Characters of chloramine decay in large looped water distribution system – the case of Tianjin, China

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ABSTRACT

In the water distribution system of a large city, chloramine could experience rapid decay as residence time extends, which may further threaten drinking water safety. A correlation analysis was conducted between the total chlorine residual of four sites on the distribution system and the water quality of the corresponding water treatment plant with data from 2016 to 2018 for the city of Tianjin. The results showed that the total chlorine residuals of all sites were negatively correlated with the temperature of the treated water, while the total chlorine residual of pipeline water did not uniformly correlate with that of the treated water. Further, a chloramine decay calculation study showed that pipe wall-induced decay contributes a lot of chloramine losses by conducting Total Chloramine Decay Model (TCDM) calibration with the monitored data. Hence, increasing the total chlorine residual of treated water, especially in the hot season, may not effectively maintain the disinfectant concentration at an ideal level.

Key words | biofilm, chloramine decay, drinking water safety

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INTRODUCTION

Disinfectant is widely applied in the field of water treatment and in distribution systems to prevent waterborne disease caused by microbial contamination. Chlorine, characterized by its high oxidation and disinfection ability, has been widely used as a secondary disinfectant for more than 100 years. Due to its rapid dissipation in drinking water and being prone to produce halogenated disinfection byproducts (DBPs) (Hoigné & Bader 1988), chlorine has been abandoned and substituted by chloramine as a secondary disinfectant in many urban cities with giant distribution networks. However, the distribution network has always been deemed to be a biochemical reactor that may make the treated water degenerate, which further threatens drinking water safety. Hence, the temporal and spatial variation in drinking water quality needs to be studied to further address the problems associated with chloraminated systems.

It is reported that the nitrification process is obviously activated in chloraminated systems, induced by ammonia doi: 10.2166/ws.2020.063 consisting of nitrifying bacteria and other heterotrophic bacteria, would consume a large amount of disinfectant in the course of sterilization. Besides, microbes could adapt to the chloraminated water upon exposure to chloramine of lower than $0.45 \text{ mg} \cdot \text{L}^{-1}$ (Herath & Sathasivan 2020), or even $0.65 \text{ mg} \cdot \text{L}^{-1}$ (Kulkarni *et al.* 2018), and further produce proteins to exhaust chloramine. Furthermore, nitrification could accelerate the process of destroying the anticorrosion coating of pipe walls through reduced pH and alkalinity (Zhang *et al.* 2008), which further leads to electrochemical corrosion of metallic iron to Fe (II) or Fe (III) by consuming chloramine. So chloramine decay induced by biochemical reactions at the pipe wall should be of great concern.

production when chloramine decays (Wilczak et al. 1996).

The increased biofilm attached to the pipe walls, mainly

To maintain the chlorine residual at the ideal level for the whole distribution system, chloramine concentration is significantly elevated in the treated water by many water



utilities, especially for the hot season. However, this strategy is barely satisfactory on the basis of practical experience. The reasonable disinfectant strategy may be deduced by resorting to well-calibrated modelling to obtain the water quality information within a distribution system. Several researchers have been working on developing kinetic models for chloramine decay in bulk water, consisting of a set of kinetic and thermodynamic reactions (Trofe et al. 1980; Kumar et al. 1987; Margerum et al. 1994; Vikesland et al. 1998; Duirk et al. 2005; Huang & McBean 2008). As a whole, these models of chloramine decay are developed in laboratory-scale batch systems, and are not capable of depicting all the decay processes, so the water quality model needs to be enriched by incorporating other reaction modules, and their usefulness can only be verified if they are applied to large-scale distribution systems.

In this article, we conducted systematic analysis for the city of Tianjin, which has a large looped distribution network with a pipeline length of more than 18,000 km. Firstly, we studied the law of variation in total chlorine residual of pipeline water at four sites with time. Secondly, we conducted a correlation analysis between the total chlorine residual of pipeline water and five water quality parameters of the corresponding treated water. Finally, we developed the Total Chloramine Decay Model (TCDM) by incorporating a nitrite oxidation module and wall decay module into the bulk decay model, and the role played by the pipe wall in overall chloramine decay was further analysed by conducting bulk decay model simulations and TCDM calibrations.

MATERIAL AND METHODS

The city of Tianjin, having more than 13 million people, is located in North China. The Lingzhuang Water Treatment Plant and Xinkaihe Water Treatment Plant are two of the four main water utilities, and use conventional water treatment technology. Their service area covers approximately half of central downtown with a design capacity of 500,000 m³·d⁻¹ and 1,000,000 m³·d⁻¹, respectively. A schematic of the Tianjin water distribution network is shown in Figure 1. The distribution network in Tianjin is constructed in looped form and

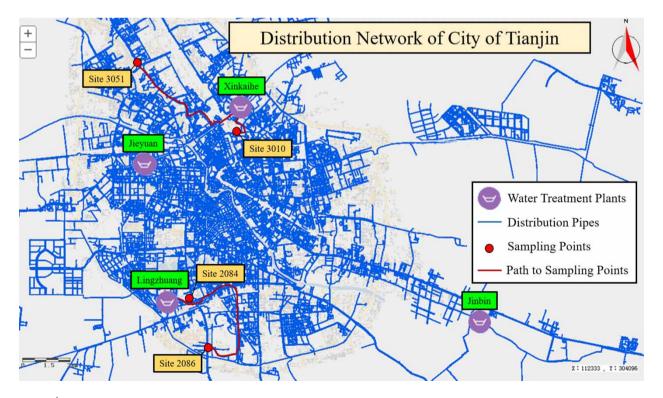


Figure 1 | Map of distribution network of city of Tianjin with treatment plant labelled by name and sampling points labelled by number. The flow paths to four sampling points from the corresponding treatment plants are shown by dark red solid lines.

mainly consists of steel pipes (main pipelines), ductile iron pipes, cast iron pipes and PE pipes (branch pipelines).

To present a precise connection between pipeline water and treated water, four sampling points (see Figure 1) were selected in the distribution network with different water ages. Also, all these sampling points are solely supplied by respectively one plant, as shown by the simulation results of BS software (Tianjin Sanbo Water Technology Co., Ltd. Tianjin, China), a calibrated GIS-based hydrodynamic calculation and visualization software. The sampling action started from January 8th 2016, through to August 21st 2018, covering different seasons for the four sampling points. A total of 248 pairs of total chlorine residuals of pipeline water and those (total chlorine residual, temperature, pH, NH₃-N, NO₂-N, turbidity) of corresponding treated water were obtained. The flow velocity varied from 1.0 to $1.2 \text{ m} \cdot \text{s}^{-1}$. The averaged pipe diameter was 0.84–1.00 m for the studied pipeline.

All water samples were collected from the four sampling sites and the corresponding utility, with a sampling interval of about 14 days for the same sampling site. The four sampling sites all have regularly used taps, without influence from any water filtration, softening or heating device. About 10 L of sample from each location was collected after initially drawing off the tap water for 3 minutes, and then flushing the container for 2 minutes. Total chlorine residual and water temperature were tested on site. The sample residuals were taken to the laboratory as soon as possible without refrigeration for further measurement of pH, NH₃-N, NO₂-N, and turbidity. Total chlorine residual, ammonia, and nitrite were measured using DPD colorimetric, Nessler's reagent, and sulphanilamide methods respectively. Turbidity and pH were tested by turbidity meter (HACH, TU5200) and pH meter (Mettler Toledo, S210-K) respectively.

Univariate correlation analysis was conducted between the total chlorine residual of the pipeline water and each of the five parameters of treated water from the corresponding treatment plant. In the course of univariate correlation analysis, only the parameters with significant correlation (p < 0.05) would be chosen as the independent variate to further do multivariate regression analysis. When carrying out multivariate regression analysis, we focused on two key statistical parameters; that is, adjusted R² and the significance of analysis of variance (ANOVA). Only when the adjusted $R^2 > 0.5$ and the significance of ANOVA <0.05 could the regression model be accepted. Univariate correlation analysis and multivariate regression analysis were conducted in the module of Bivariate Correlations and Linear Regression, respectively, in IBM SPSS Statistics (version 23). It is worth noting that the total chlorine residual was the only parameter obtained for treated water in 2016, and the monitored $NO_2^{-}N$ are uniformly lower than 0.001 mg·L⁻¹.

Chloramine loss within the distribution network could be classified into two types; that is, bulk phase decay and pipe wall induced decay. Of these, the bulk phase decay includes autodecomposition and oxidation of other substances in reduction state. We adopted the autodecomposition model containing 19 reactions, whose kinetic and thermodynamic coefficients were calibrated and validated for different pH and temperature conditions (Vikesland et al. 2001; Huang & McBean 2008; Ricca et al. 2019). As dissolved organic matter and nitrite are commonly observed in treated water or pipeline water, here we developed the bulk decay model by incorporating the total organic carbon (TOC) oxidation model and nitrite oxidation model into the autodecomposition model. The oxidation of TOC by chloramine was described as a biphasic second-order kinetic model using four specific reaction parameters. The slow and fast reaction coefficients, k_{DOC1} and k_{DOC2} , the percentage of slow and fast reactive sites, S_1 and S_2 , were set to be $3.45 \times 10^4 \text{ M}^{-1} \cdot \text{h}^{-1}$, $1.0 \times 10^5 \text{ M}^{-1} \cdot \text{h}^{-1}$, 0.016, and 0.57, respectively, as described by Ricca et al. (2019). The autodecomposition and TOC oxidation equations and the corresponding differential algebraic equations system could be referred to Ricca et al. (2019) and Wahman (2018). The oxidation of nitrite by chlorine was described as a third-order kinetic model as mentioned by Margerum et al. (1994) with $k_{\rm NO2}$ being $5.04 \times 10^{15} \,{\rm M}^{-2} \cdot {\rm h}^{-1}$. Further, the reaction of the pipe wall with chloramine is set to be a first-order kinetic reaction, and the reaction and its rate is expressed as follows:

$$NH_2Cl + Pipe wall \rightarrow Productions$$
 (1)

$$a_{\text{wall}} = -k_{\text{wall}}[\text{NH}_2\text{Cl}] \tag{2}$$

The parameter k_{wall} is the first order reaction kinetic coefficient, h^{-1} , capable of describing the mass-transfer process and wall decay process simultaneously (Rossman *et al.*)

1994; Huang & McBean 2008). Finally, the TCDM was developed by introducing pipe wall reaction into the bulk decay model to account for the chloramine decay induced by the pipe wall. The model, consisting of 19 differential equations for kinetic reactions and four algebraic equations for equilibrium reactions, was edited in C programming language on MATLAB software (version R2018b), and solved using differential algebraic equations (DAE) solver ode15 s.

The model calculation study was carried out on two utilities and the distribution network in Tianjin. Firstly, we selected eight sets of water quality data for treated water in different seasons and different utilities, see Table 1, as the initial condition to simulate the bulk decay model. Secondly, we used the total chlorine residual of the pipeline water and the corresponding water quality data of the treated water as the initial condition to calibrate the TCDM and consequently obtained the k_{wall} as the output parameter. The contribution of pipe wall-induced decay could be observed by comparing the results from the bulk decay model simulation and the TCDM calibration.

RESULTS AND DISCUSSION

Variation in total chlorine residual with time

Chloramine, as a widely used disinfectant, acts as an active substance that may react with many kinds of composites

 Table 1
 Initial conditions collected for the TCDM calibrations of the four scenarios

Troated water

dissolved or suspended in water. In the hot season, the reaction kinetics would be accelerated, which could lead to chloramine decay at a faster speed. Figure 2 presents the variation in total chlorine residual with time. As the monitoring action has a long time span, one could find the periodic variation character. For the sampling point with short water age, the total chlorine residual always maintains at a high level, which is comparative or equal to the value of the treated water (see Figure 2(a) and 2(c)). But the total chlorine residual of long distance water experiences a sharp decrease in the hot season, 6/2016-9/2016 and 6/2017-9/2017, to about $0.1 \text{ mg} \cdot \text{L}^{-1}$ or even lower (see Figure 2(b) and 2(d)). Hence, it is reasonable for the government to set the upper limit for the temperature of drinking water at the customer's taps, like the Netherlands (Agudelo-Vera et al. 2017), or shorten the time used to transport the water to customers, for example by construction of a looped system.

For sites 2,084 and 3,010, the water is pumped to the sites over about 2 h and 4 h, respectively, so there is not enough time for the treated water to deteriorate. This character is in accordance with recent research that found the wall decay could not be quantified in any period until travel time exceeded 4 h (Fisher *et al.* 2017). In other words, the water quality of short distance water is mainly controlled by the total chlorine residual of the treated water, irrespective of normal temperature changes and pipe wall effects. For sites 2,086 and 3,051, 45 h and 31 h,

Pipeline water			ireated water								
Site	Date	TCR ^a (mg·L ⁻¹)	T(°C)	pН	Alk ^b (mg·L ⁻¹)	MoCh ^c (mg·L ⁻¹)	DiCh ^d (mg·L ⁻¹)	NH ₃ -N (mg·L ⁻¹)	NO ₂ -N (mg·L ⁻¹)	TOC (mg·L ⁻¹)	
2,084	12/13/2017	0.80	7.2	7.8	85	1.00	0.01	0.46	0.001	2.00	
2,086		0.30									
2,084	5/28/2018	0.90	24.5	7.9	85	1.10	0.01	0.35	0.001	2.50	
2,086		0.10									
3,010	11/29/2017	0.80	11.0	7.9	86	1.10	0.01	0.36	0.001	1.95	
3,051		0.30									
3,010	6/19/2018	0.70	24.4	7.9	87	1.20	0.01	0.38	0.001	2.52	
3,051		0.10									

^aTotal chlorine residual.

^bAlkalinity

^cMonochloramine.

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^dDichloramine.

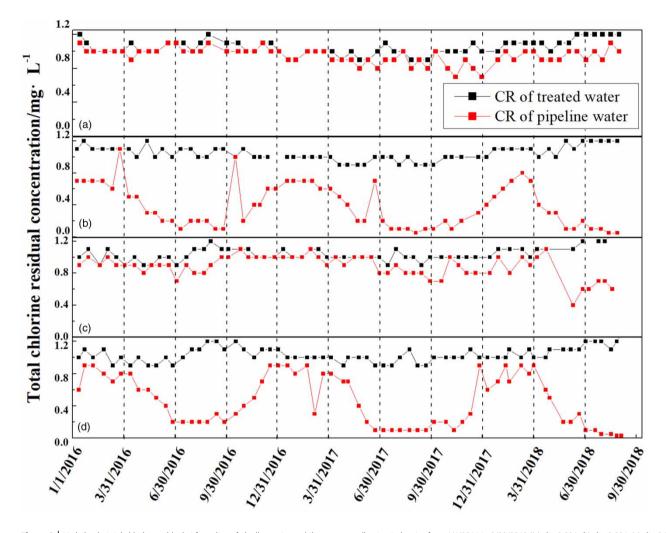


Figure 2 | Variation in total chlorine residual at four sites of pipeline water and the corresponding treated water from 1/1/2016 to 9/30/2018 ((a) site 2,084; (b) site 2,086; (c) site 3,010; (d) site 3,051).

respectively, are needed to pump the water from the utility to the sampling points. The field data show that the total chlorine residual of the two sites could be $0.4 \text{ mg} \cdot \text{L}^{-1}$ or even lower, while the modelling results under the same initial conditions show that considering the bulk phase demand only, the total chlorine residual would merely descend to 0.85 and 0.96 mg $\cdot \text{L}^{-1}$, for sites 2,086 and 3,051 respectively (see Figure 3). The sharp contrasts between field data and modelling results shed light on the potential demands on disinfectant within the pipe, including corrosive reactions with the wall material itself, with adhering biofilms and with accumulated sediments (Brown *et al.* 2017), which would be more prominent in summer and autumn. Consequently, temperature and pipe wall may play a significant role in decreasing chloramine concentration, especially in the hot season.

Correlation between total chlorine residual of pipeline water and water quality of treated water

Treated water, being the source of tap water, must affect the quality of pipeline water to some extent, such as the relationship between the temperature of the treated water and the total chlorine residual of the pipeline water, as mentioned above. Hence, a statistical analysis of the correlation between the total chlorine residual of pipeline water and five water quality parameters of the treated water was conducted for the case of the distribution network of Tianjin. As shown in

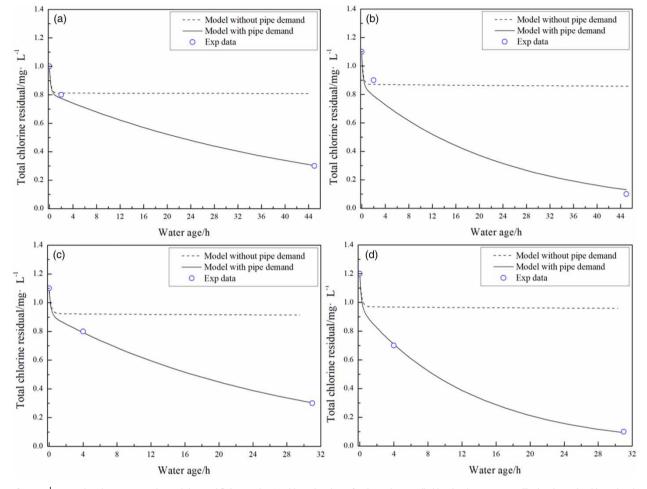


Figure 3 | Comparison between experimental data and fitting results. (a) Chloramine decay for the region supplied by Lingzhuang water utility in winter. (b) Chloramine decay for the region supplied by Xinkaihe water utility in winter. (d) Chloramine decay for the region supplied by Xinkaihe water utility in winter. (d) Chloramine decay for the region supplied by Xinkaihe water utility in summer.

Table 2, the total chlorine residual of site 3,010 is positively correlated with pH in 2017, and negatively correlated with temperature and NH₃-N in 2018, but the multivariate regression analysis further confirms that there's no significant correlation with these parameters. For site 2,084, with shorter travelling time, the total chlorine residual is positively correlated with that of treated water. As a whole, the total chlorine residual of the short distance water does not show significant correlation with the parameters of the corresponding treated water.

The total chlorine residual of site 3,051 is negatively correlated with temperature in 2017, and negatively correlated with total chlorine residual, temperature and NH_3-N in 2018, and positively correlated with pH in 2018 in the univariate correlation analysis. The multivariate regression analysis further confirms the negative correlation of total chlorine residual with water temperature in 2017, and negative correlation with total chlorine residual and water temperature simultaneously in 2018. For site 2,086, the total chlorine residual is negatively correlated with temperature, positively correlated with total chlorine residual, and pH in 2017, and negatively correlated with temperature and total chlorine residual, and positively correlated with NH₃-N in 2018. In a word, the total chlorine residual of the long distance water is strongly affected by the water temperature, as shown by the large standardized regression coefficients, while the influence from the total chlorine residual, pH, and NH₃-N of treated water is still vague.

Site	Year	Parameter	Univariate correlation analysis					Multivariate regression analysis						
			TCR ^a	ТÞ	рН	NH ₃ -N	Tur ^c	Adjusted R ²	Significance of ANOVA	TCR ^d	T ^d	рН ^d	NH ₃ -N ^d	Tur ^d
3,010	2,016	CR	NA	/	/	/	/	/	/	/	/	/	/	/
	2,017	CR	NA	NA	+	NA	NA	0.226	0.013	/	/	NA	/	/
	2,018	CR	NA	-	NA	_	NA	0.286	0.106	/	NA ^e	$^{\rm f}$	NA	/
3,051	2,016	CR	NA	/	/	/	/	/	/	/	/	/	/	/
	2,017	CR	NA	_	NA	NA	NA	0.548	0.000	/	-0.757	/	/	/
	2,018	CR	_	_	$+^{g}$	_ ^h	NA	0.915	0.000	-0.282	-0.731	NA	NA	/
2,084	2,016	CR	+	/	/	/	/	/	/	/	/	/	/	/
	2,017	CR	NA	NA	NA	NA	NA	/	/	/	/	/	/	/
	2,018	CR	NA	NA	NA	NA	NA	/	/	/	/	/	/	/
2,086	2,016	CR	NA	/	/	/	/	/	/	/	/	/	/	/
	2,017	CR	+	_	+	NA	NA	0.622	0.006	NA	-0.725	NA	/	/
	2,018	CR	_	_	NA	+	NA	0.874	0.000	NA	-0.868	/	NA	/

Table 2 | Statistical analysis of correlation between total chlorine residual of pipeline water and five parameters of treated water from the corresponding treatment plant

^aTotal chlorine residual, ^bWater temperature. ^cTurbidity. ^dThe data in the column are standardized regression coefficients. ^eNo statistical significance of that correlation. ^fNot included in the correlation analysis. ^gPositive correlation with statistical significance. ^hNegative correlation with statistical significance.

Temperature is a key environmental factor that strongly influences every biochemical reaction process pertaining to chloramine decay. Up to now, the relationship between temperature and the chloramine decay reaction in bulk water has been quantitatively studied by researchers around the world; however, the temperature dependence of the reaction of chloramine with the pipe wall, especially for the attached biofilm, has not been precisely described. Neden et al. (1992) found that microbes' activity would be stimulated when the distribution system water is 15 °C or warmer, which leads to serious microbial problems. Tianjin, affected by monsoon in the northern hemisphere, experiences obviously periodic variation in air temperature; accordingly, the water temperature of the Tianjin distribution network is higher than 25 °C in summer, and lower than 5 °C in winter. Consequently, high microbial activity induced by temperature elevation would exacerbate the chloramine loss more significantly in summer than that in winter, which results in the significantly negative correlation of total chlorine residual with water temperature.

The counter-intuitively negative correlation between total chlorine residual of treated water and that of pipeline water for site 3,051 may be caused by the high dosing of disinfectant in the water utility and strong exhaustion of chloramine after long distance travel in summer. Further, considering the lack of statistical correlation between the total chlorine residual of treated water and that of pipeline water for other sites (see multivariate regression analysis results in Table 2), it could be inferred that the disinfectant concentration of pipeline water could hardly be maintained at an ideal level only by increasing the total chlorine residual of treated water, especially in the hot season.

The role of bulk decay in the overall loss

No matter what kind of pipeline is used for water distribution, disinfectant would experience a bulk decay process, including autodecomposition and oxidation of substances in the reduction state. The simulation results for chloramine decay in bulk water are shown by a dashed line in Figure 3. It can be seen that as water ages, the total chlorine residual experiences two distinct phases in bulk water, a fast decay phase within the first few hours followed by a slow decay phase. This dual-phase character, presumably caused by initially fast oxidation of TOC in water, has further verified the conclusion drawn by Ricca et al. (2019) and Wahman (2018). After the first few hours' fast decay, the total chlorine residual for all the cases steps into the extremely slow decay phase, within which the total chlorine residual would remain stable. In other words, TOC's function in chlorine loss is transient and intense, while the autodecomposition is persistent and weak under the ambient conditions studied here.

Contribution of pipe wall-induced decay to the overall loss

Given that the bulk decay is the only cause of chloramine loss, the total chlorine residual of pipeline water with water age >4 h would be $0.8-1.0 \text{ mg} \cdot \text{L}^{-1}$. However, the monitored data (circle in Figure 3) show significant contradiction to the simulation results. Hence, with the monitored total chlorine residual of pipeline water as the initial condition (see Table 1), we further conducted TCDM calibration to tell different chloramine decay processes apart. The calibration results of overall chloramine decay are shown by the solid line in Figure 3. Firstly, it can be seen that the calibrated model could well represent the monitored data. Secondly, it is visually obvious that the overall decay also has a dual-phase character, which is similar to the bulk decay. But there's a sharp contrast between bulk decay and overall decay in the second phase; precisely, the difference in total chlorine residual concentration becomes more and more prominent as water age increases. The calibrated parameters are tabulated in Table 3.

The parameter k_b (bulk decay coefficient) varies from $1.00-1.33 h^{-1}$ to $4.36 \times 10^{-3}-8.33 \times 10^{-3} h^{-1}$, the former corresponding to the initial fast decay process mainly induced by TOC demand, the latter corresponding to the autodecomposition process. The k_b presented here is similar to those time-averaged k_b from another two field studies, one is $1.5 \times 10^{-3}-5.9 \times 10^{-3} h^{-1}$ for bulk decay in service reservoirs (Sathasivan *et al.* 2010), and the other is $1.27 \times 10^{-3}-2.13 \times 10^{-3} h^{-1}$ for bulk decay in a distribution system (Liu *et al.* 2015). Moreover, it is worth mentioning that the parameter k_b shows little regional or seasonal difference in our study. However, the calibrated parameter k_{wall} (comprehensive wall decay coefficient) remains at a low level $(2.16 \times 10^{-2}-3.54 \times 10^{-2} h^{-1})$ in winter, and ascends to a high level $(4.17 \times 10^{-2}-7.51 \times 10^{-2} h^{-1})$

summer. The seasonal changes in k_{wall} manifest the sensitivity of wall demand to the temperature variation, which is in accordance with the findings summarized in the correlation analysis. Further, the ratio, k_{wall}/k_b , appears to be very small in the early decay phase, but grows larger and larger as the travelling time increases (see the last column in Table 3). The persistent consumption of wall demand is pretty weak relative to the transient consumption of TOC oxidation, but is 5–9 times stronger than the persistent consumption of autodecomposition.

As reported previously, the parameter k_{wall} could be further expressed as follows:

$$k_{\text{wall}} = \frac{4k_{\text{f}}k_{\text{w}}}{D(k_{\text{f}} + k_{\text{w}})} \tag{3}$$

where $k_{\rm f} =$ mass transfer coefficient, m·s⁻¹; $k_{\rm w} =$ near wall decay coefficient, m·s⁻¹; D = diameter of the circular tube, m. Consequently, the comprehensive wall decay could further be subdivided into two processes; that is, chloramine transfer from the bulk phase to the near wall lamina, and chloramine consumption by the pipe wall. The free chlorine decay induced by the pipe wall could also be expressed by Equation (3); a field study on a free chlorine disinfection system reported a $k_{\rm f}$ of $2 \times 10^{-6} - 10^{-5}$ m·s⁻¹ (Huang & McBean 2008), which is similar to our modelling results, and a $k_{\rm w}$ of $1.04 \times 10^{-2} - 1.46 \times 10^{-2}$ m·s⁻¹ (Huang & McBean 2008), which is three orders of magnitude larger than the $k_{\rm w}$ for chloramine decay reported here (see Table 3). Hence, relative to chloramine, free chlorine is more reactive to the pipe wall.

Further, as shown in Table 3, k_f varies insignificantly for the four cases studied here, which is mainly caused by the little changes in tube diameter, flow velocity, and viscosity of water with region and season. However, k_w in summer is about 3 (for Lingzhuang water utility) and 17 (for

Table 3 | Summary of chloramine decay coefficients obtained from TCDM calibration and bulk decay model simulation

Region	Season	$k_{\rm b}$ (h ⁻¹)	$k_{ m wall}$ (h ⁻¹)	<i>k</i> _f (m⋅s ⁻¹)	<i>k</i> _w (m⋅s ^{−1})	k _{wali} /k _b
Lingzhuang water utility	Winter	4.36E-3-1.00	2.16E-2	3.09E-6	2.89E-6	0.02-5.0
Lingzhuang water utility	Summer	5.59E-3-1.33	4.17E-2	4.23E-6	9.04E-6	0.03-7.5
Xinkaihe water utility	Winter	6.30E-3-1.33	3.54E-2	3.64E-6	4.88E-6	0.03-5.6
Xinkaihe water utility	Summer	8.33E-3-1.33	7.51E-2	4.67E-6	8.49E-5	0.06-9.0

Xinkaihe water utility) times larger than that in winter. So the temperature elevation could remarkably enhance the reactivity of the pipe wall to consume the chloramine to some extent. The pipe wall could be deemed as a reactive integrity consisting of an attached biofilm, exposed wall material, and other sediments, the reactions of which with chloramine are temperature dependent (Li *et al.* 2019). The variation in bacterial species (Sathasivan *et al.* 2009), the production and release amount of chloramine decaying proteins (Herath & Sathasivan 2020), and so on, may lead to k_w varying over a wide range with pipelines and ambient conditions, as shown in our study.

CONCLUSION

Total chlorine residuals of four sites in the Tianjin distribution network were monitored continuously for a long time span of more than 2.5 years, and analysed by referencing to the corresponding total chlorine residual of treated water. It is observed that the total chlorine residual of pipeline water with water age >31 h would experience fast decay in summer, while pipeline waters with water age <4 h do not show seasonal changes in total chlorine residual. Not only that, the correlation analysis confirms that water temperature could govern the chloramine decay behaviour for long travelling water, but the total chlorine residual of treated water is not uniformly positively correlated with that of pipeline water, with one case showing negative correlation between the two parameters. So it is not reasonable to maintain the disinfectant concentration of long travelling water at an ideal level only by increasing the total chlorine residual of treated water, especially in the hot season. The newly developed TCDM model could well represent the monitored data under the given water quality. The model calculation results show that the wallinduced decay rate is 5-9 times the rate of autodecomposition, and larger differences are accompanied by higher temperature. Furthermore, the more prominent wall decay with temperature could be ascribed to the enhanced reactivity of the pipe wall as shown by the increased $k_{\rm w}$. But given that k_w varies with pipelines and ambient conditions, it is suggested to utilize the calibrated decay coefficients to predict the total chlorine residual of pipeline water for specific water distribution routines under similar ambient conditions.

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