

## Kinetic modelling approach as a decision support tool for chloraminated distribution systems

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### ABSTRACT

Disinfection and distribution system management of chloraminated systems can be a challenging task for water operators due to the complexity of chloramine chemistry. Formation of chloramines and maintenance of a suitable disinfection environment requires careful control of several operational parameters at the plant and at different locations along the distribution system. A mathematical model to simulate different disinfection conditions, based on chemical equilibrium and kinetic calculations, both at the point of chemical dosing and downstream in the distribution system, was developed. Common operational parameters for chloraminated systems, such as initial chemical dosages and the chlorine to ammonia ratio, were assessed. In addition, simulations of some selected operational strategies, such as breakpoint chlorination and dosing control strategies (feed-back and feed-forward) at a re-dosing station, were conducted and assessed. This modelling approach can be used as a decision support tool for water treatment operators to manage and maintain disinfection.

**Key words** | chloramination, disinfection, kinetic model, water treatment

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### INTRODUCTION

Disinfection is a very important component of drinking water treatment to ensure that water delivered to customers is free of pathogens and hence is safe to drink. The main advantage of using chloramination over chlorination is the slow decay rate of the disinfectant residual and hence it provides effective disinfection over long distribution systems. However, to manage chloramination requires more control, as the chemistry is more complex and more sensitive to other outside factors than chlorination. When considering the available tools that operators can utilise to manage disinfection, modelling has become a more popular choice. The general chemical reactions of chloramine formation and decomposition are well described in the literature (Snoeyink & Jenkins 1980). However, chloramine formations and decompositions are highly dynamic and very susceptible to changes in chlorine and ammonia concentrations as well as changes in pH. There are several kinetic

models of chloramine formation and decomposition in the literature (Jafvert & Valentine 1992; Vikesland *et al.* 2001; Liu & Ducoste 2006). One common point of these models is that chloramines are described as inherently unstable, even without the presence of reactive inorganic or organic substances. They auto-decompose by a complex set of reactions that ultimately result in the oxidation of ammonia and the reduction of active chlorine. The kinetic model developed by Valentine (1998) is widely cited and is believed to accurately represent monochloramine decay in a distribution system. This model is pH and temperature dependent and including NOH, Cl<sup>-</sup>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and several unidentified reaction products as some products are not identified, this scheme is not nitrogen conservative (Vikesland *et al.* 2001; Liu & Ducoste 2006). Furthermore, this model does not take into account breakpoint chlorination (oxidation of chloramines by free chlorine).

The kinetics of breakpoint chlorination were studied independently by Saunier & Selleck (1979) and Wei (1972) and most of the available models described in the literature were reviewed by Stenstrom & Tran (1984). This model describes dichloramines as unstable and can decompose to nitrogen hydroxide. Then, nitrogen hydroxide reacts with monochloramine, dichloramine and free chlorine to form nitrogen gas and nitrates. This model is nitrogen conservative.

The chemistry of chloramination is complex and the behaviour of the different species cannot always be easily determined. This paper describes a new numerical simulation model, after considering all the aforementioned models, to optimise chloramination. This numerical simulation can be considered as a process control simulator, based on the water quality and dosing conditions to model disinfection downstream in the distribution system. This has potential to be applied within the water industry as a decision support tool for distribution system management.

## EXPERIMENTAL

### Model development

Considering all the aforementioned models, a new model was developed. The scheme of the 15 equations used is presented in Figure 1 and the kinetic constants are given in Table 1. This model is nitrogen conservative, pH dependent and valid at 25 °C.

In this paper, ammonia refers to the sum of  $\text{NH}_3$  and  $\text{NH}_4^+$  and total nitrogen refers to the sum of ammonia and of all the nitrogen combined in chloramines. As the numerical model is based on nitrogen conservation, the following molar concentrations are constant with time.

$$[\text{NH}_3] + [\text{NH}_4^+] + [\text{NH}_2\text{Cl}] + [\text{NHCl}_2] + [\text{NCl}_3] + [\text{NOH}] + 2 \times [\text{N}_2] + [\text{NO}_3^-] \quad (1)$$

That can be considered as a fixed amount of nitrogen introduced in a given system, and the model will determine the proportion of each species at a given pH.

The above considered chemical reactions were programmed in the software package, Gepasi. Gepasi is a widely used (freeware) package for kinetic simulations

(Mendes 1993, 1997; Mendes & Kell 1998). The kinetic modelling engine used in Gepasi is based on a mass action reversible mechanism.

$$\sum_i S_i \leftrightarrow \sum_j P_j \quad (2)$$

where  $S_i$  (substrate) reacts to form  $P_i$  (product) in a reversible way, the rate of reaction is given by the following equation:

$$v = k_1 \prod_i S_i - k_2 \prod_j P_j \quad (3)$$

where:

- $k_1$  is the rate constant of the reaction

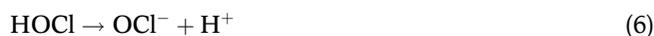
$$\sum_i S_i \rightarrow \sum_j P_j \quad (4)$$

- $k_2$  is the rate constant of the reaction

$$\sum_j P_j \rightarrow \sum_i S_i \quad (5)$$

- $S_i$  is the concentration of substrate  $i$
- $P_j$  is the concentration of substrate  $j$

Using Equation (6) as an example,



At steady state, the equilibrium expression is given by Equation (7) below:

$$\frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} = 10^{-\text{p}K_a} \quad (7)$$

and the concentration of each species is determined by the  $\text{p}K_a$  and the rate of reaction of the kinetic model is given by Equation (8) below:

$$v = k_1[\text{HOCl}] - k_2[\text{OCl}^-][\text{H}^+] \quad (8)$$

When the kinetic model has reached steady state as Equation (9) below:

$$\frac{k_1}{k_2} = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} \quad (9)$$



**Table 1** | Chloramine formation and breakpoint chlorination kinetic and decay model equilibrium constants and references

Chemical reaction	Rate constants of reaction (25 °C)	References
$\text{NH}_3 + \text{HOCl} \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_1 = 1.47 \times 10^{10} \text{ M}^{-1}\text{h}^{-1}$	$k_2 = 1.018 \times 10^{-1} \text{ h}^{-1}$ Vikesland <i>et al.</i> (2001)
$\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_1 = 1.28 \times 10^6 \text{ M}^{-1}\text{h}^{-1}$	$k_2 = 2.3 \times 10^{-3} \text{ h}^{-1}$ Vikesland <i>et al.</i> (2001)
$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \leftrightarrow \text{NHCl}_2 + \text{NH}_3$	$k_1 = k_{H^+} \times [\text{H}^+] + k_{\text{H}_2\text{CO}_3} \times [\text{H}_2\text{CO}_3] + k_{\text{HCO}_3^-} \times [\text{HCO}_3^-]$	$k_2 = 2.2 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$ Vikesland <i>et al.</i> (2001)
$\text{NHCl}_2 + \text{HOCl} \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O}$	$k_1 = 2.16 \times 10^{10} [\text{CO}_3^{2-}] + 3.24 \times 10^8 [\text{OCl}^-]^a$ $+ 1.18 \times 10^{13} [\text{OH}^-] \text{ M}^{-2} \text{ h}^{-1}$	$k_2 = \frac{19.3}{[\text{H}^+]} \text{ h}^{-1}$ Saunier & Selleck (1979); Vikesland <i>et al.</i> (2001)
$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{NOH} + 2\text{H}^+ + 2\text{Cl}^-$	$k_1 = \frac{3.24 \times 10^{-2}}{[\text{OH}^-]} \text{ h}^{-1}$	Saunier & Selleck (1979)
$\text{NH}_2\text{Cl} + \text{NOH} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^-$	$k_1 = 1.44 \times 10^7 \text{ M}^{-1}\text{h}^{-1}$	Wei (1972); Saunier & Selleck (1979)
$\text{NHCl}_2 + \text{NOH} \rightarrow \text{N}_2 + \text{HOCl} + \text{H}^+ + \text{Cl}^-$	$k_1 = 1.87 \times 10^8 \text{ M}^{-1}\text{h}^{-1}$	Wei (1972); Saunier & Selleck (1979)
$2\text{HOCl} + \text{NOH} \rightarrow \text{NO}_3^- + 3\text{H}^+ + 2\text{Cl}^-$	$k_1 = 1.44 \times 10^6 \frac{1}{1 + \frac{2.75 \times 10^{-8}}{[\text{H}^+]}} \text{ M}^{-1}\text{h}^{-1}$	Wei (1972); Saunier & Selleck (1979)
$2\text{HOCl} \rightarrow \text{Products}$	$k_1 = 400 \text{ M}^{-1}\text{h}^{-1}$	Bichani (2007); Bichani <i>et al.</i> (2008)
$2\text{OCl}^- \rightarrow \text{Products}$	$k_1 = 400 \text{ M}^{-1}\text{h}^{-1}$	Bichani (2007); Bichani <i>et al.</i> (2008)
$\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O}$	$\text{p}K_a = 14$	Vikesland <i>et al.</i> (2001)
$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$	$\text{p}K_a = 6.36$	Vikesland <i>et al.</i> (2001)
$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	$\text{p}K_a = 10.36$	Vikesland <i>et al.</i> (2001)
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	$\text{p}K_a = 9.3$	Vikesland <i>et al.</i> (2001)
$\text{HOCl} \leftrightarrow \text{OCl}^- + \text{H}^+$	$\text{p}K_a = 7.56$	Vikesland <i>et al.</i> (2001)

<sup>a</sup> with:  $k_{H^+} = 2.62 \times 10^7 \text{ M}^{-2}\text{h}^{-1}$ ,  $k_{\text{H}_2\text{CO}_3} = 4.03 \times 10^4 \text{ M}^{-2}\text{h}^{-1}$ , and  $k_{\text{HCO}_3^-} = 8.33 \times 10^2 \text{ M}^{-2}\text{h}^{-1}$ .

details can be found in [Motzko et al. \(2009\)](#). For all the simulations, the pH was set to 8 and the hardness of water was set to 112 mg/L expressed as  $\text{CaCO}_3$ .

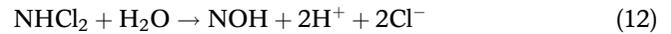
## RESULTS AND DISCUSSION

### Model development and validation

The curve of chlorine and ammonia residuals as a function of chlorine dose (generally referred to as the breakpoint chlorination curve) given by [Snoeyink & Jenkins \(1980\)](#) is the most cited in describing chloramination chemistry. [Figure 2](#) shows the simulation after 20 minutes of reaction for a fixed pH of 8. These curves confirmed that the developed model is able to reproduce the theoretical curves after a chosen time reaction with three sections of interest.

By simulating the processes at other pH values, it was found that at pH 7, the breakpoint curve was over predicted as the total chlorine decay was more advanced, and at pH 9 it was under predicted as the total chlorine decay was very slow. To understand this phenomenon, it is necessary to note that the breakpoint mechanism is based on the decomposition of dichloramine and does not account for

trichloramine or monochloramine ([Snoeyink & Jenkins 1980](#)). The equilibrium between these three species is quite fast compared to the break point mechanism



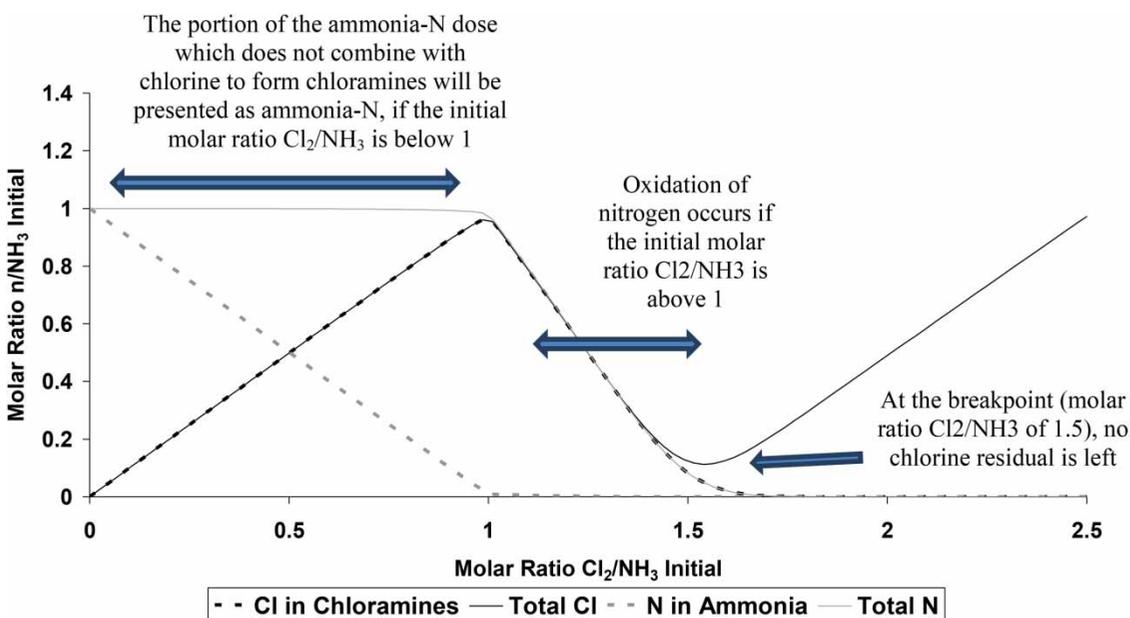
which is controlled by the pH value. Indeed the rate of this reaction is given by:

$$k_1 = \frac{3.24 \times 10^{-2}}{[\text{OH}^-]} \text{h}^{-1} \quad (13)$$

It has been shown experimentally that decomposition of dichloramines is slower at higher pH values ([Harrington & Noguera 2003](#)).

### Chloramine decay simulation with different chlorine to ammonia ratio

To illustrate the obtained breakpoint curves in more detail, three separate simulations were carried out at sections 1, 2 and 3 ([Figure 2](#)) shown in [Figures 3\(a\)–\(c\)](#) ( $\text{Cl}_2/\text{NH}_3$  molar ratio of 0.5, 1 and 1.5, respectively).



**Figure 2** | Chlorine and ammonia residual as a function of chlorine dose, results of Gepasi after 20 minutes of simulation, pH = 8.

In [Figure 3\(a\)](#), the initial concentration of ammonia is in excess compared to the initial concentration of chlorine. Therefore, there is excess ammonia remaining in the water, which can trigger nitrification problems downstream in the distribution system. In [Figure 3\(b\)](#), the initial ratio between ammonia and chlorine is ideal, hence maximum monochloramine formation occurred. Total chlorine and monochloramine curves coincide. The natural decay of monochloramine can be observed, with an expected release of ammonia in small amounts. In [Figure 3\(c\)](#), the initial concentration of chlorine is in excess compared to the initial concentration of ammonia. Therefore, breakpoint chlorination occurs and there is almost no disinfectant residual after 30 minutes.

These simulations were based upon chloramine chemistry and provided a good representation of chloramine decay with different chlorine to ammonia ratios. The relative concentrations of chlorine, ammonia and monochloramine were calculated in each case. These can be used to predict problems related to incorrect chlorine to ammonia ratio in the distribution system, such as the presence of ammonia, which will result in nitrification risk, or breakpoint chlorination which will result in rapid loss of residuals.

### Chloramine decay simulation of various initial ammonia and chlorine concentrations

The consequences of different initial chlorine and ammonia concentrations were investigated to confirm all possible combinations of initial concentrations of ammonia and chlorine, and hence to determine the optimum ratio. The initial concentrations of ammonia were chosen in uniform increments between 0 and 3 mg/L  $\text{NH}_3$  (100 increments) and the initial concentrations of chlorine between 0 and 6 mg/L  $\text{Cl}_2$  (also 100 increments). A total of  $10^4$  simulations were carried out. After 1 hour, the calculated concentrations of monochloramine, ammonia and the rate of oxidised nitrogen were saved for a simulation at a constant pH of 8.

[Figure 4](#) illustrates why the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1 is so widely used in the water industry. When chloramination is used in a distribution system the following characteristics are desired:

- maximisation of the monochloramine residual;
- minimisation of the ammonia residual;

- avoidance of the breakpoint chlorination zone.

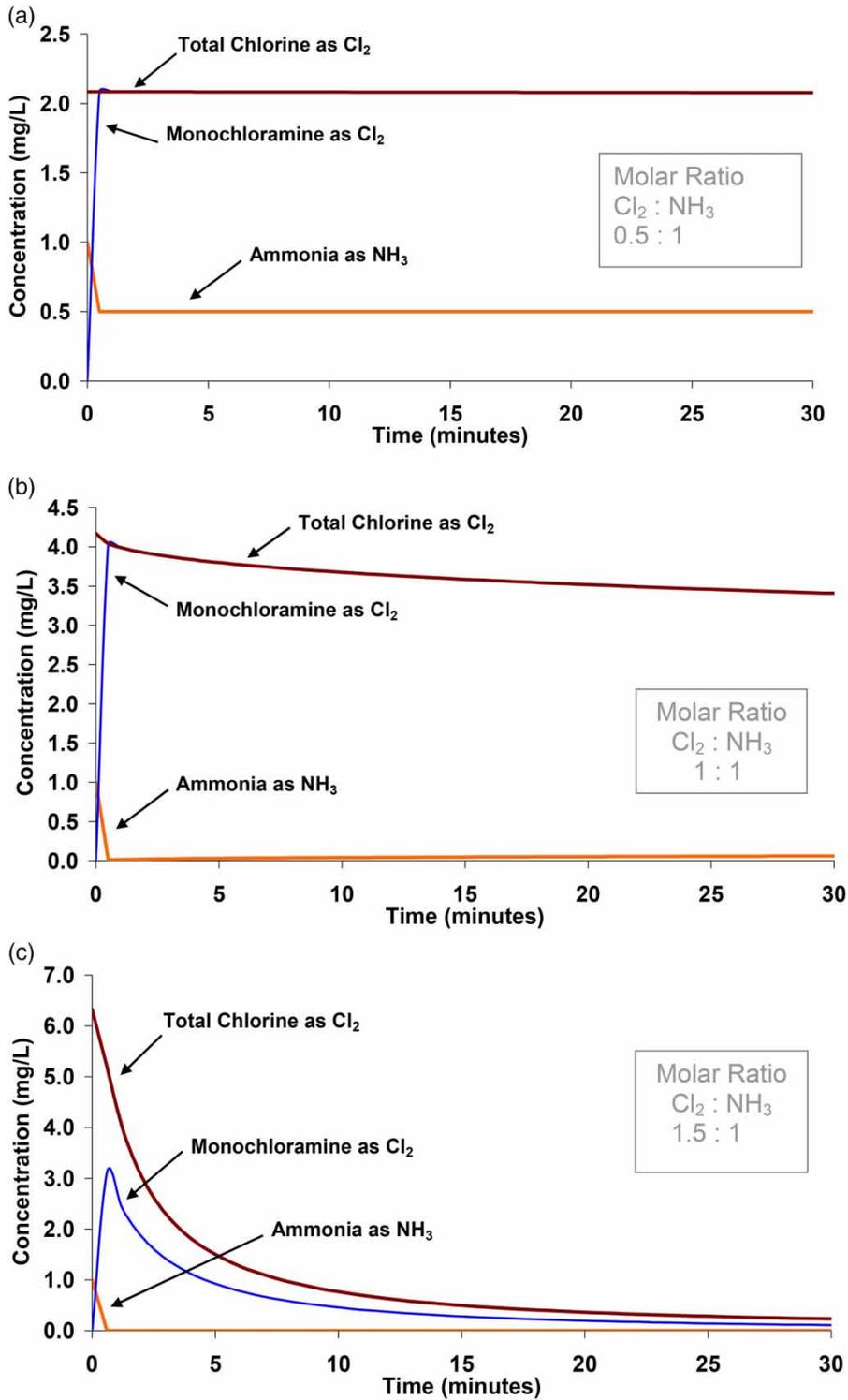
To interpret [Figure 4](#), two scenarios, initial  $\text{NH}_3$  concentration is given and initial  $\text{Cl}_2$  concentration is given, can be looked at. When the initial  $\text{NH}_3$  concentration is set, [Figure 4\(a\)](#) shows a precise range of initial chlorine concentration to form the maximum residual of monochloramine. This range is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. [Figure 4\(b\)](#) shows the minimum concentration of chlorine to add to form the minimum residual of ammonia. This minimum is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. Any extra initial chlorine dose does not help to remove more ammonia. For example, if the initial concentration of ammonia is 1 mg/L, then a  $\text{Cl}_2$  concentration of 4 mg/L is able to reach a residual ammonia concentration of 0. [Figure 4\(c\)](#) shows the maximum concentration of chlorine which can be added without entering the breakpoint chlorination zone. This maximum is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. Any extra initial chlorine will oxidise nitrogen. At a  $\text{Cl}_2:\text{NH}_3$  weight ratio of 6:1, the oxidation of nitrogen is total.

When the initial  $\text{Cl}_2$  concentration is set, [Figure 4\(a\)](#) shows the minimum concentration of ammonia to add to form the maximum residual of monochloramine. This minimum is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. Any extra initial ammonia does not help to create more monochloramine. [Figure 4\(b\)](#) shows the maximum concentration of ammonia which can be added to form the minimum residual of ammonia. This maximum is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. Any extra initial ammonia dose creates more ammonia residual. [Figure 4\(c\)](#) shows the minimum concentration of ammonia which can be added to avoid the breakpoint chlorination zone. This minimum is around the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. Any extra initial ammonia dose does not help to avoid the breakpoint chlorination zone.

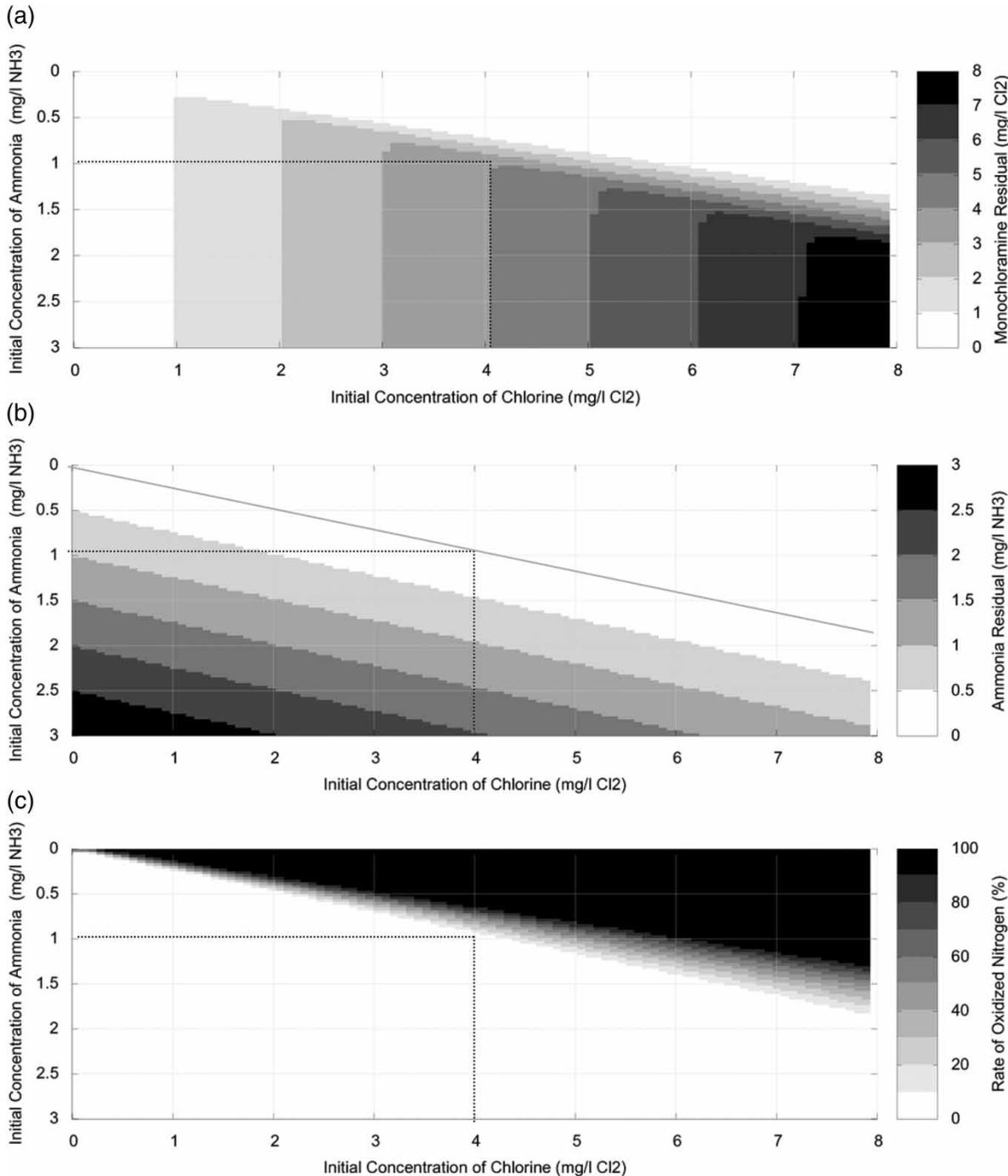
These simulations clearly show the importance of the  $\text{Cl}_2:\text{NH}_3$  ratio and they have confirmed that the weight ratio of 4:1 always achieves optimal results.

### Theoretical comparisons between different dosing strategies

In a typical distribution system, chlorine may be re-dosed to reform monochloramine when the desired level of residual



**Figure 3** | Chloramine decay simulation at pH = 8 with initial concentrations of (a) 1 mg/L  $\text{NH}_3$  and 2.1 mg/L HOCl as  $\text{Cl}_2$ , (b) 1 mg/L  $\text{NH}_3$  and 4.2 mg/L HOCl as  $\text{Cl}_2$  and (c) 1 mg/L  $\text{NH}_3$  and 6.3 mg/L HOCl.



**Figure 4** | (a) Monochloramine residual after 1 hour, pH = 8, (b) ammonia residual after 1 hour, pH = 8, and (c) rate of oxidised nitrogen after 1 hour, pH = 8.

is too low. Usually, only chlorine is re-dosed and not ammonia, as a residual of ammonia is expected to be present due to natural monochloramine decay. A typical method used in the water industry is to manually monitor the ammonia concentration and then deliver a constant concentration of

chlorine into the drinking water, with the chlorine dose being flow controlled. It is also possible to apply feed-forward control of chlorine dosing based on ammonia concentration measurement prior to the chlorine dosing, in order to maintain the  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1. The

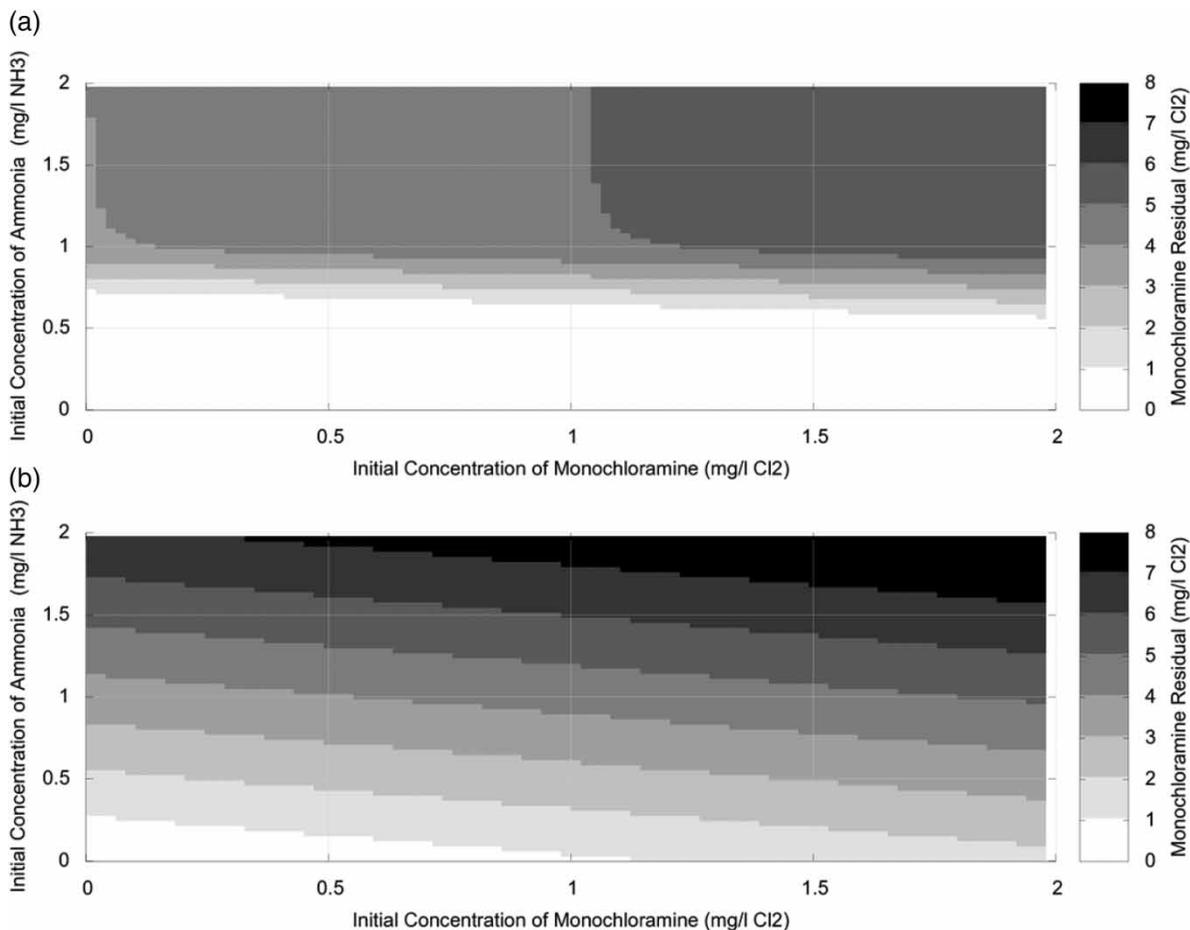
numerical model that was developed can be used to assess the fundamental differences between these two strategies by taking into account the two parameters that are likely to change at the re-dosing point, namely the ammonia and the monochloramine concentrations. For the simulations shown in Figure 5, these concentrations are called ‘initial concentrations’ as they are the input of the model.

Figure 5 shows that a constant chlorine dose of 4 mg/L as  $\text{Cl}_2$  is only effective when the initial concentration of ammonia is 1 mg/L as  $\text{NH}_3$ . Any drop of this ammonia level will lead to breakpoint chlorination, resulting in loss of monochloramine residual, and any increase of ammonia level will lead to excess ammonia in the drinking water, as no more monochloramine can be formed. In the alternative scenario, the feed-forward control enables a very efficient control as the monochloramine residual and  $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1

will always be maintained. In this situation, the ammonia residual is always minimised. As an additional benefit, Figure 5 shows that the monochloramine yield with the feed-forward control is always higher than with the conventional strategy, allowing reduced dosing to obtain an equivalent residual.

### Correlation between residual monochloramine and residual free ammonia

As seen in the previous section, the strategy of chlorine dosing to achieve constant chlorine residual works reasonably well when the initial free ammonia concentration is linearly dependent of the initial monochloramine concentration. This seems logical. Indeed it is expected that when more monochloramine is present, less free ammonia will be presented in the water (if the free ammonia comes from the



**Figure 5** | (a) Monochloramine residual after 10 hours, pH = 8, constant chlorine dose of 4 mg/L as  $\text{Cl}_2$  and (b) monochloramine residual after 10 hours, pH = 8, chlorine based on feed-forward control.

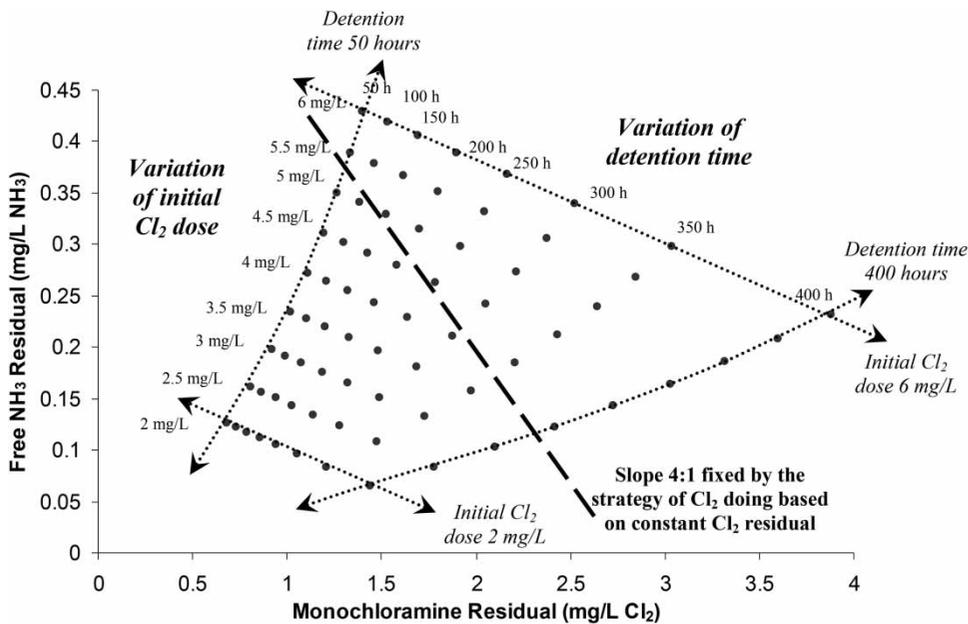
decay of monochloramine). However, whether this trend is linear or not is unknown and needs confirmation. The investigation here is to confirm this with several simulation runs to predict what would happen after the dosing at a water treatment plant and plot the residual of free ammonia as a function of monochloramine residual. The weight ratio of  $\text{Cl}_2:\text{NH}_3$  at the water treatment plant was fixed at 4 and the pH was fixed at 8. In total, nine different initial  $\text{Cl}_2$  dosings at the water treatment plant and eight different detention times were chosen for the simulations.

These two parameters are really likely to vary in the distribution system due to the variable water demand and the seasonal variation of  $\text{Cl}_2$  demand that leads to dose adjustment at the water treatment plant. That is to say, 72 different simulations were carried out and 72 points were plotted on Figure 6 showing the residual of monochloramine versus the residual of free ammonia.

In this figure, one line corresponding to the slope of the equation

$$[\text{Free NH}_3]_{\text{initial}} = \frac{[\text{Total Cl}_2]_{\text{wanted}} - [\text{NHCl}_2 \text{ as Cl}_2]_{\text{initial}}}{4} \quad (14)$$

was also plotted to establish whether this linear tendency is close to the cloud of points plotted on the graph.



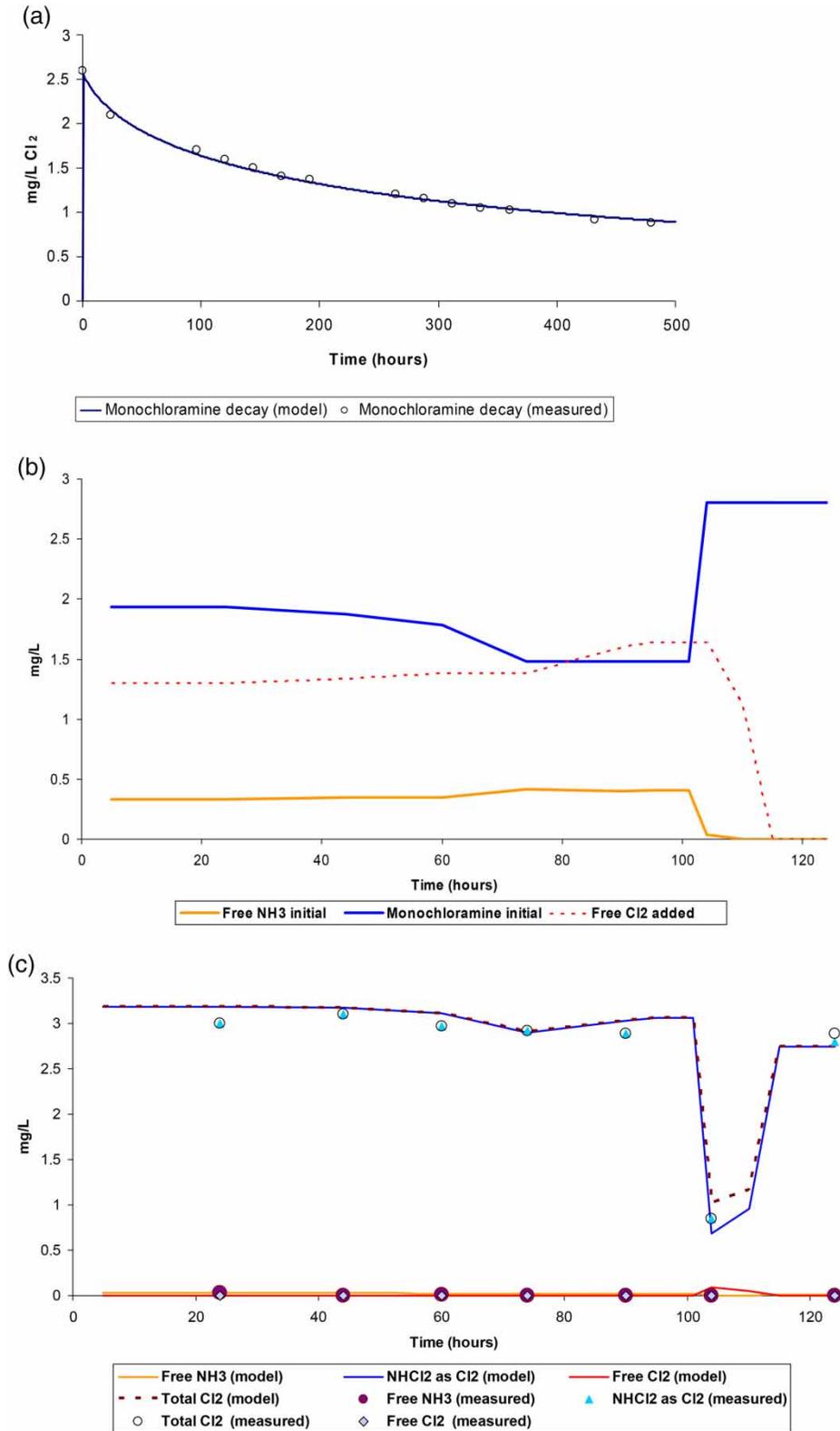
**Figure 6** | A simulation plot using nine different initial chlorine concentration and eight different detention times to illustrate the correlation between monochloramine and residual free ammonia concentration.

As seen in Figure 6, the dashed line is a really poor model and does not describe at all the cloud of points. That is to say, the re-dosing strategy based on feedback to achieve a constant  $\text{Cl}_2$  residual is clearly not appropriate for a chloraminated system. Hence the feed-forward strategy was demonstrated as the most efficient and flexible strategy among those studied.

### Using the numerical model to assess a simulated feed-forward control re-dosing strategy of a model distribution system

This feed-forward control was investigated based on using the study reported earlier (Motzko *et al.* 2009) which used the York re-dosing station, Western Australia, as model system. A 50 L tank simulated the distribution system and the free ammonia analyser was set inline after the tank. The chlorine dosing pump was located after the ammonia analyser and was controlled by the free ammonia concentration ( $\text{Cl}_2:\text{NH}_3$  weight ratio of 4:1). The available data for this experiment are shown below:

- Initially, the tank was again prepared with a monochloramine residual of 2.0 mg/L plus a free ammonia concentration of 0.3 mg/L.



**Figure 7** | (a) Monochloramine decay, (b) initial data for the numerical model and (c) results of the use of the numerical model based on feed-forward experience of the York re-dosing station, WA.

- At 62 minutes, 3 L of water ( $[\text{NH}_2\text{Cl}] = 0.16 \text{ mg/L}$ ;  $[\text{NH}_3] = 0.58 \text{ mg/L}$ ) were added to aim for a lower monochloramine residual of 1.6 mg/L and a higher free ammonia concentration of 0.4 mg/L in the tank,
- At 100 minutes, another 4 L of water was added with a free chlorine concentration of 4.73 mg/L to aim for a free ammonia residual of zero and a monochloramine residual of 2.8 mg/L.

After the optimisation process, the following kinetic factor was found:

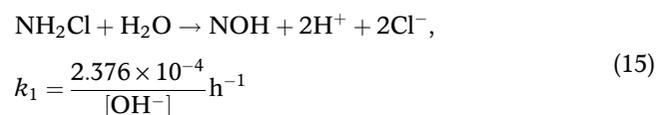


Figure 7(a) shows the plot of the calculated decay compared to the experimental one. All the input data are presented in Figure 7(b). The results of the numerical simulation (16 minutes of simulation time) are plotted on Figure 7(c). As we can see, we can observe a reasonably good match between the predicted concentrations and the measured ones, the breakpoint chlorination is especially well simulated.

## CONCLUSIONS

A kinetic model, based upon collation of published mechanisms, has been found suitable to predict chloramine chemistry, i.e. chloramine formation and breakpoint chlorination. This modelling approach was used to assess different strategies of maintaining good disinfection in the drinking water treatment plant and/or in the distribution network. The conventional re-dosing strategy based on feedback to achieve a constant total  $\text{Cl}_2$  residual was shown to be a less appropriate option for a chloraminated system. The new proposed feed-forward control re-dosing strategy was shown to be more effective.

Hence, this numerical model could be used as a tool to simulate chloramination behaviour in a water treatment plant or a distribution system and represents a very effective, quick and low cost way to assess disinfection performance. Particularly, this model would be useful for supporting

decisions concerning chloramination dose changes. The numerical model was shown to be simple and straightforward to use, requiring only the initial conditions (hardness, pH and initial concentrations of chlorine and ammonia) to predict all critical parameters for a given reaction time. If integrated into a water quality monitoring system or hydraulic model (such as EPANET), processing of real time data and assessment of performance of the disinfection process could be monitored, helping operators to improve the performance and reliability of the system.

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