

Modeling chlorine response to uncontrolled contamination events in drinking water distribution systems

S. Mohan, G. R. Abhijith and B. Aneesh

ABSTRACT

An alternating schedule of supply and non-supply adopted in intermittent water distribution systems increases the likelihood of microbial water quality deterioration, as compared to a schedule of continuous supply. Maintaining adequate levels of chlorine in water is the most common remedial strategy adopted to minimize this problem. Thus, it is imperative to understand the kinetics governing the reactions of chlorine with microbial contaminants to optimize the chlorine dosage at the dosing locations. Previous related kinetic studies focused only on controlled experiments with pure microbial cultures in chlorinated water samples. This study addresses uncontrolled contamination caused by sewage intrusion, which is a common problem in developing countries. Uncontrolled contamination is experimentally simulated by adding sewage samples to chlorinated tap water samples. The reaction kinetics is investigated by periodic monitoring of the variability in chlorine and microbial colony counts. A multi-phase kinetic model is found to fit the resulting data. The fit of the model predictions is tested through analysis of variance (ANOVA). The proposed model explains the reaction kinetics of chlorine disappearance with less than 5% error. The developed model could be applied to determine optimal chlorine dosages in drinking water distribution systems.

Key words | chlorine kinetics, contamination, intermittent water supply, water distribution systems, water quality

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INTRODUCTION

A drinking water distribution system (DWDS) is an engineered system designed and operated to meet the water demand of consumers by supplying water of desirable quality and quantity at the right time. In many developing countries, as well as in some developed countries, DWDSs are operated in an intermittent manner (Vairavamoorthy *et al.* 2007; Kumpel & Nelson 2016). The average water supply period in intermittently operated systems in developing countries is only 1–4 h a day (Ingeduld *et al.* 2006). The chances of degradation of the biological quality of water are found to be much higher in an intermittently operating system than in a continuously operating system (Kumpel & Nelson 2016).

The drinking water standards of many countries, as well as by World Health Organization (WHO), prescribe that water for drinking purposes must be free of fecal indicator bacteria (WHO 2008; Bindu *et al.* 2018). The operation of DWDSs in many developing countries mainly relies upon conventional disinfection processes like chlorination to destroy microorganisms and to prevent water quality degradation during distribution. Sufficient chlorination results in the maintenance of a minimum chlorine residual in the water supplied to consumers. This is generally considered the most practical and economical treatment strategy (Brown *et al.* 2011). The chlorine is expected to induce enzymatic inactivation and subsequently kill the microbial

contaminants present in water and provide residual action during events of contaminant intrusion. It is a complicated exercise to model the kinetics of reactions of chlorine in water distribution pipelines during uncontrolled contamination. The kinetic relationships developed solely with the consideration of pure cultures of microbial cells may not sufficiently describe chlorine kinetics in real-world operating conditions.

In this paper, we report the results of an investigation of the response of chlorine in water induced by sewage intrusion, an uncontrolled microbial contamination situation, through batch experiments. Additionally, we propose a generalized kinetic relationship between chlorine and microbial contaminants which more accurately models the disappearance of chlorine inside DWDSs.

CHLORINE RESPONSE TO MICROBIAL CONTAMINATION

Intermittent operation is characterized by cyclical pressurization and depressurization of water distribution pipelines (Fontanazza *et al.* 2015). During depressurization, zero or negative pressures arise inside the pipelines. These conditions are conducive to the entry of microorganisms from external environments through intrusion pathways (Jones *et al.* 2014). In many developing countries, the sewer lines of cities generally follow the same layout as that of drinking water distribution pipelines (USEPA 2002; Sadiq *et al.* 2006). They are laid adjacently or above distribution pipelines with only about 1 m gap, a result of unscientific planning and execution by municipal administrations. The sewer lines running in parallel with water distribution pipelines, both from the sides and above, are the main source for microbial contamination in DWDSs of developing countries (Sharma *et al.* 2015). The sewage from leaking sewer lines contains not only microbial contaminants but also chemical contaminants (USEPA 2002).

Numerous research studies have reported on the development of chlorine sensors, which use residual chlorine as a surrogate parameter for detection and quantification of microbial contamination in DWDSs (Helbling & Vanbriesen 2009). Chlorine sensors are installed as a reliable instrument for indirectly monitoring the biological quality

of water. The available chlorine concentration in water is determined by the dosage of chlorine provided at the system's inlet point (at the outlet of water treatment plant) and/or at the booster station (at an intermediate point in the DWDS). Under normal operating conditions, the available chlorine concentration of water decreases during its propagation through distribution pipelines due to the combined effects of reactions of chlorine with natural organic matter present in water and with the pipe wall material (Seyoum & Tanyimboh 2017). The former is a reaction at the bulk water zone and the latter is a reaction at the wall zone of a water distribution pipeline (Rossman *et al.* 1994). Many studies have been conducted to explain chlorine behavior in DWDSs and many kinetic models have been proposed to simulate these reactions (Powell *et al.* 2000; Clark & Sivaganesan 2002; Helbling & Vanbriesen 2009). It may be noted that the kinetics of reactions at the bulk water zone causing the decay of chlorine under conditions of uncontrolled, direct contamination may be meaningfully different from scenarios occurring under normal operation of DWDSs. Thus, all of these kinetic models may be suitable only for normal operating scenarios and may fail to describe the actual kinetics of chlorine decay during situations of uncontrolled contamination, for example, sewage intrusion.

EPANET is one of the most widely used water quality simulators to predict levels of chlorine in DWDSs (Rossman 2000). In EPANET, the user-defined reaction kinetics assume that the reactants are grouped as a single species. EPANET uses only the first-order and second-order kinetics to model the reactions of chlorine at the bulk water zone. It does not allow the use of multi-parameter kinetic models and it does not represent the reactions of chlorine in response to specific contaminants in water. To overcome this limitation, an enhanced version of EPANET known as EPANET-MSX was developed that enables customization of complex multi-species reaction expressions (Shang *et al.* 2007). Because microbial contaminants are complex and varied, it is impractical to define each and every reaction between the components of the biological matrix and chlorine and to input the same in the form of rate expressions (Helbling & Vanbriesen 2009). Therefore, the most appropriate approach is to develop a general kinetic relationship that generalizes the complex biochemical reactions between microbial contaminants and chlorine, by the selection of

appropriate parameter values. In essence, the generalized kinetic relationship considers the grouping of reactive species, but the selection of appropriate rate expression and parameter values allows better and simplified representation of the bulk phase reactions using EPANET-MSX.

Studies have been conducted in this direction by investigating the chlorine demand and microbial cell survival under different chlorine concentrations for pure microbial cultures (Shang & Blatchley 2001; Virto *et al.* 2005; Helbling & VanBriesen 2007). The kinetic relationships derived from such batch studies were used to evaluate the efficacy of using chlorine sensors as a proxy for measuring microbial contamination in DWDSs experimentally, by injecting microbial cells into laboratory-scale systems (Helbling & VanBriesen 2008). It may be noted that the overall effect of a heterogeneous contaminant community, which is present in sewage and which significantly influences the kinetics of reactions of chlorine during uncontrolled contamination events, is not accounted for in any of the above-mentioned experimental models.

Haas & Karra (1984) developed an exponential bi-phasic decay model by relating the chlorine demand present with different levels of sewage contamination. This bi-phasic model distinguished the total reaction time of chlorine into two distinct phases, namely, the fast reaction phase and the slow reaction phase. Two separate values of kinetic constants were assigned for each phase. It was reported that the kinetic constants depend on the initially available concentration of chlorine in water, initial concentration of microorganisms, and characteristics of the microbial cell species. However, the influence of chemical contaminants in the heterogeneous contaminant matrix to the value of kinetic constant was not considered. The demand for chlorine, induced by the contaminants, in any water sample contaminated with sewage will be a finite value. The chlorine demand exerted must attain a steady-state once all the reactions of chlorine with the contaminants are completed. Attainment of the steady-state condition cannot be modeled using the bi-phasic exponential decay model. Moreover, Haas & Karra (1984) left the chemical basis for the occurrence of two distinct reaction phases unexplained.

It may be concluded from the earlier studies that there is no unique kinetic model that can accurately explain the kinetics of reactions of chlorine from a fast reaction phase to

steady-state during uncontrolled contamination situations. A kinetic model of such kind, if available, could be applied to understand the behavior of chlorine in DWDSs. It could also be used towards deciding the optimal chlorine dosages at the required critical locations. This might be a step towards overcoming the management challenge of deciding the optimal chlorine dosage to control water quality degradation in intermittent DWDSs.

MATERIALS AND METHODS

Conducting batch experimental studies is deemed to be the easiest way to investigate the response of chlorine to microbial contaminants (Helbling & VanBriesen 2007). This section explains the materials that have been used and the methodology that has been adopted for conducting batch experiments to simulate uncontrolled contamination events.

Glassware and chemicals

All glassware used for the experimental study was manufactured by M/s Borosil Glass Works Ltd (India) and marketed under the brand name 'Borosil'. Before conducting the experiment, all glassware was cleaned with distilled water and dried at 150 °C for 2 h. All chemicals used in the study were of analytical reagent (AR) grade. All solutions were prepared using double distilled water (Elga Veolia, UK).

Collection and storage of sewage sample

A field scenario of sewage intrusion into distribution pipelines was simulated in this experimental study. Sewage samples used for experimentation were collected from two locations within the Indian Institute of Technology Madras campus: from the inlet of the sewage treatment plant (12.989346, 80.240729), SW1, and from the sewage outlet of one of the hostel buildings (12.986009, 80.233858), SW2. The two locations were selected to represent the characteristics of sewage in sewer lines (SW1) and at the point of generation (SW2). After collection, the samples were subjected to total organic carbon (TOC)

analysis (Shimadzu TOC-V, Japan) and heterotrophic plate count (HPC) tests. TOC content obtained was $1,749 \pm 0.1$ mg/L and 639 ± 0.1 mg/L for the sewage samples SW1 and SW2, respectively. From the HPC test, the total coliform counts were measured as 3.1×10^7 CFU/mL and 8×10^6 CFU/mL for SW1 and SW2, respectively. The sewage samples were refrigerated and used for experiments within 24 h after collection.

Chlorine solutions

The stock solution of chlorine was prepared by adding chlorine tablets of sodium hypochlorite (TCI Chemicals Pvt Ltd, India) in tap water. Water samples of different chlorine levels (2 ± 0.02 , 3 ± 0.02 , 4 ± 0.02 , 5 ± 0.02 , 6 ± 0.02 , 8 ± 0.02 , and 10 ± 0.02 mg/L) were prepared by diluting the stock solution. Final chlorine concentrations were estimated using triplicate DPD colorimetric method. The DPD colorimetric method is explained in the section below.

Available chlorine determination

The starch-iodide titrimetric method is one of the commonly used analytical methods for measuring chlorine levels in water. However, this method only yields reasonable results for chlorine concentrations greater than 1.0 mg/L. N,N-diethyl-p-phenylenediamine (DPD) colorimetric method is advocated for the determination of lower levels of chlorine (APHA/AWWA/WEF 2012). The present study adopted the DPD colorimetric method to measure chlorine concentrations in water. DPD indicator reagent and phosphate buffer solution used were procured from TCI Chemicals (India) Pvt Ltd. To determine chlorine concentration, 0.5 mL of DPD indicator and 0.5 mL phosphate buffer solution were added to 10 mL of chlorinated water sample in a test tube and mixed. The presence of chlorine is indicated by red color formation immediately following addition of DPD indicator reagent. DPD is oxidized by chlorine, and color intensity proportional to the chlorine concentration is produced. The absorption of this resulting solution is measured using the photometric method. A UV-spectrophotometer (Shimadzu UV-1800, Japan) was used for this purpose, and the light wavelength was fixed at 515 nm.

Chlorine demand assay

Two hundred mL of chlorinated water samples with concentrations 2 ± 0.02 , 3 ± 0.02 , 4 ± 0.02 , 5 ± 0.02 , 6 ± 0.02 , 8 ± 0.02 , and 10 ± 0.02 mg/L were each added to a 250 mL Erlenmeyer flask fitted with a magnetic stir bar (Remi MLH, India). The seven flasks were subjected to gentle and continuous mixing by setting the stir plate to a rotation of 155 rpm. The heterogeneous contaminants in the form of sewage samples (both the samples 1 and 2) were added at $t = 0$ min in volumetric ratios (volume of sewage, V_{sew} to volume of water, V_{wat}) of 1:500 (CT_{pre}), 1:200 (CT1), 1:250 (CT2), and 1:300 (CT3). At time $t = 3, 5, 10, 15, 30,$ and 60 min, 10 mL of water sample was drawn out in duplicate from the flask, to which 0.5 mL of DPD indicator and 0.5 mL of phosphate buffer solution were added immediately and were mixed. These samples were then analyzed for chlorine concentration using the DPD colorimetric method.

Chlorine demand exerted in water at any time is equivalent to the concentration of chlorine in water that is consumed up to that time. The chlorine demand exerted is mathematically represented as:

$$Cl_{d,t} = Cl_i - Cl_t \quad (1)$$

where $Cl_{d,t}$ = chlorine demand of the water sample exerted up to time t , Cl_i = initial chlorine concentration of the water sample, and Cl_t = chlorine concentration of the water sample at time t .

The chlorine values obtained from DPD colorimetric method were subtracted from the initial chlorine concentration of water to calculate available chlorine consumed in the reactions over time (chlorine demand) using Equation (1).

Microbial colony count assay

Total coliform bacterial colony count measurements were conducted in parallel with chlorine demand tests to ascertain the concentration of total coliform in the water samples after sewage addition. A 0.89% saline solution was prepared as the dilution water and Luria-Bertani agar medium (HiMedia Lab. Pvt Ltd, India) was used as the growth medium. Six water samples with the chlorine

concentration of 2 ± 0.02 mg/L were each added to 250 mL Erlenmeyer flasks fitted with a magnetic stir bar (Remi MLH, India). The flasks were subjected to gentle and continuous mixing by setting the stir plate to a rotation of 155 rpm. The sewage sample (SW1) was added at $t = 0$ min in V_{sew}/V_{wat} ratios of 1:200 (MT1) and 1:300 (MT2). At time $t = 3, 5, 10, 15,$ and 30 min, 9 mL of water samples were drawn out in duplicate from the flasks, to which 1 mL of 10% sodium thiosulphate solution was added to neutralize the effect of chlorine on microbial growth. One mL of the water samples were then serially diluted using 9 mL of dilution water. After autoclaving all the glassware, the agar medium was carefully transferred to each petri-dish for solidification. An amount of 0.1 mL of well-mixed sample was then aseptically inoculated on the agar medium on each plate. Using a sterile spreader device (L-rod), the diluted sample was evenly spread onto the surface of the solidified agar medium. The plates were incubated at a temperature of 35 ± 0.5 °C for a period of 48 ± 2 h. After incubation, the plates were analyzed for microbial colony formation. Each dilution was quantified in triplicate and the final microbial colony counts averaged across the three plates were reported.

Experimental methodology

To simulate a real-world sewage intrusion event in distribution pipelines, we used water that had undergone all conventional treatment processes, conveyed through the water distribution pipelines inside the Indian Institute of Technology Madras and was collected from the water tap of the Environmental and Water Resources Engineering laboratory. After measuring the actual chlorine concentration of the tap water, the stock solution of chlorine was added in required proportions to produce water samples of different initial chlorine concentrations.

The term *ultimate chlorine demand* may be duly used to define the concentration of chlorine available in water that could completely nullify the effects of any contaminant loading. If the initial chlorine concentration selected for the batch tests was equal to the *ultimate chlorine demand*, then both the chlorine concentration and the contaminant concentration left out in the water at the completion of reactions would be zero. The value of

ultimate chlorine demand may depend both on the characteristics and quantity of the contaminants present in water. Its value for a contaminated water sample may be more than or less than its available chlorine concentration. In the former case, the entire amount of chlorine present in the water will be consumed by reactions with the contaminants present. In the latter case, a residual chlorine concentration, equivalent to the difference between available chlorine concentration and the *ultimate chlorine demand*, will remain in the water after the completion of all the reactions.

We hypothesized that by conducting the experiments using chlorinated water samples having high initial chlorine concentrations, the variations in concentration of chlorine could be observed in a better way. Therefore, high values of initial chlorine concentrations, i.e., $3 \pm 0.02, 4 \pm 0.02, 5 \pm 0.02, 6 \pm 0.02, 8 \pm 0.02,$ and 10 ± 0.02 mg/L were selected for the first set of batch experiments, even though such high concentrations are generally hard to be found during normal operation of DWDSs. The same value of *ultimate chlorine demand* was maintained in every water sample during the first set of experiments. Therefore, all chlorinated water samples were injected with the same sewage sample (SW1) at the volumetric mixing ratio of 1:500 (CT_{pre}).

The drinking water standards of India suggest that the minimum chlorine level of water supplied for drinking purposes should be 0.2 mg/L at the point of delivery. The variations in concentrations of chlorine are difficult to ascertain if the tests are conducted with very low concentrations (e.g., 0.2 mg/L). However, conducting experiments with high chlorine concentrations may not help to understand the kinetics of reactions occurring under real-world operating conditions. Thus, an initial chlorine concentration of 2 ± 0.02 mg/L, which is moderately close to the levels normally maintained in DWDSs, was selected for our experiments. For the second set of experiments, the initial chlorine concentration is kept at a constant value (2 ± 0.02 mg/L). Both the sewage samples (SW1 and SW2) were used for the tests with the aim to comprehend the effects of a heterogenous contaminant matrix on the reaction kinetics of chlorine. The mixing ratio is used as a surrogate parameter for contaminant loading. Three mixing ratios (V_{sew}/V_{wat} ratios) of 1 in 200, 1 in 250, and 1

in 300 were selected for the tests CT1, CT2, and CT3, respectively.

The primary role of chlorine as a disinfectant is to kill the microbial contaminants by inactivating the enzymatic activity and to provide necessary ‘sterilization’ to the drinking water. The presence of the heterogeneous group of contaminants in sewage may significantly affect the dynamics of microbial decay (disinfection process). Batch experiments were conducted to study the microbial decay kinetics in the heterogenous contaminant pool. Two tests were conducted by injecting the sewage sample (SW1) into chlorinated tap water samples maintained with an initial chlorine concentration of 2 ± 0.02 mg/L in V_{sew}/V_{wat} ratios of 1 in 200 (MT1) and 1 in 300 (MT2), as the contaminant load.

RESULTS AND DISCUSSION

Chlorine response to contaminant intrusion

The first set of batch studies was conducted to observe the general trend of chlorine response during uncontrolled contamination situations. After the addition of SW1 at $t = 0$ min, the chlorine concentrations were measured at 3, 5, 10, 15, and 30 min. The observed temporal variations in the concentrations of chlorine are represented in Figure 1(a).

It can be inferred from Figure 1(a) that the available chlorine undergoes a relatively rapid reduction at the initial stages of the reaction, after the contaminant injection. This is eventually followed by a relatively slow reduction, followed by a very slow reduction. The same trend is observed in the results of tests with different initial concentrations of chlorine. The kinetics of the reactions causing the disappearance of chlorine is observed to be time-dependent. Hence, it may be inaccurate to generalize the reaction kinetics using a single-order kinetic model (zero-order, first-order, or second-order). It is hypothesized that the reactions follow first-order kinetics in the initial stage and zero-order kinetics in the last stage and a mixed-order reaction kinetics (between first and zero) at the intermediate stage.

Figure 1(b) depicts the relationship between the chlorine demand exerted and the initial chlorine concentrations of

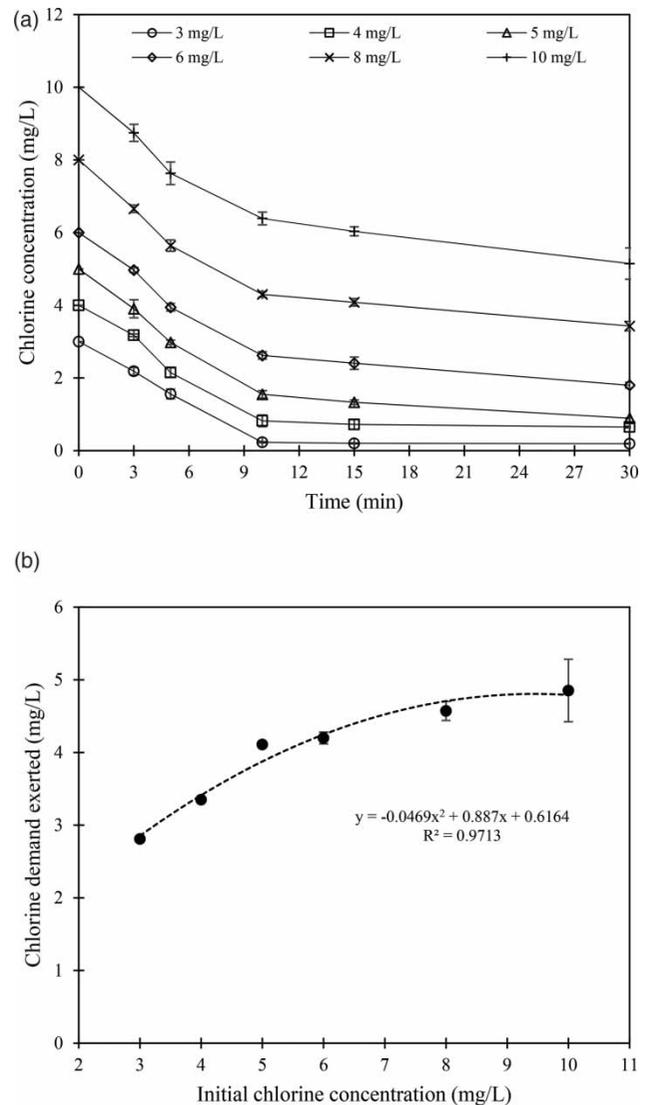


Figure 1 | (a) Chlorine response in water samples with different initial chlorine levels (3, 4, 5, 6, 8, and 10 mg/L) and (b) chlorine demand exerted versus initial chlorine concentration.

the water samples. The difference between initial chlorine concentration and the chlorine concentration of the water sample after 30 min is reported here as the chlorine demand exerted ($Cl_{d,max}$). The value of $Cl_{d,max}$ increased with increasing initial chlorine concentration (Figure 1(b)). The value of *ultimate chlorine demand* is the same for the water samples with 4 ± 0.02 mg/L and 3 ± 0.02 mg/L initial chlorine concentrations. For both these samples, the residual chlorine concentration at 30 min was found to be more than zero. Therefore, more consumption of chlorine can be related to the higher chlorine concentration

(4 ± 0.02 mg/L) maintained in the water sample. The results depicted in Figure 1(b) indicates that the chlorine demand of the water sample (consumption of chlorine) depends on the initially available chlorine concentration (Helbling & Vanbriesen 2009).

It may be illogical to assume that the chlorine demand curve shown in Figure 1(b) is always increasing. When the initial chlorine concentration equals the *ultimate chlorine demand*, induced by any contaminant load, the residual chlorine concentration becomes zero. It may be hypothesized that the chlorine demand curve will asymptotically reach the *ultimate chlorine demand* with the increase in initial chlorine concentration. This provides an opportunity to presume the existence of a specific value of chlorine concentration or a ‘threshold’ value of chlorine concentration for the water sample, for which the maximum chlorine demand exerted is equal to the *ultimate chlorine demand*. If the chlorine concentration is greater than the threshold value, corresponding to a contaminant loading, then the effect of that specific contaminant loading can be completely nullified, leaving a residual chlorine concentration.

Kinetics of the disappearance of chlorine during uncontrolled contamination

For the test described in the section ‘Chlorine response to contaminant intrusion’, the chlorine concentrations were monitored in time intervals up to 30 min after the contaminant injection. However, no significant variations were observed after 15 min (Figure 1(a)). It is hypothesized that the chlorine demand exerted in the water samples reaches a steady-state after a reaction time of 15 min. To verify this hypothesis, the chlorine concentration of the water samples was additionally monitored for 60 min after contaminant injection. The chlorine concentrations were measured at 3, 5, 10, 15, 30, and 60 min.

Figure 2 depicts the results of the batch tests conducted. The chlorine response patterns observed (Figure 2) are similar to the response patterns observed from the experiments described in the section ‘Chlorine response to contaminant intrusion’ (Figure 1(a)). The test results indicate that the reaction of chlorine in response to sewage intrusion is distinguishable into three distinct phases, based on reaction kinetics. The three phases may be described as a rapid

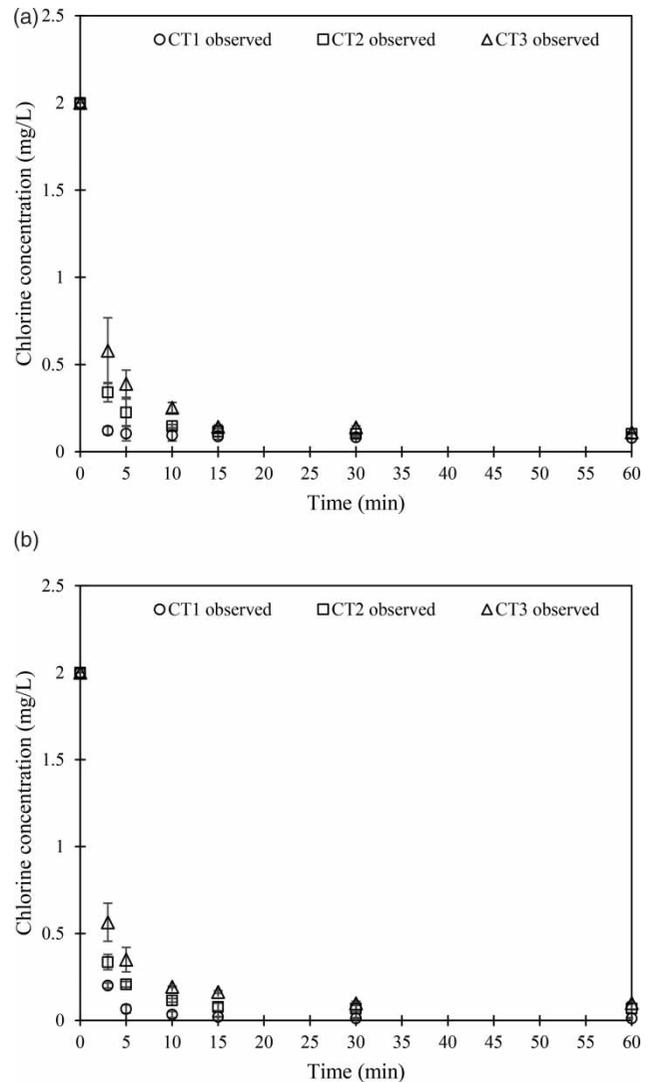


Figure 2 | Chlorine response to the injection of sewage sample (a) SW1 and (b) SW2 in volumetric mixing ratios of 1 in 200 (CT1), 1 in 250 (CT2), and 1 in 300 (CT3).

response phase, slow response phase, and very slow response phase. The rapid response phase occurs for approximately 5 min after contaminant injection. The slow response phase occurs from approximately 5 to 15 min. Beyond 15 min, only very slight variation in the chlorine concentration is observable. This corresponds to the very slow response phase. The timing of the three phases depends on the initial chlorine concentration of water and the characteristics of the contaminant load. It is evident from Figure 2 that the chlorine response curves obtained for the tests CT, CT2, and CT3 have significant differences. It is not easy to distinguish between the slow and very

slow response phases from the results of test CT1 (for both sewage samples, SW2 and SW1) because the observable variation in chlorine concentration is almost negligible after 5 min (Qualls & Johnson 1983; Brown et al. 2011). The contaminant load injected is highest for the test CT1 (V_{sew}/V_{wat} of 1 in 200) compared to tests CT2 (V_{sew}/V_{wat} of 1 in 250) and CT3 (V_{sew}/V_{wat} of 1 in 300). Accordingly, the value of *ultimate chlorine demand* is also highest for test CT1, followed by CT2, then CT3. The observed reactions for CT1 attained steady-state rapidly, within a reaction period of 5 min. For the tests CT2 and CT3, the three reaction phases are more clearly distinguishable.

The differences in reaction kinetics observable between CT2 and CT3 may be because of the comparatively high value of *ultimate chlorine demand* of water sample in the test CT2. Or, more concisely, all three tests suggest that differences in initial contaminant load result in differences in reaction kinetics (Helbling & Vanbriessen 2009). If lines were drawn to connect observed points for each test, we could see a pattern for both SW1 and SW2 showing that increased contaminant load is associated with reduced time to steady state (Helbling & Vanbriessen 2007).

The temporal variation in chlorine demand of water exerted, as a result of sewage injection, will be analogous to the variation in the concentration of chlorine. Therefore, the variations in chlorine demand exerted can also be distinguished in the three distinct phases based on the reaction kinetics. A multi-phase relationship is proposed to explain the observed reaction kinetics of chlorine. The proposed kinetic model is mathematically described as:

$$Cl_{d,t} = Cl_{d,max} \cdot \frac{t}{K_{50} + t} \quad (2)$$

where $Cl_{d,max}$ = maximum chlorine demand exerted in the water sample in mg/L; t = reaction time in minutes, and K_{50} = half-saturation constant for chlorine demand exertion in minutes. $Cl_{d,max}$ and K_{50} are the kinetic parameters. Assuming that the consumption of chlorine in water after 60 min is negligible, the chlorine demand exerted at 60 min can be approximated as the maximum chlorine demand exerted ($Cl_{d,max}$). The half-saturation constant (K_{50}) is the time at which 50% of the maximum chlorine

demand is consumed by available chlorine. Using the data derived from the experiments, the kinetic parameters of Equation (2), $Cl_{d,max}$ and K_{50} are calculated and are listed in Table 1.

By substituting the derived values of kinetic parameters in the proposed relationship, given in Equation (2), the chlorine demand exerted at different stages of the reaction are predicted. The test data and the model predicted values of chlorine demand at different stages of the reaction for the tests CT1, CT2, and CT3 (conducted both with sewage samples SW1 and SW2) are given in Figure 3.

The test data and the predicted data for the tests conducted with six contaminant loadings are statistically analyzed to evaluate the fit of the model predictions. The statistical analysis results are given in Table 2. The coefficient of determination (R^2) provides a measure of how well the test data are explained by the proposed model, based on the proportion of total variation of outcomes explained by the model. A high R^2 value may prove the suitability of the proposed multi-phase kinetic relationship in explaining the variation of the chlorine demand exerted and ability to represent the actual variation in the test data. An R^2 value very close to 1.0 indicates that the model predictions perfectly fit the test data. For all tests, R^2 values obtained are very close to 1.0 (Table 2). This suggests that the proposed kinetic relationship is perfectly predicting the variations in the concentrations of chlorine during sewage intrusion.

A regression analysis provides further insight into the accuracy of model predictions. The results of the regression analysis are presented in Figure 4. For all six tests, both with sewage samples SW1 and SW2, the proposed model explains the reaction kinetics with more than 95%

Table 1 | Values of the kinetic parameters derived from experimental data

Sewage sample	Test	Max. chlorine demand (mg/L)	Half-saturation constant (min)
SW1	CT1	1.921	0.066
	CT2	1.904	0.362
	CT3	1.888	0.886
SW2	CT1	1.988	0.189
	CT2	1.930	0.370
	CT3	1.900	0.750

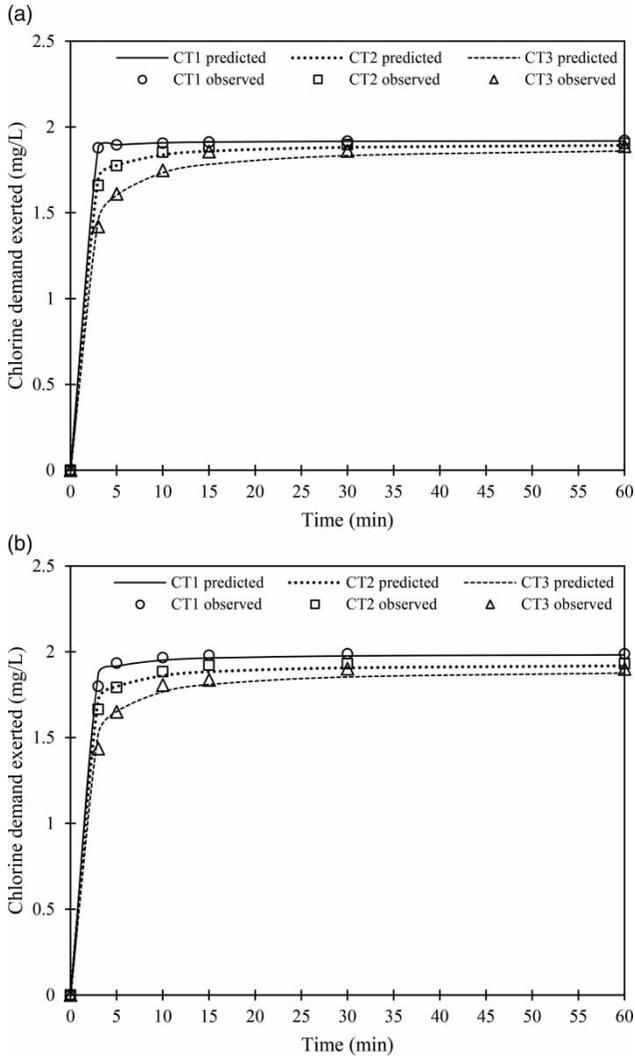


Figure 3 | Predicted and test data of chlorine demand exerted for tests conducted with sewage samples (a) SW1 and (b) SW2.

Table 2 | Results of ANOVA analysis of test data

Sewage sample	Test	R ²	P-value ^a	F-value ^b
SW1	CT1	0.9999	0.9983	4.8 × 10 ⁻⁸
	CT2	0.9990	0.9923	9.6 × 10 ⁻⁵
	CT3	0.9978	0.9658	1.9 × 10 ⁻³
SW2	CT1	0.9981	0.9990	1.72 × 10 ⁻⁶
	CT2	0.9982	0.9887	2.1 × 10 ⁻⁴
	CT3	0.9960	0.9850	3.7 × 10 ⁻⁴

^a $\alpha = 0.05$, ^bF-critical = 4.7472.

confidence (Figure 4). This proves that the proposed kinetic relationship well replicates the reaction kinetics of chlorine response during sewage intrusion.

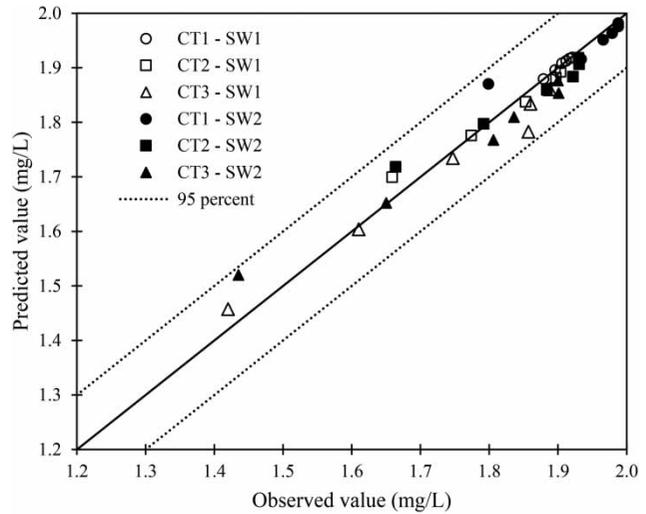


Figure 4 | Regression analysis results for the tests conducted.

Single factor analysis of variance (ANOVA) was conducted to compare the statistical significance of the test data and the predicted values. The *P*-values and *F*-values derived from the ANOVA analysis are given in Table 2. The *P*-value represents the probability by which the proposed model predicts the chlorine response with a significance level (α value) of 5%. The *P*-values for all the tests obtained are very close to 1.0. This indicates the consistency of the model predictions with the test data. The *F*-value is the ratio of the variance of group means (mean squares between) to the mean of the within the group variances (mean squared error). For all the tests, the *F*-values obtained are found to be much smaller than the *F*-critical (*F*-statistic) value (Table 2). Considering both the *P*-values and the *F*-values, it can be inferred that the model observations for all the tests are nearly identical to the test data.

Microbial decay kinetics

The chlorine response curves (Figures 1(a) and 2) show the attainment of a steady state 15 min after the contaminant injection. The batch tests (MT1 and MT2) were continued beyond this time to understand the kinetics of microbial decay during the very slow response phase. The microbial colony counts of the water samples were monitored at 3, 5, 10, 15, and 30 min. The results of the tests, MT1 and MT2, are shown in Figure 5.

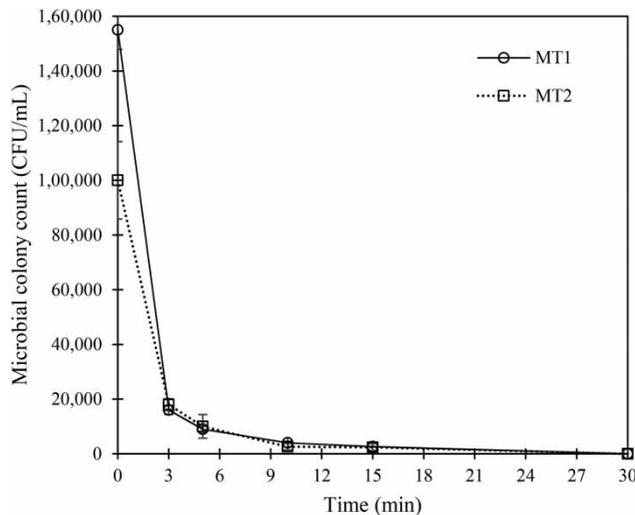


Figure 5 | Temporal variations in microbial colony count obtained by the injection of sewage sample (SW1) in mixing ratios of 1 in 200 (MT1) and 1 in 300 (MT2).

The average microbial colony count at $t = 0$ for the tests MT1 and MT2 was measured to be 1.55×10^5 CFU/mL and 1×10^5 CFU/mL, respectively. A rapid decrease in the microbial colony counts occurred by $t = 3$ min. The reaction kinetics slowed down after 3 min, and beyond this time, no significant variation in the microbial colony count was observable. The microbial decay attained saturation after 15 min. After 30 min, no colony formation was observable for both the tests MT1 and MT2.

The pattern of microbial decay observed from the tests MT1 and MT2 (Figure 5) shows a pattern similar to that of the chlorine response (Helbling & VanBriesen 2007). The rapid decrease in microbial colony counts immediately after the contaminant injection is analogous to the rapid response phase of the chlorine response curve. The rapid consumption of chlorine in the initial stages of the reaction, as observed in Figures 1(a) and 2, appears to be due to the utilization of chlorine for the inactivation of microbial cells. The relatively slow reaction kinetics of microbial decay, observed from 5 to 15 minutes, and the constant phase, observed after 15 minutes, may be analogous to the slow response and the very slow response phases of chlorine response curve, respectively. However, the microbial colony counts for both tests MT1 and MT2 are observed to be zero at 15 min. Hence, it was confirmed that decay of chlorine during the very slow response phase (after 15 min) is not due to the disappearance of microbial cells. In other

words, the initial chlorine concentrations of the water samples were sufficient to meet chlorine demand due to microbial contamination.

Chlorine has very strong oxidizing potential. The available chlorine in the water sample might cause oxidation of several chemical contaminants in the heterogenous contaminant matrix (Tian *et al.* 2017). It may be postulated that the disappearance of chlorine during the very slow response phase may be induced by these chemical contaminants. Because the maximum rate of microbial decay occurs in the first 3 min after contaminant loading, it may be inferred that the chlorine disappearance during the initial stage (rapid response phase) is predominantly influenced by the reactions causing the decay of microbial contaminants. During the intermediate stage (slow response phase), both groups of contaminants (microbial and chemical) may be contributing to the disappearance of chlorine in the water.

Kinetic parameters of the multi-phase relationship

The bi-phasic exponential relationship proposed by Haas & Karra (1984) uses three kinetic parameters, Q , k_1 , and k_2 . Q is the chlorine fraction demanded in the second phase of chlorine demand, k_1 is the chlorine decay kinetic coefficient for the initial phase of chlorine demand, and k_2 is the chlorine decay kinetic coefficient for the second phase of chlorine demand. Empirical relationships for the parameters of this expression were developed by Helbling & Vanbriesen (2009) by approximating a linear relationship between the initial chlorine concentration and chlorine remaining after a given contact time. However, this approximation does not hold well for the test results obtained here (Figure 1(b)).

We propose a simple kinetic relationship that uses only two kinetic parameters, i.e., maximum chlorine demand ($Cl_{d,max}$) and half-saturation constant (K_{50}). The values of both the parameters are dependent on the initial chlorine concentration of the water sample. The values of $Cl_{d,max}$ increase with increasing TOC values and microbial colony counts. This agrees with the basic understanding that a higher contaminant load corresponds to a higher chlorine demand. Higher contaminant loads (high V_{sew}/V_{wat} ratios) were observed to consume chlorine at a faster rate. Thus,

there is a decrease in the values of K_{50} with an increase in strength of contaminant loads.

PRACTICAL APPLICATIONS OF THE PROPOSED KINETIC MODEL

This work is a genuine attempt to understand the complex mechanisms governing the disappearance of chlorine induced by uncontrolled contamination in DWDSs. The proposed multi-phase kinetic relationship generalizes the complex biochemical reactions between microbial contaminants, chemical contaminants, and chlorine, by the selection of appropriate parameter values.

The proposed kinetic model may be utilized to investigate how the chlorine demand of water changes in real-world intermittent DWDSs in developing countries, which are commonly affected by the problem of sewage intrusion. It may be noted that more than one-third of the water utilities of Africa and South America and more than half of the water utilities of Asia are intermittently operated (Kumpel & Nelson 2016). Intermittent water supply also accounts for 17.2 million infections causing 4.52 million cases of diarrhea, and 1,560 deaths each year (Bivins *et al.* 2017). It is possible to practically safeguard water quality in a distribution pipeline from contamination via sewage intrusion if the chlorine concentration maintained is above the threshold value. By appropriate selection of chlorine dosage at the inlet point or at any intermediate point, a chlorine concentration greater than or equal to the threshold value, corresponding to an expected contaminant loading, can be maintained at points of potential contamination to adequately protect water quality. The proposed kinetic relationship can be duly incorporated for optimizing the chlorine dosages.

The proposed kinetic model can also be integrated with the monitoring framework for chlorine sensors to investigate the biological quality variations during conveyance. Chlorine sensors can be an effective tool to monitor microbial contamination in DWDSs. The proposed kinetic model may be used to relate the chlorine variations to microbial contaminant loads. By integrating chlorine sensor data with ICT cloud techniques, the water utility operators and consumers can be alerted during contaminant

intrusions. Necessary corrective and control actions can be taken this way to prevent dispersion of contaminants and potential health risks to consumers. This will help to mitigate the effects of uncontrolled contamination and will be a step towards solving the problem of water quality degradation in intermittent DWDSs of developing countries.

LIMITATIONS OF THE PRESENT STUDY

We hypothesized that no single-order kinetic model can represent the reaction kinetics of chlorine during the events of uncontrolled microbial contamination, such as sewage intrusion. A multi-phase model provides a better fit for chlorine reaction kinetics in this situation. A preliminary understanding of how the values of the kinetic parameters vary with the contaminant load (TOC and microbial colony count) in water maintained with a specific initial chlorine concentration is presented in this work. Total coliform bacteria were only considered as the potential indicator of microbial contamination. The other microorganisms that may influence the reaction kinetics of chlorine in the slow and very slow response phases were not considered, and this aspect needs further investigation. An empirical method is required for the estimation of the kinetic parameters induced by a specific contaminant load for a given chlorine concentration. It may also be noted that only the bulk phase reaction was analyzed in the present study; further research should incorporate wall zone reactions in order to understand completely the kinetics of chlorine disappearance in pipelines of real-world DWDSs.

CONCLUSIONS

Chlorine response to uncontrolled contamination (sewage intrusion) is distinguishable into three reaction phases: rapid response phase (approximately up to 5 minutes), slow response phase (between 5 and 15 minutes), and very slow response phase (beyond 15 minutes). The microbial contaminants present in the heterogeneous contaminant matrix predominantly influence the reaction rate during the rapid response phase. Both microbial and chemical contaminant groups may influence the reactions during the slow

response phase. The chemical contaminants may contribute significantly to the decay of chlorine during the very slow response phase because no total coliform count was observed after 30 minutes. A multi-phase kinetic relationship, which distinguishes the reaction into three phases, first-order, mixed-order, and zero-order, is fitted to define the chlorine response to sewage intrusion. Statistical analysis indicated that the model predictions are a good fit for the experimental data. The proposed kinetic model may be utilized to investigate how the chlorine demand of water changes in DWDSs during real-world sewage intrusion events.

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