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Meta-analysis approach to generalize chlorine decay first-order kinetic model along drinking water distribution networks

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Summary: In the last decades, research has focused on identifying the most appropriate models to describe the decay of disinfectants in drinking water distribution network (DWDN). Various kinetic models are available, but the most adopted is that of the first-order for its simplicity. However, the application of these kinetic models is not straightforward because the estimated parameters are strictly site-specific. In this work, a meta-analysis approach was used to generalize the estimation of the first-order kinetic coefficients available in literature, disengaging themselves from the site-specific boundary conditions, in order to make possible the application in real DWDN for the prediction of the residual disinfectant based on water characteristics and operating parameters.

Keywords: chlorine decay; disinfection; drinking water; meta-analysis

1. INTRODUCTION

In recent years, increasing attention has been given to the management of drinking water distribution networks (DWNs). The most recent worldwide guidelines and regulations reaffirm the importance of ensuring safe water quality from a microbiological and chemical point of view, from source to tap (Directive (EU), 2020/2184). Disinfection is the last barrier of the water treatment train to provide microbiologically safe water. However, an inefficient chemical disinfection can also lead to several drawbacks, such as (i) the alteration of water organoleptic properties, (ii) the acceleration of the wear of the pipelines, and, above all, (iii) the formation of harmful disinfection by-products (DBPs). Since chlorine is the most widely used disinfectant, several studies have focused on the description of the chlorine bulk-decay in the DWDN as a function of residence time, hydraulic conditions and water quality characteristics. Therefore, the proper selection of the kinetic model that predicts the chlorine bulk-decay along the DWDN is crucial to describe water chemical and biological stability from the outlet of the drinking water treatment plant (DWTPs) to the consumer tap. In the literature, several works have assessed and applied three main types of chlorine bulk-decay kinetic models: first-order (FO), second-order (SO), and two reactant (2R). Although SO and 2R kinetic models have been recognised as more effective in describing the decay of the disinfectant in the short and long term, today the most widely used model in software modelling the distribution network (e.g., EPANET) is still the FO kinetic model, due to its simplicity, ease of application, and direct dependence on a single parameter, namely the initial chlorine dosage. The equation describing the FO kinetic model is

$$\frac{dC_{Cl}}{dt} = -\kappa \cdot C_{Cl} \quad (1)$$

where C_{Cl} is the chlorine concentration [mg Cl_2/L] in water, t [h] is the time after initial dosing, and k is the FO reaction rate coefficient [h^{-1}] (Clark, 1998).
However, it is well known that the kinetic coefficient (κ) is site-specific and depends on water quality parameters that can affect the disinfectant demand, such as temperature, pH, organic matter, and initial dosage itself (Powell et al., 2000).
In this work, a generalized FO reaction rate coefficient κ for the chlorine bulk-decay was estimated, through a quantitative meta-analysis of available scientific literature. The actual applicability of the developed empirical model for κ was assessed through a dedicated monitoring campaign in a DWDS case study (Sirmione, Italy).

2. MATERIALS AND METHODS

Firstly, a literature review was performed by selecting the scientific articles in the SCOPUS database through appropriate keywords and limiting the query to the years 1992-2020. Then, in order to perform the quantitative meta-analysis (Borenstein et al., 2021), a database was built: for each article, the parameters for the water quality, the type of source and treatment, the disinfectant dosage, the contact time and the estimated FO coefficient κ were reported. To account for the heterogeneity between the articles, weights were formed based on the number of data collected to estimate κ and the goodness of the estimate. The weights were assigned as:

$$\text{weight} = N \times R^2 \quad (2)$$

where N is the sample size and R^2 the coefficient of determination of the estimated model. Then, a weighted least-square (WLS) regression between the FO coefficients κ and parameters (qualitative and quantitative) was performed. Weights were normalized, continuous variables were standardized, and categorical variables were transformed into dummy variables. Table 2.1 shows all the variables initially considered. To take into account pH and T in a single parameter, pH was normalized for hypochlorous acid pK_a, calculated as (White, 2010):

$$pK_a = \frac{3000}{T} - 10.0686 + 0.0253T \quad (3)$$

Table 2.1 Parameters taken into account for modelling the FO reaction rate coefficient (k)

Variable	**Type of variable**
article	dummy
water source	dummy
water treatment	dummy
chlorine initial concentration (C_{Cl})	continuous
total organic matter (TOC)	continuous
temperature (T)	continuous
pH	continuous

WLS regression was performed using R studio software, and significant variables (p-value < 0.05) were selected by the backward selection method.

The applicability of the model developed for the coefficient κ was tested in an Italian case study, monitoring the DWDS of Sirmione town. Water is taken from Garda Lake and is then treated by ozonation, adsorption of granular activated carbon and disinfection by sodium hypochlorite. In the DWDN a re-chlorination process is used to maintain an adequate chlorine residual concentration at the sections far from the DWTP. Samples were collected weekly for 10 weeks from March to August 2020, measuring chlorine residual concentration, temperature, pH and TOC. Before applying the developed model, the variables were standardized by subtracting the mean and normalizing by the standard deviation estimated by the literature reference dataset. The coefficient κ was then used to estimate the chlorine residual concentration to be compared with the measured data for model validation.

3. RESULTS AND DISCUSSION

Nine literature articles were collected, in which 78 kinetic constants were estimated, as summarised in Table 3.1.

Table 3.1 Summary of literature database

Parameter	Mean	Standard deviation	Minimum	Maximum
k [h^{-1}]	0.104	0.18	0.002	0.73
C_{Cl} [mg/L]	1.74	1.36	0.31	4.03
T [°C]	19.2	4.4	10	25
pH	7.7	0.4	6.9	8.9
DOC [mg/L]	2.13	1.41	0.48	5.87

WLS regression resulted in the following equation:

$$\kappa = -0.55 + 0.6\,DOC - 0.95\,C_{Cl} + 0.76\,C_{Cl}^2 - 0.5\,C_{cl}\cdot DOC - 0.31 C_{Cl}\cdot\frac{pH}{pKa} \quad (4)$$

with adjusted $R^2 \simeq 0.81$ and input and output parameters both standardized.
Estimated regression coefficients with their confidence intervals are shown in Figure 3.1. As expected, DOC and pK_a (i.e., temperature) positively affect κ, because of chlorine reaction with organic matter and acceleration of decay given by higher temperatures. As for the chlorine initial concentration, it has a negative correlation with κ, as confirmed in the literature (Hua et al., 1999). The positive sign of the quadratic term indicates a downward curvature of the regression due to the initial disinfectant concentration. Overall, C_{Cl} negatively influences κ, decreasingly as the chlorine concentration increases. The different sensitivity of κ to those factors and their interactions can be directly observed in the estimated model in Equation (4), because of data standardization (Figure 3.1). Regardless of the sign of the estimated dependency, the input factors can be sort according to their effect on κ as follows: $C_{Cl} > C_{Cl}^2 > DOC > C_{Cl}*DOC > C_{Cl}*pH/pKa$.
The normalized root-mean-square deviation (NRMSE) of Equation (4) with respect to data from literature was equal to 43. The differences between fitted and measured κ's are shown in Figure 3.2.

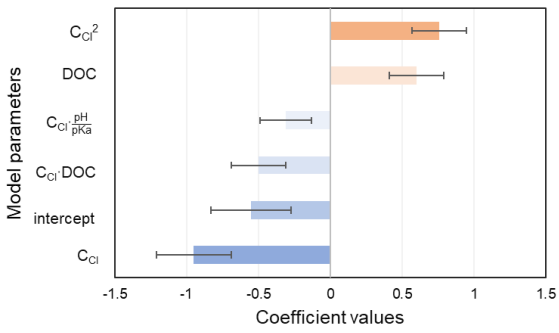

Figure 3.1 Estimates and 95% confidence intervals of the regression coefficients of Model (4) for FO coefficient κ.

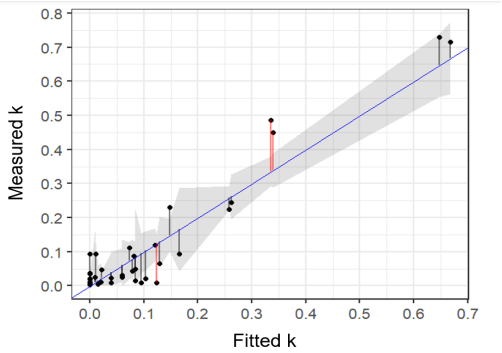

Figure 3.2 Measured κ vs fitted κ. Absolute errors greater than 0.1 are highlighted in red.

Finally, the model estimated by meta-analysis of the literature was applied to data from the full-scale DWDS monitoring. Since the FO kinetic is not always suitable in the case of systems in which re-chlorination is present (Fisher et al., 2011), to estimate κ the following water quality data were used: i) at the outlet of the DWTP, for the sampling points before the chlorination point; ii) at immediately downstream of the re-chlorination tank, for the remaining sampling points.

The residence time in the DWDSs for each sampling point was calculated using the hydraulic model in the EPANET network. The residual chlorine concentration at each sampling point was then estimated combining Equations (1) and (4) and compared with the measured residual chlorine.

The average root-mean-square deviation (RMSE) between measured and fitted values was 0.05±0.01 mg/L, with decreasing precision as the distance from the chlorination points increases. This is probably due to the lack of a sufficiently reliable calibration of the hydraulic model.

In conclusion, there are several studies in literature for the estimation of the decay of chlorine disinfectant, whose application is not straightforward because of the site-specificity of the reaction rate coefficients. In this work, we demonstrated that a quantitative meta-analysis approach allows a good generalization of the FO kinetic coefficient, making it possible to apply it for preliminary estimation of residual chlorine concentration in full-scale DWDS. Future developments will include using the meta-analysis approach for more complex kinetic models and validating it on other real-world datasets.

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