Disinfection Byproducts Rule, monochloramine (NH_2Cl) use for secondary disinfection in the United States is predicted to increase to 57% of all surface and 7% of all ground water systems (USEPA, 2005). Monochloramine use may promote nitrifying bacteria [i.e., ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria] because of naturally occurring ammonia; residual ammonia remaining from initial NH_2Cl formation; and ammonia released from NH_2Cl decay, oxidation of natural organic matter, corrosion, pipe surface reactions, and nitrite (NO_2^-) oxidation under various conditions in chloraminated water systems (Kirmeyer et al., 2004; Wilczak et al., 1996). A very rapid NH_2Cl residual loss is often associated with nitrification onset (American Water Works Association, 2013) that may result in noncompliance with existing regulations (e.g., Surface Water Treatment Rule); therefore, understanding nitrification and its control in drinking water distribution systems is of practical importance (Wilczak et al., 1996).

The most studied AOB is the pure culture *Nitrosomonas europaea*. Fig. 1 depicts *N. europaea*'s central metabolic pathway (Stein, 1998). For biological ammonia oxidation to NO_2^- , *N. europaea* uses two enzymes in two reaction steps: (i) the membrane-bound ammonia monooxygenase (AMO) enzyme catalyzes free ammonia (NH_3) oxidation to hydroxylamine (NH_2OH) and (ii) the periplasmic-residing hydroxylamine oxidoreductase (HAO) enzyme catalyzes NH_2OH oxidation to NO_2^- (Arp et al., 2002). For AMO, NH_3 is the sole reductant [i.e., electron (e^-)] source for *N. europaea* through the subsequent oxidation of NH_2OH (Fig. 1). Two of the four electrons resulting from NH_2OH oxidation are cycled back to AMO for NH_3 oxidation, while the other two electrons are used for other cellular processes (approximately 1.65 electrons passing to the terminal oxidase for ATP generation and 0.35 passing to NAD^+ to form NADH for biosynthesis) (Arp et al., 2002; Whittaker et al., 2000).

NH_2Cl inactivation studies on *N. europaea* have provided widely different estimates for inactivation rates based on the criterion used to define inactivation. For example, Oldenburg et al. (2002) reported *N. europaea* inactivation rates based on culturability were three orders of magnitude greater than those based on cell membrane integrity. In studies using NH_2Cl application to a nitrifying biofilm, Lee et al. (2011)

reported that NH_2Cl application impacted biofilm metabolic activity [based on dissolved oxygen (O_2) consumption] within 30 min; whereas, based on cell membrane integrity, minimal biofilm inactivation was seen at 2 h. In general, inactivation rates increased in the following order: (i) cell membrane integrity (Oldenburg et al., 2002; Wahman et al., 2010, 2009), (ii) culturability (Oldenburg et al., 2002), and (iii) metabolic activity (Lee et al., 2011; Pressman et al., 2012). Besides AOB inactivation from direct NH_2Cl cellular reactions, another possible inactivation mechanism impacting metabolic activity would be the direct abiotic reaction of NH_2Cl and NH_2OH . NH_2Cl and NH_2OH are known to react (Giles, 1999). Because biological NH_2OH oxidation supplies the electrons required for biological NH_3 oxidation, NH_2OH 's reaction with NH_2Cl provides a mechanism for NH_2Cl to inhibit NH_3 oxidation by competing with biological NH_2OH oxidation and starving the cell of reductant. NH_2Cl was recently shown to be biologically transformed by *N. europaea* (Maestre et al., 2013); therefore, it is reasonable to assume that NH_2Cl can be present in the periplasm, providing an opportunity for the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction. Alternatively, the $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction may benefit AOB by providing a mechanism of NH_2Cl loss and NH_3 release. To summarize, the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction represents both a possible benefit, disinfectant removal and growth substrate release, and detriment, reductant source removal, to AOB. These competing impacts should be evaluated to understand the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction's potential importance on preventing or promoting drinking water distribution system nitrification.

Before conducting biotic experiments with *N. europaea* to evaluate the possible relevance of the $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction, an abiotic model incorporating relevant NH_2Cl and NH_2OH reactions is required. To date, the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction has been investigated by a few research groups (Aoki et al., 1989; Ferriol et al., 1986; Giles, 1999; Robinson et al., 2005), but the conditions of this previous research were unrepresentative of chloraminated drinking water experiencing nitrification, including (i) mM versus μM reactant concentrations, (ii) pHs outside of 7–9, (iii) deoxygenated water versus air saturated water, or (iv) NH_2OH in great excess relative to NH_2Cl . In addition, two additional competing pathways for NH_2OH may be relevant under chloramination conditions and should be considered: reaction with (i) hypochlorous acid (HOCl) (Giles, 1999) released from NH_2Cl hydrolysis and (ii) O_2 (Anderson, 1964; Hughes and Nicklin, 1971; Kono, 1978; Moews Jr and Audrieth, 1959; Yagil and Anbar, 1964). The HOCl reaction can be considered through modeling as was done previously for the reaction of NH_2Cl and HOCl with NO_2^- (Wahman and Speitel, 2012), and the O_2 reaction can be evaluated in $\text{O}_2/\text{NH}_2\text{OH}$ control experiments.

The current study represents a first step in evaluating the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction importance on AOB by proposing and validating an abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction scheme incorporated into a well-established chloramine chemistry model (Jafvert and Valentine, 1992; Vikesland et al., 2001; Wahman and Speitel, 2012). First, a detailed literature evaluation was conducted to propose a relevant reaction scheme for the abiotic $\text{NH}_2\text{Cl}/\text{NH}_2\text{OH}$ reaction under chloraminated drinking water relevant conditions, including incorporation of revised nitroxyl (HNO) chemistry and

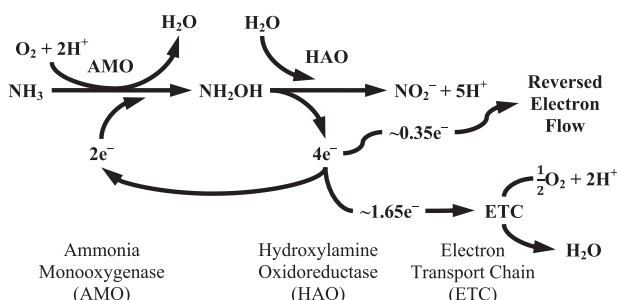


Fig. 1 – Central metabolism of *N. europaea* (Stein, 1998; Ward et al., 2011).

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