

PREFORMED MONOCHLORAMINE FOR MAINTENANCE OF DISINFECTANT RESIDUALS IN CHLORAMINATED DRINKING WATER DISTRIBUTION SYSTEMS

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INTRODUCTION

The Goldfields Agricultural Water Supply Scheme (GAWSS) in Western Australia is the longest and most extensive distribution system managed by the Water Corporation of Western Australia. The GAWSS source water is initially chloraminated and then re-chlorinated to maintain disinfectant residual. Under certain conditions, chloraminated distribution systems are prone to nitrification which leads to loss of disinfectant residual. Loss of disinfectant efficacy causes the risk of pathogen outbreaks, particularly *Naegleria* in the GAWSS. However re-chlorination to maintain disinfectant residual results in increased formation of potentially harmful disinfection by-products (DBPs), which are detrimental to water quality. This project addresses these issues by proposing the use of concentrated preformed monochloramine solutions for disinfectant redosing into tanks and reservoirs to re-establish disinfectant residual. In addition, this method offers more control over chloramine speciation compared to re-chlorination. Preventing dichloramine formation, which has been reported to promote the formation of potentially harmful nitrogenous disinfection by-products, is a key advantage of preformed monochloramine. Only a small number of applications of preformed chloramination in drinking water disinfection have been reported. However, this technique can provide a practical solution for maintaining disinfectant residual, improve water quality and prevent pathogen detections in extensive distribution systems such as the GAWSS. The objectives of this project were,

- To understand the optimum conditions for, and limitations on, the formation of concentrated monochloramine solutions,
- To develop a kinetic model that is able to predict the speciation (dichloramine formation) and stability of a concentrated chloramine solution over time, and
- To determine the practicality of application of preformed monochloramine for dosing into tanks and reservoirs on a pilot scale.

METHODOLOGY

Several factors can affect the stability and speciation of chloramine solutions including pH, Cl: NH₃ ratio, and temperature. The stability of concentrated monochloramine was investigated at several pH values. A range of chloramine decomposition products were measured (NH₃, Cl⁻, NO₃⁻, and an unidentified monochloramine decomposition product 'U') to elucidate the most important degradation pathways. The monochloramine decomposition kinetics proposed by Jafvert and Valentine in the Unified Model (Table 1, developed for low concentrations <2mM) were expected to describe the behaviour of concentrated monochloramine solution. A kinetic model based on this model was developed to optimise the conditions for monochloramine stability, and minimise dichloramine and disinfection by-product formation.

Dichloramine formation in concentrated monochloramine solutions was also measured, to assist in developing the kinetic model. Conventional chloramine measurement methods were ineffective at identifying dichloramine because of interference from the high concentration of monochloramine. A method was developed to qualitatively identify dichloramine in the presence of high concentrations of monochloramine using High Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD). HPLC-DAD was able to resolve monochloramine and dichloramine peaks and also separate the unidentified decomposition product.

RESULTS

Preliminary results from this study have shown that pH control is imperative for maintaining the stability of concentrated monochloramine solutions. In laboratory-scale studies, pH control can be achieved using buffers, however, this is not applicable on a field-scale. Additionally, previous studies have shown that certain buffers have a catalytic effect on monochloramine decomposition. Borate buffer was proposed for pH control in laboratory experiments. A comparison of the stability of monochloramine in unbuffered (pH maintained by the addition of aliquots of NaOH or H₂SO₄ solutions) and borate buffered conditions showed no difference in monochloramine concentrations. Hence, borate has no catalytic effect on monochloramine decomposition. The outcomes of laboratory-scale experiments using borate buffered solutions would therefore be directly applicable to field-scale, unbuffered conditions.

The stability of concentrated monochloramine at pH 8.3, 9 and 10 was modelled based on the Unified Model. It was found that the rate of decomposition of monochloramine at high concentrations was not accurately described by this model. Figure 1 shows the fit of the model to experimental data at high monochloramine concentration and pH 8.3, compared to the fit of the model to similar data at low monochloramine concentration also at pH 8.3. The slight difference between the model prediction and experimental data at low concentration is exaggerated at higher monochloramine concentrations. This suggests that, at high monochloramine concentration, rate constants pertaining to monochloramine decomposition are too low, or that there are important reaction pathways that are unaccounted for by the model. Additionally, previous studies indicate the maximum stability of monochloramine (at low concentrations <2mM) is observed at pH 8.3; however this stability was not observed at this high concentration of monochloramine.

CONCLUSION

Concentrated monochloramine solution has been found to be unstable over a short time period at certain pH values. Further investigation is being carried out to refine the kinetic model, which will be able to predict the optimum conditions for stability of a concentrated monochloramine solution. This will determine whether the solution can be prepared and stored for an extended period or needs to be prepared 'on-site' and used by a certain time period. Redosing using preformed monochloramine will re-establish disinfectant residual quickly and over longer distances in long, chloraminated distribution systems. This will provide important benefits for the water industry, with better control of pathogen risks, DBP formation and less nitrification instances.

Table 1: Key equations describing monochloramine formation and decomposition in the Unified Model as proposed by Jafvert and Valentine (1992) and Cimetière (2009)

Reaction Number	Equation
E1	$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$
E2	$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$
E3	$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$
E4	$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$
E5	$\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow \text{P} \quad \text{P} = \text{Cl}^-, \text{NO}_3^-, \text{N}_2$
E6	$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$
E7	$\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^-$

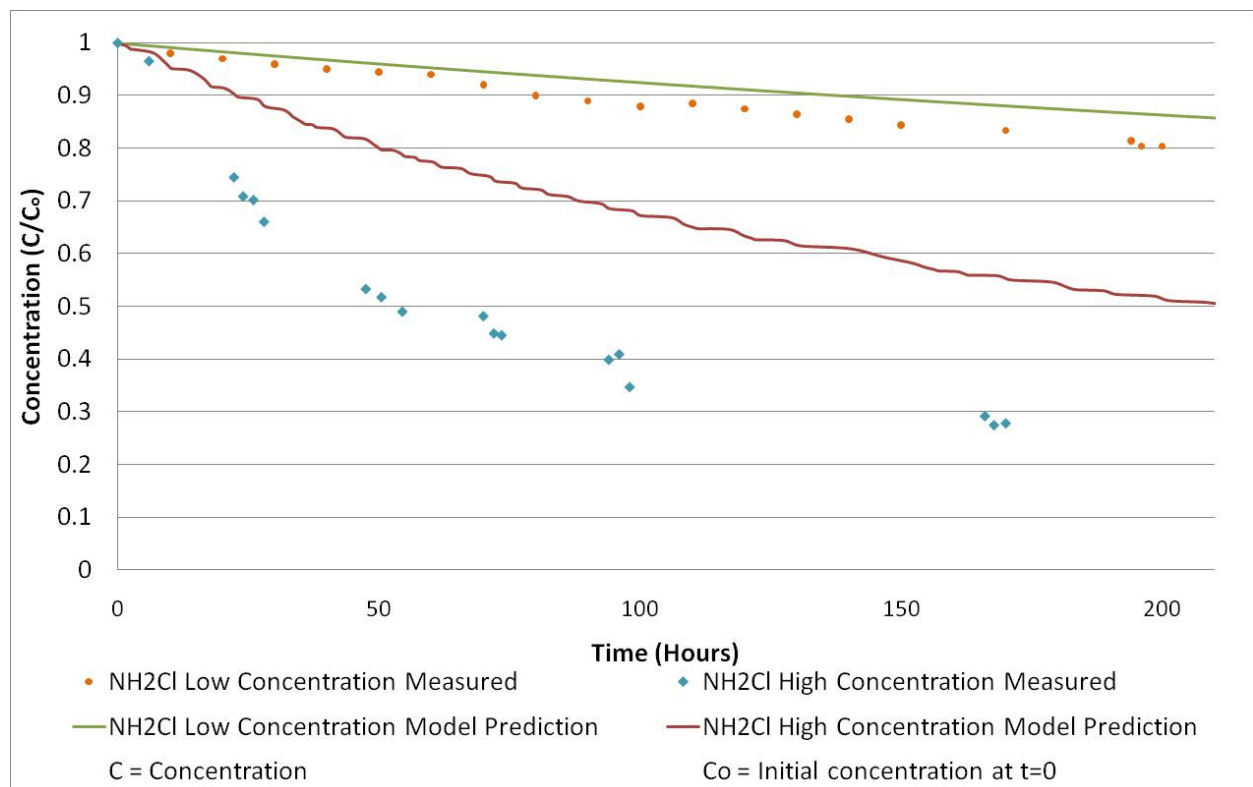


Figure 1: Monochloramine stability at pH 8.3, experimental data (points) compared to predictions of the Unified Model (lines). High concentration is 19.4 mM, low concentration is 1.5 mM.