“Achieving safe free residual chlorination at point-of-use in emergencies: A modelling approach”

by

Hongjian Wu

B.Sc., University of Toronto, 2018

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

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in the Department of Civil Engineering

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Supervisory Committee

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Abstract

While free (breakpoint) chlorination is widely utilized in humanitarian water treatment, a main challenge limiting its effective application is in determining the initial dose to satisfy both health requirements and aesthetic considerations (i.e. taste and odour). International guidelines and studies showed varying recommendations for the initial chlorine dose and many did not consider chlorine decay during water transportation and storage for up to 24 hours. The main objective of this thesis is to develop a tool for humanitarian staff to accurately determine the initial chlorine dose for achieving free chlorine residual (FCR) objectives with the limited instrumentation and information in the field. The first manuscript included in the thesis gathered and evaluated seven basic chlorine decay models' applicability in humanitarian treatment contexts. All seven models were found able to accurately describe chlorine decay in water representative of humanitarian treatment contexts with more than half of the regression resulted in R^2 over 0.95. However, each model had its own limitations, which were discussed. The second manuscript involved conducting extensive chlorine decay tests in water with different characteristics, explored the relationships between the estimated chlorine decay constant and several water parameters including pH, turbidity, ultraviolet absorption at 254 nm wavelength (UVA_{254}), temperature and 30-minute chlorine demand. It was found that the UVA_{254} of water followed linear and exponential relationships with the decay constant in Feben and Taras's empirical model and that in the first order model respectively. Arrhenius-type relations were verified between the decay constant and water's temperature. A model developed to predict FCR decay in water with known 30-minute chlorine demand accurately predicted FCR level in synthetic water (with humic acid being the main constituent) but underpredicted FCR decay in water with additional chlorine consuming

matter. Further research on additional chlorine decay mechanisms are needed to expand the applicability of the model.

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List of Abbreviations

Abbreviation	Meaning
CDC	Centers for Disease Control
DBP	Disinfection-by-products
FCR	Free chlorine residual
FMH	Federal Ministry of Health, Government of Sudan
IFRC	International Federation of Red Cross and Red Crescent Societies
JHU	Johns Hopkins University
POU	Point-of-use
RMSE	Root mean square error
SSR	Sum of square of residuals
SST	Total sum of squares
TOC	Total organic carbon
USEPA	United States Environmental Protection Agency
UVA_{254}	Ultraviolet absorbance at 254 nm wavelength
WASH	Water sanitation and hygiene
WHO	World Health Organization

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Introduction

Background

Inadequate quantity and quality of water supplied in humanitarian emergency situations underlie most public health problems, including the transmission of water- and excreta-related diseases, as classified by Mara and Feachem (1999). Supplying water that is safe for drinking is important in humanitarian water supply. However, providing water in sufficient quantity is equally if not more important as it supports personal and domestic hygiene, which is another major factor accounting for the transmission of diseases (Dorea, 2012). The SPHERE handbook (2018) specifies a minimum requirement of 15 liters of water per person per day in crisis situation, and the exact quantity should be based on the context and phase of the response. It is a priority to fulfill the quantity requirement of water supply, but efforts should be made towards improving the water quality.

Free (breakpoint) chlorination is a widely employed disinfection method in humanitarian water interventions due to its advantages. Some of them include easy to be obtained, easy to be verified, effective in inactivating most bacterial and viral pathogens and having residual protective effects in the water during transportation and storage (Murray & Lantagne, 2015). Chlorine can be applied at different stages of humanitarian water provision and in different locations. Common chlorination programmes for emergencies include centralized treatment (i.e. water treated in bulk in water storage tanks or other containers), point-of-delivery (i.e. water chlorinated in tanker truck during water collection), point-of-source (i.e. water chlorination at the source – pot chlorination for wells), point-of-collection (i.e. chlorine dispenser at water tap stand) and point-of-use (i.e. chlorination of water in household containers) (Ali et al., 2015; Branz et al., 2017; Garandeau et al., 2006; Gupta & Quick, 2006; Yates et al., 2015). Chlorine is typically applied in powder (i.e.

Sodium dichloroisocyanurate (NADCC) and calcium hypochlorite), liquid (i.e. bleach solution) or tablet (i.e. NADCC tablet) form in humanitarian water treatment (Clasen & Edmondson, 2006; Lantagne & Clasen, 2012; Yates et al., 2015). The solid chlorine products are easier to be transported to sites and liquid sodium hypochlorite is usually available locally (Branz et al., 2017). The established chlorination strategies and the variety of chlorine products facilitate its application in humanitarian emergencies.

Despite the advantages and widespread usage of free chlorination in humanitarian water supply, one main challenge limiting its effective application is the determination of the initial chlorine dose (Branz et al., 2017). Due to a strong oxidant nature, chlorine reacts with different inorganics (i.e. metals, ammonia etc.) and organics (i.e. humic acid and fulvic acid) in the water (Crittenden et al., 2012; Fisher et al., 2011). Most of these reactions happen in the first 30 minutes after dosing, and the amount of chlorine consumed to complete these reactions is called the "chlorine demand" of the water. Only after the chlorine demand of the water is met, additional chlorine then forms FCR for disinfection purposes (Branz et al., 2017). The FCR concentration continues to decrease due to slower reactions with some of the organics and physical losses such as evaporation and dissociation (Abdel-Gawad & Bewtra, 1988; Fisher et al., 2011). An indicator of safe drinking water in humanitarian water supply is the presence of sufficient free chlorine residual (FCR) in the water. The FCR level in the water should be maintained to meet both health-based limits and aesthetic considerations (i.e. taste and odour) for up to 24 hours during transportation and storage in the field (USEPA, 2018; Lantagne, 2008; WHO, 2017). Chlorine dose determination is challenging because the chlorine demand and FCR decay characteristics are site specific and are usually unknown for water sources identified in humanitarian contexts.

Unlike conventional (i.e. non-emergency) contexts in which water is treated in engineered reactors under relatively stable environmental conditions, chlorination in humanitarian contexts has its unique set of challenges. Firstly, in humanitarian contexts, chlorination may happen in different places, ranging from centralized storage tank to household's storage containers (i.e. jerrycans, plastic buckets, ceramic pots, etc.), and containers without proper maintenance add chlorine demand to the water (Meierhofer et al., 2019). Secondly, relatively elevated temperatures and intense sunlight exposure are usually associated with humanitarian water contexts. Such environmental conditions may accelerate both the chlorine reaction kinetics and the losses of chlorine through evaporation and dissociation (Abdel-Gawad & Bewtra, 1988). Thirdly, many of the FCR verification techniques are subjective with regard to field personnel interpretation. Instead of outputting an exact value, humanitarian staff estimate values by visually assessing color changes shown by the measuring devices. Six commercially available FCR measuring devices used in the field showed 5.1% to 40.5% measurement error in accuracy under laboratory condition (Murray & Lantagne, 2015).

There are international guidelines and studies with recommendations for determining initial chlorine doses in humanitarian water supply (Branz et al., 2017). However, the recommended values vary across guidelines, and most guidelines do not consider chlorine decay during water storage for up to 24 hours. The variability in recommendations can create confusions for humanitarian staff.

Goal of thesis

To tackle the challenges presented earlier, a tool/method is warranted to accurately determine the adequate chlorine dose for achieving FCR targets in humanitarian treatment contexts with the limited available information in the field. The goal of the thesis is to work towards the development

of such tool. For achieving this goal, two main activities were conducted, namely: (1) the evaluation of existing chlorine decay models' application in humanitarian contexts and (2) the development of predictive model based on chlorine decay impacting factors.

Structure of thesis

The thesis is comprised of two manuscripts, which details the two steps undertaken to move towards achieving the goal of the thesis. The main objective of the first manuscript, "Evaluation and Application of Chlorine Decay Models for Humanitarian Emergency", was to identify available chlorine decay models used in conventional water treatment and evaluate their applicability in contexts of humanitarian water supply. This manuscript was originally designed to be a systematic review on published chlorine decay models in peer-reviewed literature. However, three papers identified during the process together evaluated and summarized most of the available chlorine decay models for the applications in conventional treatment contexts (Fisher et al., 2011; Haas & Karra, 1984; Kim et al., 2015). The focus was then shifted to the evaluation of the identified models on their applicability in contexts of humanitarian water supply. A systematic approach was still employed to gather available chlorine decay data in identified papers. The search was conducted in December 2018 in three databases (i.e. Web of Science, Engineering Village, PubMed), and 250 tests data were extracted from 32 papers. Combining with 324 data from the study by Gallandat et al. (2019) and 62 data generated from experiments conducted for the second manuscript, a total of 636 test data were available for evaluating these models' applicability in humanitarian contexts.

The second manuscript, "Towards a Predictive Model for Initial chlorine Dose in Humanitarian Emergencies" built on the results from the first manuscript. The models evaluated in the first manuscript were used to study chlorine decay in synthetic test waters with different concentrations

of humic acid and under different temperature conditions. Pearson correlation analysis was conducted between water parameters and the estimated chlorine decay constant from regression analysis for each of the model separately. The models and developed relations between parameters were then used to develop a method for predicting chlorine decay in specific water types (including natural sources) and to back-calculate the initial dose. Verifications with natural water sources showed that additional chorine decay mechanisms should be examined to further improve the predictive tool.

In the Discussion section, a brief recap of the two manuscripts was provided, followed by discussion on how 30-minute chlorine demand of water could be an appropriate proxy for estimating chlorine decay in humanitarian treatment contexts. The relations between the fast and slow decay phases of typical chlorine decay curves were then discussed. The limitations of applying the developed model from the thesis was also mentioned and future research activities were recommended.

Manuscript 1

Manuscript Title

Evaluation and Application of Chlorine Decay Models for Humanitarian Emergency Water Supply Contexts

Authors

J. Wu, C. Dorea

State of Publication:

This manuscript is intended to be submitted as an Article in the *Journal of Water & Health* (IWA Publishing).

Abstract

Chlorine is a widely used water disinfectant in humanitarian emergency water supply. However, its effective application can be limited by the uncertainty in initial dose determination. The target free chlorine residual in water should achieve both health objectives and aesthetic considerations, but the varying field conditions and changing source water quality may affect the performance of chlorination strategies. A predictive chlorine dose tool could be useful to assist initial dose determination. To this end, an accurate chlorine decay kinetic model can serve as a strong foundation for developing such a tool. In this study, a literature search identified 7 basic chlorine decay kinetic models that were subsequently tested with 610 different chlorine decay test data (from a semi-systematic literature search and laboratory-generated results). The models were then ranked based on their goodness of fit (R^2) and root mean square error. An empirical model, power models and parallel models were found able to fit most decay data with more than half of the regression resulting in R^2 value over 0.97. First order models can achieve R^2 value above 0.95 when the data points in the rapid phase are excluded from the model fitting. The power models and parallel models can form a strong basis for developing a chlorine dose predictive tool if the power term and the ratio term (adjustable terms in the model) can be controlled. An essential next step is to evaluate the relationships between easily obtainable water parameters in the field and the decay term in the models to allow rapid model calibration.

Keywords:

Chlorination; Decay; Kinetics; Models; Emergency Water Supply; WASH; Container Chlorination; Point-of-Use Water Chlorination;

Introduction

A humanitarian emergency can arise when the impacted communities are unable to cope with the disruptions induced by natural or man-made hazards. The affected population is at higher risk to water- and excreta-related diseases, as classified by Mara and Feachem (1999), due to the combined impacts from insufficient water supply, inadequate sanitation and poor hygiene practices. Humanitarian emergency water supply should, therefore, provide water of safe quality for drinking and of sufficient volume for personal and domestic hygiene practices (Dorea, 2012). Chlorination is a widely used disinfection method in humanitarian emergency water supply because chlorine inactivates most viral and bacterial pathogens in a rapid and cost-effective manner while leaving a free chlorine residual (FCR) in the water for protective effects. (Branz et al., 2017; WHO, 2017).

A major challenge in chlorination is in determining the correct chlorine dose to attain adequate FCRs whilst avoiding overdosing, which could cause taste and odour issues (Branz et al., 2017; WHO, 2017). Humanitarian contexts present unique challenges due to the differences in resources (e.g. equipment, staffing, expertise, etc.) relative to the conventional (non-emergency) water treatment contexts (Dorea et al., 2006). In a conventional treatment approach, chlorination takes place in engineered contact tanks under relatively stable conditions, and chlorine doses can be determined by measuring the chlorine decay characteristics and by modeling the FCRs in the distribution network (Fisher et al., 2011; Hua et al., 1999). The chemistry of water (i.e. pH) can also be adjusted to achieve optimum chlorination conditions. In humanitarian emergencies, chlorination can take place in a variety of places, ranging from centralised bulk tanks to decentralised household containers in point-of-use (POU) water treatment, and they might be exposed to elevated temperature and intense sunlight, which alter the chlorine decay kinetics (Abdel-Gawad & Bewtra, 1988; Ali et al., 2015; Branz et al., 2017; Yates et al., 2015). Some

chlorine dose recommendations are determined primarily based on the turbidity of the source water (JHU & IFRC, 2008; Lantagne, 2008). In the field, only certain water parameters (i.e. pH, temperature, turbidity) are measurable due to limited instrumentation typically available (Dorea & Simpson, 2011). In addition, the results from some measurement devices rely on personal judgements and hence, show greater variability compared to results from methods used in conventional water treatment (Murray & Lantagne, 2015). In humanitarian contexts, FCR decay of stored water can be for up to 24 hours after collection, which is a notable contrast to conditions in conventional water supply systems. Considering the differences between conventional and humanitarian water supply, a bespoke predictive chlorine dose tool for humanitarian emergencies is needed to facilitate the effective application of chlorination.

There is limited research on chlorine decay modelling in humanitarian contexts, which can help determining the initial chlorine dosing. One study by Ali et al. (2015) utilized a modelling approach to study FCR decay across three refugee camps in South Sudan. They used their model to determine a 1.1 mg/L initial dose to achieve their FCR target (i.e. 0.2 mg/L FCR after 12 hours of storage). The power model they employed achieved an average R^2 value of 0.76 from 220 water samples, and this demonstrates how modelling can be helpful for determining the chlorine dose in the field. The power model was originally developed for modelling chlorine decay in the conventional treatment context, but Ali et al. (2015) showed that it is also applicable in the humanitarian context. However, there is a variety of published models to assist in the design and planning of chlorination in conventional (i.e. non-emergency contexts) water systems (Fisher et al., 2011). These models are potentially applicable in humanitarian water supply, and their applicability should be evaluated.

An adequate chlorine decay model should capture the characteristics of the chlorine decay curve, which has both a fast and a slow decay region. When chlorine is dosed into water, it tends to react with an array of substances due to its nature as a strong oxidant, causing a reduction in chlorine's concentration over time (Crittenden et al., 2012). Generally, reactions between chlorine and easily oxidizable matter, dissolved metals, and ammonia take place rapidly. These happen usually during the initial 30 minutes after dosing, forming the fast chlorine decay region. When these reactions are complete, chlorine reacts with the remaining organic matter (i.e. humic acid) in the water at a slower kinetic rate, creating the slow decay phase (Fisher et al., 2011).

This study is aimed at evaluating the applicability of different available chlorine decay models to humanitarian chlorination contexts. Specifically, the study tries to answer the following questions: What models are available for describing chlorine decay in water? Which ones are more applicable in humanitarian water treatment context? What are the constraints on these models?

Methodology

To evaluate the applicability of different chlorine decay models in humanitarian emergency water supply, a first step was to identify available models from literature. The identified models were then evaluated based on how well they accurately describe the chlorine concentration change in water, over a range of water types (i.e. surface water, ground water, grey water etc.) and in both the conventional and emergency settings. The applicability is quantified by checking the coefficient of determination (R^2) and root mean square error (RMSE) of the results from data regression analysis. In this study, only chlorine decay models, whose rates are based solely on the concentration of chlorine, were examined and a semi-systematic approach was utilized to gather available chlorine decay test data for testing the models.

Published Model Identification

Most of the chlorine decay kinetic models were summarized and evaluated in three papers identified during literature search. Haas and Karra (1984) fitted five chlorine decay kinetic models to the chlorine decay test data in secondary effluents provided by Lin and Evans (1974), and they found the parallel first order model resulted in more satisfactory fit compared to other models. Kim et al. (2015) tested 14 chlorine models and the relationship of their parameters' relations with their respective Reynolds numbers in a pilot distribution system. Fisher et al. (2011) summarized and evaluated most published models based on several features: accuracy, simplicity, computational efficiency, ability to describe effects of initial dose, temperature condition and re-chlorination. Seven models which had an analytical solution to the decay rate equation and the rates based solely on the concentration of the chlorine (a quantifiable parameter in field conditions) were identified as basic models. Other identified models were expansions (expanded models) of the basic models, which included multi-stage models, higher order models concerning both the concentration of chlorine and the reactants, and empirical solutions for basic models where the parameters were estimated based on water quality and/or environmental conditions.

Data acquisition

A semi-systematic approach was used to identify and extract relevant chlorination datasets in three databases (i.e. Web of Science, Engineering Village, PubMed) based on the keyword strategy as follow: [(Chlorin*) AND (Water) AND (Total OR Residual OR Free OR Combined) AND (Decay OR Decrease OR Demand OR Reduction OR Kinetics OR Mechanism*) AND (Model OR Models OR Modelling)].

The search was conducted in December 2018, and the results were restricted to peer-reviewed journal articles. Additional relevant studies were identified through searching the cited articles from the selected studies. Only papers published in English were included in the search.

All journal articles identified through the keyword search were imported into Zotero (Version 5.0), a reference management software. After duplicate removal and title screening, the remaining studies which met any two of the following three criteria were determined eligible for this study:

1. At least one chlorine decay model is presented/proposed
2. The model/method was tested on water sample(s) and the sources of water are specified.
3. At least one water characteristic (i.e. pH, turbidity, conductivity, temperature etc.) is quantified.

The open source WebPlotDigitizer software (https://automeris.io/WebPlotDigitizer/, accessed: February 28, 2019) was used to digitally extract the data points plotted on chlorine decay plots presented in identified journal articles. All extracted data were arranged and saved in an Excel spreadsheet for analysis. This resulted in 250 test data.

There are three data groups in this study based on the data sources and the context they represent. Table 1 shows the number of test data included in each data group.

Table 1. Number of test data from each of the three sources.

Group	For ranking determination (90%)	For ranking verification (10%)	Total test data	Context	Sources
A	225	25	250	Conventional	Papers listed in S1 - Literature data sources
B	268	30	298 (324 originally)	Humanitarian Emergency	(Gallandat et al., 2019)
C	55	7	62	Conventional and Humanitarian Emergency	(Wu, 2020)

Group A contains all extracted data from the semi-systematic literature search, and it represents the treatment context of a conventional water system. The two components of chlorine decay planning in a conventional water system are chlorine bulk decay and chlorine wall decay. Data in

Group A originate from chlorine bulk decay studies, which were conducted in controlled close containers. The 324 test data from Group B were those from a previous study (Gallandat et al., 2019). These 324 test data originate from tests conducted in 16-L plastic buckets simulating the treatment setting of a humanitarian emergency. After data analysis, 26 test data were excluded for the evaluation exercise, leaving 298 remaining test data. Data in Group C comes from author's experiments (Wu, 2020). The water used was a synthetic water with added humic acid to control the water's organics content. The temperature settings were at 10℃, 20℃, and 30℃. 40 tests were conducted in bulk water and 22 tests were conducted in jerry cans. In total, 610 test data were used in this study.

For each group, the test data were separated randomly into a 90% pile and a 10% pile. The 90% pile were used to generate a model ranking based on the R^2 value from regression analysis; such ranking is then verified by running the same process and checking the RMSE of models calculated for the remaining 10% pile.

Model fitting analysis

MATLAB (R2019a) was used to fit the selected models to the test data extracted. The model fitting was done using the least square error method, which is widely accepted and utilized for such purposes. MATLAB program (S2-Matlab Codes) automatically searched for the combination of parameters which result in the smallest error from the model compared to the original data. The R^2 value was then calculated based on the fitted model using Equation 1.

Equation 1. Formula for R^2 calculation.

$$R^2 = 1 - \frac{SSR}{SST}$$

$$SSR = \Sigma(y_i - \hat{y}_i)^2$$

$$SST = \Sigma(y_i - \bar{y})^2$$

Where SSR is the variation explained by the model, and SST is the total variation in the data. y_i is the y value for observation i, $\bar{y}$ is the mean value of y, and $\hat{y}_i$ is the predicted value of y for observation i.

The remaining 10% of test data were fitted with the same models, and their RMSE were computed using Equation 2.

Equation 2. Formula for RMSE calculation.

$$RMSE = \sqrt{\frac{\sum(\hat{y}_i - \mathrm{y_i})^2}{n}}$$

Where $\hat{y}_i$ is the predicted value of y for observation i, $\mathrm{y_i}$ is the y value for observation i, and n is the number of observations. Based on the ranking from analysis of the 90% of the test data, higher ranking models should generate the smallest error when fitted to the 10% test data. This provides verification for the model ranking.

Results

Literature model summary

The seven basic models identified are summarized in Table 2. Expanded models were not included for evaluation due to several reasons: 1. The empirical models required certain water quality data (i.e. temperature, TOC, chlorine demand, etc.) to estimate parameters in the decay equation, and test data gathered from the literature did not consistently contain these values; 2. The multi-stage models combined different basic models and selected certain reaction times as the divides. The variation in times of measurements and missing data points at the divides in the extracted data did not allow the effective comparison among these models. Only the basic models could be evaluated

with all the extracted data with their readily available analytical solutions. From here on, all models will be referred to their corresponding numbers in Table 2.

Table 2. Basic Chlorine Decay Models.

Basic Models			
Single Reactant Models	**Name**	**Equation**	**References**
1	Empirical Model – "Feben and Taras"	$C=C_0-kt^n$	(Feben & Taras, 1951)
2	First Order Model	$C=C_0*e^{-kt}$	(Haas & Karra, 1984)
3	Limited First Order Model	$C=C_*+(C_0-C_*)e^{-kt}$	(Haas & Karra, 1984)
4	Power Decay Model	$C=[kt*(n-1)+(1/C_0)^{n-1}]^{-1/(n-1)}$	(Haas & Karra, 1984)
5	Limited Power Decay Model	$C=C_*+[kt*(n-1)+(1/(C_0-C_*))^{n-1}]^{-1/(n-1)}$	(Haas & Karra, 1984)
Two Reactants Models			
6	Parallel First Order Model	$C=(w)*C_0*e^{-k1t}+(1-w)*C_0*e^{-k2t}$	(Haas & Karra, 1984)
7	Limited Parallel Power Model	$C=C^*+[k_1t*(n_1-1)+(1/(w)*(C_0-C^*))^{n1-1}]^{-1/(n1-1)}\}+[k_2t*(n_2-1)+(1/(1-w)*(C_0-C^*))^{n2-1}]^{-1/(n2-1)}$	(Kim et al., 2015)

Model fitting results

The extracted data from literature covers chlorine decay in water from a variety of sources. The 250 literature-extracted test data were divided into six categories as shown in the pie chart in Figure 1.

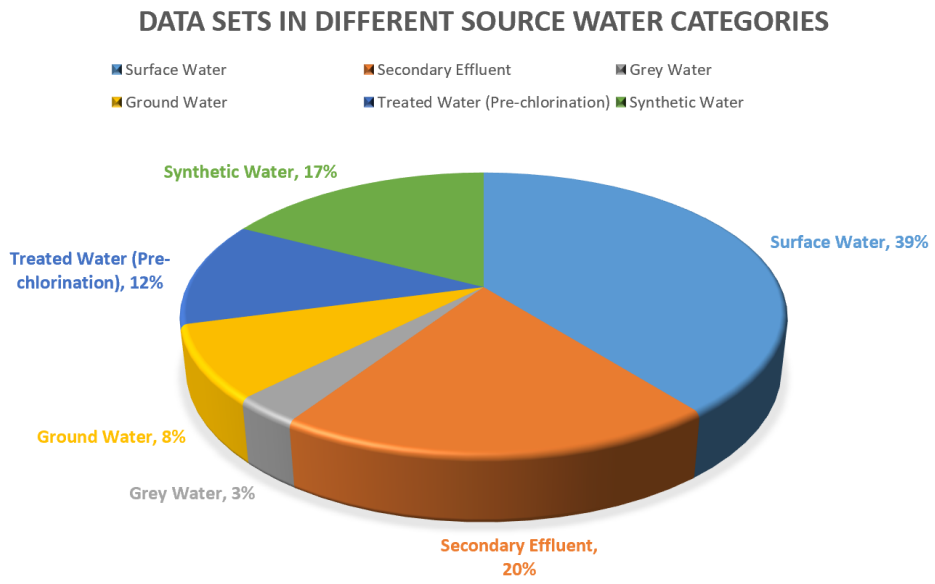

Figure 1. Distribution of extracted test data (250 in total) from different source water categories.

The R^2 distribution of results from regression of the 225 test data (90% of Group A) are shown in the box and whisker plot (Figure 2) below. Based on the results, Model 7 resulted in the best fitting capacity (median $R^2 = 0.995$) compared to other models on the extracted test data. It also had the narrowest dispersion of values among all models evaluated. Model 6 (median $R^2 = 0.987$), Model 1 (median $R^2 = 0.984$), Model 5 (median $R^2 = 0.974$) and Model 4 (median $R^2 = 0.971$) closely followed Model 7 with similar performance but greater dispersion of values. Model 3 and Model 2 resulted in median R^2 values of 0.937 and 0.866 respectively, which were comparatively lower than other models.

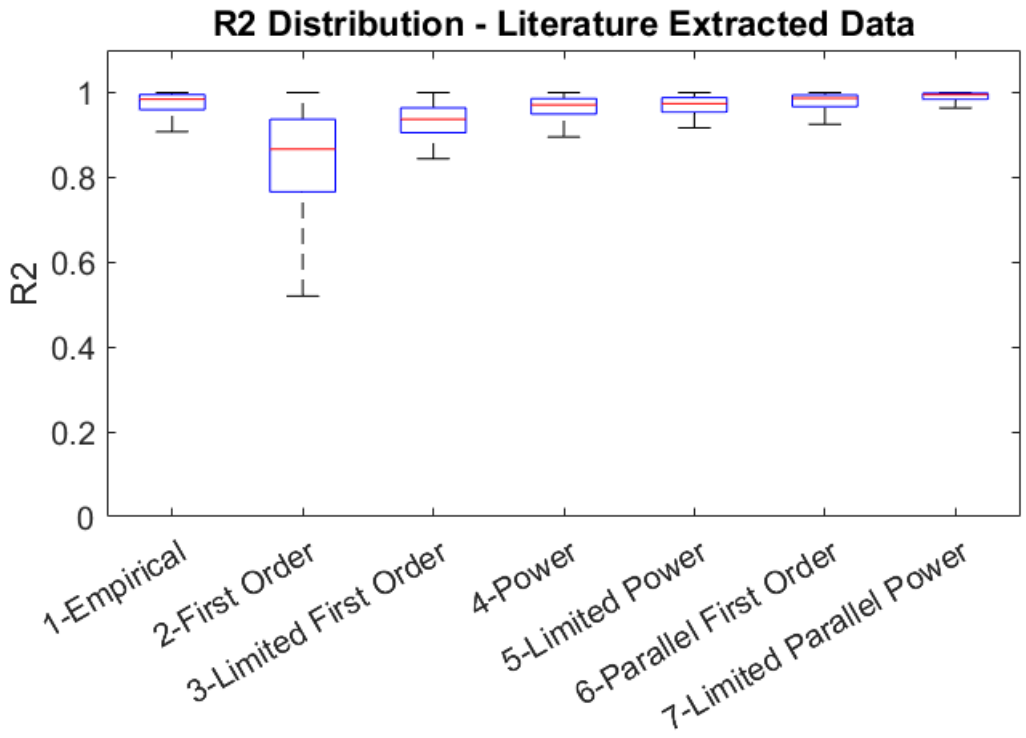

Figure 2. R^2 distribution results from the fitting of seven distinct models on 225 (90% of Group A) test data extracted from literature. From top to bottom of each box are the maximum value, third quartile, median, first quartile, and minimum value of R^2 for the specific model it represents.

By calculating the RMSE from the seven models on the remaining 25 chlorine tests (i.e. 10 % pile of Group A), a distribution of RMSE values can be seen in the box and whisker plot in Figure 3. A ranking of models from the smallest RMSE values to the largest are Model 7 (RMSE = 0.056 mg/L), Model 6 (RMSE = 0.071 mg/L), Model 1 (RMSE = 0.089 mg/L), Model 4 (RMSE = 0.094 mg/L), Model 5 (RMSE = 0.104 mg/L), Model 3 (RMSE = 0.157 mg/L) and followed by Model 2 (RMSE = 0.224 mg/L).

This result verified that Model 7 had the best performance (smallest median RMSE and smallest value dispersion). However, all models except for Models 2 and 3 achieved similar performance when modelling literature extracted data.

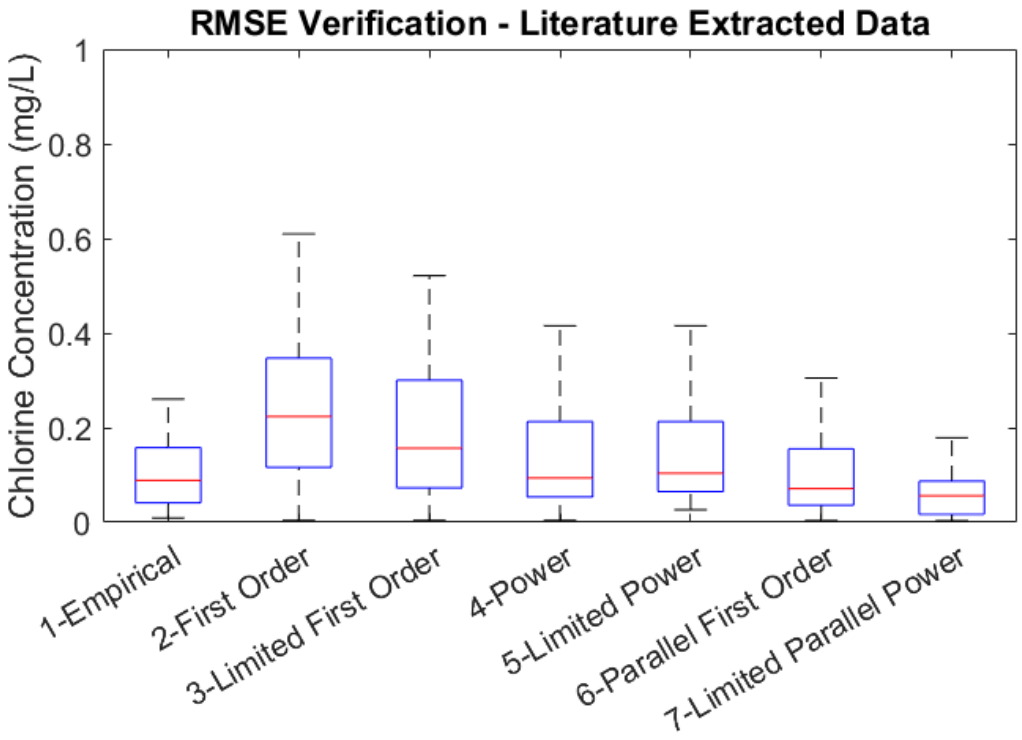

Figure 3. RMSE results from the fitting of seven distinct models on the remaining 25 (10% of Group A) test data extracted from literature. From top to bottom of each box are the maximum value, third quartile, median, first quartile, and minimum value of RMSE for the specific model it represents.

When fitting the models on data from Gallandat et al. (2019), 26 test data resulted in negative R^2 values. Figure 4 shows an example of the case. Because the regression line (red line in figure) always passes through the first data point and the remaining values can only be smaller if not equal to the initial FCR, the best fitting line for data in the figure resulted in a close-to-horizontal line passing the first point. Based on the formula for R^2 (Equation 1), SSR is greater than SST, meaning error from using the fitted line to describe the data is greater than the error from using the average of the data (blue line in the figure), R^2 ended up being negative. The data shown in Figure 4 has an issue, which is having larger measured FCR in water than the initial value as the residence time (value on x-axis) increases. It was uncertain what lead to such observations in the data set, but the 26 test data were considered inadequate to be used for the model evaluation purpose. The 26 test data were excluded from the later analysis, leaving 298 sets of data.

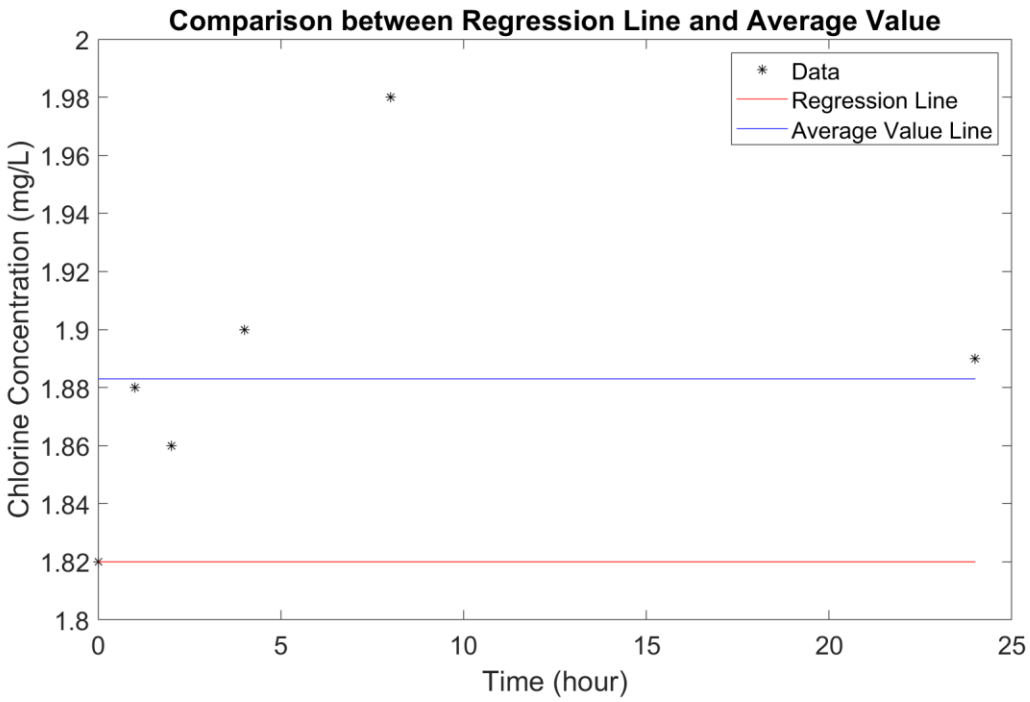

Figure 4. Comparison of data prediction with the fitted first order model and with the horizontal line (average value of data).

The R^2 distribution of the seven models on modified test data from Gallandat et al. (2019) are shown in the box and whisker plot (Figure 5) below. Based on the results, the median R^2 values (0.961, 0.934, 0.973, 0.984, 0.984, 0.992 and 0.991 for Models 1 through Model 7 respectively) were very similar to the results from modelling literature data besides a greater dispersion of R^2 values for all seven models.

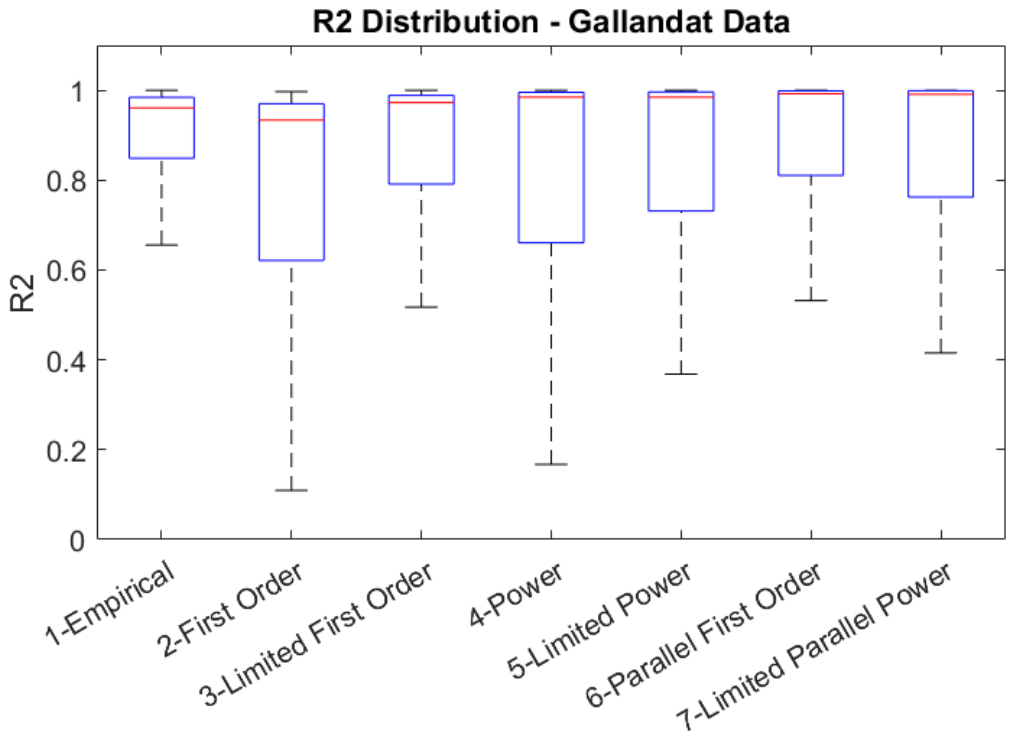

Figure 5. R^2 distribution results from the fitting of seven distinct models on 268 (90% of Group B) test data from Gallandat et al. (2019).

Figure 6 shows the RMSE of all seven models on the remaining test data (10% of Group B) from Gallandat et al. (2019). The results indicated that all models performed similarly in the bucket system that attempted to simulate humanitarian emergency water treatment conditions.

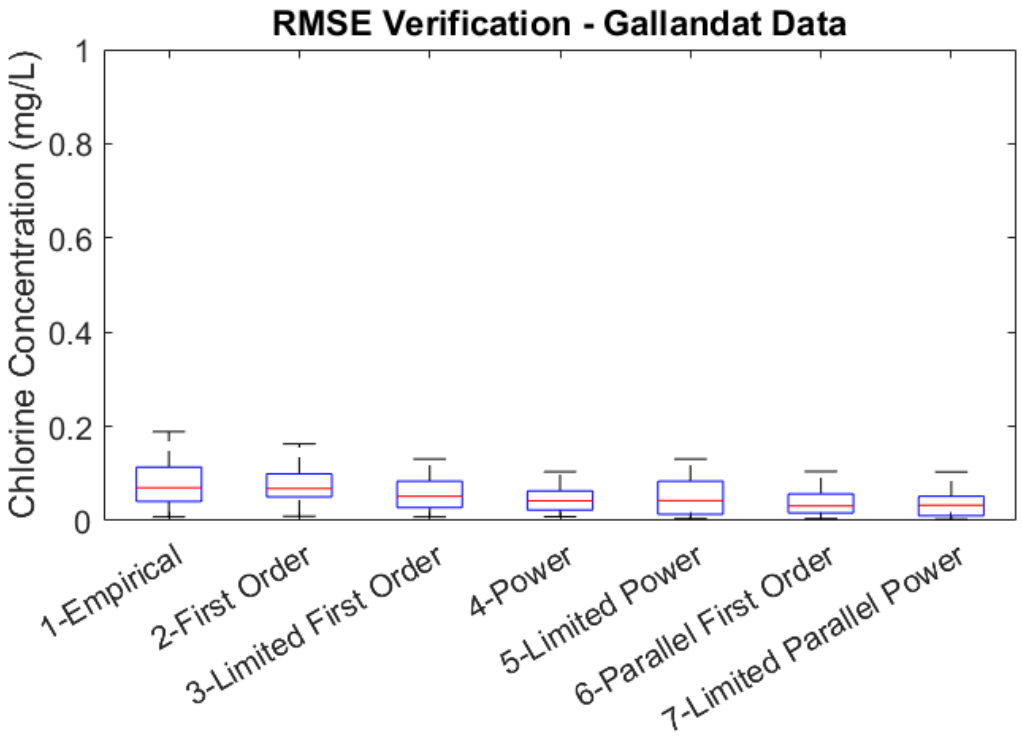

Figure 6. RMSE results from the fitting of seven distinct models on the remaining 30 (10% of Group B) test data from Gallandat et al. (2019).

Figure 7 below shows the model fitting results for the 51 tests data from Wu (2020). Model 7 performed the best among all models based on the median R^2 of 0.995. It is followed by Model 1 with a median R^2 value of 0.992, which is very closed to that of Model 7. The most used model in the conventional system, Model 2, performed the worst among all evaluated models with the lowest median R^2 value (0.797) and a largest dispersion of R^2 values. Figure 8 shows the RMSE from model fitting on the remaining 7 test data in Group C, and it verifies the ranking based on the results in Figure 6.

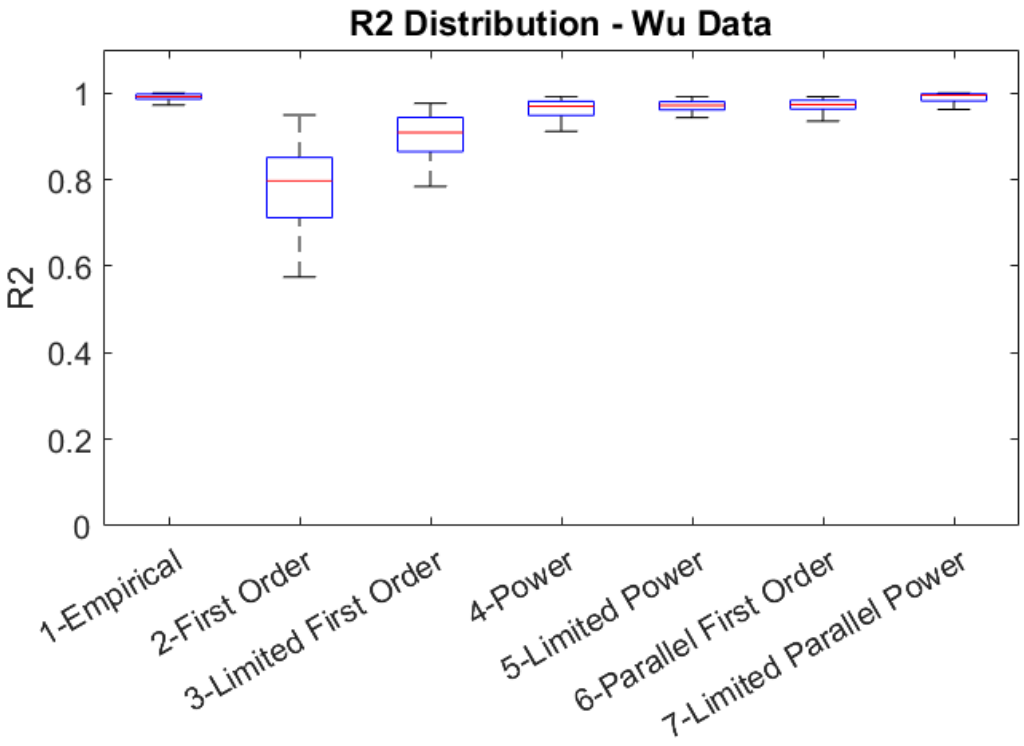

Figure 7. R^2 distribution results from the fitting of seven distinct models on 44 (90% of Group C) test data from Wu (2020).

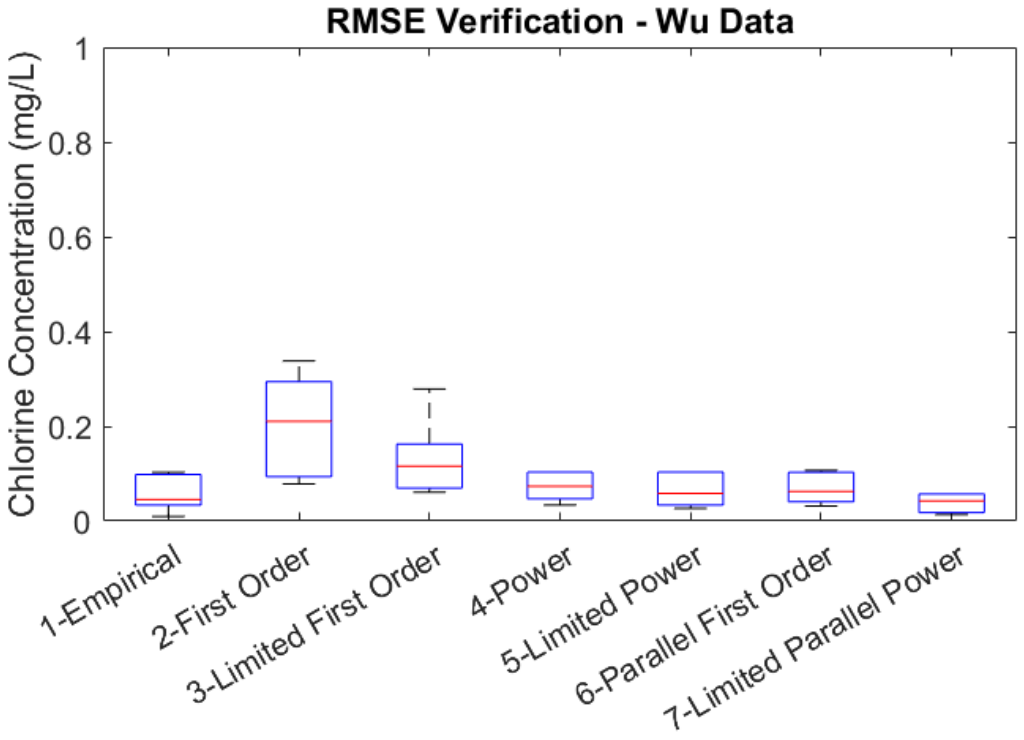

Figure 8. RMSE results from the fitting of seven distinct models on the remaining 7 (10% of Group C) test data from Wu (2020).

The box and whisker plots (Figure 9) show the distribution of estimated power term ‘n’ and ratio term ‘w’ (Figure 10) from applying the power models (Models 1, 4, 5 and 6) and models with two components (Models 6 and 7) on test data from Wu (2020). Compared to Model 1 (power model in nature), other power models show much greater dispersion of the value of their power terms. The ratio term of Model 6 and Model 7 ranged from 0.02 to 0.82 and from 0.03 to 1.0 respectively, covering most of the possible value range (0 to 1). This implies unpredictability in the estimation of the power term and ratio term in these models (except Model 1).

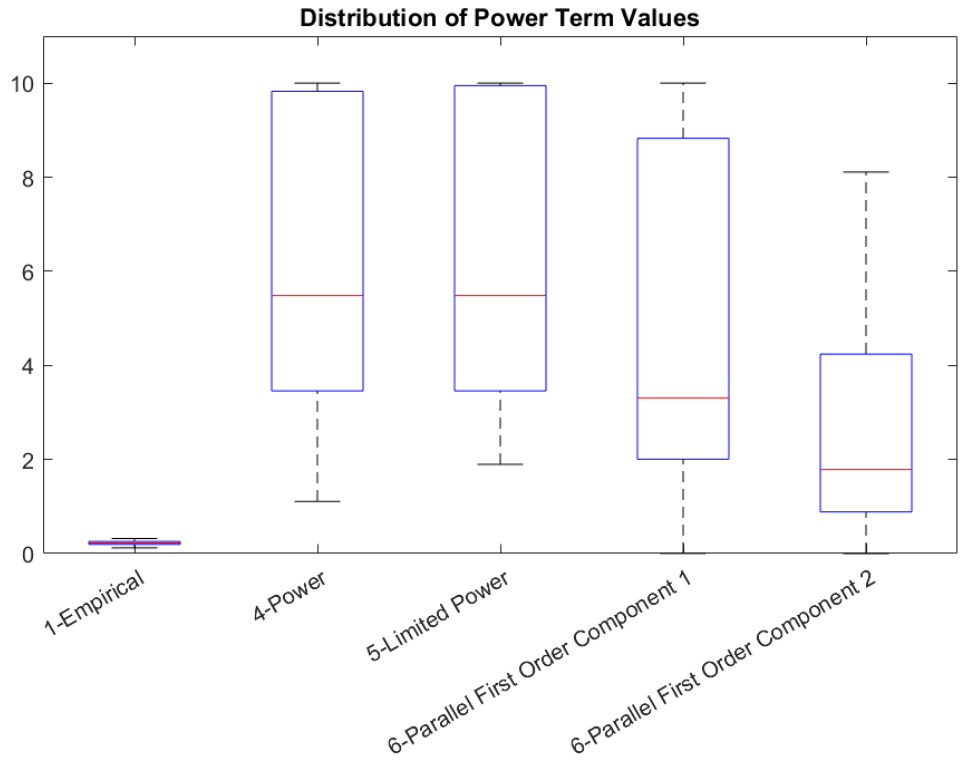

Figure 9. Distribution of the estimated power term in the corresponding models on data from Wu (2020).

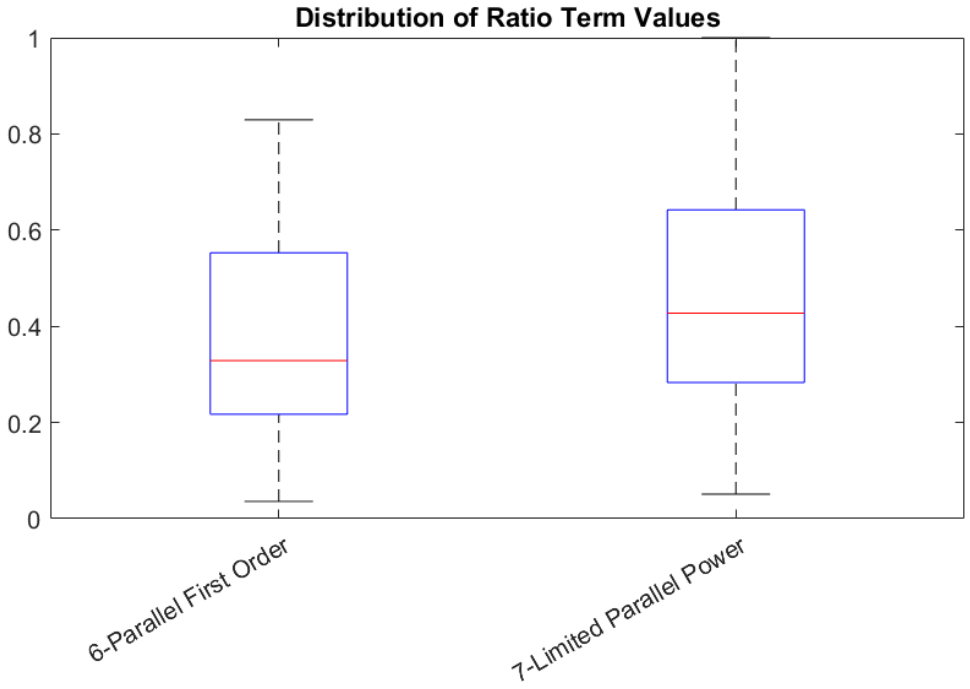

Figure 10. Distribution of the estimated ratio term in the corresponding models on data from Wu (2020).

Discussion

Overall Application

Six basic kinetic models (Models 1, 3, 4, 5, 6, 7) could describe chlorine decay across a range of source water types and in both conventional and humanitarian contexts with more than 50% of the data regression resulted in R^2 values over 0.97. The same analysis resulted in relatively lower R^2 value at 0.9 for Model 2. Even though these models were developed for application in a conventional treatment context, they were deemed applicable for modelling chlorine decay in systems representative of humanitarian water treatment contexts.

Overall, the tested models fitted better on data from Group A compared to those from Group B, shown by smaller dispersion of R^2 values for all seven models. Firstly, most of the chlorination tests in literature were conducted in controlled conditions, minimizing the impact from the environment (i.e. effects from temperature, surrounding lighting, evaporation etc.). Secondly, because most papers were published to show successful applications of certain models, the extracted data may have been subjected to publication bias, resulting in higher R^2 values overall.

Model Limitations

The empirical model developed by Feben and Taras (1951) (Model 1) was one of the earliest models developed for describing chlorine decay. The nature of Model 1 is a power model. For this model to include the two-phase characteristic of a typical chlorine decay curve, the n value needs to be between 0 and 1 ($0<n<1$). A main reason this model is not utilized in the conventional treatment system is because the chlorine value may turn negative as time increases (Fisher et al., 2011). In humanitarian water supply contexts, recommendations state that FCR in water should be not less than 0.2 mg/L at 24 hours of storage time (Lantagne, 2008). Model 1 is suitable for the emergency context because the contact time is limited to around 24 hours, unlike in a conventional system where water residence time (including distribution system) may reach several days.

The most widely utilized model in conventional treatment system, the first order model (Model 2), fit all three groups of test data the poorest among all tested models. The model assumed that chlorine was reacting with organics having higher concentrations than that of chlorine. Therefore, the rate of reaction was based solely on the concentration of chlorine. This model did not perform satisfactorily because, firstly, when the organics in the water was in relatively small quantities, the model assumption might not hold true. Secondly, this model assumed chlorine reacts with one category of substance, which was incapable of capturing both the fast and slow decay regions with very different kinetic properties. One common strategy used was to exclude the fast decay phase in model fitting. Here, after trying to fit Model 2 to the data from Wu (2020), 30 minutes after dosing, the average R^2 increased from 0.797 to 0.948.

The nature of Models 4, 5, and 7 are all power models, and they achieved relatively high R^2 values in describing chlorine decay in water based on the results. For models of the same nature, the more components the model has (i.e. more freedom in regression analysis), the better fit it could achieve for the same data. Model 5 (limited power model) built on Model 4 (power model) by adding a stable component 'C*' in the formula, and it resulted in higher R^2 values from regression on data from all three groups. The addition of the stable component gives the model freedom to account for cases where a portion of the chlorine is not consumed over time potentially due to limited availability of reactants. Similarly, Model 7 not only included an additional stable term on top of Model 4, but also added another component to the equation. This resulted in Model 7 reaching median R^2 close to 1 for all three groups of data.

Even though models with more components could result in better fitness of data, the inclusion of additional parameters created challenges in understanding the models. The inclusion of the stable term in Model 5 increased the overall fitness of the model compared to that of Model 4, but the

stable term showed no correlation to any of the known parameters. So far, the stable term could only be determined by conducting model regression.

There is another concern with the power models: Their power terms are highly unpredictable. In humanitarian emergencies, the limited time and instrumentation make it impossible to measure all required information to predict every term in the model. Having an unpredictable power term makes it unfeasible to study the relationship between the decay term with other parameters. In the study by Ali et al. (2015), all predicted power terms from regression were consistently around 2. It was uncertain whether the limit was set to approximately 2 in their regression analysis or the values were consistent due to random chance, but such results allows them to focus on the prediction of decay term. When the power models are used as base models to develop the dose predictive tool, the power term should be constrained to certain values or be linked to certain water properties or environmental conditions for accurate understanding of the decay kinetics. However, in this study, no relations were identified to guide the model restrictions on the power terms.

Parallel models (Models 6 and 7) performed well in all circumstances tested since they had two components for effectively capturing both the fast and slow regions of a typical chlorine decay curve. The only disadvantage for the models were that the assumption of chlorine being divided into two parts and reacted with two different reactants separately was not true, causing the ratio of chlorine for the two reaction parts being hard to predict. The parallel second order model proposed by Kastl et al. (1999) resolved this issue; however, there are four variables involved in the decay equation and an analytical solution is available only when additional assumptions are made (Kohpaei & Sathasivan, 2011). Despite this fact, Models 6 and 7 worked well in describing chlorine concentration change in the water based on the analysis.

All seven basic models evaluated in this study have the potential to be used to model chlorine decay in a humanitarian treatment context. However, each of these models has its own constraints. Feben and Taras's empirical model (Model 1) can turn negative when residence time increases, and its power term needs to be constrained for better analysis of the decay term. First order models (Models 2 and 3) cannot effectively capture both the fast and slow decay regions of the chlorine decay curves, and they work best when only data from the slow regions (after ~30 minutes contact time) are modelled. For power models (Models 4, 5 and 7), the constraints on the power term should be set, and there are currently no criteria based on which we may select the values. The ratio between the two reactions in parallel reaction models (Model 6 and 7) is hard to predict, similar to the power term in power models.

Field Application

Based on the results of this study, first order models (Model 2 and 3) are the simplest to be applied in the field because the only undetermined term is the decay kinetics term. The first 30 minutes of FCR data should be excluded from the regression analysis to estimate the value of the kinetics term. After that, the developed model can be used to back calculate initial dose based on desired FCR for a specific storage time. In addition, correlation analysis can be run between water parameters and the decay term to discover potential influencing factors on chlorine decay kinetics. For Models 1, 4, and 5, if the power term can be constrained in the regression analysis, these models can be utilized in ways similar to those mentioned for Models 2 and 3. For Models 6 and 7, similarly, if the ratio term can be constrained, they can be used to perform the same tasks.

Even though these models can be used in the way Ali et al. (2015) did to predict chlorine dose for a specific site. The analysis requires substantial amount of chlorine decay data to calibrate the model parameters. In humanitarian emergency water supply, there may be no chlorine decay data

available. It is therefore key to understand chlorine decay mechanisms, discover the impacting factors from the field on chlorine decay kinetics, then use the limited available information (i.e. chlorine demand, temperature, turbidity etc.) in the field to estimate the decay term in the model rather than spending days to determine the term through regression.

Conclusions

Seven basic models were evaluated on their applicability on describing chlorine decay data in both conventional and humanitarian treatment context. A total of 610 chlorine decay test data from three sources were used to evaluate the models, and more than half of the regression analysis using the models resulted in R^2 value over 0.9. The study shows that all seven models have the potential be applied in humanitarian emergency context for initial chlorine dose prediction when sufficient chlorine data are available. Several challenges exist for effective applications of the models, specifically, first order models require exclusion of data from fast decay region of the chlorine decay curve to improve its accuracy in data fitting, power models and parallel first order model require understanding of the power term and ratio term respectively to effective evaluate the decay kinetics term(s) in the models.

When there is no or limited chlorine decay data available for model calibration, a necessary approach is to fundamentally understand chlorine decay and use available impacting factors to estimate decay term models. In humanitarian contexts, the chlorine demand, pH, turbidity, and temperature of water are usually obtainable. The next step is to evaluate the relationships these parameters have with the decay term and use the relationships information to quickly estimate decay term in the models without needing chlorine decay data for model calibration.

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Manuscript 2

Manuscript Title

Towards a Predictive Model for Initial chlorine Dose in Humanitarian Emergencies

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State of Publication:

This manuscript is intended to be submitted as an Article in the open access journal *Water* (MDPI).

Abstract

Free chlorination is a widely employed disinfection method in humanitarian water provision due to its many advantages. However, its effective application is hindered by the challenge in determining adequate initial doses to achieve free chlorine residuals that satisfy both health and aesthetic requirements. Current guidelines show varying recommended dosing strategies, and many of them do not adequately consider chlorine decay mechanisms that occur during water storage. Even though turbidity is commonly used as a criterion for deciding chlorine dose, it may not be an adequate proxy for the water quality in many cases. This paper addresses the fundamental relationships between chlorine decay kinetics and selected key water parameters (i.e. natural organic matter, water temperature, chlorine demand) by conducting chlorine decay tests in controlled conditions and in jerrycans (i.e. simulating humanitarian water treatment conditions). Chlorine decay constant from the empirical model by Feben and Taras's and first order model formed linear and exponential relationships with two water parameters (UVA_{254} and 30-minute chlorine demand). With these relationships, chlorine decay prediction models were developed. 30-minute chlorine demand was found able to incorporate different factors on chlorine decay kinetics. Three developed models can predict chlorine decay in water having a main chlorine demand-inducing constituents as natural organic matter. However, it underpredicted chlorine decay in surface water with additional chlorine reactants. Further research on additional chlorine decay mechanisms are needed to expand the applicability of the model.

Keywords:

Chlorine decay; Natural organic matter; Temperature; Humanitarian emergency; WASH; Bucket chlorination.

Introduction

Humanitarian emergency situations arise when natural or man-made hazards bring serious disruptions to a society, causing widespread human suffering and stretch the community's coping mechanisms to a breaking point (Davis et al., 2002). Damages to local water systems or mass migration in some cases may lead to a lack of water to meet the community's basic needs. Insufficient quantity of water for consumption and hygiene, together with poor water quality underlie most public health problems such as transmission of diarrheal diseases during crisis situations (SPHERE, 2018). Therefore, it is critical for humanitarian relief organizations to provide water of safe drinking quality and in adequate volume to support lives and hygiene in the community (Dorea, 2012; SPHERE, 2018). For humanitarian water provision, disinfection is an essential step to produce water of safe drinking quality as it aims to inactivate disease-causing microorganisms in water.

There are a variety of water disinfection methods for application in the context of a humanitarian emergency (referred to as "the field" hereinafter) such as water boiling, chlorination, ultraviolet disinfection, etc. (Lantagne & Yates, 2018; WHO, 2015). However, free (or breakpoint) chlorination is usually the method of choice because chlorine is relatively easy to obtain, apply, measure, and it can inactivate most viral and bacterial pathogens in a rapid and cost-effective manner, in addition to leaving a residual protection in the water (Branz et al., 2017; Murray & Lantagne, 2015).

Despite the various advantages of free chlorination in the field, a key challenge for its effective application is finding the appropriate dose to achieve protective residual at a target storage time at the point of use (Branz et al., 2017). Storage time is typically 24 hours, assuming water is fetched daily. Within the 24-hour storage time, the free chlorine residuals (FCR) need to be within both

recommended health-derived and aesthetic limits (Lantagne, 2008). This creates the challenge because chlorine is a strong oxidant and may react with a variety of constituents (i.e., metals, organics, ammonia, etc.) in water, hence its concentration decays over time at a rate, which depends on various factors (Abdel-Gawad & Bewtra, 1988). Some of these factors include quality of the treated water, water temperature, initial chlorine dose and/or the reaction container (details of which are discussed later).

Field conditions set humanitarian water treatment apart from conventional treatment contexts. In the latter, chlorination is achieved in engineered tanks and pipelines under relatively stable environmental conditions. In humanitarian water treatment, chlorination may take place in locations ranging from centralized water tanks to decentralized collection and storage containers (e.g. buckets, jerry cans, etc.) at the point of collection or point of use in a humanitarian context (Lantagne, 2008). The treated water may often be subjected to relatively elevated temperatures (Ali et al., 2015), which accelerates chemical reactions in the water, leading to higher FCR decay rates (Crittenden et al., 2012; Monteiro et al., 2015). For FCR verifications, pool testers and several other measuring devices are often used, and the results are less consistent compared to those resulted from using a colorimeter because pool testers require operators' personal judgement (Murray & Lantagne, 2015). The limitation of imprecise readings with the field instruments makes it challenging in obtaining key information (i.e. chlorine demand, FCR decay data, etc.). Both the environmental conditions and instrumentation in humanitarian contexts add uncertainties to initial dose prediction.

To guide chlorination application in humanitarian contexts, varied international guidelines and research studies provide recommendations on the initial doses based on source water characteristics. A comparison of the recommendations is provided in Table 1.

Table 1. Chlorine dosages recommendations from several guidelines and studies.

Guidelines/Studies	Dose Recommendations	References
Descriptive based		
CDC	1/8 teaspoon (8 drops) of bleach (5-6% or 8%) for each gallon of clear water; Double value for cloudy water	(CDC, 2019)
USEPA	2 drops to ½ teaspoon of bleach (6% or 8.25%) to certain amount of water (1 liter to 8 gallons)	(USEPA, 2017)
Empirical based		
WHO	Find the dose to reach at least 0.5 mg/L free chlorine at 30 minutes after dosing	(WHO, 2005)
Exact values		
Lantagne	1.875 mg/L for water with turbidity <10 NTU 3.75 for water with turbidity 10-100 NTU	(Lantagne, 2008)
JHU & IFRC	2.5 mg/L, verify that there is at least 1 mg/L free chlorine at 30 minutes after dosing	(JHU & IFRC, 2008)
FMH	2mg/L and aim to result in 0.5 mg/L FCR	(FMH, 2017)

Based on the comparison of listed recommendations, there are four points to be noted. Firstly, the descriptive based guidelines are comprehensive, which allow for most people to execute. However, the bleach solution may have degraded (Nicoletti et al., 2009), and no information was included for FCR verification. This can lead to underdose of water. Secondly, several guidelines use turbidity (or cloudiness of the water) as a quantifiable indicator of water quality and use it for deciding the chlorine dose. Turbidity is an optical property of a suspension mainly attributed to the presence of suspended particles and can be measured with simple devices like a turbidity tube in the field (Dorea & Simpson, 2011). Arguably, suspended matter may not be the best indicator of chemical properties of dissolved compounds in water. Gallandat et al. (2009) suggest that water

turbidity from inorganic matter has no impact on chlorine decay kinetics. Thus, showing that the type of turbidity matters in terms of how it affects chlorine demand. Ali et al. (2015) explored relationships between FCR decay and water quality in 220 unique samples and concluded that ambient air temperature and water conductivity show potential direct relationships with decay kinetics, while other water parameters including turbidity only accounted for about 25% of the variance in their data. To this end, parameters directly related to chlorine demand inducing compounds such as natural organic matter (NOM) (e.g. UV absorbance, dissolved or total organic carbon, etc.) could be a better metric to use (Crittenden et al., 2012). Thirdly, several recommendations suggest verifying FCR at 30 minutes after dosing but do not consider chlorine decay for longer storage time (JHU & IFRC, 2008; WHO, 2005). Sometimes, it may be impractical to reach the recommended minimum FCR value of 0.2 mg/L for 24 hours storage time (Ali et al., 2015). Based on the assumption that households fetch their water daily, to ensure effective residual protection, dose recommendations should evaluate FCR decay during storage to up to 24 hours. Lastly, the values recommended by different guidelines vary, and it may create confusion for humanitarian staff in guideline selection.

To tackle the series of challenges present in determination of the correct chlorine dose, a predictive tool, which uses the obtainable information in the field to rapidly and accurately estimate chlorine decay kinetics would be of use towards determining the appropriate initial dose for achieving safe free chlorination objectives. This paper examines several water parameters including NOM, water temperature and 30-minute chlorine demand and their impacts on chlorine decay kinetics. Chlorine decay models were also developed based on the discovered relationship between the water parameters and the chlorine decay kinetics. These models could be used towards developing such a predictive tool.

Background

Two-phase chlorine decay behavior

A typical chlorine decay curve (FCR versus time) contains two phases, a rapid decay phase takes place usually within the first 30 minutes after chlorine dosing and a slow decay phase afterwards (Al Heboos & Licskó, 2016; Crittenden et al., 2012; Fisher et al., 2011). Based on the chemistry of chlorine reactions, major contributors to the rapid decay phase are easily oxidizable substances, metals, fast reacting NOM, ammonia, etc. For the slow decay region, slow reacting NOM is considered the main reactant consuming chlorine, and the reaction rate is influenced by water temperature.

Temperature

The temperature dependence of chemical reaction rates can be described using the Arrhenius equation (Equation 1) (Crittenden et al., 2012).

Equation 1. Arrhenius equation for linking reaction kinetics to reaction temperature

$$k = A * e^{-\frac{E_a}{RT}}$$

where A is the frequency term, meaning the frequency of collisions in the right orientation; E_a is the activation energy of the reaction; R is the universal gas constant; k is the reaction rate, and T is the temperature of the reaction in Kelvin. Powell et al. (2000) has shown that an Arrhenius type relation exists between chlorine decay constants and the water temperature.

Decay kinetic models

There are a variety of kinetic models available in the literature for describing chlorine decay curves (Fisher et al., 2011). Wu (2020) evaluated the application of seven basic chlorine models in humanitarian contexts. After excluding three models containing an additional stable term in the

equation, which did not impact the model fitness significantly, five models were included in this study as shown in Table 2. They are: Feben and Taras's empirical model, first order model, power model, parallel first order model and limited parallel power model.

Table 2. Five Models evaluated by Wu (2020) and their analytical solutions.

Model	Equation	Data Modification OR Model Restrictions	References
Feben and Taras's empirical model	$C = C_0 - kt^n$	Optionally fix n value based on regression results	(Feben & Taras, 1951)
First order model	$C = C_0 * e^{-kt}$	Exclude data prior to 30 minutes reaction time	(Haas & Karra, 1984)
Power model	$C = (kt * (n-1) + \left(\frac{1}{C_0}\right)^{(n-1)})^{(\frac{-1}{n-1})}$	Optionally fix n value based on regression results	(Haas & Karra, 1984)
Parallel first order model	$C = w * C_0 * e^{-k_1 t} + (1-w) * C_0 * e^{-k_2 t}$	N/A	(Haas & Karra, 1984)
Limited parallel power model	$C = C^* + (k_1 t * (n_1 - 1) + \left(\frac{1}{(w)(C_0 - C^*)}\right)^{(n_1-1)})^{(\frac{-1}{n_1-1})}$ $+(k_2 t * (n_2 - 1) + \left(\frac{1}{(1-w)(C_0 - C^*)}\right)^{(n_2-1)})^{(\frac{-1}{n_2-1})}$	N/A	(Kim et al., 2015)

For first order model, it is the most widely used chlorine decay model in conventional treatment system as it only has one parameter, 'k', to be determined (Fisher et al., 2011). Wu (2020) suggested that first order model was potentially applicable to the humanitarian context when only data from the slow decay phase (30 minutes after dosing) were used as the model was unable to capture both phases at once.

Materials and Methods

The development of a chlorine dose predictive tool contained three main stages: 1. Establishment of base relationships between the chlorine decay kinetic constant and selected water quality parameters using synthetic water (i.e., "brown bottle" tests); 2. Verification of the base findings in scaled up systems (i.e., 20-L jerrycans); 3. Verification of the models by conducting chlorine decay tests on water from three different natural sources.

To evaluate the relations between chlorine decay rate and several water quality parameters, synthetic water with different amounts of added humic acid (Sigma-Aldrich) and in different temperature settings were dosed with chlorine and the decay of FCR were monitored over time. Selected models from Wu (2020) were used to fit the decay data, and correlation analysis was conducted between the estimated decay constant term and water parameters, including organics (by measuring ultraviolet absorbance at wavelength of 254 nm (UVA_{254})), temperature, and 30-minute chlorine demand. A total of 64 chlorine decay tests, in both 125-mL glass brown bottles (Fisher Scientific, Canada) and 20-L plastic jerrycans (ULINE, Canada) were conducted from August 2019 to January 2020.

Apparatus and cleaning

The containers used in the tests were either 125-mL brown bottles or 20-L jerrycans. The brown bottles were used for testing bulk chlorine decay, which means factors other than the characteristics of the tested water were minimized. The jerrycans were used to simulate chlorination in the field and the results were compared to those obtained from bulk chlorine decay tests.

All glassware involved in the experiments were treated according to the Environmental Technology Verification Protocol before the test (USEPA, 2003). This cleaning protocol involves

using Fl-70 detergent and chlorine solution with 10-20 mg/L available chlorine to remove the chlorine demand-inducing substances (i.e. adsorbed organics) on the inner surface of glassware.

Synthetic water preparation

Synthetic water was prepared in batches prior to testing. Humic acid (Sigma-Aldrich) was added to the Milli-Q water based on the relationship described by Equation 2 to achieve specific readings of UVA_{254}, representing the amount of natural organic content in the water. This relationship was determined and used for the stock humid acid in the Public Health and Environmental Engineering (PH2E) laboratory at the University of Victoria (Victoria, Canada). The prepared water was then distributed into three 2-L Erlenmeyer flasks for temperature adjustments.

Equation 2. Relation between UVA_{254} of water and humic acid added to 1 liter of water

$$Y = 0.0281 * X - 0.0043$$

where Y is the water UVA_{254} value measured in cm^{-1}, and X is the concentration of humic Acid measured in mg/L.

Temperature control

The test water was placed in three different incubators set at 10℃, 20℃, and 30℃ respectively to reach the designed temperature. For tests in jerrycans, a water bath was set up to keep the water temperature at 30℃. Figure 1 illustrates the experimental setup of the tests.

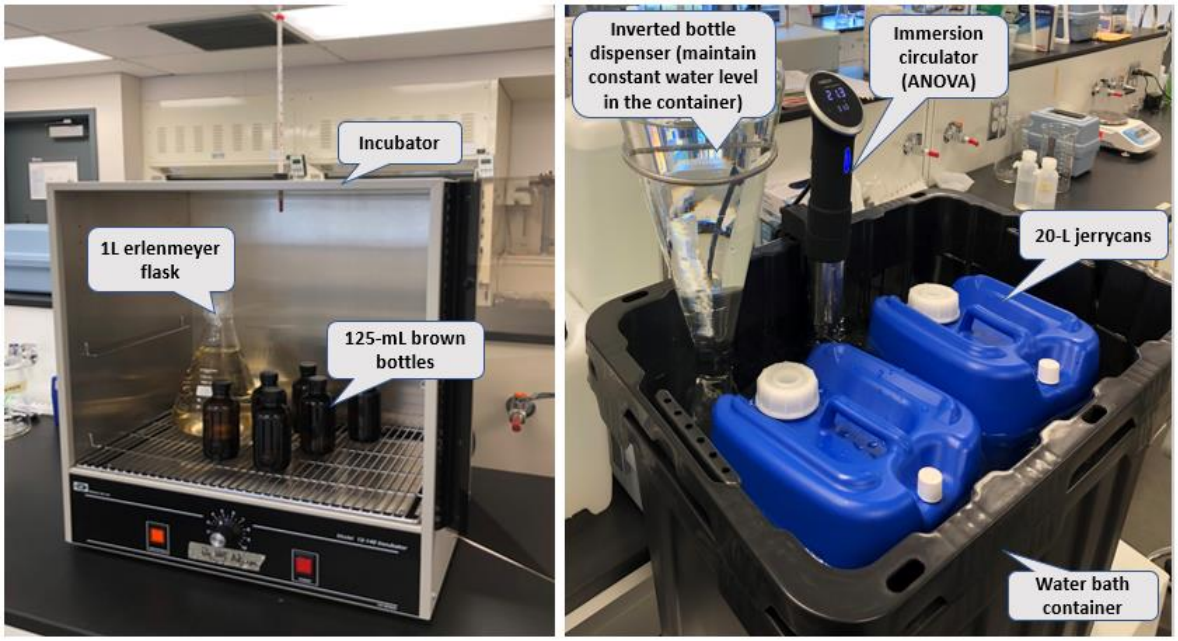

Figure 1. Experimental setup for chlorine decay tests in bulk "brown bottles" tests (left) and in jerrycans (right).

Chlorine stock solution

Chlorine stock solution was prepared by diluting commercially available bleach solution using Milli-Q water to reach a concentration of approximately 600 mg/L available chlorine. The strength of the stock chlorine solution was verified (HACH Method 8209) at least three times prior to each use. For each test, the stock solution was dosed to a separate container with Milli-Q water, parallel to the one with actual test water for dose verification.

Matrix for test conditions

The first stage of the study involves conducting a series of 24-hour chlorine decay tests under various organics and temperature conditions. Figure 2 illustrates the matrix for the tested conditions inspired by the approach adopted by Gallandat et al. (2019).

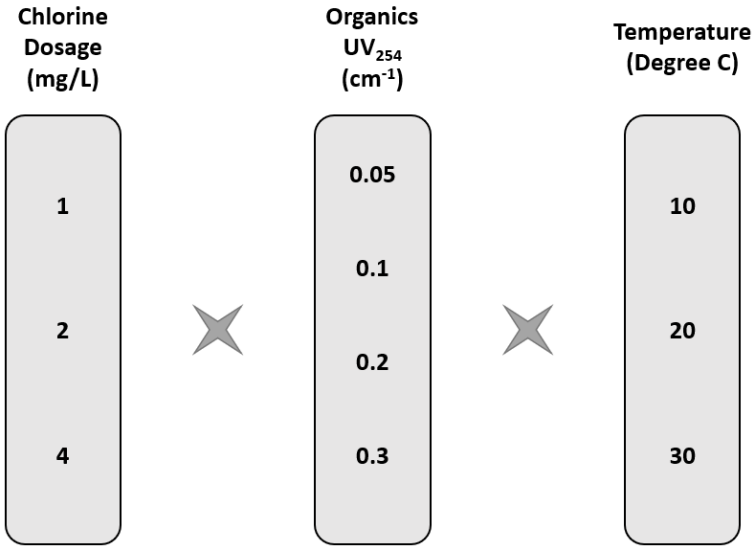

Figure 2. matrix for the test conditions.

These 24-hours decay tests were conducted in 125-mL brown bottles with synthetic water, incubated at the desired temperature. Chlorine readings were performed at 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45 min, 1 hr, 2 hr, 4 hr, 20 hr, and 24 hr. These frequent readings increased the resolution of the chlorine decay curve, especially for the rapid decay phase in the first 30 minutes. The second stage of the test was to conduct the same chlorine decay tests in 20-L jerrycans, which simulated the conditions of field water chlorination in a similar fashion to the setup used by Gallandat et al. (2019). The final stage of the test was to use water from three water sources, to verify the relationships developed in the first two stages.

For chlorine dose selection, the 2 mg/L and 4 mg/L for clear and turbid water respectively were tested based on current recommendations (Lantagne, 2008; WHO, 2017). Additionally, 1 mg/L was selected to study lower dose conditions.

For UVA_{254} settings, the selections were based on several studies with UVA_{254} of numerous water sources (e.g., river and reservoir) ranging from 0.0 to 0.8 cm^{-1} (Bond et al., 2011; Edzwald et al.,

1985; Volk et al., 2002), with the value for most cases below 0.3 cm^{-1}. Therefore, the selected values of 0.05, 0.10, 0.20, 0.30 cm^{-1} represented most cases studied.

As for the temperature settings, 10℃, 20℃, and 30℃ were used to represent temperate climate conditions, room temperature conditions, and hot climate conditions respectively. Even though specific values were selected to construct the test matrix, once the relationships between parameters were determined, any condition in between the extreme values tested could be interpolated and determined.

Natural water samples

Three water samples, representing three natural water types, were obtained for verifying the developed model. Water from an observation well located in the University of Victoria was used to represent groundwater sources. Water from the source reservoir, which supplies Victoria's drinking water was selected to represent surface water. In addition, water from a pond located in a local golf course was tested to represent cases of more contaminated surface water. The sampled water was carried to the laboratory immediately and tested for turbidity, pH, UVA_{254}, and ammonia concentration. The water was then tested at 30 ℃ for chlorine decay. All the water quality parameters were tested again before chlorine dosing.

Data Analysis

All three selected models were fitted to test data in MATLAB (R2019a) using the least squares method. Pearson's correlation analysis between parameters were conducted in Excel (2020) using its built-in Data Analysis toolbox.

Results

Overall, all models except first order model achieved satisfactory fitting on all 64 data sets, which were chlorine decay data in synthetic test water. The R^2 distribution from data fitting for all five models are demonstrated in the box and whisker plot (Figure 3). Figure 4 shows three randomly selected representative tests from the experiments and the regression curves from the four models to demonstrate their fitness.

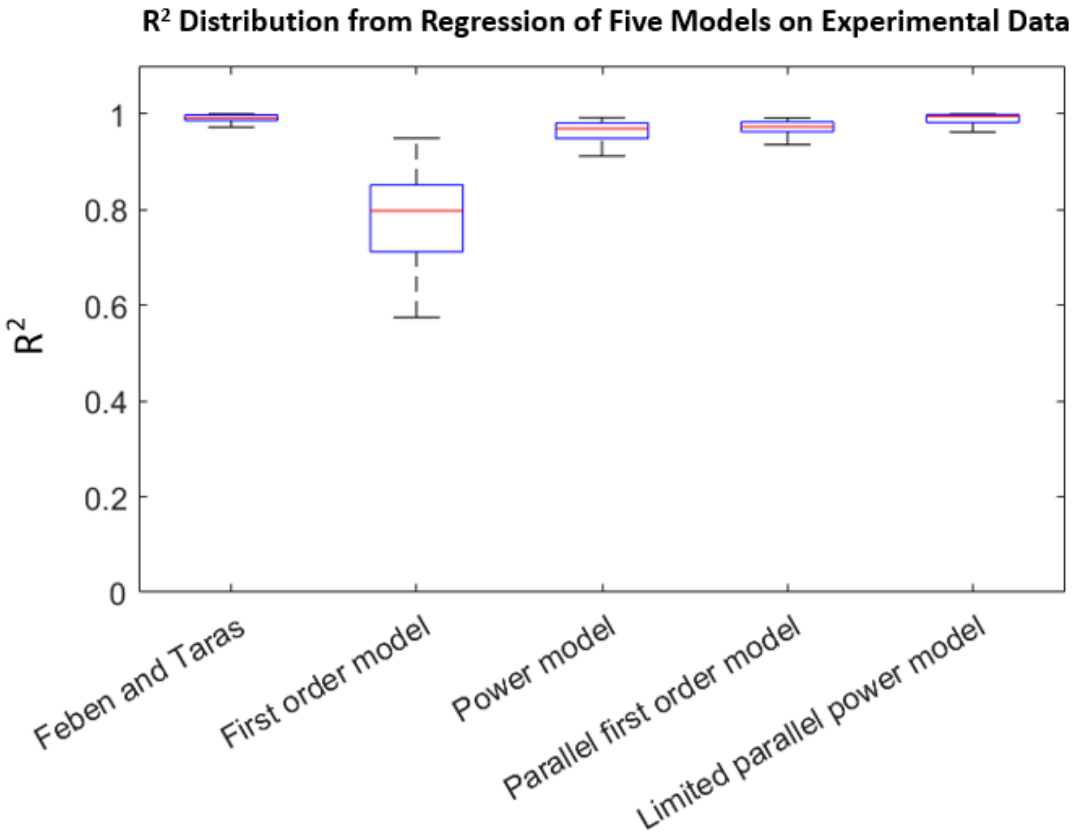

Figure 3. R^2 from model fitting on all 64 chlorine decay tests using the five models. From top to bottom of each box are the maximum value, third quartile, median, first quartile, and minimum value of R^2 for the specific model it represents.

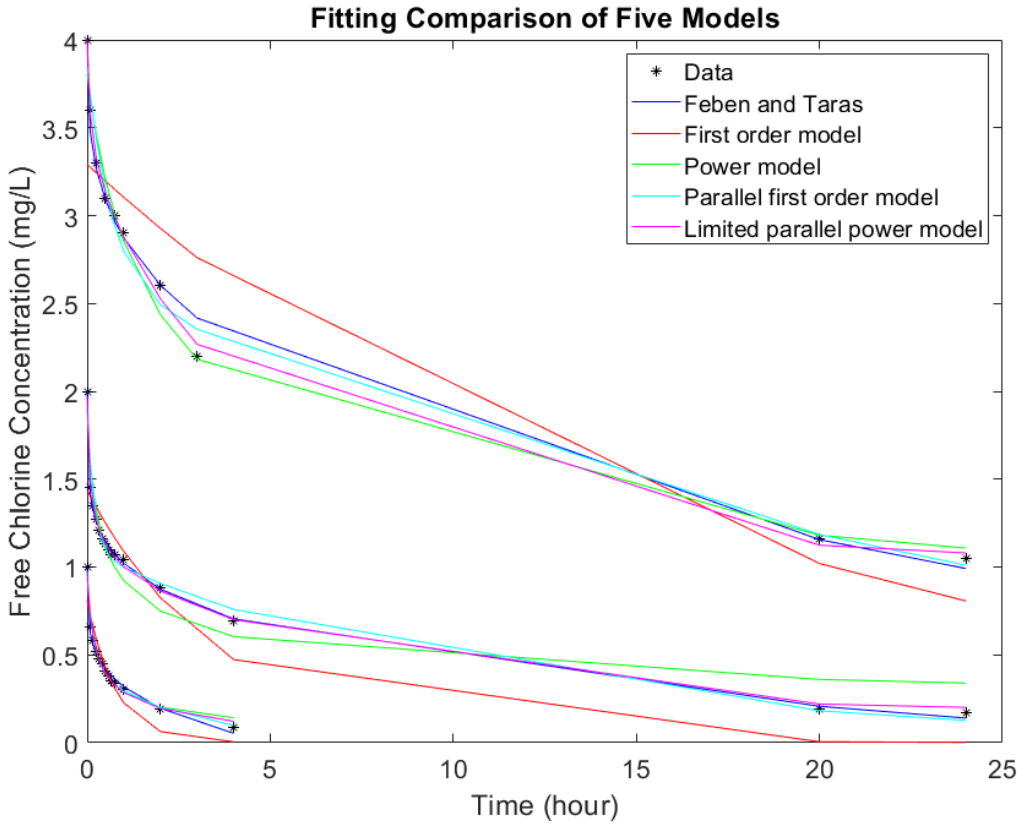

Figure 4. Model regression from the five models on three random tests from experiments.

Correlation and mathematical relations

Pearson's correlation analysis was conducted between estimated decay rate of the 36 bulk decay tests and their corresponding water quality parameters. The results from the analysis are shown in Table 3. Based on the results, UVA_{254} and 30-minute chlorine demand of water appear to have significant impacts on chlorine decay rates.

Table 3. Pearson correlation results between chlorine decay term in the model and water parameters.

Models	Parameters	UVA_{254}	Temperature	30-minute Chlorine Demand
Feben and Taras's empirical model	k	0.86	0.18	0.78
First order model	k	0.67	0.24	0.77
Power model	k	0.35	0.09	0.51
Parallel first order model	k_1	-0.32	-0.19	-0.28
Parallel first order model	k_2	0.43	0.10	0.38
Limited parallel power model	k_1	0.26	-0.06	0.30
Limited parallel power model	k_2	0.00	-0.22	-0.04

Parameters from both Feben and Taras's empirical model and first order model show mathematical relationships with water's UVA_{254} value, and the temperature (Figure 5). The decay constants for Taras's empirical model and first order model increased linearly and exponentially with the increase in UVA_{254} respectively (Figure 6). Both models' decay constants followed Arrhenius relationship with the water temperature, specifically, linear relationship between the natural log of decay constant and the reciprocal of water temperature in Kelvin (Figure 6). When the water parameters were determined in the field, the predicted k value could be interpolated and extrapolated among all identified relations.

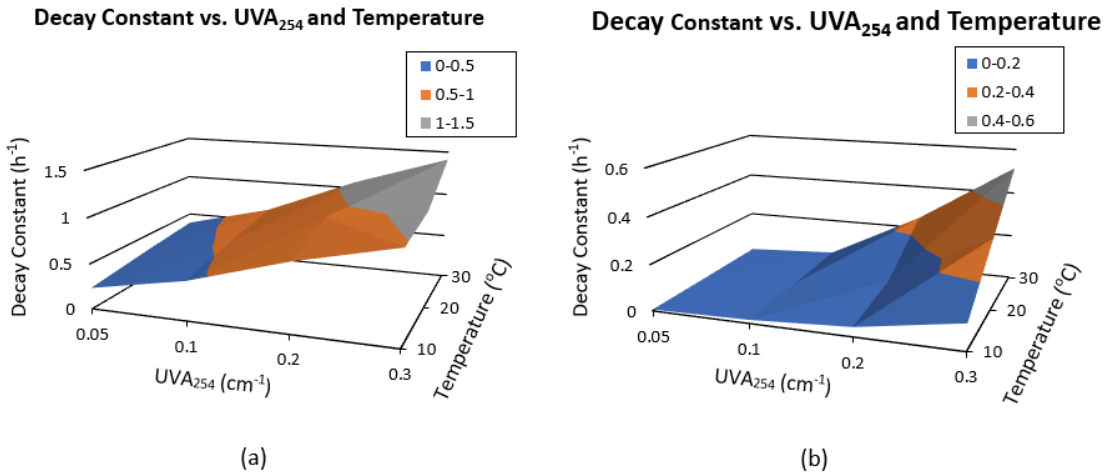

Figure 5. (Plot a) The combined impacts on chlorine decay constant in Feben and Taras's empirical model from temperature and water organics content (2 mg/L initial dose). (Plot b) The combined impacts on chlorine decay constant in first order model from temperature and water organics content (2 mg/L initial dose).

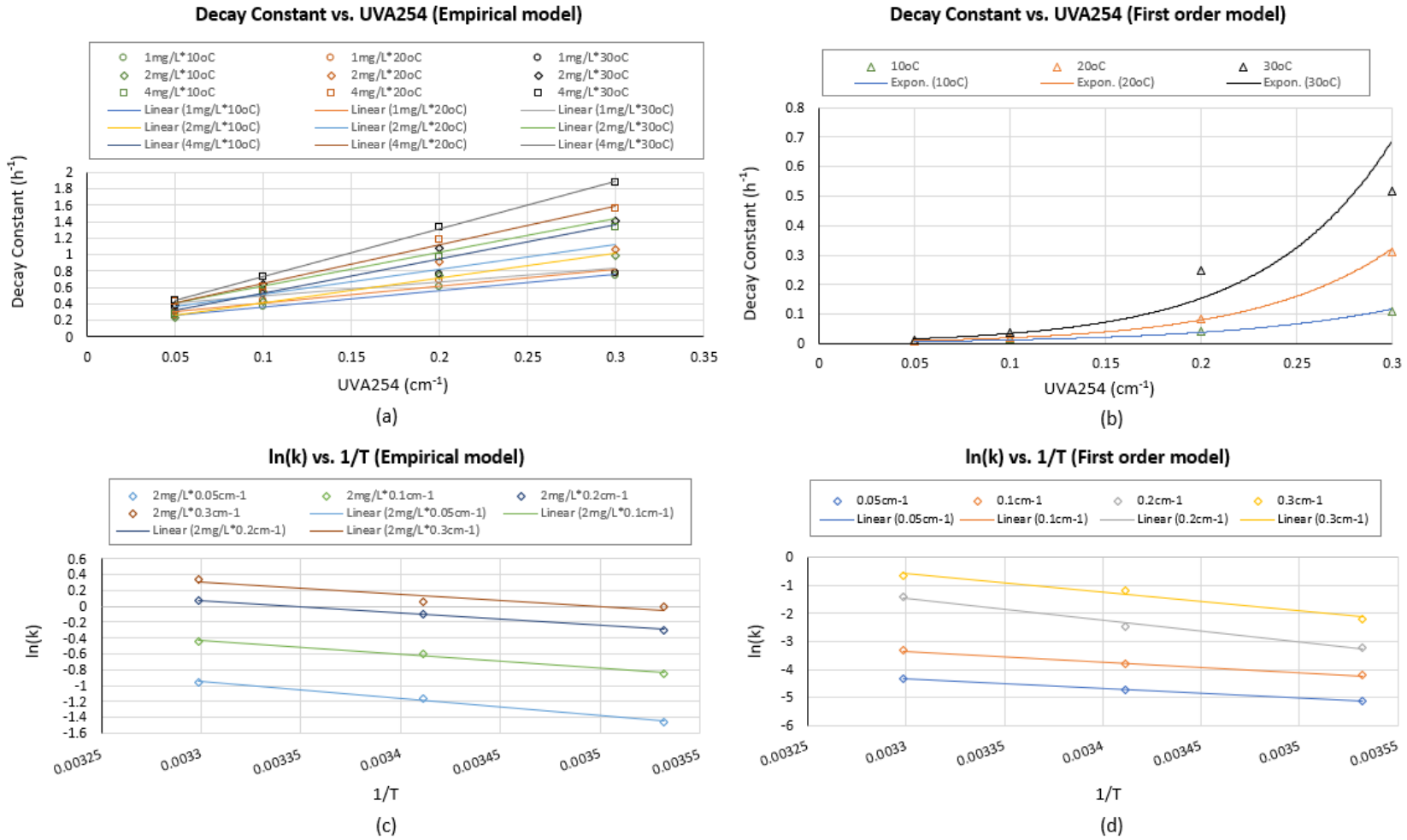

Figure 6. (Plot a) Decay constants from Feben and Taras' s empirical model versus the organic content in the test water. (Plot b) Decay constants from first order model versus the organic content in the test water for the cases with 2 mg/L initial dose. (Plot c) ln(k) versus 1/T for all organic content cases with 2 mg/L initial dose – Feben and Taras' s empirical model. (Plot d) ln(k) versus 1/T for all organic content cases with 2 mg/L initial dose – first order model.

Decay kinetics and water chlorine demand

The relations between decay constants estimated from data fitting and the 30-minute chlorine demand of the tested water are shown in Figure 7. For Feben and Taras's empirical model and a specific initial dose, the decay constant followed nearly linearly with the 30-minute chlorine demand. For the first order model, the relation was not obvious between the two parameters for each specific dose. However, generally, an exponential relation could be observed.

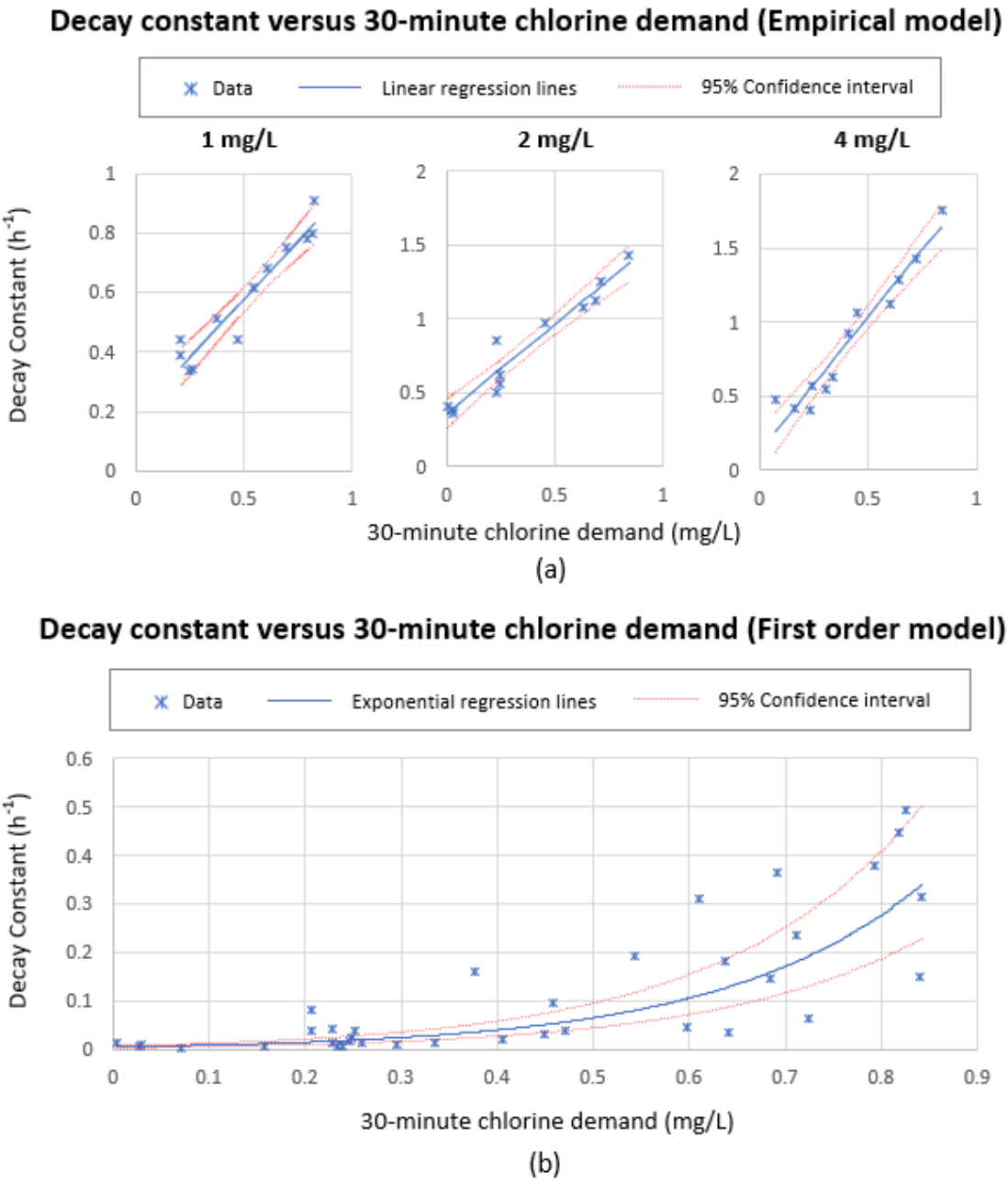

Figure 7. Mathematical relationship between decay constant and 30-minute chlorine demand of test water. Top figure (a) is for decay constant in Feben and Taras's empirical model. Bottom figure (b) is for decay constant in first order model.

Quality control

Four replicates were conducted for quality control purpose for the 36 bulk water tests. The four tests were selected randomly and measured FCR were compared between the original and the replicates. Of the 36 FCR measurements in the four tests, the average error was 1% (-1% to 5%). For the eight replicates conducted for the 20-L jerrycans, the 96 measurements were all within 10% of the values from the initial tests.

Verification

Water quality data of the three natural water samples obtained in Victoria were summarized in Table 4 below. These values were measured right before the water was dosed with chlorine. The three water were dosed with pre-determined doses of chlorine, and the chlorine decay curves were predicted using the developed methods and compared with the actual measurements. A comparison of the predicted chlorine curves and actual decay curve can be seen in Figure 8.

Table 4. Water quality parameters of the three natural water sampled

Water ID	Turbidity (NTU)	pH	UVA254 (cm^{-1})	Ammonia (mg/L)	30-minute chlorine demand (mg/L)
Well Water	12.6	7.52	0.009	0.01	0.11
Reservoir Water	0.43	7.27	0.05	0.04	0.52
Pond Water	9.67	6.3	0.212	0.43	3.12

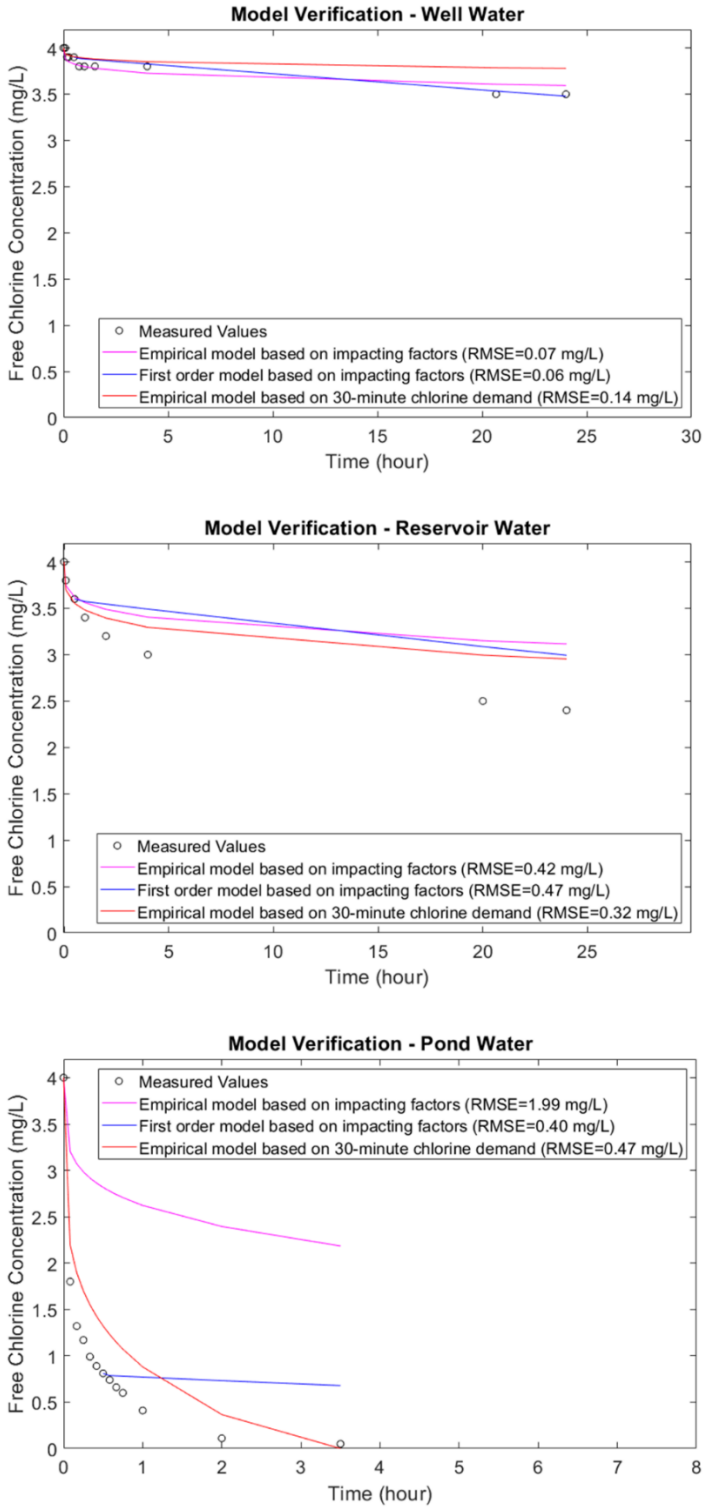

Figure 8. Predictions of chlorine decay in three natural water using the three developed approaches, and their comparisons with the measured values.

All three models performed similarly in prediction of chlorine decay for well water. Feben and Taras's empirical model with the decay constant estimated based on water's 30-minute chlorine demand could best capture the trend of chlorine decay with a relatively small root mean square error value for both reservoir water and pond water.

Discussion

There were four potential models proposed for chlorine decay prediction in this study. These models were based on the two basic models (Feben and Taras's empirical model and first order model) from the literature with their chlorine decay term being estimated using either the actual impacting factors (i.e. UVA_{254}, temperature) or a proxy (30-minute chlorine demand). The models are listed below:

1. Feben and Taras's empirical model with decay term estimated using UVA_{254} and temperature of water.
2. First order model with decay term estimated using UVA_{254} and temperature of water.
3. Feben and Taras's empirical model with decay term estimated using water's 30-minute chlorine demand.
4. First order model with decay term estimated using water's 30-minute chlorine demand.

Decay estimation using impacting factors and their mathematical relations

Feben and Taras's empirical model contains two parameters, decay constant 'k' and power term 'n', to be determined from regression analysis. To evaluate relations between decay constant 'k' and impacting factors, the influence from the power term 'n' needs to be minimized. After the initial model fitting, 'n' values generated from fitting the experimental data varied from 0.12 to 0.32, with 50% of the values located between 0.2 and 0.26. A second round of model fitting set

the 'n' value fixed at 0.22 (the average value from the first round) to remove the influence from 'n'. As a result, the median R^2 value decreased from 0.988 to 0.960. The decay constant term was found linearly related to the change in water's organic content under all doses and temperature conditions but with different slope. The $\ln(k)$ over $1/T$ plot (Figure 6, plot c) showed linear relations between natural log of decay constant and the reciprocal of temperature in Kelvin. This verified the Arrhenius-type relationship. The slopes of the lines were very similar for all doses and organic content combinations with an average value of $1397K$. Based on this result, the decay constant at a certain temperature from 10℃ to 30℃ can be estimated according to Equation 3 when the decay constant is known for the same water at any known temperature from 10℃ to 30℃.

Equation 3. formula for finding decay term in temperature 1 when decay term at temperature 2 is known. (Feben and Taras's empirical model as basis)

$$k_1 = k_2 * e^{-1397*(\frac{1}{T_1}-\frac{1}{T_2})}$$

The analysis for the first order model was similar to those for the Feben and Taras's empirical model, the decay constant increased with the increase in water organic content and water temperature. The relationships between the UVA_{254} value and the decay constant under all three initial dosages conditions and all temperature settings were exponential. Noticing the points for 0.2 and 0.3 cm^{-1} for the 30-degree curve in Figure 6 (c) did not follow the exponential trend, it was because the chlorine residual was completely reacted within 24 hours and the decay kinetics for the entire period was not able to be calculated. This also meant that the initial chlorine was not sufficient to maintain a chlorine residual of greater than 0.2 mg/L for 24 hours for the tested conditions. Otherwise, all chlorine decay kinetics increased exponentially with the increase in water organics content. For impacts from temperature, the $\ln(k)$ over $1/T$ plot (Figure 6, plot d)

showed similar slopes of the regression lines for all doses and organic content combinations with an average value of $4818K$. Therefore, Equation 4 can be used to adjust the k value based on the water's temperature.

Equation 4. formula for finding decay term in temperature 1 when decay term at temperature 2 is known. (First order model as basis)

$$k_1 = k_2 * e^{-4818*(\frac{1}{T_1}-\frac{1}{T_2})}$$

Decay estimation using 30-minute chlorine decay

The model which used first order model as basis and predict chlorine decay term using 30-minute chlorine demand information was not feasible because the decay term did not strictly follow the exponential relation with the 30-minute chlorine demand of water. However, it was possible when Feben and Taras's empirical model was used as the basis as clear linear relationships were identified between estimated chlorine decay term and 30-minute chlorine demand of water. It was possible to estimate the chlorine decay based on the 30-minute chlorine demand and selected initial dose. This model produced best prediction of chlorine decay in the natural water tested. This approach was convenient since it incorporated other factors impacting chlorine decay, including temperature and chlorine consuming constituents. 30-minute chlorine demand is also easily obtainable in the field. One disadvantage was that the relations between decay constant and measured 30-minute chlorine demand for different initial doses differ, and it did not permit the chlorine decay rate estimation at intermittent doses. Currently, only relations for doses of 1 mg/L, 2 mg/L and 4 mg/L were determined.

For achieving minimum FCR of 0.2 mg/L at 24 hours of storage time, the maximum decay constant term was determined for the three doses. Corresponding maximum 30-minute chlorine demand of

the water can be determined based on the identified relationships shown in Figure 7. For an initial dose of 1 mg/L, 2 mg/L, and 4 mg/L chlorine, the 30-minute chlorine demand of the water cannot exceed 0.26 mg/L, 0.44 mg/L, and 0.97 mg/L respectively to meet the FCR objective.

Discussion on parameter relationships

Analysis from the tested waters showed that chlorine decay constant followed linear relationships with the UVA_{254} in the water. Humic acids mostly contain organics with aromatic compounds, and the dominate reactions between chlorine and the aromatic compounds are electrophilic substitution follows by stepwise substitutions (Deborde & von Gunten, 2008). A linear increase in the UVA_{254} of water lead to linear increase in chlorine consumption demonstrated by the consumption term, kt^n, in Feben and Taras's empirical model. The decay constant increased exponentially in the case of first order model because it is positioned in the exponent of the equation.

We hypothesized that humic substances and temperature were the two main factors impacting the chlorine slow decay, and the results from reservoir and pond water showed that there were more substances in the water leading to higher chlorine decay in the slow decay phase. Potential mechanisms including chlorine consumption from ammonia, chloramines and other organics such as fulvic acids.

From tests in the study, the 24-hour chlorine consumption ranged from 0.5 mg/L to 4 mg/L depending on the UVA_{254} values. However, the turbidity of all test water was below 10 NTU. This suggested that turbidity was indeed not an adequate indicator for chlorine decay in test water in the study.

Impacts from storage container

For all 16 tests conducted in the jerrycans, the chlorine decay kinetics were similar to those from tests in brown bottles under the same organics and temperature conditions. This implies that

chlorine reactions in (new/clean) jerrycans can be treated as bulk water decay. Within 24 hours, there were insignificant impacts from the environmental factors such as radiation and evaporation on chlorine decay. Additional chlorine reduction is possible in the field due to chlorine demand on the inner surface of the jerrycans. Frequent cleaning of the storage container can reduce chlorine demand from the containers and reduce the risk of water re-contamination (Meierhofer et al., 2019).

Additional chlorine reduction mechanisms

The organic and temperature-based model underpredicted the decay rate of chlorine in surface water sources where additional chlorine consuming substances might present. Either a coagulation/flocculation pre-treatment was needed before applying the predictive tool, or more chlorine reactions need to be researched to expand the tool's applications.

Conclusion

Three models for FCR decay prediction were proposed based on results from chlorine decay testing in water with varying UVA_{254} and under different temperature settings. Feben and Taras's empirical model with chlorine decay constant based on the 30-minute chlorine demand of the water adequately described chlorine decay in most of the test water samples (including tests in brown bottles and jerrycans). The model underpredicted chlorine decay in reservoir water and pond water, but the estimated values were closer to the actual FCR measured compared to estimation from models with chlorine decay term estimated from UVA_{254} and temperature of water.

30-minute chlorine demand was shown able to reflect actual chlorine decay kinetics. Together with the fact that it can be easily obtained in the field, it is recommended that 30-minute chlorine demand be used as an indicator for chlorine dose design instead of using turbidity. Based on the relations discovered in the study, for an initial dose of 1 mg/L, 2 mg/L, and 4 mg/L chlorine, the

30-minute chlorine demand of the water cannot exceed 0.26 mg/L, 0.44 mg/L, and 0.97 mg/L respectively for achieving minimum FCR of 0.2 mg/L at 24 hours of storage. Since the 30-minute chlorine demand incorporates the impacts such as UVA_{254} and temperature on chlorine decay kinetics. The exact values of the parameters were not required to be determined. Only 30-minute chlorine demand is needed to evaluate if the initial doses were feasible for the test water in field.

To develop the tool for finding the appropriate initial dose, Feben and Taras's empirical model can be used as the basic model. The power term 'n' in the equation can be set fixed at 0.22 and the decay term 'k' can be estimated with embedded formula based on the three mathematical relations developed for the three initial doses in the study. The three doses, 1 mg/L, 2 mg/L and 4 mg/L can be evaluated at once on whether they are able to reach 0.2 mg/L FCR at 24 hours based on the input value of 30-minute chlorine demand. Doses able to achieve the objective are output for the humanitarian staff. In future research, additional initial dose condition should be tested to expand the applicability of the model.

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Discussion

Recap

Two steps were undertaken to move towards the overall goal of develop a field-relevant chlorine dose predictive tool for humanitarian water supply applications. The first step (first manuscript) gathered chlorine decay models originally developed for assisting chlorination planning in conventional treatment systems and evaluated their performance in simulated humanitarian treatment contexts. The second step (second manuscript) built on findings from the first manuscript, used the evaluated models as basis to discover the relationships between estimated chlorine decay constant and several water parameters including pH, turbidity, UVA_{254}, temperature and 30-minute chlorine demand. Based on the relationships, the developed models in the second manuscript achieved accurate prediction of chlorine decay in synthetic test water with humic acid as the main constituent. The methods underpredicted chlorine decay in water with additional chlorine consuming chemicals.

30-minute chlorine demand as a proxy for chlorine dose determination

Chlorine demand is a water parameter which indicates the minimum amount of chlorine to be added to the water before FCR can form for a given contact time. 30 minutes is commonly used as the standard contact time in both conventional and humanitarian water chlorination (Crittenden et al., 2012; SPHERE, 2018). In humanitarian emergencies, 30-minute chlorine demand can be measured by conducting jar testing with several (typically 5) chlorine doses (USAID, 2019).

For the water tests conducted in brown bottles in manuscript 2, 24-hour chlorine consumption ranged from 0.5 mg/L to 4 mg/L with turbidity of all test water tested below 10 NTU. The test water which consumed 4 mg/L over 24 hours could not reach the minimum requirement (0.2 mg/L FCR) suggested by Lantagne (2008). This result showed that turbidity was not adequate for

chlorine dose determination. Although 30-minute chlorine demand requires more time to measure comparing to turbidity in the field, its correlation with the chlorine decay terms in kinetic models shows its great potential as a chlorine dose indicator in the field. Comparing to turbidity, an optical property of water which can be made up of inorganic suspended particles which do not affect chlorine consumption in the water, 30-minute chlorine demand incorporates a variety of chlorine decay impacting factors such as pH, temperature, chlorine dose, reactants etc., which reflects the actual chlorine reduction rates.

FCR verification is important in field application

Since the modelling approach proposed in manuscript 2 uses water's 30-minute chlorine demand to estimate chlorine decay in the water, finding the correct value is critical. While there are tradeoffs (i.e. accuracy, difficulty to use, cost etc.) in the selection of FCR verification tools (Murray & Lantagne, 2015), for jar tests, accuracy should be prioritized. A colorimeter is recommended for the jar test. However, for verification of FCR after dosing, less accurate results are acceptable since we are only checking if the FCR reaches the desired level. Other factors such as costs of tests and ease of use could be prioritized in this case.

Relations between fast and slow decay phases

30-minute chlorine demand can be used for quantifying the fast reacting substances such as fast reacting organics, fast reacting nitrogen compounds and inorganics in the water, contributing to the fast decay phase (Jegatheesan et al., 2006). However, its correlation with chlorine decay constant for the slow decay phase shows potential connections between the two phases. Possible explanation is that some dissolved organic matter (DOC) resulted in lower reactivity as the amount decreases (reacted with chlorine). Hua et al. (2015) proposed a variable reaction rate coefficient in

the chlorine decay model to account for the reducing reactivities of reactants and achieved satisfactory prediction of chlorine decay (R^2 over 0.9) in their test waters.

The two phases of the chlorine decay curve might not be caused by completely different mechanisms. Reactants with decreasing reactivity or possible sequential reactions with chlorine potentially form connections between the fast and slow decay phases of typical chlorine decay curves. This can be further researched by monitoring different chlorine reactants' concentration in water chlorination tests.

Limitations of the modelling approach

The modelling approach which uses Feben and Taras's empirical model as basis and predict chlorine decay constant using water's 30-minute chlorine demand can accurately predict chlorine decay in water with humic acid being the main constituent. It underpredicted decay in natural water samples with additional chlorine reacting substances (i.e. ammonia) by around 0.5 mg/L as shown in results of manuscript 2. This approach has several limitations such as not considering chlorine decay due to container wall contamination and other physical mechanisms (i.e. turbulence during transportation, evaporation etc.)

The jerrycans used in manuscript 2 were in brand new condition which had minimum chlorine demand on its inner wall surface. The chlorine decay kinetics of test water with the same constituents under the same temperature were similar for reactions in brown bottles and reactions in jerrycans. Chlorine decay of test water in jerrycans were essentially bulk decay. In field application however, containers wall may have chlorine demand due to adsorbed matter or growth of microorganisms on the inner wall surface (Meierhofer et al., 2019; String et al., 2019). An effective container cleaning strategy can be applied to minimize chlorine demand from the

container for more accurate application of developed models. An ongoing study is being conducted at Tufts University to evaluate several jerrycans cleaning strategies (String et al., 2019).

During water transportation, water in the containers can be subjected to turbulence, Abdel-Gawad & Bewtra (1988) showed that FCR reduction in water with stirring was double of that without stirring. Their test water was stirred for 1.5 day straight. In the field, 30 minutes is typically the maximum travel time for fetching water. Therefore, the impact from water turbulence was lower but still need to be evaluated in future study.

As for chlorine decay from evaporation, the jerrycans used in manuscript 2 were not completely filled with test water during chlorine decay tests as opposed to brown bottles where no air gap was left after water filling. Because of the similar decay results in similar water from both jerrycans and brown bottles, evaporation was deemed not a major factor of chlorine decay in humanitarian treatment contexts.

Trial development of dose predictive tool - Spreadsheet

A feasible approach determined was to use the empirical model with the power term ‘n’ set to 0.22 and the decay term estimated based on water’s 30-minute chlorine demand. In humanitarian contexts, the 30-minute chlorine demand of a source water can be measured relatively easily. Then the value could be input into the programmed spreadsheet which evaluated the FCR residual at 24 hours from the three initial doses (1 mg/L, 2 mg/L and 4mg/L). The spreadsheet (S3) then output the dose(s) able to maintain a minimum of 0.2 mg/L FCR during 24 hours of storage for the humanitarian staff to select. In cases the minimum FCR of 0.2 mg/L was not achievable, the maximum storage duration for which water would be safe for consumption will be shown to the staff.

Conclusion

The goal of the thesis was to work towards a tool/method to accurately determine the initial chlorine dose for achieving FCR objectives in humanitarian water supply. The findings in this work advance us towards achieving the goal, but additional research is needed to fully arrive there. The thesis took a two-step approach to develop tools for chlorine does prediction. The first step (first manuscript) gathered and evaluated seven basic chlorine decay models' applicability in contexts of humanitarian water supply and summarized their advantages and limitations. All seven models could describe chlorine decay in simulated humanitarian treatment conditions accurately, but they required chlorine decay data for model calibrations. The second step (second manuscript) utilized the models from the first manuscript as basis to study the relationship between chorine decay constant and several water parameters. The empirical model by Feben and Taras (1951) was selected because its power term 'n' could be fixed to 0.22 based on regression results. First order model was also used but data from the fast decay region (first 30 minutes after chlorine dosing) were excluded in regression. Power models and parallel models were excluded due to the variation in their power term 'n' and ratio term 'r' respectively. It was discovered that mathematical relationships existed between the chlorine decay constant and water parameters including UVA_{254}, temperature and 30-minute chlorine demand. Based on the discovered relationships, three methods were developed to predict FCR decay in three natural water samples. The methods accurately predicted FCR level in water with humic acid being the main constituent but underpredicted FCR decay in water with additional chlorine consuming matter. 30-minute chlorine demand was found to be an appropriate proxy for chlorine decay kinetics and FCR estimation based on it showed higher accuracy in the three natural water samples compared to those based on water's UVA_{254} and temperature. Additional research on chlorine decay due to reactions with ammonia and fulvic

acid and physical mechanisms such as water turbulence, dissociation in sun exposure are needed to improve the accuracy of the predictive tool.

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Appendix

Appendix 1

Table. Literature data sources used in Manuscript 1.

Category 1	**Surface Water**
Total: 98 Test data	(Fisher et al., 2011, 2012, 2015, 2017; Gang et al., 2003; Hua et al., 2015; Jegatheesan et al., 2006; Kohpaei et al., 2011; Monteiro et al., 2015)
Category 2	**Municipal Wastewater (In some cases: Secondary Effluent)**
Total: 50 Test data	(Abdel-Gawad & Bewtra, 1988; Wang et al., 2019)
Category 3	**Grey Water (Residential Water)**
Total: 8 Test data	(March et al., 2005; March & Gual, 2009)
Category 4	**Ground Water**
Total: 20 Test data	(Fisher et al., 2011, 2015; Vieira et al., 2004)
Category 5	**Treated Water (Pre-chlorination)**
Total: 31 Test data	(Fisher et al., 2012; Gang et al., 2003; Hua et al., 1999; Hua et al., 2015; Jegatheesan et al., 2006; Kastl et al., 2003; Kohpaei et al., 2011; Li et al., 2016; Liu & Qi, 2010; Monteiro et al., 2015)
Category 6	**Synthetic Water**
Total: 43 Test data	(Fisher et al., 2015; March & Gual, 2009)

Sources of literature test data

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Appendix 2.

MATLAB (2019a) codes for data fitting and generating R2 value from regression analysis used in Manuscript 1.

```
clear all
close all
clc

matrix = xlsread('Literature_My_Data','MyData_2020_A','C1:AL260');

%this line reads the chlorine decay test data pair and put them in "matrix"

%Create result matrix
result = zeros(100,10);

%for i value, enter number of test - 1; (42 tests, write i = 1:41);
for i=0:51
    a = 1+2*i;
    b = 2+2*i;
```

```
xm = rmmissing(matrix(a,:));
ym = rmmissing(matrix(b,:));
yave = mean(ym)
c0 = matrix(b,1);

%%%%%first order model
a0 = [c0,0.5];
% (1) Initial Value; (2) Decay Constant
ya = @(a0) a0(1)*exp(-a0(2).*xm);
objectivea=@(a0) sum((ya(a0)-ym).^2);
optimum_ya = fmincon(objectivea,a0,[],[],[],[],[0,0],[c0,5]);
resultsa = objectivea(optimum_ya);
R2_a = 1-((sum((ym-ya(optimum_ya)).^2))/(sum((ym-yave).^2)));
%%%%%first order model

%%%%%power model
b0 = [c0,0.1,2];
% (1) Initial Value; (2) Decay Constant; (3) Power Term
yb = @(b0) ((b0(2).*xm*(b0(3)-1))+(1/b0(1)).^(b0(3)-1)).^(-1./(b0(3)-1));
objectiveb=@(b0) sum((yb(b0)-ym).^2);
optimum_yb = fmincon(objectiveb,b0,[],[],[],[],[0,0,1],[c0,5,10]);
resultsb = objectiveb(optimum_yb);
R2_b = 1-((sum((ym-yb(optimum_yb)).^2))/(sum((ym-yave).^2)));
%%%%%power model

%%%%%Limited First Order model
d0 = [c0,0.8,0.05];
% (1) Initial Value; (2) Decay Constant; (3) Stable Component
yd = @(d0) d0(3)+(d0(1)-d0(3))*exp(-d0(2).*xm);
objectived=@(d0) sum((yd(d0)-ym).^2);
optimum_yd = fmincon(objectived,d0,[],[],[],[],[0,0,0],[c0,5,c0]);
resultsd = objectived(optimum_yd);
R2_d = 1-((sum((ym-yd(optimum_yd)).^2))/(sum((ym-yave).^2)));
%%%%%Limited First Order model


%%%%%Limited Power model
e0 = [c0,0.05,0.01,2];
% (1) Initial Value; (2) Decay Constant; (3) Stable Component; (4)
% Power Term
ye = @(e0) e0(3)+(e0(2).*xm*(e0(4)-1)+(1/(e0(1)-e0(3))).^(e0(4)-1)).^(-
1/(e0(4)-1));
objectivee=@(e0) sum((ye(e0)-ym).^2);
optimum_ye = fmincon(objectivee,e0,[],[],[],[],[0,0,0,1],[c0,5,c0,10]);
resultse = objectivee(optimum_ye);
R2_e = 1-((sum((ym-ye(optimum_ye)).^2))/(sum((ym-yave).^2)));
%%%%%Limited Power model

%%%%%Parallel First Order model
f0=[c0,0.05,0.05,0.3];
% (1) Initial Value; (2) Decay Constant; (3) Decay-2 (4) ratio
yf=@(f0) f0(1)*f0(4)*exp(-f0(2).*xm)+f0(1)*(1-f0(4))*exp(-f0(3).*xm);
objectivef=@(f0) sum((yf(f0)-ym).^2);
optimum_yf = fmincon(objectivef,f0,[],[],[],[],[0,0,0,0],[c0,5,5,1]);
resultsf = objectivef(optimum_yf);
R2_f = 1-((sum((ym-yf(optimum_yf)).^2))/(sum((ym-yave).^2)));
```

```
    weightf_2 = 1-optimum_yf(4);
    %%%%%Parallel First Order model

    %%%%%Limited Parallel Power Model
    g0=[c0,0.05,2,0.5,2,0,0.01];
    % (1) Initial Value; (2) Decay-1; (3) Power term-1; (4) Decay-2; (5)
    % Power term-2; (6) Stable Term; (7) Ratio
    yg=@(g0) g0(6)+((g0(2).*xm*(g0(3)-1)+(1/(g0(7)*(g0(1)-g0(6)))).^(g0(3)-
    1)).^(-1/(g0(3)-1)))...
    +((g0(4).*xm*(g0(5)-1)+(1/((1-g0(7))*(g0(1)-g0(6)))).^(g0(5)-1)).^(-
    1/(g0(5)-1)));
    objectiveg=@(g0) sum((yg(g0)-ym).^2);
    optimum_yg =
    fmincon(objectiveg,g0,[],[],[],[],[0,0,0,0,0,0,0],[c0,5,10,5,10,c0,1]);
    resultsg = objectiveg(optimum_yg);
    R2_g = 1-((sum((ym-yg(optimum_yg)).^2))/(sum((ym-yave).^2)));

    %%%%%Limited Parallel Power Model

    %%%%%Empirical Model
    i0=[c0,0.5,0.01];
    % (1) Initial Value; (2) Decay Constant; (3) Power Term
    yi=@(i0) i0(1)-(i0(2)*(xm.^(i0(3))));
    objectivei=@(i0) sum((yi(i0)-ym).^2);
    optimum_yi = fmincon(objectivei,i0,[],[],[],[],[0,0,0],[c0,5,5]);
    resultsi = objectivei(optimum_yi);
    R2_i = 1-((sum((yi(optimum_yi)-ym).^2))/(sum((yi(optimum_yi)-yave).^2)));
    %%%%%Last line for codes finding R2 for Parallel First Order + Limited
    model

    %%%%%Below codes are for finding R2 for Empirical Model
    z=1+i;
    result(z,1) = R2_a;
    result(z,2) = R2_b;
    result(z,3) = R2_d;
    result(z,4) = R2_e;
    result(z,5) = R2_f;
    result(z,6) = R2_g;
    result(z,7) = R2_i;


    %%%%%Last line for codes finding R2 for Empirical Model

end
```

Appendix 3.

Spreadsheet for determining chlorine doses to achieve 0.2 mg/L free chlorine residual for 24 hours of storage. In cases where the above objective is not achievable, the spreadsheet outputs the longest duration of safe storage time based on the measured 30-minute chlorine demand of water. (Please contact the author for a copy of the file)