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The Dependence of Chlorine Decay and DBP Formation Kinetics on Pipe Flow Properties in Drinking Water Distribution

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Abstract

Simultaneous chlorine decay and disinfection byproduct (DBP) formation have been discussed extensively because of their regulatory and operational significance. This study further examines kinetic variability of the water quality changes responding to hydrodynamics in drinking water distribution. The variations of kinetic constant for overall chlorine decay (k_E), trihalomethane (THM) formation were determined under a set of physiochemical and flow conditions using three devices of different wall demand and two types of natural organic matters (NOM) in water. The results from the comparative experiments and modeling analyses show the relative importance of wall demand (k_w), DBP-forming chlorine decay (k_D), and other bulk demand (k'_b) for pipe flow $Re=0-52500$. It is found that chlorine reactivity of virgin NOM is the overriding factor. Secondly, for tap water NOM of lower reactivity, pipe flow properties (Re or u) can significantly affect, the THM yield (T), formation potential (Y), and the time to reach the maximum THM concentration (t_{max}) through their influence on kinetic ratio $k_D/(k'_b + k_w)$. These observations, corroborating with turbidity variations, cannot be explained alone by chlorine dispersion to and from the pipe wall. Mass exchanges through deposition and scale detachment are most likely the other mechanism depending on the flow velocity and shear stress on pipe walls. Thus for the simultaneous occurrence of chlorine decay and DBP formation, model considerations of NOM reactivity, pipe types (wall demand), flow hydraulics, and their interactions are essential.

1.0 Introduction

Better water quality management and energy saving in water distribution often require accurate water quality prediction through modeling and quantitative analysis. However, mass transfer and interrelated kinetic variables are complex affecting the water quality in distribution (e.g., Rossman et al., 2001; Zacheus et al., 2001; Lehtola et al., 2006; Sadiq and Rodriguez, 2004; Wang et al., 2013; and Kim et al., 2014). Many controlling factors are not fully characterized.

For chlorine decay and disinfection by-product (DBP) formation, a flowing water pipe essentially acts as a tubular plug flow reactor, where mass transport and chemical reactions

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are intimately related to the hydraulic properties. Such relationships have long been discussed in chemical engineering (e.g., Laidler, 1958; Ottino, 1994; Poirier and Carr, 1971); for example, experiments and model simulations have shown that pipe flow micromixing and microchanneling affect solute transport and hereby product yield (Forney and Nafia, 2000; Chakraborty and Balakotaiah, 2002; Kockmann et al., 2006). Similarly, flow-controlled kinetic variability occurs in drinking water distribution pipes, a subject that has been examined since the 1990s (e.g., Biswas et al., 1993; Clark, 1998; Piriou et al., 1998; Rossman et al., 2001; Yang et al., 2008b; Stoianov and Aisopou, 2014). Continuing research is needed, however, to understand how pipe flow affects the simultaneously occurring chlorine decay and DBP formation because of the regulatory and operational importance (e.g., Clark et al., 2001, 2009; U.S. EPA, 1998 and references therein).

Concentration of non-selective free chlorine and other disinfectants decreases in water distribution by biological and chemical reactions, some of which produce carcinogenic DBPs. Chlorine reactions in bulk water and at pipe walls are known as chlorine bulk and wall demand, respectively. Many identified organic matters in a pipe have diverse chlorine reactivity and DBPs formation potentials, and complex relationships with pipe flow hydrodynamics (See Chan et al., 2002; Yang et al., 2008b; Stoianov and Aisopou, 2014; Mathieu et al., 2014; and Wang et al., 2012, 2013). Examples include chlorine mass transport to pipe walls, multi-species competitive reactions with chlorine in the bulk phase, changing DBP-forming fractions of organic matters, pipe scale formation and biofilm detachment returning to the bulk phase, all of which are related to pipe flow hydrodynamics. Previously examined controlling factors include pipe materials (Rossman et al., 2001), disinfectant chemical properties (Hua and Reckhow, 2007), total organic carbon (TOC) compositions and concentration in water (Clark et al., 2001; Gang et al., 2003; White et al., 2003; Anastasia et al., 2003), and hydrodynamic regimes of pipe flow (Lu et al., 1995; Clark and Haught, 2005; Yang et al., 2008b; Mathieu et al., 2014; Stoianov and Aisopou, 2014; and Kim et al., 2014). Many results are used in water quality simulation programs such as EPANET and its extension EPANET-MSX (Rossman, 2002; Shang et al., 2012), in re-chlorination and DBP formation models (Rossman et al., 2001; Boccelli et al., 2003; Sadiq and Rodriguez, 2004, and references therein), and in other earlier water quality models (Biswas et al., 1993; Clark, 1998).

Our attention is focused on three important factors in water quality analysis: reaction kinetic constant, the time to reach steady state, and the concentration of chlorine residual and DBP compounds. In water distribution, it is conceivable that flow hydrodynamic changes create numerous scenarios of interactions among aqueous contaminants, disinfectants, other solutes in bulk water, the pipe and attached biofilm/scale. Figure 1 shows a few typical scenarios; each has different fractions of reaction kinetic constants in wall demand (k_w), bulk demand consisting of DBP-forming reactions (k_D) and other bulk reactions (k'_b). For simplicity, earlier studies (Rossman et al., 1994; Clark, 1998; and Clark et al., 2009, 2002) lumped the effect of flow hydraulics into an overall mass transport coefficient in a reaction kinetic constant. The accuracy of this kinetic representation has not been examined since then.

This paper aims to examine the effects of hydrodynamics on reaction kinetics by using a set of comparative experimental and modeling analysis. The dependency of reaction kinetics on pipe flow Reynolds number (Re), initial chlorine and NOM concentrations in water, and the pipe materials is the focus of analysis. The results lead us to propose a set of considerations to model the hydrodynamic effects.

2.0 Methods

2.1. Modeling Analysis

Chemical reactions—Total free chlorine [Cl] – the sum of hypochlorous acid [$HClO$] and hypochlorite ion [ClO^-] in a water-flowing pipe, react with natural organic matters [NOM_{DBP}] (e.g., humic and fulvic acids) in bulk demand [BCD] to form DBPs. A fraction of [Cl] also reacts with other bulk demand [BCD'] without DBP formation. Bulk demand consists of organic materials present in the post-treatment water and those forming from detachment of biofilms and pipe scales in distribution. Chlorine also reacts with pipe wall materials and attached biofilm, with both terms lumped together as the wall demand. Generally, the multi-component chlorine reactions are written as:

(1)

(2)

(3)

(4)

(5)

In this study, DBPs formation is represented by trihalomethane (THM) compounds – trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM), collectively as total THM (TTHM). They form during chlorination through stepwise NOM-oxidation and hydrolysis. This process is illustrated below using model compound propanone CH_3COCH_3 and m as the Br molar fraction:

(6)

(7)

Mathematical models—For chlorine decay and THM formation in Eqs.1–7, chlorine concentration (C_A) in a water pipe is given by:

$$\frac{\partial C_A}{\partial t} = u \frac{\partial C_A}{\partial x} + \frac{1}{Pe_L} \left(\frac{\partial^2 C_A}{\partial x^2} \right) + \left(\frac{\partial C_A}{\partial t} \right)_D + \left(\frac{\partial C_A}{\partial t} \right)_{b'} + \left(\frac{\partial C_A}{\partial t} \right)_w$$

where Pe_L is the axial Péclet number; u is the area-averaged axial flow velocity; x is distance from a reference point in the pipe; subscripts D , b' and w refer to DBP-forming bulk demand, other non-DBP forming bulk demand, and wall demand, respectively. The concurrent chlorine decay and DBP formation follow the first and second kinetic laws. Modified from Clark (1998), chlorine and DBP molar concentrations at t (C_A and C_B) are:

$$\frac{\partial C_A}{\partial t} = -k_{DBP}\theta C_A^2 - k_E C_A$$

(9)

$$\frac{\partial C_B}{\partial t} = k_{DBP}[C_{E,0} - \theta(C_{A,0} - C_A)]C_A$$

(10)

$$\frac{\partial C_B}{\partial C_A} = \frac{k'_b + k_w}{k_{DBP}[C_{E,0} - \theta(C_{A,0} - C_A)] + k'_b + k_w} - 1$$

(11)

$C_{E,0}$ is the chlorine-molar equivalent of reactive NOM in water. The overall decay kinetic constant for chlorine (k_E) and particularly pseudo first-order DBP formation kinetic constant (K_D) are:

$$k_E = K_D + k'_b + k_w = \gamma \cdot k_{DBP}, \text{ and}$$

$$K_D = (C_{E,0} - \theta C_{A,0})k_{DBP}$$

(12)

Notably k_E in Eq.12 consists of three elements. The first two terms K_D and k'_b represent bulk demand for DBP-forming and non-DBP forming chemical reactions, respectively; the total bulk demand kinetic constant is $k_b = K_D + k'_b$. The third term for chlorine wall demand (k_w) depends on flow hydrodynamics, the relationship that will be examined later by experiments and data modeling. The governing equations have two fractional parameters: θ is a proportional factor for the DBP-forming fraction of the total chlorine decay; and γ is a ratio of the reaction rate constants; namely the contribution of DBP formation to the rate of overall chlorine decay.

Assuming solute transport is predominant in pipe flow, Clark et al. (2009) noted that k_w varies between the two end members governing solute dispersion: the wall reaction-limited decay at k'_w and mass transfer from the bulk phase onto the pipe wall at k_{mt} :

$$k_w = \frac{2k_{mt}k'_w}{a(k_{mt} + k'_w)}$$

(13)

For $C_A = C_{A,0}$ at $t = 0$, governing Eq.9 yields to the analytical solution:

$$C_A = \frac{C_{A,0}}{\left(1 + \frac{\theta}{\gamma}C_{A,0}\right)e^{\frac{k_E t}{\gamma}} - \frac{\theta}{\gamma}C_{A,0}}$$

(14)

for which, $C_A \rightarrow 0$ when $t \rightarrow \infty$ at total chlorine consumption by decay. For $\gamma \gg \theta$ or $\theta \rightarrow 0$, a small fraction of chlorine decay is attributed to DBP formation and Eq.14 becomes the familiar form of first-order chlorine decay:

$$C_A = C_{A,0}e^{-k_E t}$$

(15)

Integrating Eq.11 using Taylor series and replacing C_A by Eq.14 yields the analytical solution for DBP concentration in the pipe (See the supplemental materials):

$$\frac{\Delta C_B}{C_{A,0}} \cong \frac{k_{DBP}(1 - C_A/C_{A,0})}{(k'_b + k_w)}C_{E,0} - \frac{k_{DBP}\theta \cdot C_{A,0}}{2(k'_b + k_w)}(1 - C_A/C_{A,0})^2$$

(16)

For drinking water of small θ and $C_{E,0} \gg C_{A,0}$ particularly in the late-time reactions, Eq.16 can be further simplified to yield the THM concentration C_B , THM yield T and formation potential Y :

$$\Delta C_B \approx Y \cdot C_{A,0} - \frac{k_D}{(k'_b + k_w)} \cdot C_A$$

(17)

$$Y = \lim \left(\frac{\Delta C_B}{C_{A,0}} \right)_{t \rightarrow \infty} = \frac{k_D}{(k'_b + k_w)} + \frac{\theta \cdot k_{DBP}}{2(k'_b + k_w)} C_{A,0}$$

(18)

$$T = - \frac{\partial C_B}{\partial C_A} = \frac{k_D}{(k'_b + k_w)} + \frac{\theta \cdot k_{DBP}}{(k'_b + k_w)} C_A$$

(19)

Note that T and Y share the same kinetic ratio $\frac{k_D}{(k'_b + k_w)}$. The potential Y is a constant for a given water-chlorine reaction system, while T varies with time because of its dependence on reactive chlorine concentration in water. Among the 25 predictive models that Sadiq and Rodriguez (2004) evaluated, only three (Clark, 1998; Clark and Sivaganesan, 2002; and Gang et al., 2003) are mechanistic, relating DBP formation to chlorine consumption by kinetic laws. Clark (1998) and other subsequent publications (e.g., Clark and Sivaganesan, 2002; Boccelli et al., 2003) approximated T' from the overall $\frac{\Delta C_B}{\Delta C_A}$ in a time period with the second order of chlorine decay:

$$C_B = C_{B,0} + T'(C_{A,0} - C_A) = C_{B,0} + T' C_{A,0} \left(\frac{e^{K_E t} - 1}{e^{K_E t} - \frac{C_{A,0}}{\alpha C_{E,0}}} \right)$$

(20)

The Clark's (1998) model Eq.20 is similar to the full analytical solution in Eq.16 or $T' \approx T$ under a small $\theta C_{A,0}/C_{E,0}$, a condition common in drinking water pipes. When $\frac{\gamma}{\theta} \gg C_{A,0}$ or θ is very small, Eq.16 becomes the well-known first-order equation for DBP formation:

$$C_B \approx C_{B,0} + \frac{k_{DBP}C_{E,0}}{(k'_b + k_w)}C_{A,0}\left(1 - e^{-k_E t}\right) \quad (21)$$

2.2 Comparative Experimental Testing

The relative importance of k_D , k'_b , and k_w varies among drinking water pipes of a distribution network. Their implication on simultaneous chlorine decay and DBP formation is further examined using comparative experimental testing (Table 1). Three devices were used in testing at the U.S. EPA Testing and Evaluation Facility: a 1-L glass bottle, pilot-scale water distribution simulators that are constructed of new PVC pipes and aged ductile iron (DI) pipes of 22.7-m long and 102-mm diameter. The simulators are equipped with a heat exchanger to maintain a fairly constant temperature during the ~36-hour testing (Table 1).

By design, the glass bottle bench testing yields k_b for chlorine bulk demand (Figure 1a). Pilot-scale distribution simulators of new PVC and aged DI pipes were tested to determine the reaction kinetic rates in flow-dependent reaction scenarios (Figure 1b and 1c) under stagnant-laminar-turbulent flow field conditions ($Re=0, 1700, 3200, 5400, 52500$). Other testing variables include two contrasting TOC types: local tap water NOM, and the tap water spiked with virgin Biohume® humic acid after NOM removal by GAC filtration. The local tap water is produced from the Ohio River by coagulation, flocculation, filtration, GAC adsorption, and UV disinfection. TOC concentrations averaged 0.9 ± 0.2 mg/L ($n=6$). For the humic acid synthetic water, TOC is ~3 or 4 mg/L and the used commercial grade humic acid contains insoluble humin.

THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) were measured by a high-resolution GC-MS using the EPA method 555.1. Free chlorine and TOC grab samples were quenched using sulfuric acid and sodium sulfite after collection, and measured using DPD colorimetric EPA methods 330.5 and 415.1. Other chemical parameters (turbidity, temperature, and dissolved oxygen) were measured using sensors inserted into the simulator pipes (See Panguluri et al., 2007). Analytical results for the experiments are contained in the supplemental materials.

3.0 RESULTS

Measured chlorine and THM concentrations show typical t - C variations (Figure 2), from which three characteristic properties are determined: the maximum TTHM concentrations (C_B^*), time to reach the maximum (t_{max}), and the TTHM overall yield ($\Delta C_B/\Delta C_A$) where $\Delta C_B = C_B^* - C_{B,0}$. The results are listed in Table 2. Overall, chlorine decay proceeded rapidly

in the DI pipe and for water spiked with virgin NOM. In contrast, the residual chlorine in the PVC pipe experiments remained detected after 36 hrs, for which C_B^* and $t_{\max}$ values are likely underestimated. Nonetheless, $t_{\max}$ for the PVC pipe is significantly larger than for DI pipe of large wall demand (Table 2).

On THM composition, TCM is the dominant species formed; BDCM and DBCM were detected at a small fraction of the remaining ($<5\%$ M/M), while TBM was absent. Referring to the THM formation reactions in Eqs.6–7, this TTHM composition reflects the dominance of Cl over Br in the testing water and are consistent with their common relative chemical activities.

3.1. Chlorine decay and THM formation kinetics

3.1.1. k_E variability—Model analysis of the chlorine decay data yields k_E using the second-order model (Eq.14), the classic first-order decay model (Eq.15), and the two-stage decay model of Gang et al. (2003). The two-stage model comprises of a fast chlorine decay followed by a slow reaction phase, in order to mathematically describe the deceleration of chlorine decay with time. Compared to the two-stage model, the other two kinetic models adequately, or mostly better represent the chlorine decay and THM formation data. This observation agrees with previous conclusions in evaluating the second-order kinetic models (See Clark, 1998; Yang et al., 2008a; Shang et al., 2012; Di Cristo et al., 2014). A systematic difference in k_E is observed between the second-order and the first-order models (Table 3). These two models yield comparable results, but diverge at large k_E values (Figure 3). As noted above, model errors using Eq.15 give arise from the assumption $\theta \rightarrow 0$, which becomes problematic at large k_E values. For this reason, the second order k_E values are reported here, despite poor confidence in data regression (ρ) for the obtained k_E values (Table 3). Bulk demand k_b is taken to be the average $k_E = 0.018 \pm 0.002 \text{ hr}^{-1}$ ($N=6$) from glass bottle tests of the tap water. This value is similarly small to the average $k_E = 0.022 \pm 0.005 \text{ 1/hr}$ for all the k_E PVC pipe testing. In comparison, the values for aged DI pipe at stagnant flow are larger by an order of magnitude (Table 3). The other extreme values are observed for the reactive new NOM. They show extremely fast chlorine decay and large $\Delta C_B / \Delta C_A$ (Figure 2b and Table 2). Their k_E values are significantly larger, up to an order of magnitude, than those for the tap water NOM (Table 3).

3.1.2. THM formation kinetic properties—Five characteristic kinetic parameters in THM formation are determined from the experiments: T , Y , $t_{\max}$, the kinetic ratio $\frac{k_D}{(k'_b + k_w)}$, and the THM overall yield $\Delta C_B / \Delta C_A$. Determined $t_{\max}$ values (Table 2) differ significantly between the DI and PVC pipes of contrasting t_w , and between tap water NOM and the virgin NOM of higher t_b . These differences, as shown in different t - C variations (e.g., Figure 2), are directly attributed to the different THM formation kinetics and the characteristic ratio $\frac{k_D}{(k'_b + k_w)}$.

Linear correlation between C_A and C_B is observed for all tap-water and virgin NOM experiments (See Supplemental Materials). Y and $\frac{k_D}{(k'_b + k_w)}$ from data regression using Eq.17 are listed in Table 3. In addition, the other kinetic parameter – THM yield T is consistent in concept but slightly different from the THM yield T' of Clark (1998). T' is determined in regression by substituting chlorine k_E into Eq.20. When k_E is not determined from chlorine data, it is directly obtained from regression of the TTHM data, despite of the uncertainty associated with obtained k_E and T . The tap water results for the DI pipe (Table 3) are 0.0069 – 0.0202 with a mean of 0.0124 ± 0.0051 . For the PVC pipe, T' is slightly lower ranging 0.0059 – 0.0219. These measurements are similar to those kinetic results reported for dichloroacetic acid formation by Duirk and Valentine (2006). Figure 4a further shows $T' \sim \frac{k_D}{(k'_b + k_w)}$ (Figure 4a), indicating a small θ and $C_{E,0} \gg C_{A,0}$ for the tap NOM; thus $T \approx T'$ for this study.

The determined T , Y and $\frac{k_D}{(k'_b + k_w)}$ in comparative experiments between PVC and DI pipes are further examined in Figure 5. First, the PVC pipe using tap water NOM is kinetically different. Because of small k'_b and k_w , low levels of residual chlorine still remained after 36 hrs (Table 2). All experiments fall into the area of $\frac{k_D}{(k'_b + k_w)}$ or $T < \frac{\Delta C_B}{\Delta C_A}$ (Figure 4b). Thus the characteristic $\frac{k_D}{(k'_b + k_w)}$ is overestimated by $T < \frac{\Delta C_B}{\Delta C_A}$ using model regression of short-duration C - t data because of incomplete chlorine reaction.

Second, the determined Y values are similar in magnitude with, but consistently greater than T' (thus T) and $\frac{k_D}{(k'_b + k_w)}$; all experiments fall into T'/Y ratio 1–1.3 (Figure 4a). Compared to DI pipe of large k_w , the clean PVC pipe shows slightly but consistently larger Y and $\frac{k_D}{(k'_b + k_w)}$ values than the DI pipe. This is in apparent conflict with the general fact that the more chlorine consumed by wall demand, the less in bulk demand for THM formation and thus the smaller $\frac{k_D}{(k'_b + k_w)}$ and Y . One possible explanation for the disagreement lies within the contribution of DBP precursors from the DI pipe walls, as examined in later sections.

3.2. Kinetic Variability with Flow Properties

3.2.1. k_E and T variability with Re —For each pipe and NOM types, the determined k_E varies with Re (Figure 6a). This relationship is more complex than the theoretical predictions of Clark's (1998) model for reaction-limited solute transport. The k_E variation for PVC pipe is muted; a small but apparent increase in k_E occurs from stagnant to turbulent

flow. The overall values are very close to the bulk demand $k_b = 0.018 \text{ hr}^{-1}$ measured from the glass bottle testing.

In contrast, the DI pipe shows large variations in k_E and T with Re (Table 3). To isolate the flow effects, k_E in PVC pipe is subtracted from that in DI pipe under same experimental conditions. The resulted net values in Figure 6a are compared to a family of theoretical k_E curves calculated using Eq.13 and assuming an elevated $k_b = 0.195 \text{ hr}^{-1}$ for stagnation DI pipe. The resulting net k_E values fall into two groups. For stagnant-laminar-transitional flow ($Re=0\text{--}3200$), the net k_E is approximately consistent with $k_w \sim 0$ of the Clark (1998) model (Figure 6a). The ratio $k_D/(k'_b + k_w)$ is $\sim 20\%$ lower in the DI pipe than in the PVC pipe. In turbulent flow ($Re=3200\text{--}54000$), the net k_E increased rapidly indicating a $k_w \sim 0.0008 \text{ cm/s}$ and 0.0020 cm/s . The THM yield is <0.010 , approximately 2 times lower than it is under laminar flow conditions (Figure 6b).

3.2.2. Turbidity changes with Re and TTHM—For the same pipe and NOM type, we consider that the kinetic variability with Re is related to the mass exchange between bulk water and pipe walls. This mass exchange cannot be explained alone by the solute dispersion (Figure 6a). Mass exchange between the bulk water and the pipe wall is the most likely primary contributor. Turbidity is proposed as an indicator of the deposition and detachment affecting NOM availability in chlorine reactions.

Figure 7 shows a broad correlation between turbidity and the ratio $k_D/(k'_b + k_w)$ for the comparative testing. A large decrease in turbidity with time is observed for all the virgin NOM experiments. At $t > 10\text{--}20$ hrs, turbidity decreased significantly from initial 51–130 NTU levels (e.g., Figure 8a). One experiment at a lower initial turbidity of 1.7–2.1 NTU followed the same trend. Because the humins has limited solubility, the particles of Biohume® humic acid apparently have deposited onto pipe walls causing the changes in turbidity. The particle deposition decreased at higher flow rate or pipe shear stress (Figure 8b). The more virgin NOM in bulk water, indicated by the average turbidity concentrations, the higher THM formation and the kinetic ratio (Figure 7).

For tap water NOM experiments, DBP precursors in bulk phase are enhanced by scale sloughing and detachment at pipe walls (Yang et al., 2008a; Zacheus et al., 2001; Stookey et al., 2002). This hydrodynamically dependent process is clearly evident in the turbidity increase with time (Figure 8a). The turbidity increase is persistent and significant in all DI pipe experiments, and at a lesser degree for PVC pipes. The degree of change varies the shearing stress or flow velocity (Figure 8b). Both DI and PVC pipes show the largest turbidity increase in stagnant and laminar flow, and subsequent decrease in the transitional flow regime. Under the turbulent flow, turbidity increase is the largest for the PVC pipe and remained subdued for the DI pipe of heavy buildup in scales and biofilms. This diverse response in biofilm cohesiveness and turbidity variability among pipe types has been reported previously (e.g., Mathieu et al., 2014; Choi and Morgenroth, 2003). The kinetic

ratio $k_D/(k'_b + k_w)$ is positively related to the turbidity changes with a large degree of scattering among the experiments (Figure 7).

4.0 DISCUSSIONS AND SUMMARY

4.1. Flow and mass transfer effects

. Models for molecular diffusion and solute dispersion in pipe flow have been extensively examined (Biswas et al., 1993; Lu et al., 1995; Clark, 1998; Clark et al., 2010; Shang et al., 2012); one example is shown in Eq.8. Model analysis of the experimental results on chlorine-TTHM-turbidity changes demonstrated that the k_D , k'_b and k_w vary as a result of wall deposition and scale detachment. The process persists even in the PVC pipes. Based on numerical model simulation of the same datasets, Abokifa et al (2016) suggested the same mechanism as being responsible to the increasing TTHM concentrations in the DI pipes in turbulent flows.

To account for the mass transfer effects on reaction kinetics is not straight forward. Model Eq.13 for solute transfer addresses only solute dispersion. Mass exchange between the bulk water and the pipe wall is another important mechanism (Stooley et al., 2002; Yang et al., 2008b; Dudde et al., 2009; Wang et al., 2012, 2013; Abokifa et al. 2016). Wall surfaces, particularly those of aged pipes, accumulate inorganic and organic scales and soft deposits rich in extracellular polymeric substances, which can serve as the DBP precursors (Gauthier et al., 1999; Zacheus, 2001; Hallam et al., 2002; Peng et al., 2010). The surfaces also differ in roughness, pipe age, and scale materials of diverse chlorine reactivity, all resulting in variations of the mass exchange and chemical reactions among the flow regimes. The nature of this interaction, however, is not universally agreed upon. Hallam (2002) suggested that chlorine decay at unreactive wall is limited by chlorine reactivity, while for reactive pipe it is controlled by chlorine mass transfer, k_{mt} , to the pipe wall. Others (e.g., Lu et al., 1995; Lehtola et al., 2006; Kim et al, 2014) argued that the flow properties and disinfectant consumption at the pipe wall often define the water quality changes.

Doubtlessly, variations in biofilm and pipe scale, their reactivity with chlorine, and associated substrate changes in pipe flow, all contribute to the k'_w variations in chlorine consumption and TTHM formation that were considered in early modeling efforts (See Lu et al., 1995; Rossman et al., 2001). There is a need to incorporate both solute transport and the water-wall mass exchange into the modeling equations. For analytical solutions in Eqs.14 and 16, one approach is to define the model parameters to reflect the kinetics of NOM and chlorine transport over the flow Re range. Exact model solutions are not presented here. For considerations, we have identified three major variables in this study: the NOM reactivity, pipe scale, and pipe flow hydraulics. Their relationship changes among pipe types and flow regimes:

- Small and invariant k_E for clean PVC pipe

Pipes with clean surfaces, such as the PVC pipe in this study, have small k_E values and little variation across the flow range (Figure 6), for which

$k_E \approx k_b; k_b (= k'_b + k_D)$ is often determined through bench glass bottle testing.

Negligible k_w and a clean PVC pipe surface permit little mass exchange between the pipe wall and bulk water. It is worth to note, however, that turbidity increase can be expected once new PVC pipes are in service. TTHM formation at $\mu\text{g/L}$ levels only require a small degree of increase in wall-derived chlorine demand to produce a substantially change in the TTHM formational potential proportional to $k_D/(k'_b + k_w)$. This kinetic variation is evident in experimental results of k_E and $k_D/(k'_b + k_w)$ (See Figure 6), which is in line with measurable wall demand and DBP formations reported in previous studies (e.g., Chan et al., 2002).

At $k_w \approx 0$, chlorine decay and THM formation potential directly depend on chlorine-NOM reactivity. We have shown that virgin NOM has significantly larger k_E and $k_D/(k'_b + k_w)$ than the tap water NOM, and a far greater Y in THM formation. This observation lends support to the importance of reactive NOM removal to reduce in water treatment and management.

- Large k_E for DI pipe in flows $Re < 2300$

The kinetic variations for both new PVC pipe and aged DI pipe are worthy of attention among stagnant, laminar and transitional flow. In a flow of $Re < 3200$, the ratio $k_D/(k'_b + k_w)$ is the largest, while k_E is relatively small and has little variation with Re (Figure 6a). A large internal variation in both kinetic properties is also found among experiments under transitional flow at $Re = 1700$ (Figure 6). We attribute the higher DBP-forming potential or $k_D/(k'_b + k_w)$ to the release of DBP-forming organic reactants from the pipe wall. This is supported by the large turbidity change for stagnant flow experiments (Figure 8b). In general, deposits accumulating at pipe wall are composed of iron, microbiologically available organic matter, bacterial and other inorganic matters. Precursors for DBP formation, such as polysaccharides and proteins, are shown to be released from the breaking down of bacterial cells and extracellular polymeric substances (Wang et al., 2012, 2013). Even in relatively clean plastic pipes, biofilm and scale, some in the form of soft deposits, can be an important factor (Ndiongue et al., 2005; Lehtola et al., 2006). These deposits, mobilized from erosion by pipe flow (Choi and Morgenroth, 2003; Dudde et al., 2009), are related to chlorine decay and THM formation (Rossman et al., 2001; Hallam et al., 2002; Chan et al., 2002).

Recently Liu et al. (2017) reported geochemical and biological changes in field experiments under stagnant and laminar flows in pipe dead ends. They reported the largest changes in water chemistry (pH, ORD, etc.), turbidity, and biological growth. Their findings support the turbidity and k_E variations of this study as shown in Figure 6 and Figure 8b, respectively. Periodic stagnation and transit flow can result in a compounding effect that increase biofilm development, mass and solute (e.g., nutrients, chlorine) transfer, and thus chlorine decay and THM formation (Hallam et al., 2002; Chan et al., 2002; Stoianov and Aisopou, 2014;

and Liu et al., 2017). The net effect can significantly depart from the solute dispersion predictions (See Figure 6).

- Large k_E with low and steady THM formation in turbulent flow

The Re -dependent k_E variations under turbulent flow conditions indicate that besides solute dispersion, other mass transfer mechanisms such as deposition and scale detachment may be the primary mechanism affecting the reaction kinetics. This process is indicated by the changes in turbidity as a function of Re .

Similar conclusions were proposed for turbidity variability in pipe flow hydrodynamics (Choi and Morgenroth, 2003). Scale adhesion and detachment is flow-dependent. Increasing flow velocity and hydraulic turbulence in a pipe supply nutrients to pipe wall, and thus enhance biofilm growth (Abe et al., 2012). They also increase shear stress acting upon biofilm, leading to scale detachment through erosion or sloughing (Stooley et al., 2002; Choi and Morgenroth, 2003; Abe et al., 2012). This produces new chlorine reaction sites on the pipe wall, an increase of, but a potential decrease of $k_D/(k'_b + k_w)$.. The balance of two counter processes limits biofilm growth and enable particle detachment to approach a steady state.

4.2. Practical implications

The findings of this study have direct implications on network modeling and management in three areas. First, the simultaneous occurrence of chlorine decay and THM formation depends on the kinetic ratio $k_D/(k'_b + k_w)$. that in turn is a function of pipe flow hydrodynamics. Several common water quality parameters, including total organic carbon (TOC), residual chlorine, UV256, water pH and temperature, have been used to estimate the THM formation potential (Clark and Sivaganesan, 2002), mostly in the form of location-specific empirical formulations (See Sadiq and Rodriguez, 2004; and references therein). As shown here, the non-DBP forming bulk demand and the wall demand also affect the THM formation potential in competitive reaction. Therefore, one may find it useful to obtain accurate $k_D/(k'_b + k_w)$. through experiments using targeted pipe types under field hydraulic conditions. Simple bench-scale testing in current practice using glass bottles may underestimate the total chlorine decay, and overestimate the THM formation potential, albeit slightly.

Second, NOM properties and specifically the chlorine-reaction fraction are controlling variables for the competitive reactions. For the reactive virgin NOM, $k_E, k_D > k_w$ and $k_E \approx k_b$. In this system, the chlorine decay and THM formation potential are insensitive to pipe flow variability. Removal of reactive NOM fractions in treatment is the only effective approach to decrease, T and Y , in order to maintain the required chlorine residual level and reduce the THM formation potential simultaneously. For aged NOM with small, such as the tap water NOM used in this study, the hydrodynamic effects on k_E and $k_D/(k'_b + k_w)$. cannot be neglected. The reaction competition from Re -dependent wall demand becomes comparable with THM-forming and other bulk demand. This concept

yields new insights on the variance of chlorine decay and THM-formation kinetics reported previously.

Finally, the kinetic constants and the time to reach a pseudo-steady state are all related to pipe flow hydrodynamics. Many parts of a distribution network have water ages exceeding 24 hours, and re-chlorination is necessary to compensate for the excessive loss of chlorine residuals for biological control. Re-chlorination, however, will further increase the DBP levels (Boccelli et al., 2003) even to the extent of violating drinking water standard. Therefore, a fundamental objective in the model analysis is to compute the flow field using the governing Eq.1 and mass transport equations with the Re -dependent reaction kinetics. Then, simulated water age and Re distribution can make it possible to determine the variations of chlorine residuals and THM concentrations for simultaneous regulatory compliance.

5.0 CONCLUSIONS

Experimental testing and modeling analysis presented in this paper demonstrate the effects of flow hydrodynamics on chlorine decay and THM formation kinetic constants:

k_E, k'_D, k_w and k_E . Their ratio $k_D/(k'_b + k_w)$, characteristic of competitive chlorine reactions, defines the rate and levels of THM formation and is the primary component to the THM yield and formation potential in a water pipe. This kinetic effect, schematically shown in Figure 1, also depends on THM-forming precursors' transport and availability in pipe flow in form of both solute dispersion and mass exchange between the bulk water and the pipe wall (Rossman et al., 2001; Gauthier et al., 1999; Hallam et al., 2002). Major findings are:

- The existing water quality models only consider solute dispersion to and from pipe walls. This study calls attention on the importance of mass exchange in NOM deposition and scale detachment. The Re -dependent mass exchange is a principal factor affecting the availability of DBP-forming NOM in the bulk water, and thus the chlorine decay and THM formation.
- Pipe flow Re , NOM and pipe types define the characteristic, $k_E, k_D/(k'_b + k_w)$, and $t_{\max}$ for tap water NOM in drinking water. For virgin and reactive NOM, however, their chlorine reactivity is the predominant factor overshadowing the flow-dependent pipe wall contributions or $k_b \sim k_d > k_w$.
- The Re -dependent K_E and K_D can be incorporated into governing equations for the second-order kinetic models of THM formation. Such model improvement may offer a window to identify controlling operational parameters in order to control chlorine decay and THM formation in a network. This potential warrants future research.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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7.0 NOMENCLATURE

C	Concentration; subscript A, B, E for chlorine, DBP compound, chlorine-molar equivalent of reactive NOM, respectively, and subscript 0 for the starting time.
C_E	The chlorine-molar equivalent of NOM in water
$\frac{\Delta C_B}{\Delta C_A}$	THM overall yield for a period of time, dimensionless
k_E	Overall decay kinetic constant for chlorine
K_D	Pseudo first-order DBP formation kinetic constant, equal to $(C_{E,0} - \theta C_{A,0})k_{DBP}$, where k_{DBP} is the second-order kinetic constant of DBP formation and is the chlorine fraction for DBP formation.
k_w	Kinetic constant for the first order chlorine in wall demand
k_{mt}	Chlorine mass transfer coefficient
k_b, k'_b	Kinetic constant for total bulk and non-DBP forming chlorine decay, respectively.
$\frac{k_D}{(k'_b + k_w)}$	Characteristic kinetic ratio for DBP formation
Re	Pipe flow Reynold number
T	THM yield, dimensionless
T'	THM yield of Clark (1998) model, dimensionless
Y	THM formation potential, dimensionless
u	Area-averaged axial flow velocity
θ	Molar fraction of chlorine decay in DBP formation
γ	Ratio of the reaction rate constants

8.0 Reference

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Figure 1.

Chlorine wall demand, bulk demand, and DBP formation in relation to three typical cases of flow, pipe materials, particle deposition and scouring. Schematic illustrations: A) bulk demand only; B) and C) Bulk demand and wall demand dominant, respectively.

Figure 2. Typical variations of Cl_f and TTHM molar concentration ratios for (A) tap water NOM, and (B) fresh NOM. Model fitting curves are based on the first-order models and the second-order model of this study. S&F is the fast and slow reaction kinetic model of Gang et al. (2003).

Figure 3.
Comparison of determined values between the first-order and the second-order chlorine decay models

Figure 4.

Correlations in Y, T', THM overall yield $\Delta C_B / \Delta C_A$, $\frac{k_D}{(k'_b + k_w)}$, and kinetic ratio for the comparative experiments.

Figure 5.
The relationship in determined chlorine decay and THM formation kinetic properties between DI and PVC pipes of different wall demand.

Figure 6.

KE and KD variations with Re in DI and PVC pipe flows. Also plotted are model values of Clark (1998) for varying K_w (cm/s) according to Eq.12.

Figure 7.

Positive correlations between the absolute turbidity change and the THM yield from tap-water NOM experiments. For virgin NOM, the average turbidity in water (Turbidity_m) is plotted.

Figure 8.

Turbidity changes and correlation for the tap water NOM and the virgin NOM. (A).

Turbidity variations in experiments 3a and 3b at $Q=0.379$ m/s. (B). The turbidity changes of each set of experiments as a function of detachment in form of v^b .

Table 1.

Experimental conditions of comparative testing.

Test No.	DI Pipe				PVC pipe				
	Q (L/sec)	V (m/s)	Re	T (C) (C°)	[TOC] ₀ (mg/L)	[Cl] ₀ (mg/L)	T (C) (C°)	[TOC] ₀ (mg/L)	[Cl] ₀ (mg/L)
<i>Tap NOM, CI</i>									
1a	0	0	0	23.7±0.7	0.88	2.10	24.3±2.1	0.92	2.30
2a(i)	0.189	0.011	1,700	20.1±0.7	0.96	1.90	20.4±0.9	0.99	2.40
2a(ii)	0.189	0.011	1,700	21.2±2.3	0.72	4.30	20.6±1.9	0.72	4.30
3a	0.379	0.023	3,200	19.5±0.4	1.06	1.90	19.3±0.5	1.07	2.10
4a	0.631	0.038	5,400	19.3±0.7	0.50	2.20	19.4±0.8	0.62	2.50
5a	6.314	0.379	52,500	17.9±0.5	1.16	2.10	18.2±2.3	1.19	2.30
<i>Virgin NOM, CI</i>									
1b	0	0	0	27.2±0.6	4.04	0.60	27.2±0.9	3.51	1.60
2b(i)	0.189	0.011	1,700	21.8±2.0	3.31	1.00	25.8±1.3	3.27	0.10
2b(ii)	0.189	0.011	1,700	20.9±1.5	4.23	3.50	20.9±1.6	3.78	4.00
3b	0.379	0.023	3,500	21.9±1.2	3.72	0.60	23.3±2.2	3.68	0.40
4b	0.631	0.038	5,000	17.1±1.5	3.17	1.50	18.2±1.0	3.63	1.70
5b	6.314	0.379	52,500	18.5±0.9	3.69	3.90	18.4±1.2	3.76	4.70

Table 2.

TTHM yield and maximum TTHM concentrations observed in experiments.

Test	DI Pipe						PVC Pipe					
	C_B^*	t_{max}	$C_{A,o}$	C_B/C_A	TOC _o	Range (m $\pm\sigma$)	Turbidity	Range (m $\pm\sigma$)	TOC _o	C_B/C_A	$C_{A,o}$	Range (m $\pm\sigma$)
Tap NOM												
1a	117.68	25	2.10	0.027	0.88	0.96 $\pm$ 0.05	1.43	0.72 $\pm$ 0.48	0.92	0.030	2.30	1.06 $\pm$ 0.29
2a(i)	74.99	30	1.90	0.017	0.96	1.13 $\pm$ 0.15	1.39	1.21 $\pm$ 0.46	0.99	0.017	2.40	1.05 $\pm$ 0.09
2a(ii)	83.66	35	4.30	0.007	0.72	0.76 $\pm$ 0.08	0.69	0.62 $\pm$ 0.25	0.72	0.021	4.30	0.73 $\pm$ 0.05
3a	76.28	24	1.90	0.017	1.06	1.15 $\pm$ 0.06	0.91	0.67 $\pm$ 0.30	1.07	0.014	2.10	1.12 $\pm$ 0.04
4a	65.12	9	2.20	0.010	0.50	0.59 $\pm$ 0.05	0.53	0.56 $\pm$ 0.15	0.62	0.022	2.50	0.58 $\pm$ 0.06
5a	60.82	28	2.10	0.012	1.16	1.25 $\pm$ 0.07	0.76	0.54 $\pm$ 0.22	1.19	0.021	2.30	1.24 $\pm$ 0.04
Virgin NOM												
1b	106.71	20	0.60	0.082	4.04	3.52 $\pm$ 0.68	-124.7	103.3 $\pm$ 49.4	3.51	0.036	1.60	3.01 $\pm$ 0.62
2b(i)	70.67	25	1.00	0.024	3.31	3.15 $\pm$ 0.25	-22.0	124.3 $\pm$ 6.8	3.27	0.471	0.10	3.29 $\pm$ 0.27
2b(ii)	213.88	25	3.50	0.027	4.23	3.42 $\pm$ 0.62	-2.5	2.7 $\pm$ 0.8	3.78	0.034	4.00	3.17 $\pm$ 0.43
3b	72.36	36	0.60	0.045	3.72	3.09 $\pm$ 0.44	-37.4	98.6 $\pm$ 12.5	3.68	0.103	0.40	3.40 $\pm$ 0.26
4b	68.62	24	1.50	0.026	3.17	2.84 $\pm$ 0.63	-12.8	94.4 $\pm$ 3.3	3.63	0.040	1.70	3.19 $\pm$ 0.61
5b	62.11	36	3.90	0.003	3.69	3.25 $\pm$ 0.44	-53.7	44.0 $\pm$ 16.5	3.76	0.014	4.70	3.47 $\pm$ 0.23

Note: TTHM average yield (C_B/C_A) calculated from C_B^* in M/M. Units: C_B^* in $\mu\text{g/L}$, t_{max} in 1/hr, $C_{A,o}$ and TOC in mg/L, and turbidity in NTU.

Table 3.

Determined k_E , T^* and Y values from the chlorine measurements in comparative experimental testing.

Test	DI Pipe							
	K_E (1/h) [*]	P	K_E (1/hr) ^{**}	P	T^* #	P	$K_D/(K'_b+K_w)^{\$}$	P
Tap NOM								
1a	0.20 ± 0.01	<0.0001	0.09 ± 0.01	<0.0001	0.020 ± 0.0011	<0.0001	0.018 ± 0.0012	<0.0001
2a(i)	0.17 ± 0.05	0.069	0.18 ± 0.02	<0.0001	0.016 ± 0.0003	<0.0001	0.013 ± 0.0010	<0.0001
2a(ii)	0.15 ± 0.04	0.006	0.14 ± 0.01	<0.0001	0.007 ± 0.0001	<0.0001	0.007 ± 0.0005	<0.0001
3a	0.23 ± 0.04	<0.0001	0.24 ± 0.01	<0.0001	0.013 ± 0.0003	<0.0001	0.011 ± 0.0006	<0.0001
4a	0.47 ± 0.05	<0.0001	0.32 ± 0.02	<0.0001	0.008 ± 0.0006	<0.0001	0.009 ± 0.0005	<0.0001
5a	0.75 ± 0.11	0.0001	0.44 ± 0.03	<0.0001	0.010 ± 0.0009	<0.0001	0.012 ± 0.0008	<0.0001
Virgin NOM								
1b	NM		NM		0.077 ± 0.001 [#]	<0.0001	NM	NM
2b(i)	NM		NM		0.022 ± 0.001 [#]	<0.0001	NM	NM
2b(ii)	0.20 ± 0.07	0.017	0.39 ± 0.03	<0.0001	0.025 ± 0.001	<0.0001	0.023 ± 0.002	<0.0001
3b	NM		1.00 ± 0.25	0.001	0.044 ± 0.002 [#]	<0.0001	NM	NM
4b	0.60 ± 0.73	0.496	0.80 ± 0.06	<0.0001	0.023 ± 0.001	<0.0001	0.021 ± 0.003	<0.0001
5b	0.39 ± 0.39	0.332	0.88 ± 0.15	<0.0001	0.003 ± 0.0001	<0.0001	0.003 ± 0.0003	<0.0001
PVC Pipe								
Test	K_E (1/h) [*]	P	K_E (1/hr) ^{**}	P	T^* #	P	$K_D/(K'_b+K_w)^{\$}$	P
							$Y^{\$}$	P
Tap NOM								
1a	0.071 ± 0.015	0.001	0.030 ± 0.0019	<0.0001	0.022 ± 0.0019	<0.0001	0.023 ± 0.0020	<0.0001
2a(i)	0.015 ± 0.029	0.62	0.016 ± 0.0016	<0.0001	0.016 ± 0.0033	0.0006	0.014 ± 0.0016	<0.0001
2a(ii)	0.010 ± 0.009	0.34	0.010 ± 0.0004	<0.0001	0.014 ± 0.0031	0.001	0.018 ± 0.0014	NM
3a	0.040 ± 0.042	0.35	0.017 ± 0.0018	<0.0001	0.015 ± 0.0036	0.0008	0.012 ± 0.0012	<0.0001
4a	0.062 ± 0.020	0.01	0.012 ± 0.0016	<0.0001	0.006 ± 0.0007	<0.0001	0.010 ± 0.0012	<0.0001
5a	0.027 ± 0.023	0.26	0.019 ± 0.0023	<0.0001	0.008 ± 0.0013	0.0003	0.020 ± 0.0024	<0.0001

Test	PVC Pipe									
	K_E (L/h) [*]	ρ	K_E (L/hr) ^{**}	ρ	T_r [#]	ρ	$K_D/(K_t+K_w)$ ^{\$}	ρ	Y ^{\$}	ρ
Virgin NOM										
1b	NM		NM		0.035 ± 0.001 [#]	<0.0001	NM		NM	
2b(i)	NM		NM		0.456 ± 0.007 [#]	<0.0001	NM		NM	
2b(ii)	0.04 ± 0.02	0.06	0.093 ± 0.008	<0.0001	0.033 ± 0.002	<0.0001	0.033 ± 0.002	<0.0001	0.032 ± 0.001	<0.0001
3b	NM		NM		0.103 ± 0.007 [#]	<0.0001	NM		NM	
4b	0.31 ± 0.03	<0.0001	0.337 ± 0.021	<0.0001	0.037 ± 0.001	<0.0001	0.028 ± 0.002	<0.0001	0.027 ± 0.001	<0.0001
5b	0.28 ± 0.13	0.06	0.672 ± 0.065	<0.0001	0.009 ± 0.001	<0.0001	0.012 ± 0.001	<0.0001	$0.007 \pm 4.1E-04$	<0.0001

Note: K_E calculated using two different models:

* - 2nd-order Eq.14;

** - 1st-order Eq.15.;

[#] - determined in TTHM regression (See text);

^{\$} - obtained from Eq.19. NM - Regression not meaningful.