



Effectiveness of re-chloramination to control nitrification in chloraminated bulk waters

K.C. Bal Krishna^{a,*}, Gaganraj Singh Bhullar^{a,b}, Arumugam Sathasivan^{a,c},
Ralph Henderson^b

^aDepartment of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia,
emails: bal.krishna@curtin.edu.au (K.C. Bal krishna), Raj.Bhullar@watercorporation.com.au (G.S. Bhullar),
A.sathasivan@uws.edu.au (A. Sathasivan)

^bDrinking Water Quality Branch, Water Corporation, Western Australia, Australia,
email: Ralph.Henderson@watercorporation.com.au

^cSchool of Computing, Engineering and Mathematics, University of Western Sydney, Locked Bag 1797, Penrith, NSW 2751, Australia

Received 6 March 2015; Accepted 24 July 2015

ABSTRACT

Managing chloramine residuals in water distribution systems after the onset of nitrification is a major challenge for water utilities that employ chloramine as a disinfectant. One of the strategies adopted by utilities is re-chloramination, but its effectiveness may vary depending on the stage (immediately after the onset or later) at which re-chloramination is practiced. Therefore, a systematic study of the effectiveness of re-chloramination was conducted by collecting bulk water samples from full-scale and laboratory-scale water distribution systems. The findings of this study revealed that in addition to initial dose of chloramine residuals, effectiveness of re-chloramination largely depend on the stage at which re-chloramination is practiced. Comparatively slow chloramine decay rates were observed when re-chloramination was carried out just after the onset of nitrification or after chloramine residuals dropped close to zero. However, the recurrence of nitrification is inevitable if only single dosing is practiced.

Keywords: Chlorine; Chloramine; Re-chloramination; Nitrification

1. Introduction

For water utilities, the greatest risk to public health is the presence of pathogenic micro-organisms in drinking water distribution system. To mitigate this risk, disinfectants, especially chlorine or chloramine have been commonly employed as secondary disinfectants to inactivate the accidentally entered pathogenic micro-organisms and to prevent their regrowth in the

water distribution system. The use of chloramine as a disinfectant has been gaining popularity because of their tendency to form lower level of regulated disinfection by-products (DBPs) [1–3]. Additionally, the lower reactivity of chloramine is advantageous for use in long and extensive distribution systems in which maintaining disinfectant residual levels over longer distances or longer period is required [4].

Chloramine, however, is inherently unstable in water as it decays by itself even in the absence of oxidisable matter. The decay of chloramine results in the

*Corresponding author.

liberation of free-ammonia, which in turn becomes an energy source for indigenous micro-organisms, mainly nitrifiers. The accumulation of free-ammonia leads to biological instability by promoting nitrifiers growth in the water distribution systems, resulting in nitrification. Nitrification is a microbiological process in which ammonia is sequentially oxidized to nitrite and then nitrate by ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), respectively. The consequences of a nitrification episode can be serious and include loss of disinfectant residual, proliferation of pathogenic micro-organisms, and possible regulatory compliance issues [4]. Consequently, water utilities are often forced to route nitrified waters from the potable supply and either employ them for other non-consumable purposes (e.g. irrigation) or dispose the water.

To maintain adequate chloramine residuals and minimize the occurrence of nitrification, water utilities have been implementing different strategies which are: (a) reducing the water retention time in distribution systems [5–7], (b) dosing free chlorine to maintain the total chlorine to total ammoniacal nitrogen (TAN) ratio close to five thus diminishing the free-ammonia residuals [4,5,7], (c) regularly carrying out break point chlorination [5,7], (d) draining and refilling the service reservoirs (tanks) or diluting the nitrified water with freshly chloraminated water in winter [7,8], (e) frequently flushing the distribution systems [5] and (f) re-chloramination. Out of these, break point chlorination is known to be one of the most effective control methods. However, it suffers from drawbacks due to the occurrence of increased heterotrophic bacteria and coliform numbers in water distribution systems [9,10]. Additionally, prolonged use of breakpoint chlorination forms DBPs and also increases consumer complaints about chlorineous taste [11]. The application of break point chlorination hence compromises the advantages offered by chloramination, despite it being an effective measure in maintaining disinfectant residuals after the onset of nitrification.

The reduction of free-ammonia by increasing chlorine-to-TAN ratio or by topping up of free-chlorine to maintain chlorine-to-TAN ratio close to five is also considered as an effective long-term preventive measure [9]. Some Australian water utilities such as Sydney Water distribution system and Goldfield and Agricultural Water Supply System (G&AWSS) have been adding free-chlorine once chloramine residuals dropped below a certain level to achieve chlorine-to-TAN ratio close to five in their distribution systems. Regardless of the continuous practice of re-chloramination, especially by minimizing free-ammonia residuals, a systematic investigation on the efficacy of this method is lacking.

The efficiency of re-chloramination or chloramine topping up for controlling nitrification could be improved by considering the application time based on the bulk water characteristics. Therefore, this study collected bulk water samples from the G&AWSS, Western Australia and incubated over a long period and samples of different bulk water characteristics were obtained and re-chloramination was carried out. The results obtained were then verified with the nitrified bulk water samples obtained from a laboratory-scale distribution system.

2. Materials and methods

2.1. Stock chemical solutions, sampling bottles and glassware preparation

Stock solutions for all chemicals were prepared in reverse osmosis (RO) treated water (IbisIS0006, Ibis Technology, Australia). The RO treated water had dissolved organic carbon (DOC) and conductivity of $<0.15 \text{ mg L}^{-1}$ and $<1 \mu\text{S cm}^{-1}$, respectively. Stock solutions of ammonium chloride (500 mg N L^{-1}) and sodium hypochlorite ($500 \text{ mg Cl}_2 \text{ L}^{-1}$) were used to re-chloramine the bulk waters. All the chemicals used in this experiment were of analytical grade.

Sample bottles (500 mL polyethylene terephthalate (PET)) and glassware were cleaned by immersing them into a 1.0% sodium hypochlorite solution and High Density Polyethylene (HDPE) container of 25 L by filling the same (a 1.0% sodium hypochlorite) solution, followed by rinsing five to six times with RO treated water to ensure they were free of chlorine by measuring total chlorine for added RO treated water sample.

2.2. Bulk water samples collection from full-scale distribution system

The G&AWSS is located in Western Australia and details of this distribution system can be found in Bal Krishna et al. [12]. Chloraminated bulk water samples were collected from a sampling point on one of the branches of the G&AWSS located approximately 121 km from the initial chloramination point. HDPE containers (25 L) cleaned using sodium hypochlorite solution as detailed in the above section were used to collect the bulk water samples. The containers were rinsed three times with sampling water at the point of collection to remove possible contaminants prior to collection. Physicochemical characteristics (total chlorine, TAN, nitrite, nitrate, pH and DOC) of the collected waters are detailed in Section 3.1. Once the collected samples were transported to the laboratory,

a constant temperature ($20.0 \pm 2.0^\circ\text{C}$) was maintained using a submersible AquaOne™ 100 Watt glass heater. Afterwards, total chlorine, TAN, nitrite and nitrate concentrations were periodically monitored.

2.3. Experimental design

After the occurrence of severe nitrification (rapid drop of TAN and total chlorine and rapid increase of nitrite and NO_x residuals) in the stored (25 L HDPE container) chloraminated bulk water samples, subsamples were extracted at 692.0, 718.0 and 861.0 h of the incubation time (Fig. 2) and they were named as subsamples (A), (B) and (C), respectively. In each sampling time, the subsample collected was split into four 500 mL PET bottles. Two of these PET bottles were spiked with initial chloramine residuals of $1.5 \text{ mg Cl}_2 \text{ L}^{-1}$ and other two were spiked with $2.5 \text{ mg Cl}_2 \text{ L}^{-1}$ residuals using stock solutions of ammonium chloride (500 mg N L^{-1}) and sodium hypochlorite ($500 \text{ mg Cl}_2 \text{ L}^{-1}$). For both chloramine residuals, total chlorine-to-TAN ratio of 4.5:1 was maintained. Afterwards, they were incubated in a water bath at a constant temperature ($20.0 \pm 2.0^\circ\text{C}$) and chemical parameters (total chlorine, TAN, nitrite and nitrate residuals) were periodically monitored.

2.4. Sample collection from a laboratory-scale distribution system and experimental design

In order to verify the results obtained from full-scale water distribution system, nitrified bulk water samples were collected from Reactors-3 to 5 of a laboratory-scale system (Fig. 1). Details of laboratory-scale system can be found in Bal Krishna and Sathasivan [13] and Bal Krishna et al. [14]. Physicochemical parameters were monitored in each sample prior to

re-chloramination. Similar to the full-scale distribution system, the bulk water samples collected from each reactor was split into four subsamples. Two of the subsamples from each reactor were spiked with initial chloramine residuals of $1.0 \text{ mg Cl}_2 \text{ L}^{-1}$ and remaining two were spiked with $2.0 \text{ mg Cl}_2 \text{ L}^{-1}$ maintaining a chlorine-to-TAN ratio of 4.5:1. Samples were incubated in a water bath maintaining a constant temperature ($20.0 \pm 2.0^\circ\text{C}$) and total chlorine residuals were then periodically monitored.

2.5. Use of NO_x-N to determine the nitrification rate

AOB activity in chloraminated water can be determined by monitoring the changes in NO_x-N residuals. Nitrite can be oxidized to nitrate chemically (in the presence of chloramine residuals) and biologically (by NOBs). Oxidation of nitrite to nitrate does not alter NO_x-N residuals. The only means of nitrite production is through the microbial conversion of TAN to nitrite by AOBs, which results in the increase in NO_x-N concentration. Hence, AOBs activity can be easily determined by monitoring the changes in NO_x-N concentrations.

2.6. Determination of chloramine decay coefficient

To determine the total chlorine decay rate, first-order decay kinetics as detailed in Eq. (1) was used.

$$\text{Cl}_t = \text{Cl}_0 e^{(-kt)} \quad (1)$$

where Cl_t is chloramine residual (measured as total chlorine), in $\text{mg Cl}_2 \text{ L}^{-1}$ at time t h; Cl_0 is the initial chloramine residual, in $\text{mg Cl}_2 \text{ L}^{-1}$ and k is the total chloramine decay rate coefficient, in h^{-1} .

2.7. Analytical procedures

Total chlorine, TAN, nitrite, nitrate and DOC were measured immediately after collecting the samples. The Aquakem 200, a high precision wet chemistry automated analyser, was employed to measure TAN, nitrite and NO_x concentrations. The analyser has a low detection limit for TAN, nitrite and NO_x level of $0.002 \text{ mg N L}^{-1}$. TAN and NO_x were measured spectrophotometrically according to EPA method 350.1 [15]. Nitrite was measured using the APHA sulphanilamide method (4,500-NO⁻² B) [16]. Detailed measurement methods are given in Bal Krishna and Sathasivan [13]. Total chlorine residual was measured by DPD colorimetric method using a HACH pocket

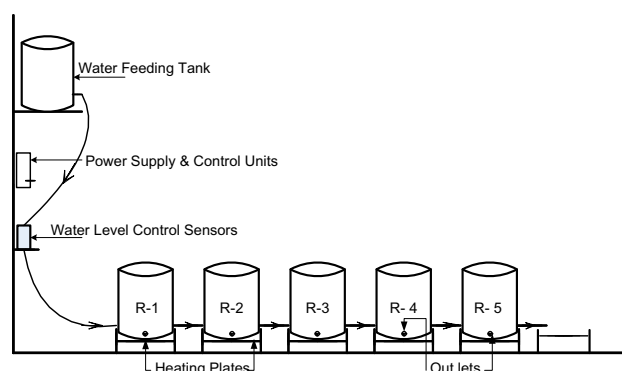


Fig. 1. Schematic diagram of laboratory-scale system (adopted from [13]).

colorimeter. Total chlorine measurement had an experimental error of $\pm 0.05 \text{ mg Cl}_2 \text{ L}^{-1}$. The DOC concentration was measured using a TOC analyser connected to an auto sampler (TOC-L_{CSH/CSN}, Shimadzu Co., Kyoto, Japan). A portable pH meter (HACH 40d) with a pH probe (HACH, PHC101) was used to measure pH and the measurement error was ± 0.1 .

3. Results and discussion

3.1. Chloramine decay behaviour in the bulk water sample

Total chlorine: $1.66 \pm 0.05 \text{ mg Cl}_2 \text{ L}^{-1}$, nitrogenous species (TAN: $0.496 \pm 0.003 \text{ mg N L}^{-1}$, nitrite: $0.12 \pm 0.005 \text{ mg N L}^{-1}$ and nitrate: $0.453 \pm 0.01 \text{ mg N L}^{-1}$), DOC: $1.30 \pm 0.30 \text{ mg L}^{-1}$ and pH: 7.23 ± 0.10 were measured in the bulk water sample collected from the G&AWSS prior to incubation at a constant temperature ($20.0 \pm 2.0^\circ\text{C}$). The nitrite and nitrate residuals represent upstream nitrification or raw water characteristics. Gradual decrease in total chlorine residuals with steady nitrogenous species residuals were noted until 524 h of incubation (Fig. 2). Once total chlorine residuals dropped below $0.55 \text{ mg Cl}_2 \text{ L}^{-1}$ (after 524 h of incubation), accelerated drop in total chlorine and TAN residuals with a rapid increase in nitrite and NO_x residuals were observed in bulk water samples (Fig. 2), demonstrating the onset of nitrification. This result corroborates with the observation made in bulk water samples obtained from the Sydney water distribution system where onset of nitrification was noted when total chlorine residuals were in the range of $0.43\text{--}0.49 \text{ mg Cl}_2 \text{ L}^{-1}$ [17]. A similar total inorganic

nitrogen (TIN) concentrations (summation of TAN and NO_x-N) prior to incubation ($0.88 \pm 0.01 \text{ mg N L}^{-1}$), at different time periods (as detailed in Table 1) and at the end of the incubation ($0.86 \pm 0.02 \text{ mg N L}^{-1}$) confirms the changes in nitrogen species residuals in the bulk water as a result of nitrification. After the onset of nitrification, total chlorine decay rate increased by 7.6 times (before and after the onset of nitrification: 0.0023 and 0.0176 h^{-1} , respectively) signifying the role of nitrification in accelerating chloramine decay.

3.2. Effectiveness of re-chloramination to maintain chloramine residuals

This study reveals nitrified bulk water characteristics (such as total chlorine and nitrogenous species) and chloramine residuals to be dosed at the time of re-chloramination are the critical parameters which play a major role in improving the stability of disinfectant. For example, accelerated drop in total chlorine residuals were observed in subsamples (A) and (B), but comparatively slow decay was noted in subsample (C) (Fig. 3(A)) when re-chloramination was carried out with chloramine residual of $1.5 \text{ mg Cl}_2 \text{ L}^{-1}$. The differences among the subsamples were they had experienced different bulk water characteristics, especially total chlorine and nitrogenous species residuals (Table 1 and Fig. 2). Chloramine residuals dropped below the detection limit in subsamples (A) and (B) after incubation period of 150 h, whereas around 350 h was required to reach the same level in subsample (C) (Fig. 3(A)). The decay rate coefficients presented in Fig. 4(F) further supported the observation showing

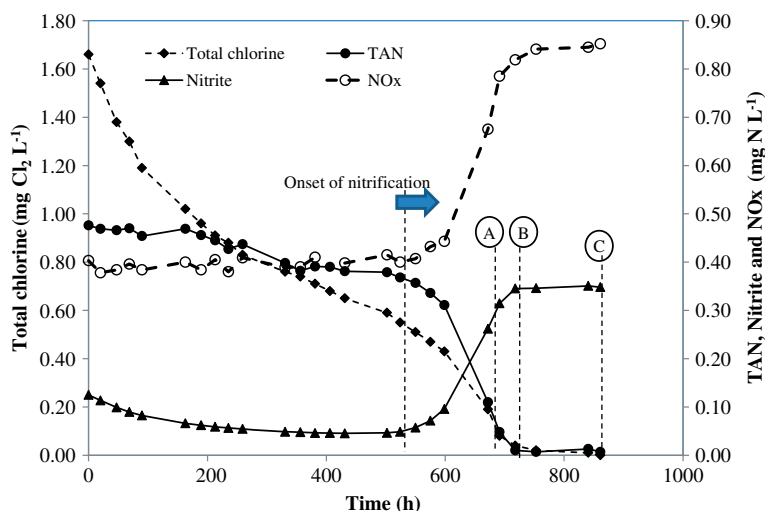


Fig. 2. Total chlorine and nitrogenous species residuals profiles before and after onset of nitrification. Points (A), (B) and (C) represent the samples extraction time for subsamples (A), (B) and (C), respectively.

Table 1

Total chlorine and nitrogenous species residuals measured in subsamples A, B and C prior to re-chloramination

Parameters		Subsamples		
		A	B	C
Total chlorine	mg Cl ₂ L ⁻¹	0.14 ± 0.05	0.04 ± 0.05	ND
TAN	mg L ⁻¹	0.07 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
Nitrite	mg N L ⁻¹	0.32 ± 0.01	0.35 ± 0.01	0.35 ± 0.01
Nitrate	mg N L ⁻¹	0.47 ± 0.01	0.47 ± 0.01	0.50 ± 0.01
NOx	mg N L ⁻¹	0.79 ± 0.01	0.82 ± 0.01	0.85 ± 0.01
TIN	mg N L ⁻¹	0.86 ± 0.02	0.84 ± 0.02	0.86 ± 0.02

Notes: ND: Below the detection limit.

±: Analytical error.

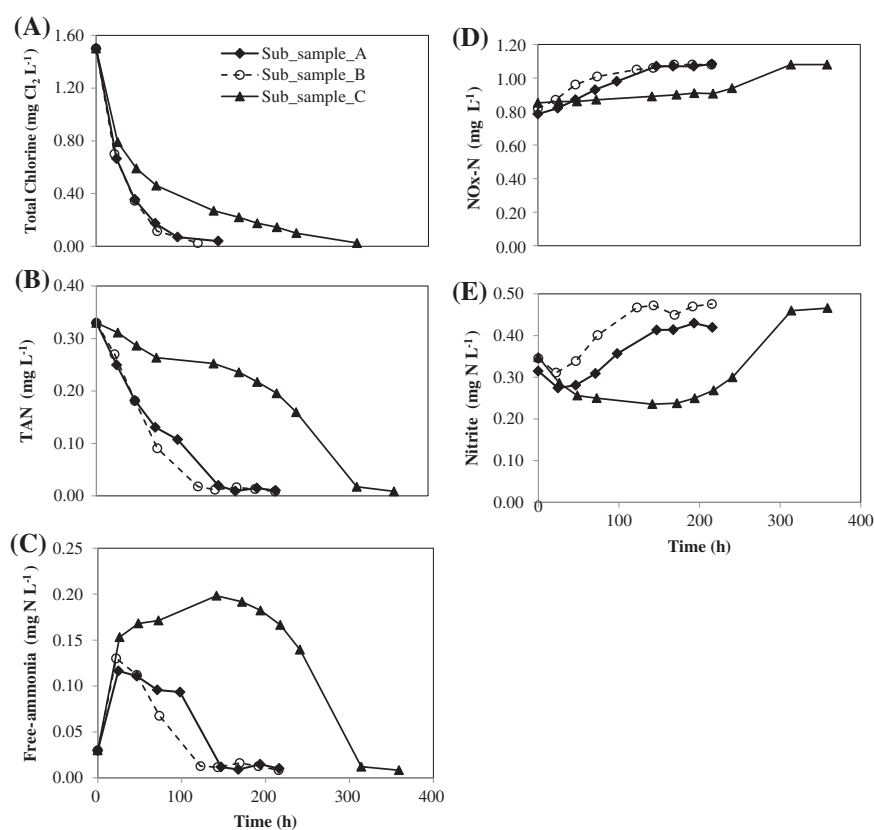


Fig. 3. Chemical parameters profiles in the nitrified bulk water samples after re-chloraminating with 1.5 mg Cl₂ L⁻¹ of total chlorine. (A) total chlorine, (B) TAN, (C) free-ammonia (D) NOx-N and (E) nitrite profiles.

far less chloramine decay rate in subsample (C) than in other two subsamples.

Further improved total chlorine residual profiles were observed in subsamples when they were spiked with increased chloramine residuals (Figs. 3(A) and 4(A)). For example, when re-chloramination was carried out by maintaining initial chloramine residual of 2.5 mg Cl₂ L⁻¹, total chlorine residual dropped below

the detection limit after 200 h of incubation in subsamples (A) and (B), whereas the residual lasted for only 150 h when initial chloramine residual of 1.5 mg Cl₂ L⁻¹ was maintained in the same sample. This observation was further supported by the decay rate coefficients (Fig. 4(F)) which were found to be decreased by half when the initial chloramine residual was increased. High chloramine residuals are known to be

effective for inactivating bacteria including nitrifiers [18,19] which could be a potential reason to observe improved chloramine residuals in the subsamples dosed with high chloramine residuals.

Comparing to subsamples (A) and (B), better stability of chloramine residual was noted in subsample (C) (Figs. 3(A), 4(A) and 3(F)) at both re-chloramination conditions demonstrating the effectiveness of re-chloramination mainly depending on nitrified bulk water characteristics. Bacterial communities' compositions including nitrifying bacteria largely depend on nitrified bulk water characteristics [14]. Therefore, bacterial direct and indirect roles towards degrading chloramine residuals could vary depending on community composition. However, determining nitrifying bacterial activities based on nitrification rate discussed in the following section could further clarify the observation made.

3.3. Impact of re-chloramination on onset of nitrification

This study confirms the effectiveness of re-chloramination on delaying the onset of nitrification not only depends on chloramine residual to be dosed, but also on the bulk water characteristics. Onset of nitrification was observed in subsamples (A) and (B) after 22–24.5 h of incubation whereas nitrification took place after 172 h of incubation in subsample (C), despite all subsamples being spiked with the same initial chloramine residual of $1.5 \text{ mg Cl}_2 \text{ L}^{-1}$ (Table 2). At the time of onset of nitrification, free-ammonia residuals were $0.12\text{--}0.13 \text{ mg N L}^{-1}$ in subsamples (A) and (B) and 0.20 mg N L^{-1} in subsample (C) (Fig. 3(C)). Delayed onset of nitrification was observed in subsamples when high initial chloramine residual of $2.5 \text{ mg Cl}_2 \text{ L}^{-1}$ was maintained and nitrification onset times varied between the subsamples (Table 2). Increased

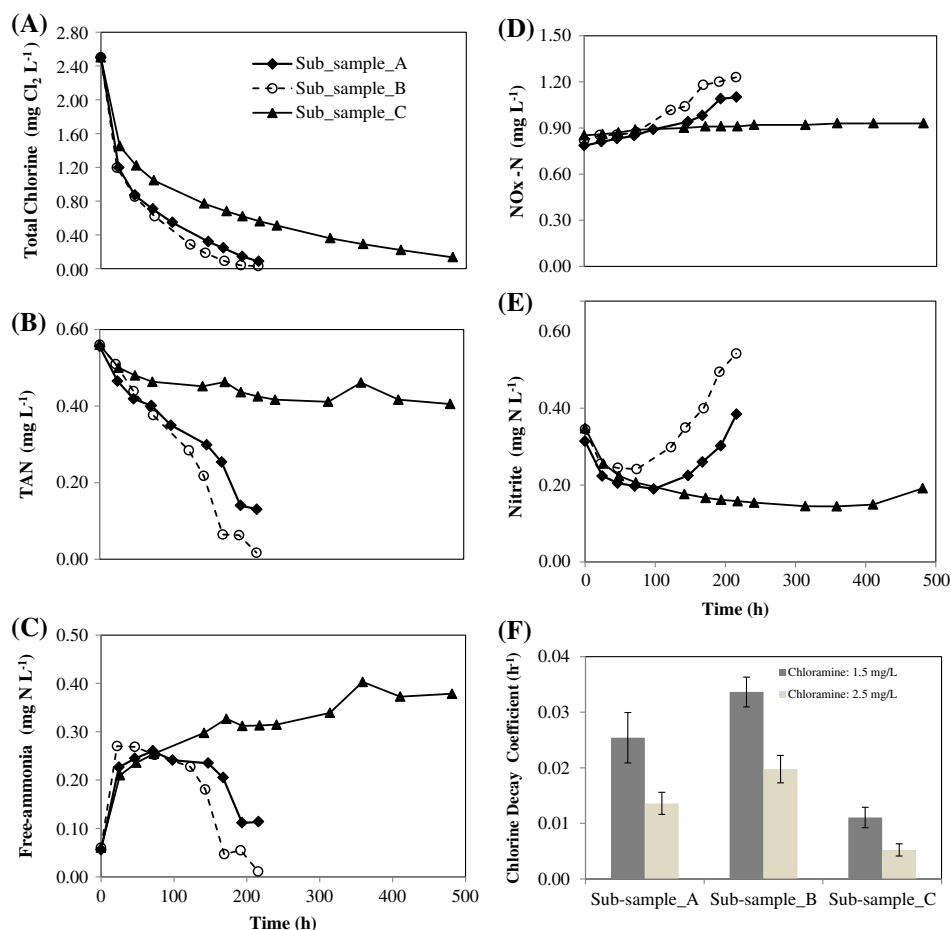


Fig. 4. Chemical parameters profiles in the nitrified bulk water samples after re-chloraminating with $2.5 \text{ mg Cl}_2 \text{ L}^{-1}$ of total chlorine. (A) total chlorine, (B) TAN, (C) free-ammonia, (D) NOx-N , (E) nitrite profiles and (F) total chlorine decay rates.

Table 2
Onset of nitrification time and corresponding total chlorine residuals

Parameters		Subsample A	Subsample B	Subsample C
Total chlorine dosed: 1.5 mg Cl ₂ L ⁻¹	Nitrification onset time (h)	24.5	22.0	172.0
	Chlorine residuals at onset of nitrification (mg Cl ₂ L ⁻¹)	0.67 ± 0.05	0.70 ± 0.05	0.22 ± 0.05
Total chlorine dosed: 2.5 mg Cl ₂ L ⁻¹	Nitrification onset time (h)	98.0	73.5	459.0
	Chlorine residuals at onset of nitrification (mg Cl ₂ L ⁻¹)	0.55 ± 0.05	0.62 ± 0.05	0.29 ± 0.05

free-ammonia residuals 0.26 mg N L⁻¹ in subsamples (A) and (B) and 0.40 mg N L⁻¹ in subsample (C) were noted at the time of onset of nitrification (Fig. 4(C)). Free-ammonia residual is known to be one of the key parameters for AOBs activities. However, nitrification had taken place at different free-ammonia residuals when re-chloraminated with different initial chloramine residuals. As reported by Bal Krishna et al. [14] and Vicente et al. [20] nitrifying bacterial species and their abundance could be different among the subsamples and their ability towards resisting chloramine residuals could be different, which could be one of the possible reasons to observe such variation on nitrification onset time.

TIN at the beginning and end of re-chloramination were in the range of 1.12 ± 0.09–1.18 ± 0.09 mg N L⁻¹ and 1.0 ± 0.09–1.07 ± 0.09 mg N L⁻¹, respectively in the subsamples dosed with chloramine residual of 1.5 mg Cl₂ L⁻¹. Similarly, initial and final TIN were 1.34 ± 0.1–1.43 ± 0.1 mg N L⁻¹ and 1.18 ± 0.1–1.25 ± 0.1 mg N L⁻¹, respectively in the subsamples dosed with chloramine residual of 2.5 mg Cl₂ L⁻¹. Not much difference in initial and final TIN in each subsample demonstrate conversion of nitrogen species is largely due to oxidation of TAN to nitrite by AOBs and subsequent oxidation of nitrite to nitrate by NOBs and total chlorine. The minimal difference in initial and final TIN could be the result of TAN conversion into nitrogen gas as a result of auto-decomposition in the presence of total chlorine as reported by Sathasivan and Bal Krishna [21].

Higher NO_x-N production rates at an earlier stage of incubation in subsamples (A) and (B) were observed when they were spiked with low chloramine residuals (Table 3). In contrast to this observation, increased NO_x-N production rate were noted at a later stage of incubation in the same subsample dosed with a high chloramine residual of 2.5 mg Cl₂ L⁻¹ (Table 3). This observation shows that a higher dose of chloramine residual adversely impacts on the nitrifiers' activities as demonstrated by Oldenburg et al. [18,19] and Zhang

and DiGiano et al. [19] however, recurrence of their activities are inevitable. This observation reveals maintenance of high chloramine residuals with single dosing alone at the time of re-chloramination is not an effective solution.

Total chlorine residuals at the time of nitrification in subsamples (A) and (B) (Table 2) were in the range of 0.55–0.70 mg Cl₂ L⁻¹ and the observation reveals maintaining chloramine residuals more than 0.70 mg Cl₂ L⁻¹ could facilitate in delaying the recurrence of nitrification or this residual could be used as an indicator to manage the residuals in distribution system. The observation, however, could be influenced by distribution system environment (such as temperature, retention time, biofilm, sediments, pipe materials and pipe ages) and water quality (pH, total chlorine, TAN, nitrite and nitrate residuals).

3.4. Re-chloramination in bulk water samples obtained from the laboratory-scale system

In order to verify the results obtained from full-scale distribution system, nitrified bulk water samples experienced different chemical concentrations (mainly total chlorine and nitrogenous species residuals) were collected from a laboratory-scale distribution system as detailed in Bal Krishna et al. [13,14]. The chemical parameters measured in Reactors-3–5 are shown in Fig. 5(A). The rapid drop of total chlorine and TAN residuals with sharp increase in NO_x concentration along the reactors demonstrates the bulk water samples experienced different nitrification stages. The pH of the bulk water samples obtained from Reactors-3 to 5 were 7.8, 7.7 and 7.65 and DOC were 2.86, 2.84 and 2.80 mg L⁻¹, respectively.

In agreement with the result obtained from full-scale bulk distribution system, this result further confirms a crucial role of bulk water characteristics at the time of re-chloramination in maintaining stable chloramine residuals. For example, lower chlorine decay rates were noted in the bulk water samples obtained

Table 3
NO_x-N production rate mg N L⁻¹ h⁻¹ for different incubation period

Sample	Nitrification rate (mg N L ⁻¹ h ⁻¹)		Time h
	Total chlorine 1.5 mg Cl ₂ L ⁻¹	Total chlorine 2.5 mg Cl ₂ L ⁻¹	
Subsample A	0.0014 ± 0.0001	0.0010 ± 0.0001	0–25
	0.0024 ± 0.0002	0.0009 ± 0.0001	25–75
	0.0011 ± 0.0001	0.0017 ± 0.0001	>75
Subsample B	0.0023 ± 0.0002	0.0015 ± 0.0001	0–25
	0.0027 ± 0.0002	0.0011 ± 0.0002	25–75
	0.0005 ± 0.0001	0.0023 ± 0.0002	>75
Subsample C	0.0003 ± 0.0001	0.0003 ± 0.0001	0–25
	0.0002 ± 0.0001	0.0006 ± 0.0001	25–75
	0.0007 ± 0.0001	0.0001 ± 0.0001	>75

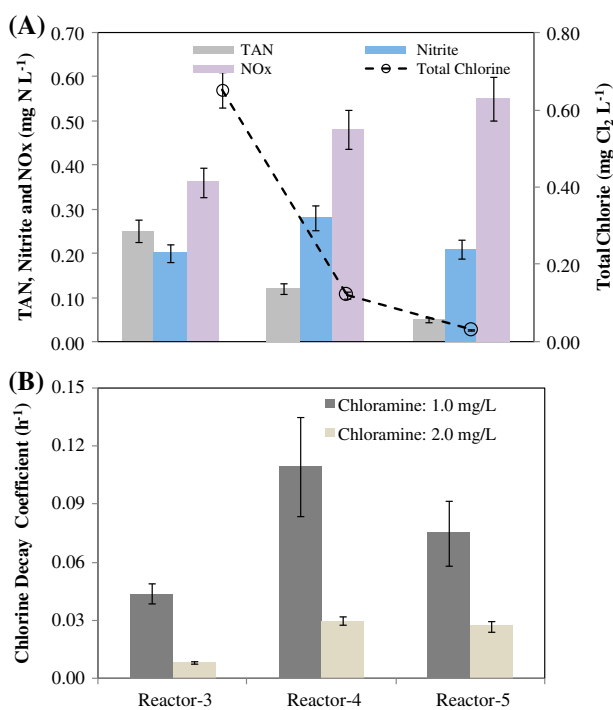


Fig. 5. Chemical parameters and total chlorine decay rates measured in bulk water samples obtained from the laboratory-scale system. (A) total chlorine and nitrogenous species profiles and (B) total chlorine decay rates.

from Reactor-5, while compared with Reactor-4 in both re-chloramination conditions (Fig. 5(B)). Similar to subsample (C), Reactor-5 experienced less TAN and total chlorine residuals (Fig. 5) than other two samples. Far lower decay rates (Fig. 5(A)) were noted in the samples obtained from Reactor-3. Although Reactor-3 experienced nitrification, the total chlorine and TAN residuals were higher than in other two reactors prior to re-chloramination. This observation further

reveals onset of nitrification could be delayed by carrying out re-chloramination at either early stage of the nitrification (such as Reactor-3) or near complete oxidation of TAN (such as Reactor-5 and subsample (C)).

3.5. Practical implication

Reverting chloramine residuals after the onset of nitrification is one of the biggest challenge for many water utilities. It has been reported that after the onset of nitrification, dosing a very high chloramine residual of 8.0 mg Cl₂ L⁻¹ was not enough to bring it under control [10]. This study, which was carried out using the bulk water samples obtained from the laboratory- and full-scale distribution systems, demonstrate that it is possible to delay the recurrence of nitrification and maintain a chloramine residual for an extended period of time. The study highlighted the importance of consideration of bulk water characteristics and initial chloramine residuals to be dosed prior to re-chloramination. According to this study, nitrification could be significantly delayed if either re-chloramination was carried out at an early stage of nitrification or when chloramine and TAN residuals dropped below the detection limit. However, considering the public health aspect, re-chloramination at latter stage of nitrification would be an inappropriate for water utilities. It is further essential to note that since these investigations were carried out using bulk water samples obtained from both systems, the required dose of re-chloramination in real distribution systems could vary as a result of demand from biofilm, sediments, pipe wall interactions, etc. [22]. Other factors not considered in the study were such as water temperature, bulk water characteristics (pH, DOC and other constituents, etc.), pipe materials and their age might also influence the observation.

4. Conclusions

This study investigates the effectiveness of re-chloramination in nitrified bulk water to control the recurrence of nitrification and to maintain sufficient chloramine residuals. Chloraminated bulk water samples collected from full- and laboratory-scale distribution systems were re-chloraminated with different doses of chloramine residuals at varying stages of nitrification and the conclusions made from this study are as follows:

- (1) Effectiveness of re-chloramination is largely dependent on nitrified bulk water characteristics and the initial chloramine residuals to be dosed. Chloramine decay rates were found to be comparatively slow when re-chloramination was carried out just after the onset of nitrification or after chloramine residuals dropped close to zero.
- (2) Chloramine residuals below $0.70 \text{ mg Cl}_2 \text{ L}^{-1}$ were found to be critical for the onset of nitrification.
- (3) By dosing a suitable chloramine residual at a proper time (based on bulk water characteristics), stability of chloramine residual could be improved.
- (4) The recurrence of nitrification could be delayed after redosing chloramine, but could not be completely prevented.

Acknowledgements

The authors acknowledge the funding offered by Curtin University. The authors would like to acknowledge Water Corporation, Western Australia for providing the samples and assisting during the sample collection.

References

- [1] J.A. Cotruvo, THMS in drinking water, *Environ. Sci. Technol.* 15(3) (1981) 268–274.
- [2] N.V. Brodtmann, P.J. Russo, The use of chloramines for reduction of trihalomethanes and disinfection of drinking water, *J. Am. Water Works Assn.* 71(1) (1979) 40–42.
- [3] X. Chen, P.S. Stewart, Chlorine penetration into artificial biofilm is limited by a reaction-diffusion interaction, *Environ. Sci. Technol.* 30(6) (1996) 2078–2083.
- [4] G.J. Kirmeyer, K. Martel, G. Thompson, L. Radder, W. Klement, M. LeChevallier, *Optimizing Chloramine Treatment*, AWWA Research Foundation, Denver, CO, 2004.
- [5] R.L. Wolfe, E.G. Means, M.K. Davis, S.E. Barrett, Biological nitrification in covered reservoirs containing chloraminated water, *J. Am. Water Works Assn.* 80(9) (1988) 109–114.
- [6] N.R. Ike, R.L. Wolfe, E.G. Means, Nitrifying bacteria in a chloraminated drinking-water system, *Water Sci. Technol.* 20(11–12) (1988) 441–444.
- [7] N.I. Lieu, R.L. Wolfe, E.G. Means, Optimizing chloramine disinfection for the control of nitrification, *J. Am. Water Works Assn.* 85(2) (1993) 84–90.
- [8] A. Sathasivan, I. Fisher, G. Kastl, Application of the microbial decay factor to maintain chloramine in large tanks, *J. Am. Water Works Assn.* 102(4) (2010) 94–103.
- [9] L.H. Odell, G.J. Kirmeyer, A. Wilczak, J.G. Jacangelo, J.P. arcinko, R.L. Wolfe, Controlling nitrification in chloraminated systems, *J. Am. Water Works Assn.* 88 (7) (1996) 86–98.
- [10] J. Skadsen, Nitrification in water distribution system, *J. Am. Water Works Assn.* 85(7) (1993) 95–103.
- [11] J.W.A. Charrois, S.E. Hrudey, Breakpoint chlorination and free-chlorine contact time: Implications for drinking water N-nitrosodimethylamine concentrations, *Water Res.* 41(3) (2007) 674–682.
- [12] K.C. Bal Krishna, A. Sathasivan, S. Garbin, Wider presence of accelerated chemical chloramine decay in severely nitrifying conditions, *Water Sci. Technol. Water Suppl.* 13(4) (2013) 1090–1098.
- [13] K.C. Bal Krishna, A. Sathasivan, Does an unknown mechanism accelerate chemical chloramine decay in nitrifying waters? *J. Am. Water Works Assn.* 102(10) (2010) 82–90.
- [14] K.C. Bal Krishna, A. Sathasivan, M.P. Ginige, Microbial community changes with decaying chloramine residuals in a lab-scale system, *Water Res.* 47(13) 2013 4666–4679.
- [15] EPA, *Methods for the Examination of Waters and Associated Materials, Ammonia in Waters*, 1981.
- [16] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*, twentieth ed., Washington, DC, 1998.
- [17] A. Sathasivan, I. Fisher, T. Tam, Onset of severe nitrification in mildly nitrifying chloraminated bulk waters and its relation to biostability, *Water Res.* 42 (14) (2008) 3623–3632.
- [18] P.S. Oldenburg, J.M. Regan, G.W. Harrington, D.R. Noguera, Kinetics of *Nitrosomonas europaea* inactivation by chloramine, *J. Am. Water Works Assn.* 94(10) (2002) 100–110.
- [19] W.D. Zhang, F.A. DiGiano, Comparison of bacterial regrowth in distribution systems using free chlorine and chloramine: A statistical study of causative factors, *Water Res.* 36(6) (2002) 1469–1482.
- [20] V. Gomez-Alvarez, K.A. Schrantz, J.G. Pressman, D.G. Wahman, Biofilm community dynamics in bench-scale annular reactors simulating arrestment of chloraminated drinking water nitrification, *Environ. Sci. Technol.* 48(10) (2014) 5448–5457.
- [21] A. Sathasivan, K.C. Bal Krishna, Major mechanism(s) of chloramine decay in rechloraminated laboratory scale system waters, *Desalin. Water Treat.* 47(1–3) (2012) 112–119.
- [22] A. Sathasivan, K.C. Bal Krishna, I. Fisher, Development and application of a method for quantifying factors affecting chloramine decay in service reservoirs, *Water Res.* 44(15) (2010) 4463–4472.