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Modeling of chlorine decay in drinking water supply systems using EPANET MSX

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Abstract

The modelling of chlorine residual in water supply systems is of great importance in managing disinfectant concentrations throughout the network. First order decay kinetics are currently often used to describe both bulk and wall chlorine consumption. However, more complex approaches have been proposed, namely a parallel, two-reactant second order decay model (2R model) that has been reported as yielding better accuracy for simulating chlorine bulk decay in laboratory tests. The recent EPANET Multi-Species Extension (EPANET MSX) brought enhanced capabilities for the simulation of chlorine residuals in water supply systems, including the use of the 2R model or any other formulation. In the current paper, the performance of the 2R model as well as of first and n[th] order decay kinetics was assessed for full scale modelling of chlorine in a transmission system. Results have shown that a similar level of accuracy can be achieved with the three tested kinetic models, provided that a good calibration of the wall decay coefficient is accomplished. Although with improved modelling capabilities, the use of the stand-alone EPANET MSX was less user-friendly than normal EPANET application by the lack of a graphical interface allowing for the visualization of chlorine concentration profiles along the system. The use of the 3D-enabled Epanet Java web application circumvented such limitations. This tool together with a better characterization and estimation of the bulk and wall decay components allow for a more practical and accurate modelling of chlorine in water supply systems, while taking advantage of EPANET MSX's enhanced capabilities.

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1. Introduction

Chlorine is used worldwide as a disinfectant residual to counteract microbial contamination and proliferation in drinking water supply systems. However, chlorine residual concentration decays as the water travels through the systems mainly due to its reaction with the water's natural organic matter (NOM) (bulk decay) and with the pipe's internal surface materials (wall decay). Keeping an effective residual concentration of the disinfectant, while maintaining it at levels for a minimal formation of disinfection by-products, is essential for the water's safety (World Health Organization, 2011). Hence, the management of chlorine residual concentration within defined limits in drinking water systems is a major concern for utilities.

Water quality models that simulate chlorine decay are valuable tools for the management of chlorine residual. Such models are currently used for dosage optimization, chlorination facilities siting and prediction of critical locations where chlorine may decay to ineffective levels. Although many efforts have been made in the last decades (Rossman et al., 1994; Shang et al., 2008), the modeling of chlorine residuals is still complex, as it relies on the accuracy of hydraulic models to describe flows and flow velocities (Blokker et al., 2008; Pasha and Lansey, 2010) and on the adequacy of chlorine decay kinetic models (Fisher et al., 2011a).

The nth order bulk decay kinetic model with respect to chlorine is described by the following equation:

$$\frac{dC}{dt} = -k_b C^n \tag{1}$$

where C is chlorine concentration, k_b is the bulk decay rate coefficient and n is the order of the reaction with respect to chlorine. First order bulk decay is a particular case of nth order kinetics with respect to chlorine. It has been extensively used in the simulation of chlorine decay in water supply systems (Rossman et al., 1994). Several authors have reported that this kinetic approach is not frequently the most accurate for describing bulk decay and, therefore, a number of alternative models have been proposed (Clark, 1998; Jonkergouw et al., 2009; Kastl et al., 1999). Recently, Fisher et al. (2011a) reported on a two reactant (2R) second order model as the most simple and generally suitable model for simulating chlorine concentration profiles in distribution system networks. The model assumes that chlorine reacts with two groups of water compounds, one reacting rapidly and the other reacting slowly:

$$\frac{dC}{dt} = \frac{dC_f}{dt} + \frac{dC_s}{dt} = -k_f C C_f - k_s C C_s \tag{2}$$

where C_f and C_s are, respectively, the concentrations of fast and slow reducing agents in the water that react with chlorine (as mg Cl-equivalent/L) and k_f and k_s are decay rate coefficients for fast and slow reactions (L/mg Cl/h). The model requires the estimation of four parameters, namely the reaction rate coefficients and initial concentrations of C_f and C_s, which can be inferred from laboratory decay tests data. Although the model has very accurately described chlorine decay in a several decay tests, its performance has not previously been confirmed for full scale water supply systems.

For wall decay in non-metallic pipes, a first order kinetic model is generally used (Rossman et al., 1994; Vasconcelos et al., 1997):

$$\frac{dC}{dt} = \frac{2k_w k_F}{R(k_w k_F)} C \tag{3}$$

where k_w is the wall reaction rate coefficient, k_F is the mass transfer coefficient and R is the pipe's radius.

EPANET MSX (Shang et al., 2008) is an extension of the standard hydraulic modeling software EPANET that enables the user to freely define which chemical reactions are the most relevant for wall and bulk decay and to use

the equations that more accurately describe these reactions. Thus, this feature allows the application of chlorine bulk decay kinetics other than the ones included on EPANET 2.0.

In the studies described herein, the utilization of a 2R model to describe bulk decay at full-scale conditions was assessed. For this purpose, an EPANET MSX chlorine decay model was developed and tested in a large water supply system. Results were compared to those obtained with first and optimized nth order models. In addition, Epanet Java (Baseform), an innovative web-based application for hydraulic and water modeling, with 3-D graphical visualization, Google Earth® integration and enhanced MSX simulation features, was tested.

2. Methodology

2.1. Case study description

The case study was carried out in a sector of the drinking water transmission system that supplies eastern Algarve, Portugal. It comprises a 23 km long, large-diameter trunk main with 6 delivery points. At each point, water is delivered to service storage tanks that are managed by municipal water utilities. The system is supplied by the Tavira Water Treatment Plant (WTP) and carries water to Cabeço service tank at the downstream end (Figure 1). Pipe diameters range from 1500 mm to 450 mm in the main line, with delivery branches ranging from 100 mm to 400 mm. Water flows by gravity and uni-directionally. Flow is controlled by water levels in the tanks and, therefore, depends on the demand patterns at the delivery points.

Tavira WTP is supplied with water from the Beliche reservoir through a raw water transmission pipeline. Water is treated by a conventional process for superficial waters consisting of pre-oxidation with ozone, followed by coagulation/flocculation/sedimentation, sand filtration and final disinfection with gaseous chlorine. Average chlorine content is 0.83 mg/L at the WTP outlet and 0.6 mg/L at the inlet of Cabeço tank. Water has relatively low, organic (1.5 mg C/L as total organic carbon) and inorganic contents (iron, ammonia and manganese concentrations below detection limits) and therefore, low chlorine demand is expected.

Predominant pipe materials are ductile iron with aluminous cement lining and steel. Average infrastructure service age is about 15 years.
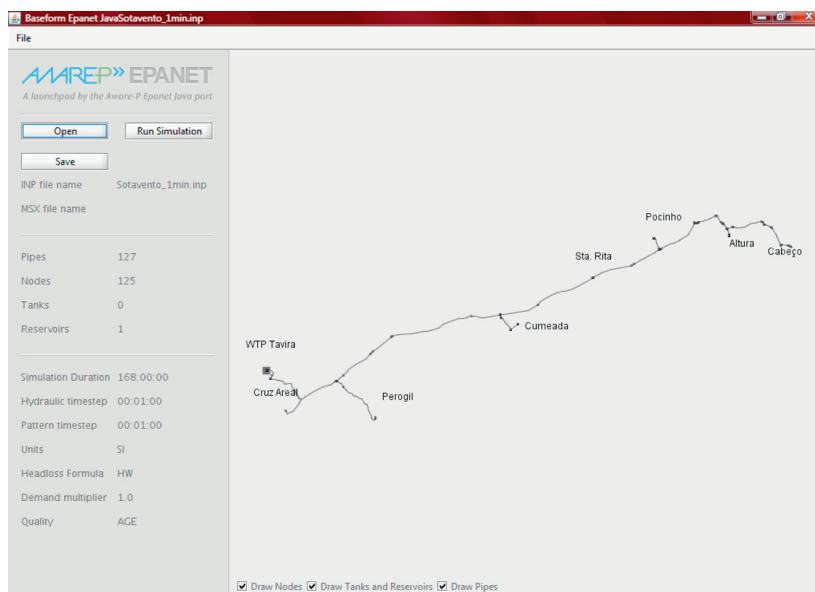

Figure 1. Case study's EPANET model.

2.2. Kinetics study

Bottle tests, carried out according to the procedure described by Powell et al. (2000), were used to assess chlorine consumption kinetics and estimate bulk decay rate coefficients (k_b). Tests were carried out at different temperatures (10, 15, 20, 25 and 30ºC) in a refrigerated incubator (model FOC225E, Velp Scientifica) in order to investigate temperature effect on k_b. The DPD colorimetric method (APHA et al., 1998) was used for free chlorine concentration determination (Pocket Colorimeter II, Hach). Chlorine decay tests lasted until concentration reached 0.1 mg/L or seven days, whichever came first.

First and n^{th} order kinetic models with respect to chlorine were fitted with laboratory data on chlorine decay. Model parameters (k_b, n) were estimated by the sum of residuals minimization using Solver function on Excel® (Microsoft). For the 2R model, the same data were used and the Scientist® software (Micromath) was utilized for parameter estimation. The ability of each of these bulk decay models to describe laboratory tests data was assessed by Root Mean Square Error (RMSE) between observed and predicted chlorine concentrations.

An Arrhenius model (Equation 4) was used to assess the temperature effect on chlorine bulk decay rate coefficient (Monteiro et al., 2012; Powell et al., 2000) for each kinetic model.

$$k_b = A \cdot \exp(\frac{-E_a}{RT}) \tag{4}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature (K). Equation 4 was used for bulk decay coefficient estimation for the average water temperature within the modeling time period.

2.3. Chlorine modeling

The hydraulic model was developed by the water utility using EPANET 2.0. Water demand records at each of the six delivery points were obtained from the telemetry system for a one-week time period (13th to 19th February 2013), with one minute time steps.

For chlorine modeling, EPANET MSX was used and the Epanet Java web app was tested. Chlorine was modeled for 1st and n^{th} order decay kinetics (in order to chlorine), and with the 2R model for bulk decay simulation. For wall demand, a first order kinetic model was assumed. Time steps of 1 min, were used for both hydraulic and quality simulation.

A pattern of chlorine concentration at WTP outlet was developed by using online measurements with a chlorine analyzer (Polymetron). Data was registered at 1 min time intervals.

Additionally, chlorine was measured online by two other analyzers placed at Perogil (Polymetron) and Santa Rita (Fischer-Porter) delivery points. Analyzers performance was checked 3 times a week at WTP outlet and once a week at Perogil and Santa Rita delivery points.

For model's calibration and validation, a field data collection programme was carried out consisting of *in situ* chlorine measurements at several points throughout the system. Free chlorine concentration was measured at five delivery points (Cruz do Areal, Perogil, Cumeada, Pocinho, Santa Rita) and at the downstream end of the system (Cabeço), for four times at each point, over a two-day period. An additional measurement was made at another delivery point (Altura).

For chlorine wall reaction rate coefficient calibration, 12 random chlorine measurements were used. These included all measuring points. The remaining set of chlorine measurements were used for model's validation.

Model calibration was performed by sequentially adjusting the chlorine wall reaction rate coefficient to give the best fit between predicted and observed field measurements. The suitability of k_w was evaluated by examining the correlation plots and minimization of RMSE between predicted and observed values. Wall decay coefficient was assumed to be the same for all pipes, as both materials and service age are identical.

Two different approaches were developed for chlorine model validation. One was done by comparing chlorine concentrations produced by the models with synchronous field measurements. The other, allowing to assess

models results over an extended time period, relied on chlorine analyzers measurements at Perogil (average travel time of 6.3 h) and Santa Rita (average travel time of 13.7 h) delivery points, herein referred as locations 1 and 2 respectively, over a 48 h period (80 to 127 hours of simulation). This approach was also used to evaluate the calibration of the hydraulic model. For both approaches, models best performance criteria was the minimization of RMSE.

3. Results and Discussion

3.1. Kinetics study

Bulk decay kinetic model fitting with laboratory test data was evaluated by RMSE (Table 1). Results do not show significant chlorine decay simulation improvements with the use of the 2R model, as it could be expected, except for the 15ºC assay. For the 10ºC and 25ºC assays, all kinetic models performed similarly well and for the 20ºC assay the 2R model performed as well as the nth order one and both performed better than the first order model. At the extreme temperature of 30ºC, the 2R model performed better than the nth order one, but worse than the first order model.

The estimated value of n that most minimized the error of the nth model was not the same for all tests, ranging from 0.7 to 2.0 (Table 1). For modeling purposes, an optimized value for n was determined by the sum of square difference between model and measured values minimization of all laboratory tests. The obtained value was 1.2 and therefore the nth order model referred herein is a 1.2 order model.

Table 1. RMSE calculated for bulk decay models fitting to laboratory test data.

T (ºC)	RMSE (mg/L)		
	1st order	n^{th} order	2R
10	0.031	0.027 (0.7)[*]	0.032
15	0.021	0.010 (1.4)[*]	0.004
20	0.045	0.010 (2.0)[*]	0.010
25	0.017	0.015 (1.2)[*]	0.015
30	0.015	0.080 (0.8)[*]	0.023

[*] estimated value of n that minimized the error of the nth order model fitting

After estimation of the Arrhenius parameters, the coefficients of the kinetic models were determined for the average temperature (13ºC) of water in the system during the simulation time period (Table 2).

Table 2. Estimated bulk decay models parameters at average temperature (13ºC).

1st order	n^{th} order (n = 1.2)			2R model		
k_b (/day)	k_b ($L^{0.2}/mg^{0.2}$/day)	C_{f0} (mg Cl-equivalent/L)	C_{s0} (mg Cl-equivalent/L)	k_f (L/mg/day)	k_s (L/mg/day)
-0.27	-0.35	0.03	1.85	-6.74	-0.17

3.2. Chlorine modeling

Chlorine modeling using estimated parameters for bulk decay models was tested with EPANET MSX. In a first approach, a k_w equal to zero was tested. Modeling bulk decay alone led to poor simulations, mostly with overestimated chlorine concentrations (correlation plot in Figure 2a). These results were observed for all tested bulk decay models. Similarly to what was observed for laboratory decay tests at 15ºC, 1st order kinetics led to the higher RMSE than 1.2 order model and the 2R model was the one which better described bulk chlorine decay in the water supply system (Table 3).
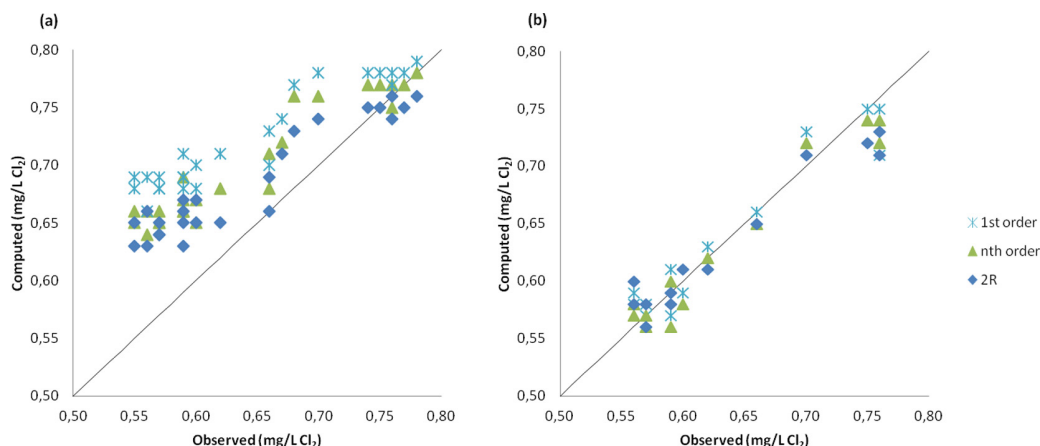

Figure 2. Correlation plot for field measured and computed values by the three kinetic models assuming (a) only bulk decay; (b) bulk and wall decay.

The difference between calculated and measured values increased with the distance of the point of measurement to the WTP (i.e., with travel time). These differences were probably due to factors that exert chlorine demand, other than chemical reaction between chlorine and NOM in the water. This is traditionally ascribed to reactions with pipe material and biofilm in the pipes internal surface and acknowledged as wall decay, even in pipes of low reactivity materials. Nevertheless, this difference might also be interpreted as the result of the lack of accuracy of bulk decay models that do not include the influence of additional factors, such as flow velocity, in bulk decay rates (Menaia et al., 2003).

When including a wall decay component, correlation plot showed better agreement between measured and simulated results (Figure 2b), alike it has been observed by Vasconcelos et al. (1997).

Calculated RMSE (Table 3) for all developed decay models is within measurement uncertainty (0.05 mg/L), which means that all models were able to accurately simulate chlorine concentration decay. In addition, no significant differences in overall decay model accuracy were observed between the tested bulk decay kinetic models. This suggests that uncertainties in bulk decay simulations are being confused with the ones associated with wall decay coefficient calibration, thus in accordance with Fisher et al. (2011b) findings. These may likewise explain why slightly lower k_w coefficients were needed for model calibration as bulk decay simulation accuracy was higher. Accordingly, the more accurate bulk decay modeling was, the smaller was the involved wall decay component, which may then have been closer to the occurring one.

Table 3. RMSE based on field chlorine measurements and calibrated k_w.

Bulk decay model	k_w (m/day)	RMSE (mg/L)	
		Bulk decay	Overall decay
1st order	0.040	0.089	0.021
nth order	0.035	0.067	0.018
2R	0.025	0.057	0.023

On average the models were able to reproduce individual chlorine measurements with an absolute error in the order of 0.02 mg/L, which is an average relative error of ca. 3%.

When comparing overall chlorine predicted concentrations with the measured ones at locations 1 and 2 by online chlorine analyzers over a 48 h period, results in the models performance were quite similar (Table 4) as RMSE remained equal to 0.02 mg/L (at location 2) and only slightly higher at location 1 (0.03 mg/L) for all tested models.

Table 4. RMSE for overall decay based on online chlorine measurements.

Bulk decay model	RMSE (mg/L)	
	Location 1	Location 2
1st order	0.030	0.025
nth order	0.034	0.017
2R	0.035	0.019

Figure 3 shows chlorine concentration profiles at locations 1 and 2 during the simulated time period, as well as the values predicted by the three tested models. The first 50 hours of simulation, which represented two and a half times the average travel time from the WTP to the node farer away, were neglected in this analysis as hydraulic stabilization of the system might still be occurring.
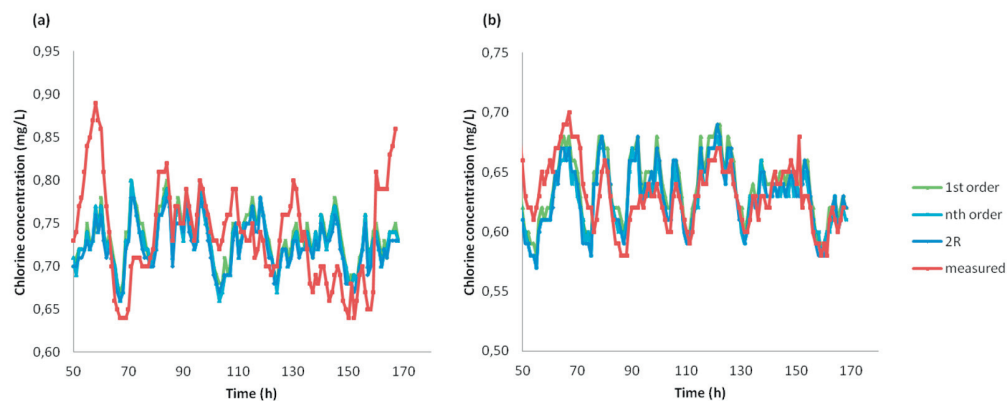

Figure 3. Comparison of computed and measured chlorine concentration over the simulation period at locations 1 (a) and 2 (b).

At location 2, predicted concentrations were quite similar to the measured ones. The models were able to simulate chlorine peaks at the exact times they were detected by the online analyzer, thus denoting that the hydraulic model was well calibrated. On the other hand, differences between values computed by the different formulations were very small, as would be expected from the previous evaluations of the models.

Although the performance of the chlorine analyzers was frequently assessed, some unreliable measurement periods were detected during the one-week study period. At location 1 (Figure 3) at least two situations could be

easily identified, as it is the case of the peak detected at 58 h and the rapid chlorine concentration increase at 160 h. The first corresponds to an impossible chlorine concentration that is higher than the measurement at the WTP outlet 6.6 h before (the travel time at this delivery point on that time step). The other corresponds to a sensor recalibration that was then performed. These conditions made it difficult to understand whether such discrepancies between online measurements and modelled values were due to limitations of the models to describe chlorine decay or to unreal chlorine measurements during maintenance or any other change on analyzers' operating conditions. On the other hand, all the models were based on a chlorine concentration time pattern that was built in WTP outlet analyzer measurements and were therefore vulnerable to this analyzer possible incorrect measurements. Nevertheless, good agreement between modelled and measured chlorine concentrations at location 2 indicates that the WTP outlet analyzer had a good performance through the study period. Hence, model validation, as well as chlorine concentration time pattern set up, should not rely only on online analyzers but also on field sample measurements.

3.3. EPANET MSX

Chlorine modeling with EPANET MSX is not as practical as standard EPANET 2.0, given the lack of a graphical user interface. It requires MS-DOS user capabilities and it does not allow for rapid visualization of results. In addition, calibrating a wall decay rate coefficient with MSX extension can be quite a time-consuming and complex task. Epanet Java was faster and more effective to use due to the innovative use of its 3-D graphical interface and integration with Google Earth®. It allowed for immediate visualization of results of chlorine decay simulation with the 2R model (Figure 4).
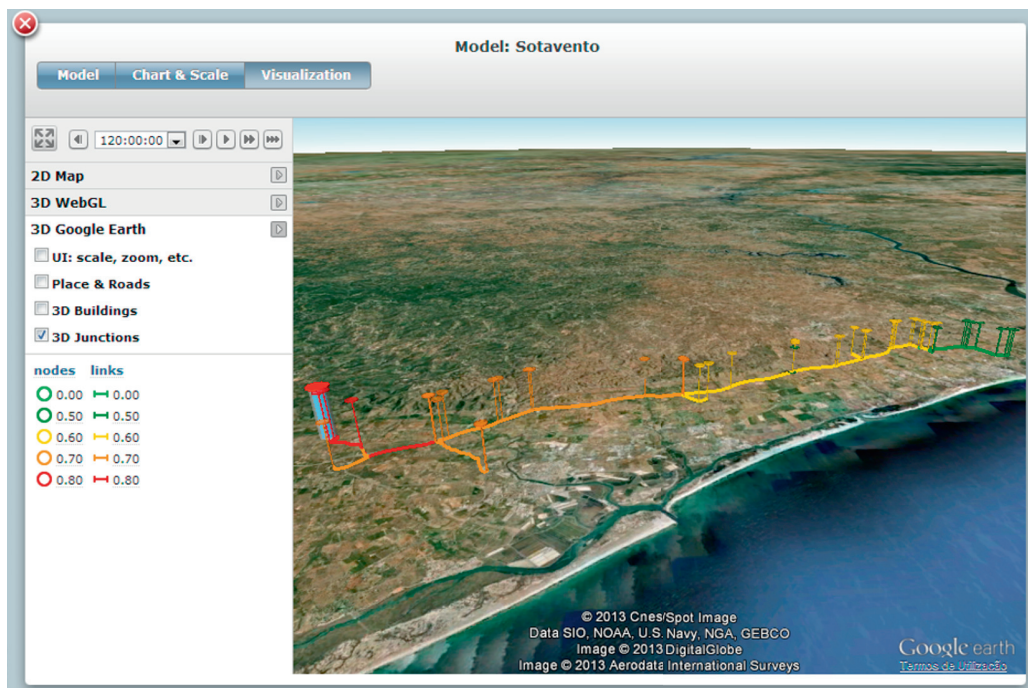

Figure 4. EpanetJava web app showing the results of the 2R model simulation at hour 120 in terms of chlorine concentration at nodes. (http://baseform.org/np4/apps/epanetApp.html, accessed 2013/04/26)

4. Conclusions

While the 2R model conceptually approaches better the processes involved in bulk chlorine consumption in supply systems, namely by incorporating fast and slow decay terms, and depending less on wall decay calibration, similarly satisfactory descriptions of chlorine decay were produced with the 1st and n^{th} order models. Hence, 2R and 1st and n^{th} order less complex models may be successfully used alike for simulating chlorine decay in supply systems, provided that a sound calibration of wall reaction rate coefficient is performed. Accordingly, the use of the current EPANET MSX version may not be always advantageous, owing to the use of MS-DOS and the lack of a graphical interface. This limitation may be effectively overcome with the use of Epanet Java as herein demonstrated. A deeper understanding of the mechanisms underlying chlorine consumption in piped systems, namely the effect of pipe material and surface conditions, including those associated with biofilm, is still needed for a more accurate estimation of k_w and chlorine decay modeling improvement.

Acknowledgements

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