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Batch test to evaluate microbial disinfectant decay and the onset of nitrification

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ABSTRACT

A batch test procedure was investigated to provide insight into the microbial contribution to disinfectant decay in drinking water distribution systems using chloramines. A modified method for determining the critical threshold residual (CTR), the intersection point on a semi-log plot between first-order total chlorine fitted decay curves before and after the breakpoint, was developed. Unlike the CTR as originally defined, initial sample conditions were retained rather than artificially raising the monochloramine concentrations. The CTR calculated with this modified method can more easily be applied to distribution system scenarios. In addition, four types of decay curves were identified and could distinguish differences in the microbial contribution to disinfectant residual decay. This study revealed that chloramine decay batch tests should be evaluated based on decay curve type, decay rates, and the CTR value, in addition to the microbial decay factor, which has been used alone in previous studies. The batch test approach and evaluation criteria established here can be used to predict conditions favorable for rapid chloramine decay and nitrification, and that monitoring and control strategies should be implemented.

Key words: chloramine, chlorine residual, critical threshold residual, decay curve, microbial decay factor, nitrification

HIGHLIGHTS

- The developed batch test procedure distinguishes between chemical and microbial contributions to chloramine decay and determines nitrification potential.
- The critical threshold residual (CTR) was identified as the intersection of fitted first-order total chlorine decay curves before and after a breakpoint.
- Batch tests were evaluated by decay curve type, decay curve rate, CTR, and microbial decay factor.

INTRODUCTION

In distribution systems using monochloramine as a secondary disinfectant, nitrification can result in accelerated decay of the chloramine residual, which can lead to regulatory compliance issues and potentially decrease robustness. Nitrification is the process in which ammonia-oxidizing microorganisms, such as ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA), convert ammonia to nitrite, which can be further oxidized to nitrate (e.g., Scott *et al.* 2015). Monitoring for nitrification can be a challenge as indicators, such as a rise in nitrite and nitrate concentrations, may not be present or may not provide advance warning of nitrification episodes before they are fully established (Pintar *et al.* 2005). Some tools have been developed to indicate that conditions in a distribution system could lead to nitrification events, and that monitoring and control strategies should be implemented. One approach is a batch test method developed by Sathasivan *et al.* (2005, 2008). This test inhibits microbial activity and compares the chloramine decay to parallel uninhibited samples, and as a result, the chemical and microbial contributions to monochloramine decay can be identified.

Sathasivan *et al.* (2005) defined a quantity called the microbial decay factor (F_m) as the ratio between the microbial decay coefficient (k_m) and the chemical decay coefficient (k_c) that contribute to the overall chloramine decay rate. One of the advantages of this batch test method is that it provides a way to quantify the role of microbially mediated chloramine decay without direct enumeration. In a follow-up study, Sathasivan *et al.* (2008) extended the batch test method to identify

the critical threshold residual (CTR), which is the point at which the total chlorine decay rate begins to increase rapidly in some situations. The phenomenon of two phases of the total chlorine decay in these batch tests was also observed by Sathasivan *et al.* (2010). The batch test method of Sathasivan *et al.* (2005, 2008) has been applied to studies on full-scale drinking water distribution systems. Fisher *et al.* (2009) applied the F_m to reservoir stratification. The method was able to show that microbial stratification persisted in winter, even though the reservoirs were no longer thermally stratified and chemical indicators did not show stratification. Sathasivan *et al.* (2010) implemented a successful reservoir management strategy using the F_m as a performance metric. However, relying on F_m alone can be misleading, as it can have similar values in waters with very different rates of chloramine decay. As well, F_m cannot provide direct evidence of microbially mediated nitrification, only the overall contribution of microorganisms to the chloramine decay rate (Sathasivan *et al.* 2005; Herath *et al.* 2015; Sawade *et al.* 2016). Thus, there is a need to develop a holistic approach for determining the potential for rapid chloramine decay and the onset of nitrification in distribution systems.

In this study, a batch test method was applied to water samples collected from two full-scale chloraminated drinking water distribution systems. These systems were previously shown to have indicators of nitrification, including sporadic occurrences of nitrite concentrations above the threshold value of 0.025 mg-N/L that may be indicative of a nitrification episode and the presence of ammonia-oxidizing microorganisms as measured by both PCR and culture methods (Scott 2012; Scott *et al.* 2015). The objectives of the current study were to analyze the approach in Sathasivan *et al.* (2005, 2008) for determining the potential for microbially mediated chloramine decay and the onset of nitrification at sites that had previously shown evidence of nitrification in the City of Toronto and the Region of Waterloo drinking water distribution systems in Ontario, Canada, and to further develop the evaluation criteria for analyzing test results. The evaluation criteria identified can be more readily applied to monitoring and operational practices in distribution systems where chloramine decay and nitrification are potential concerns.

METHODS

Sample collection

Sampling locations were selected from sites in two full-scale chloraminated drinking water distribution systems that had been previously monitored over a 9-month period (2009–2010) (Scott *et al.* 2015). The City of Toronto uses Lake Ontario as a source water, and the Region of Waterloo blends water from the Grand River with groundwater. Water entering both distribution systems had an average pH of 7.5, and water temperatures over the 9 months were 10 ± 2 °C (Toronto) and 12 ± 6 °C (Waterloo). A more detailed description of the drinking water treatment and distribution systems is provided in Scott *et al.* (2015). Based on this previous information, a range of sites that had shown differing water quality characteristics were included in the present study. Samples were collected from the City of Toronto distribution system on 17 August 2010 and 17 October 2010, and the Region of Waterloo distribution system on 12 October 2010 and 24 November 2010. The sample locations that were selected included the water leaving each treatment facility and entering the corresponding distribution system (T-WTP and W-WTP), the sites with the lowest disinfectant residual (T-2 and W-7), the sites with the highest concentration of AOB (T-5 and W-4), and the sites with a stable disinfectant residual (T-3 and W-6) (refer to Supplementary Material, Figures S1 and S2). Samples collected at the treatment plants were taken from continuous-flow sampling taps. Prior to sampling in the distribution systems, taps were flushed until the water had reached a steady temperature, indicating that the collected water was from the distribution system and not the premise plumbing. The samples were then collected in sterile 1 L glass bottles. Additional details on the sampling procedure can be found in Scott *et al.* (2015).

Parameters measured

Total chlorine, monochloramine, nitrate, nitrite, and ammonia were measured in accordance with Hach Methods 8167, 10171, 8171, 8507, and 10200, respectively (Hach Water Analysis Handbook Procedures 2008).[1] The pH was measured with standard method 4500-H^+ (Standard Methods for the Examination of Water and Wastewater 2005) with an Orion 290A pH meter and an Ag/AgCl electrode probe. Heterotrophic plate counts were measured based on standard method 9215 (Standard Methods for the Examination of Water and Wastewater 2005). See Scott *et al.* (2015) for additional details on the analytical methods that were used to measure the water quality parameters. The pH was measured on-site, while the

[1] The 5th edition handbook is no longer available; the new version can be found at https://www.hach.com/wah.

other parameters were measured at the University of Waterloo. The background water quality of the samples used in the experiments is shown in Table 1. Additional water quality data for samples collected at these sites based on previous experimental work can be found in Scott *et al.* (2015).

Batch test procedure

Each sample was divided into 15 sterile plastic 50 mL vials. Half of the vials were unamended, and the other half were inhibited by adding 0.25 mL of 20 mg-Ag/L $AgNO_3$, resulting in a final concentration of 100 μg-Ag/L. The effectiveness of silver nitrate as a microbial inhibitor was demonstrated in Scott (2012) by comparing decay results from inhibited and 0.2 μm filtered samples. While these methods can remove the effect of ongoing microbial activity, there may be soluble microbial products (SMPs) still present that can also contribute to accelerated decay of the disinfectant residual (Herath *et al.* 2018). Vials were incubated stationary at room temperature (20–22 °C). Initially, total chlorine was measured at the start of the experiment and after every 2 days during the batch test experiments, with the vials being sacrificed after each measurement. The experiments were continued until the chlorine concentrations were below the detection limit, up to a maximum of 648 h (27 days). The monitoring frequency was then adjusted as necessary depending on its decay rate. Monochloramine was measured in parallel with total chlorine in the batch test experiment using water collected from Toronto (17 October) and Waterloo (12 October), and at the start and end only for Waterloo samples collected on 24 November. Free ammonia and nitrite were measured at the beginning and end of batch tests conducted using water collected from Toronto (17 October) and Waterloo (12 October and 24 November) and nitrate at the beginning and end of samples collected on 24 November.

Analysis of results

After the completion of the batch test, chlorine decay curves were constructed and evaluated. The k_c and k_m for the total chlorine residual and the F_m were calculated as described by Sathasivan *et al.* (2005, 2008). Briefly, total chlorine residuals were plotted against time on a semi-log plot, and the slopes (equivalent to the first-order coefficients due to the logarithmic transformation) were calculated. The inhibited subsamples had a steady slope, but the uninhibited subsamples often displayed two phases, with decay rates designated as k_{T1} and k_{T2}, respectively. The difference between the inhibited (k_c) curve and the first phase of the uninhibited (k_{T1}) curve first-order decay rates was attributed to microbial processes (k_m). The first-order k_m

Table 1 | Water quality parameters for samples used in batch tests

Sample	pH	Total chlorine (mg-Cl_2/L)	Monochloramine (mg-Cl_2/L)	Ammonia (mg-N/L)	Nitrate (mg-N/L)	Nitrite (mg-N/L)	HPC (CFU/mL)
17 August							
T-WTP[a]	n.m.	1.20	n.m.	n.m.	n.m.	n.m.	n.m.
T-2	n.m.	0.80	n.m.	n.m.	n.m.	n.m.	n.m.
T-5	n.m.	0.81	n.m.	n.m.	n.m.	n.m.	n.m.
17 October							
T-WTP	7.15	0.96	0.31	0.40	n.m.	0.003	9
T-2	7.19	0.54	0.17	0.32	n.m.	0.007	122
T-3	7.10	0.80	0.30	0.31	n.m.	0.003	20
T-5	7.28	0.60	0.24	0.43	n.m.	0.005	256
12 October							
W-WTP[a]	7.17	1.67	0.63	>0.50	n.m.	0.002	1
W-4	7.24	0.64	0.26	0.44	n.m.	0.005	387
W-6	7.31	1.11	0.58	0.54	n.m.	0.002	25
W-7	6.71	0.78	0.36	0.47	n.m.	0.038	32
24 November							
W-WTP	7.46	1.72	1.49	0.36	3.6	0.003	n.m.
W-4	7.65	1.11	0.98	0.51	3.6	0.006	n.m.

HPC, heterotrophic plate count; CFU, colony-forming unit; n.m., not measured.

[a]Samples beginning in T are from the City of Toronto distribution system, and samples beginning in W are from the Region of Waterloo distribution system.

and the F_m were determined from the following equations:

$$k_m = k_{T1} - k_c \quad (1)$$

$$F_m = \frac{k_m}{k_c} \quad (2)$$

Acceleration in the residual first-order decay rate (k_{T2}) in the uninhibited curve defines the start of the second phase of chloramine decay. The CTR was determined by finding the intersection point of straight lines fitted using linear regression through the two phases of the total chlorine decay on a semi-log plot (with slopes of k_{T1} and k_{T2}). Data that were included as part of k_{T1} and k_{T2} were determined by visual inspection. This was altered from the method of Sathasivan *et al.* (2008) to simplify the calculation process and make it more robust against deviations from first-order decay.

RESULTS AND DISCUSSION

Batch testing results

F_m and CTR

Batch tests to measure chloramine decay and the onset of nitrification were successfully carried out on water samples from sites in the two full-scale drinking water distribution systems. For each sample, the chlorine decay curves for both inhibited and uninhibited batches were plotted, and as an example, the curves for W-6 collected on 12 October 2010 are displayed on a semi-log plot in Figure 1. For some samples, including W-6 collected on 12 October 2010, chlorine decay in the uninhibited batch test occurred in two distinct phases. The intersection of the fitted uninhibited batch decay curves before and after the breakpoint was defined as the CTR. The CTR represents the chlorine residual where a rapid decay in disinfectant residual occurs. Using Equations (1) and (2), the k_m and F_m were determined from k_{T1} and k_c and are listed for each sample in Table 2.

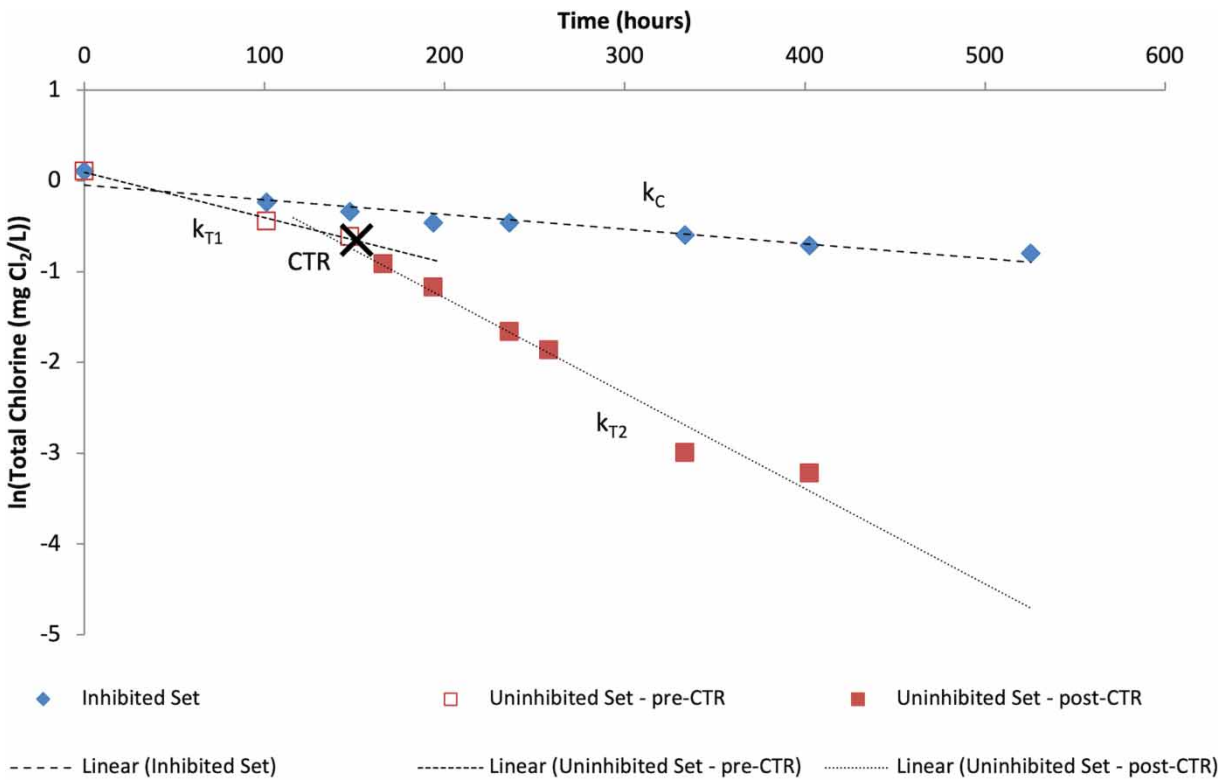

Figure 1 | Semi-log plot of the total chlorine decay curves from a batch test; the sample shown is from site W-6 collected on 12 October 2010. The CTR is the intersection point between the decay curves for the first phase (slope is k_{T1}) and the second phase (slope is k_{T2}) of decay in uninhibited sets. The k_c is the decay rate for the inhibited set.

Table 2 | Coefficients, chlorine decay curve types, CTR, and the incubation time to reach the CTR for the batch tests

Sample	k_{T1} (h^{-1})	k_{T2} (h^{-1})	k_c (h^{-1})	CTR (mg/L)	Time to CTR (d)	k_m (h^{-1})	F_m (–)	Type
17 August								
T-WTP[a]	0.0010	0.0010	0.0011	NA[b]	NA	0.0000	0.0	I
T-2	0.0069	0.0069	0.0014	NA	NA	0.0055	3.8	IV
T-5	0.0039	0.0080	0.0014	0.45	6.3	0.0025	1.8	II
17 October								
T-WTP	0.0022	0.0237	0.0016	0.49	12.5	0.0006	0.4	II
T-2	0.0065	0.0125	0.0013	0.39	2.1	0.0052	4.0	III
T-3	0.0022	0.0022	0.0014	NA	NA	0.0008	0.6	I
T-5	0.0033	0.0302	0.0016	0.38	5.4	0.0017	1.1	III
12 October								
W-WTP[a]	0.0057	0.0090	0.0026	0.57	7.5	0.0031	1.2	II
W-4	0.0075	0.0072	0.0042	0.28	4.6	0.0033	0.8	II
W-6	0.0050	0.0105	0.0016	0.52	6.3	0.0034	2.1	III
W-7	0.0062	0.0134	0.0042	0.22	8.3	0.0020	0.5	II
24 November								
W-WTP	0.0044	0.0069	0.0026	0.50	12.1	0.0018	0.7	II
W-4	0.0040	0.0106	0.0024	0.52	8.3	0.0016	0.7	II

Sampling dates (in 2010) are indicated.
[a]Samples beginning in T are from the City of Toronto distribution system, and samples beginning in W are from the Region of Waterloo distribution system.
[b]CTR is not available (NA) for decay curves of types I and IV.

Samples collected from the two treatment plants and distribution systems had k_m values that ranged from 0 h^{-1} in T-WTP (17 August 2010) to 0.0055 h^{-1} in T-2 (17 August 2010) and F_m values that ranged from 0 in T-WTP (17 August 2010) to 4.0 in T-2 (17 October 2010) (Table 2). As F_m is the ratio of k_m to k_c, biological processes were relatively more responsible for chloramine decay in samples with a higher F_m. As suggested in Sathasivan *et al.* (2005), samples with a higher F_m may be more susceptible to rapid chloramine decay due to nitrification. As expected, samples with the highest F_m were collected from the distribution systems and not in the effluents of the treatment plants. This is indicative of the increased potential for microbial regrowth of nitrifying bacteria and associated chloramine decay. Nitrifying bacteria (both AOB and AOA) were previously found to be present in both distribution systems, and AOB in particular showed regrowth (Scott *et al.* 2015) which correlated with chlorine and ammonia concentrations; therefore, it was likely that nitrification contributed to rapid chloramine decay in the batch test samples. However, as discussed later, F_m can have the same value in different situations and can lead to incorrect conclusions with potentially severe consequences.

In this study, the method of finding the CTR differs from Sathasivan *et al.* (2008). Modifications to the analyses described in Sathasivan *et al.* (2008), which calculated pair-wise first-order decay coefficients between adjacent points, had to be made to accommodate the fact that chloramine decay as a first-order process was not a perfect fit in every sample. Conversely, in the present study, the CTR was determined as the intersection point on a semi-log plot between first-order decay curves fitted to measurements before and after the point where chloramine decay accelerates. All calculations were performed using total chlorine measurements rather than monochloramine data to calculate the decay rates and the CTR. This decision was made due to the lower variability of the total chlorine measurements. As well, unlike Sathasivan *et al.* (2005), monochloramine levels were not increased to at least 1.0 mg-Cl_2/L at the beginning of the batch tests. This simplified the test and preserved the initial sample conditions. Sathasivan *et al.* (2005) raised the initial monochloramine concentration in samples where it was low to ensure a sufficient number of measurements before the residual was depleted and to improve the accuracy of the rate calculations. However, by retaining the initial sample conditions from the distribution system, the time taken to reach the CTR becomes a useful basis for comparison between samples.

The majority of the samples that had a discernible CTR had values that were in the range of 0.4–0.6 mg-Cl_2/L (Table 1). Krishna & Sathasivan (2012) reported that severe nitrification episodes can begin once the disinfectant residual drops

below 0.5 mg/L, so the results in this study agree with other applications of this batch test method. The time taken to reach the CTR may be interpreted as a prediction of the hydraulic retention time in the distribution system before the decay rate of the chloramine residual accelerates. Since batch tests undergo bulk water processes rather than wall/biofilm processes, they can be considered to be analogous to reservoirs. As a result, the batch test method may be particularly useful in the operation of reservoirs, by providing values for the minimum disinfectant residual and the maximum retention time. The site W-6, for example, is a reservoir and the results from the batch testing performed in this study suggest that the chlorine residual should be above 0.52 mg/L by operating at a retention time of less than 6.3 days, at least with the water quality conditions at the time that the sample was taken. However, it must be recognized that CTR provides only an indirect measure of biostability and nitrification potential. Sathasivan *et al.* (2008) found that CTR values can underestimate the disinfectant concentration required to prevent microbial regrowth (or the biostable residual concentration). As well, Sathasivan *et al.* (2008) indicated that the nitrification potential at a given location can be influenced by upstream biofilms, and also by the presence and type of AOB. Therefore, maintaining a disinfectant residual value well above the CTR will be important to allow for these and other contributing factors. Another important point when applying the results of this batch test to the operation of a distribution system is the impact of temperature. The distribution systems studied here have maximum annual temperatures in the same range at which the test was conducted (20–22 °C), and the warmest months are when there is the greatest need to be vigilant about nitrification events and other reactions accelerating the decay of the disinfectant residual. In cooler months, or in distribution systems where the peak temperatures differ from the temperature at which the batch test is conducted, a correction could be made to account for the impact of temperature, for example, using the approach described by Sathasivan *et al.* (2009).

The results in Table 2 support the observations of Sathasivan *et al.* (2008) that monochloramine decay often occurs in two phases, with a greater decay rate in the second phase (k_{T2} higher than k_{T1}). The mechanisms responsible for the increase in the total chlorine decay rate below the CTR are unclear. One possible reason could be that a point is reached where the ammonia levels begin to decline. A monochloramine residual is more chemically stable in the presence of ammonia (Vikesland *et al.* 2001), so the consumption of ammonia by nitrifiers could trigger a more rapid decay of the disinfectant residual. Another factor could be the production of nitrite by AOB and AOA, since nitrite will react with monochloramine (Vikesland *et al.* 2001). In addition, nitrifier cometabolism of monochloramine can be a significant contributor to the total chlorine decay at low chlorine residuals (Maestre *et al.* 2013, 2016; Wahman *et al.* 2016). As well, chloramine-decaying proteins can have a larger impact at lower chloramine residuals resulting in an increase in the decay rate after the CTR (k_{T2}) (Herath *et al.* 2018). The results of Sathasivan *et al.* (2008) showed that the beginning of the second phase of the total chlorine residual decay coincided with a decrease in the ammonia concentration and an increase in the nitrite concentration. Differences in the presence and abundance of AOB and AOA may also explain why in some samples k_{T2} was substantially larger than k_{T1}, while in some samples the difference was only marginal. Two phases of chloramine decay were also observed in the results of a batch test conducted by Zhang *et al.* (2002). In the present study, ammonia and nitrite concentrations were not monitored, while the batch tests were in progress but were measured before and after the batch tests on 17 October, 12 October, and 24 November (Table 3). In general, increases in nitrite and nitrate concentrations were noted, indicating that nitrification had occurred. However, the ammonia concentrations increased in many circumstances which were not expected.

Decay curve categorization

In addition to calculating the F_m and CTR values, this study defined four decay curve types and evaluated the batch test results by assigning each sample to one of these types based on visual examination. This approach was taken to provide a robust method for interpreting data collected from the batch test results without relying on any single parameter. The types of total chlorine decay curves that were observed in the current study were the following:

Type 1: Inhibited and uninhibited samples track closely together (Figure 2(a)).
Type 2: Inhibited and uninhibited samples track together initially and then diverge at the CTR (Figure 2(b)).
Type 3: Inhibited and uninhibited samples have some initial divergence, with an increase in divergence at the CTR (Figure 2(c)).
Type 4: Inhibited and uninhibited samples diverge initially, and no second phase of accelerated decay in the uninhibited batch is observed (Figure 2(d)).

Table 3 | Change in ammonia, nitrite, and nitrate during uninhibited batch tests

	Ammonia (mg-N/L)			Nitrite (mg-N/L)			Nitrate (mg-N/L)		
Sample	Initial	Final	Change	Initial	Final	Change	Initial	Final	Change
17 October									
T-WTP[a]	0.40	0.46	0.06	n.m.	0.003	–	n.m.	n.m.	n.m.
T-2	0.32	>0.5	>0.18	0.004	0.007	0.003	n.m.	n.m.	n.m.
T-3	0.31	>0.5	>0.19	0.002	0.003	0.001	n.m.	n.m.	n.m.
T-5	0.43	>0.5	>0.07	0.004	0.005	0.001	n.m.	n.m.	n.m.
12 October									
W-WTP[a]	>0.50	0.51	–	n.m.	0.002	–	n.m.	n.m.	n.m.
W-4	0.44	n.m.	–	0.004	0.005	0.001	n.m.	n.m.	n.m.
W-6	0.54	0.42	−0.12	n.m.	0.002	–	n.m.	n.m.	n.m.
W-7	0.47	0.41	−0.05	0.003	0.038	0.035	n.m.	n.m.	n.m.
24 November									
W-WTP	0.36	>1.0	>0.64	0.003	0.003	–	3.60	3.90	0.30
W-4	0.51	0.98	0.47	0.006	0.004	−0.002	3.60	3.88	0.28

n.m., not measured.

[a]Samples beginning in T are from the City of Toronto distribution system, and samples beginning in W are from the Region of Waterloo distribution system.

Categorizing results from these batch tests into the four distinct types provides a better description of the trends observed and facilitates a comparison between sites. The chlorine decay curve types defined here can be compared to the categorization system used by Sathasivan *et al.* (2008), in which three representative sample types (A, B, and C) were presented. Representative samples A and B in their work would both be classified as Type III according to the criteria used here. This is because the total chlorine decay rates were greater in the uninhibited batches than in the inhibited batches at the beginning, and there were clear points where the rates accelerated. In contrast, their representative sample C did not show two phases of the total chlorine decay and had no significant difference between inhibited and uninhibited samples (i.e., $F_m = 0$); these characteristics make it equivalent to Type I in the classification system in this study.

The trends observed in Type II and Type IV chlorine decay curves, however, are believed to be novel to the current research. Type II fits between Types I and III, with the chloramine decay rate approximately equal in uninhibited and inhibited batches, until the CTR when the decay rate in the uninhibited batch accelerates. Type IV trends likely occur in samples where the initial total chlorine residual is at or less than the CTR, since having the sample start in the accelerated chlorine decay phase would preclude observing a residual where acceleration in the decay rate occurs. This idea is supported by the initial decay coefficients (k_{T1}) in the uninhibited batch of the Type IV sample (see Table 2), which is greater than in the other samples.

The primary benefit of including a qualitative evaluation of the decay curve type is to give context to the numerical results and avoid misinterpretations. This is important, because some of the numerical parameters, especially F_m, as discussed in the following section, can have the same value under differing circumstances. Overall, the results show that the three complementary approaches of evaluating the results from the nitrification batch tests, the F_m (and the decay coefficients used in its calculation), the CTR including the time required to reach the CTR, and the decay curve type, provide useful information for evaluating the potential for nitrification in a given location.

Interpretation of batch test results

The procedure of Sathasivan *et al.* (2008) for determining the CTR involves calculating the first-order decay rate between each pair of successive measurements and finding the point when the first-order slope reaches double its baseline value. However, when initial measurements did not follow a smooth first-order curve due to noise in the data or second-order effects, it was difficult to establish an accurate baseline. The modified method discussed above, of calculating the CTR as the intersection between the fitted first-order decay curves from the first and second phases of the total chlorine decay, was adopted as an alternative that is intended to be simpler and more robust to calculate.

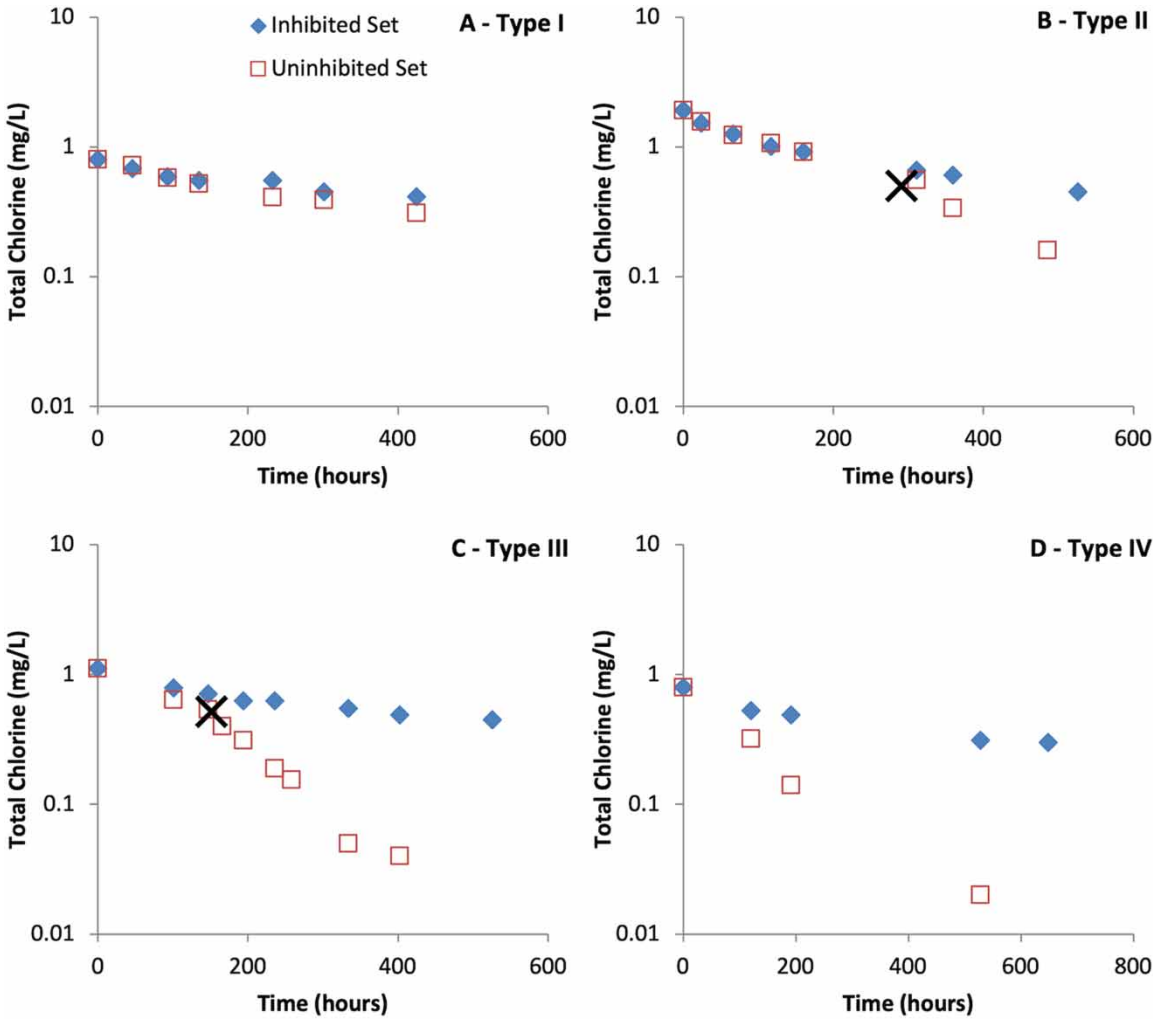

Figure 2 | (A) Representative Type I chlorine decay curve from site T-3 collected on 17 October 2010. In this type of trend, the inhibited and uninhibited samples track closely together for the entire incubation period. (B) Representative Type II chlorine decay curve from site W-WTP collected on 24 November 2010. In this type of trend, the inhibited and uninhibited samples track closely together initially and then diverge at a point known as the CTR. (C) Representative Type III chlorine decay curve from site W-6 collected on 12 October 2010. In this type of trend, the inhibited and uninhibited samples have some initial divergence, and then the decay rate in the uninhibited batch accelerates at the CTR. (D) Representative Type IV chlorine decay curve from site T-2 collected on 17 August 2010. With this type of trend, a CTR cannot be determined due to the lack of a clear breakpoint in the decay rate of the uninhibited portion of the sample.

As previously mentioned, as F_m is the ratio between k_m and k_c, it can have the same value under vastly different sample conditions. Consequently, comparing samples on the basis of their F_m values alone could result in misleading interpretations of batch test results, which could potentially have severe implications for reservoir management. Figure 3 illustrates this weakness of the F_m by plotting pairs of k_m and k_c values from batch test experiments performed in this study and from the literature (Sathasivan *et al.* 2005, 2008, 2010; Fisher *et al.* 2009; Krishna & Sathasivan 2012). A variety of samples and experimental conditions are included, providing a range of k_c (from inhibited samples) and k_m (difference between inhibited and uninhibited samples) values. Each line is a single F_m number (recall that $F_m = k_m/k_c$). Reporting the results of chloramine decay batch tests as an F_m value alone can miss some important details, since any point along one of these lines will have the same F_m, but the residual decreases more rapidly for points further from the origin.

As evidenced in Figure 3, in many batch tests from both the current study and the literature (Sathasivan *et al.* 2005, 2008, 2010; Fisher *et al.* 2009; Krishna & Sathasivan 2012), when k_c was elevated, k_m was elevated as well. Thus, many batch tests with a high k_m had an F_m ratio that was similar to batch tests with a normal k_m. Due to this effect, reporting both k_c and k_m should be seen as more useful and informative than just reporting the ratio F_m. Figure 3 also shows that the results for this type

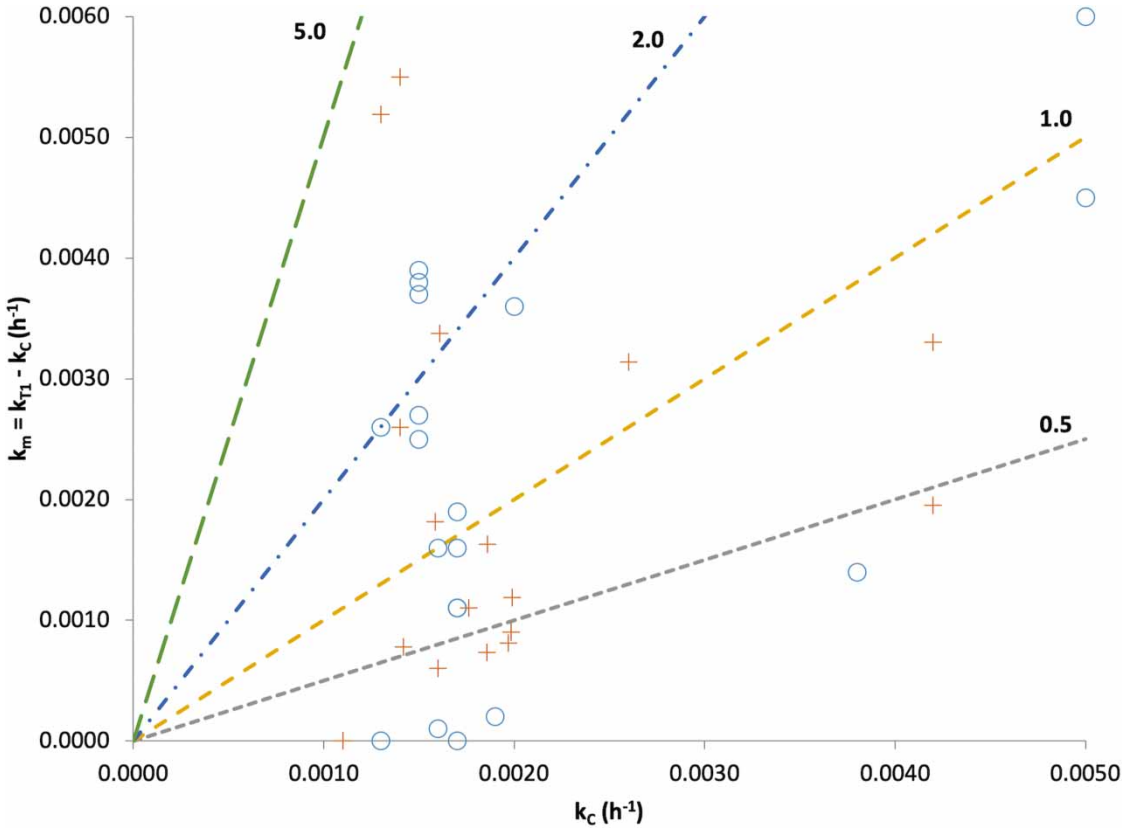

Figure 3 | An illustration of the range of observed F_m values from batch tests completed in this study (+), and from the literature (o) (Sathasivan *et al.* 2005, 2008, 2010; Fisher *et al.* 2009; Krishna & Sathasivan 2012). Constant F_m numbers are shown as straight lines and labeled with their value.

of batch test typically cluster together. In this study, the values of k_c normally fall in the range of 0.001–0.002 h^{-1}, which is similar to the range of 0.0011–0.0019 h^{-1} reported by Sathasivan *et al.* (2005). k_m values also clustered in this experiment and in the literature (Sathasivan *et al.* 2005, 2008, 2010; Fisher *et al.* 2009; Krishna & Sathasivan 2012), albeit in a wider range than k_c of 0.000–0.004 h^{-1}, as indicated in Figure 3. Results falling outside of this region had more rapid than normal rates of chloramine decay. Possible reasons for a high k_c in a water sample include low pH, a high chlorine to ammonia nitrogen ratio, high temperature, and elevated concentrations of carbonate, nitrite, bromide, and natural organic matter (Vikesland *et al.* 2001; Duirk *et al.* 2005). Meanwhile, k_m can be elevated due to the consumption of ammonia by nitrifiers, the production of nitrite by ammonia-oxidizing bacteria and archaea, and nitrifier cometabolism of monochloramine (Vikesland *et al.* 2001; Maestre *et al.* 2013, 2016; Wahman *et al.* 2016). Furthermore, the presence of chloramine decaying organisms that are not nitrifiers, chloramine decaying proteins, or SMPs may also influence k_m and F_m (Sathasivan *et al.* 2005; Herath *et al.* 2015, 2018). However, although SMPs have a microbial source, they would likely remain in the sample following inhibition or filtration and, therefore, would be measured as k_c. Future research should attempt to further elucidate and quantify the mechanisms leading to increases in k_m and k_c.

An important factor to consider when interpreting results from these batch tests is that only bulk water processes will be represented (Sathasivan *et al.* 2005). Therefore, this batch test method could significantly underestimate the total chlorine decay rate for samples from distribution system locations where pipe-wall processes, such as corrosion and biofilm-associated reactions, are important factors. However, this test should be useful for samples from reservoirs, since their relatively low surface-to-volume ratios imply that bulk water reactions will usually be the dominant effects on water quality changes. In addition, reservoirs also have residence times that are much easier to determine compared to other parts of distribution systems (provided that the extent of potential short-circuiting can be determined). For these reasons, this batch test method is especially recommended for reservoir operation. The CTR and the incubation time taken to reach it in a reservoir sample

can be regarded as the minimum allowable disinfectant residual and the maximum allowable retention time for that reservoir after safety factors are added to the batch test results. For example, Sathasivan *et al.* (2010) used F_m to develop an operational strategy for a reservoir to prevent nitrification episodes. Those authors used the batch test method developed in Sathasivan *et al.* (2005) to determine a target dilution that would yield an acceptable F_m (and overall decay rate), since diluting the stagnated reservoir water with freshly treated water was their strategy for improving water quality. In addition, temperature can also influence the time required to reach CTR, since lower water temperature will reduce microbial growth rates and can affect the biostability and onset of nitrification in disinfected waters (Sathasivan *et al.* 2009; Sarker *et al.* 2013). However, batch test results can provide an early warning that conditions at a site can be susceptible to rapid chloramine decay caused by nitrification at warmer temperatures.

In view of these points, the strengths and weaknesses of the three methods to convey the results of these chloramine decay batch tests can be compared. The F_m is prone to misinterpretation if it is used in isolation but reporting the decay coefficients that were used in its calculation can mitigate this. However, these decay coefficients are based on the assumption that the residual decay during the batch test is a first-order process (although having the potential for two phases with differing rate constants). The validity of this assumption should be checked when using these decay coefficients. The CTR was difficult to determine via the original procedure of Sathasivan *et al.* (2008) when there were deviations from first-order trends, but the new calculation procedure utilized in this study is simpler yet more robust (Scott 2012). Classifying a chloramine decay batch test result into one of the four types as previously discussed has the limitation of being qualitative rather than quantitative but does provide a useful broad categorization of the trends observed. Viewing the results through all of these lenses in combination provides a robust, holistic view of the results of these batch tests.

Application of batch test method

The results of the batch tests were compared to disinfection times from the literature (*Ct* concept) and to the full-scale results reported in Scott *et al.* (2015). *Ct* values (Chick–Watson disinfection times) for the monochloramine decay batch tests conducted in this study were calculated for comparison with published disinfection kinetics for nitrifying microorganisms. This was accomplished by finding the area under the total chlorine decay curves in uninhibited samples, where the area is the product of the disinfectant concentration and contact time. The comparison included samples from each decay curve type is shown in Figure 2. Microbial activity (non-negligible k_m) was detected despite *Ct* values above literature values for 99% inactivation (Wahman *et al.* 2009), suggesting higher chloramine resistance in the chloramine decaying organisms in these samples. The full-scale distribution systems from which the samples collected were monitored as part of the research described in Scott *et al.* (2015). It was difficult to draw direct comparisons to the present work since both distribution systems were well controlled with respect to nitrification during that sampling campaign, which concluded before most of the samples were collected for this study. The sites that had the highest AOB gene counts (T-5 and W-4) did not have the highest k_m values. The disinfectant residual at all sites sampled remained above the CTR values found here during the full-scale sampling campaign, except for W-4, which had two samples that were below its CTR of 0.52 mg/L in July and August 2010 (the minimum was 0.46 mg/L). Since maintaining a total chlorine residual greater than the CTR to the far end of the distribution system should be a means of controlling nitrification, it is thus logical that nitrification was found to be well controlled in these drinking water distribution systems in Scott *et al.* (2015).

CONCLUSIONS

The batch test methodology for investigating the potential for rapid chloramine decay and nitrification potential that was developed and applied in this study can be useful in future research and for drinking water system operations, provided that its limitations are kept in mind. The following conclusions were made from the results of this study:

- The two phases of decay of the total chlorine residual first noted by Sathasivan *et al.* (2008) were confirmed.
- The batch test methodology developed here was able to isolate the microbially mediated and chemical components of the total chlorine decay rate.
- Four types of decay trends that can be used to classify samples were identified.
- The assumption of first-order decay is only an approximation but is usually valid; the calculation procedure for determining the CTR was modified to depend less on this assumption.

- The CTR and the incubation time required to reach CTR will be particularly useful for monitoring reservoir operations. Based on information from this study and the literature, a CTR of at least 0.5 mg/L (as total chlorine) represents a useful guideline.
- A normal range of 0.001–0.002 h^{-1} was identified for the k_c; samples that fall outside of this range should be examined more closely.
- The F_m should be used with caution (not in isolation, but in conjunction with other parameters), since this ratio can have the same value under contrasting conditions.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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