Modeling and testing of reactive contaminant transport in drinking water pipes: Chlorine response and implications for online contaminant detection

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ABSTRACT

A modified one-dimensional Danckwerts convection–dispersion–reaction (CDR) model is numerically simulated to explain the observed chlorine residual loss for a "slug" of reactive contaminants instantaneously introduced into a drinking water pipe of assumed no or negligible wall demand. In response to longitudinal dispersion, a contaminant propagates into the bulk phase where it reacts with disinfectants in the water. This process generates a U-shaped pattern of chlorine residual loss in a time-series concentration plot. Numerical modeling indicates that the residual loss curve geometry (i.e., slope, depth, and width) is a function of several variables such as axial Péclet number, reaction rate constants, molar fraction of the fast- and slow-reacting contaminants, and the quasi-steady-state chlorine decay inside the "slug" which serves as a boundary condition of the CDR model. Longitudinal dispersion becomes dominant for less reactive contaminants.

Pilot-scale pipe flow experiments for a non-reactive sodium fluoride tracer and the fast-reacting aldicarb, a pesticide, were conducted under turbulent flow conditions (Re = 9020 and 25,000). Both the experimental results and the CDR modeling are in agreement showing a close relationship among the aldicarb contaminant "slug", chlorine residual loss and its variations, and a concentration increase of chloride as the final reaction product. Based on these findings, the residual loss curve and its geometry are useful tools to identify the presence of a contaminant "slug" and infer its reactive properties in adaptive contaminant detections.

1. Introduction

Small quantities of contaminant can enter a water distribution system due to back siphonage induced by transient pressures at pipe joints, leaks and breaks (LeChevallier et al., 2003; Kirmeyer et al., 2001), cross-connections and biological sloughing (US EPA, 2002) and through intentional sabotage and terrorist activities (US EPA, 2005). Such contamination is generally limited in time and space (Boyd et al., 2004), but can result in water quality deterioration and possibly unacceptable health risk (Burrows and Renner, 1999; GAO, 2005; WHO, 1996; Whelton et al., 2003). Detection and monitoring of the contamination events is a technical challenge, but is essential to the delivery of safe drinking water and to the security of...
critical water infrastructure. Contaminant detection methodologies combined with model simulations have been suggested to detect and manage such incidents (Jain and McLean, 2006; Boulos et al., 1994; Harding and Walski, 2000; Caputo and Palagagge, 2002; Uber et al., 2004).

Most research on predictive modeling in water supply has centered on chlorine transport in a distribution network (e.g., Lu et al., 1993; Rossman et al., 1994; Clark and Haught, 2005; Harding and Walski, 2000) and the reaction with stationary biofilm and pipe wall surfaces (Clark et al., 2001). Models such as EPANet (Rossman, 2002) and its commercial derivatives have been widely used in engineering design, network operation and management (Harding and Walski, 2000; US EPA, 2006). In describing chemical (chlorine) transport in water pipes, mass conservation principles apply. Biswas et al. (1993) and Rossman et al. (1994) used these principles and developed the widely used chlorine transport models that were evaluated and further extended by Clark and Haught (2005). Wang and Postlethwaite (1999) developed mass transfer models for the flow of low Reynolds numbers in pipe corrosion studies. Heinz and Roekaerts (2001) explored mass conservation models for multi-scale mixing and reaction in turbulent pipe flows. Leonenko et al. (2005) applied the principles to pipe flow modeling of reactive droplets and polydisperse systems. Lu et al. (1993) derived simplified models for study of steady-state multi-species transport in a water distribution system, and Islam and Chaudhry (1998) numerically simulated state multi-species transport in a water distribution system, and Islam and Chaudhry (1998) numerically simulated state multi-species transport in a water distribution system, and Islam and Chaudhry (1998) numerically simulated state multi-species transport in a water distribution system, and Islam and Chaudhry (1998) numerically simulated state multi-species transport in a water distribution system.
chemical and kinetic heterogeneity in bulk phase. Research by Powell et al. (2000) on UK water supplies showed the dependence of bulk demand on temperature, pH, total organic carbon and other water quality parameters. Clark and Sivaganesan (2002) proposed empirical equations that relate chlorine decay kinetics to several water quality parameters. When a discrete “slug” of contaminant is introduced to bulk flow, it will change the parameters of the receiving water cited by Powell et al. (2000) and consequently will generate local heterogeneity in chlorine decay rates. The associated convection–dispersion–reaction (CDR) process has not been fully investigated for water quality in drinking water distribution, nor represented in the chlorine decay models. In contrast, the phenomenon has been extensively studied in chemical and pharmaceutical engineering (Baldyga et al., 1996; Levien and Levenspiel, 1999; Forney and Nafia, 2000; Chakraborty and Balakotaiah, 2002) where an understanding and control of micro-scale mixing and reaction are important to product quality and quantity.

Hladik et al. (2005) showed that chlorine and other disinfectants in drinking water can oxidize a number of herbicide compounds. Similar reactions occur resulting in the decomposition and transformation of recalcitrant pharmaceutical compounds subject to chlorination (Stackelberg et al., 2004). Some investigators (Khordagui, 1995; Burrows and Renner, 1999; Hamilton et al., 2006) have suggested that maintaining a high level of chlorine residual can protect against health risks from a number of hazardous contaminants in drinking water. The level of risk reduction depends on the quantity and composition of the contaminant “slug”, the contaminant-chlorine reaction rate, and the traveling time of contaminated water reaching a consumer.

Because of the importance of these types of localized reactions, new models and additional research are needed to adequately predict fate and transport of a small volume of contaminants introduced into drinking water. For this purpose, a series of experiments coupled with computer modeling have been undertaken using pilot-scale pipe flow devices. The objective is to define contaminant-chlorine reactions taking place during the transport of water in a pipe, to characterize the hydraulic dispersion of non-reactive chemicals, to assist in detecting contamination events using water quality sensors, and to establish a working model for predicting the fate and movement of a reactive contaminant “slug”. This paper is the first of a series that describe these studies. It begins with an introduction followed by description of experiment testing and its results. To further explore temporal and spatial changes in chlorine residual concentrations, a CDR model is proposed to examine the relationships between the concentration changes, reactive properties of the contaminants and flow hydrodynamic properties in a water pipe. Finally, these results will be discussed in light of real-time contaminant detection in drinking water distribution systems.

2. Experiments and results

For the purpose of this paper, results from two sets of experiments are presented. The first was conducted to investigate the dispersion of non-reactive sodium fluoride in a pilot-scale pipe flow device. The second was conducted on reactive aldicarb in a fiberglass-lined water pipe to qualify the effect of both dispersion and the fast reactions between aldicarb and chlorine disinfectant. The difference in results between the two sets of experiments is used to identify the effects of CDR process.

2.1. Sodium fluoride tracer experiments

Li (2000) studied the transport of sodium fluoride in a 14.60-cm inside diameter, horizontally placed new polyvinyl chloride (PVC) pipe with three 90° bends (Fig. 1a). Water exited at the end of the pipe 112.2 m downstream from the tracer injection port, where samples were collected and analyzed for fluoride ion concentration using a Hach 2000 spectrophotometer. In the experiments at $Q_p = 69.1–69.3$ L/min, 450-mL sodium fluoride solution (7300–16,900 mg/L) was injected into the pipe to form an instant fluoride “slug” at a calculated concentration of 208–562 mg/L after mixing. Based on the fluoride concentration measurements at the end of pipe (Table 1), tracer exit age (Levenspiel, 1972) and the fluoride dispersion coefficient in water are calculated:

\[
E^* = \left( \frac{C_i}{\sum_{i=1}^{n} C_i} \right) \Delta t^*,
\]

\[
l^* = \left( \frac{D_{\text{eff}}}{L^2} \right)^{1/2} \left( 1 - e^{-uL^*/D_{\text{eff}}} \right),
\]

\[
\frac{L^2}{u^2} = 2 \left( \frac{D_{\text{eff}}}{L^2} \right)^{1/2} \left( 1 - e^{-uL^*/D_{\text{eff}}} \right)
\]

The tracer exit age defined a nearly symmetric E-curve (Levenspiel, 1972) with the peak around the hydraulic retention time (Fig. 2). In a 112.2-m flow distance, the instantaneously injected “slug” of tracer was dispersed into a water column of 7–13 min pipe flow at the pipe exit (Table 1). Maximum concentration detected was 1.45–3.33 mg/L after background corrections, representing >97 times of concentration decrease from the initial concentration 208–562 mg/L at the injection port. Li (2000) reported the conservation of recovered tracer mass in the experiments and attributed the large concentration reduction as a result of dispersion in the pipe. From Eq. (2), the experimental data yielded effective dispersion coefficients of 59.8–216.1 cm²/s for fluoride which can be used in chlorine transport modeling.

2.2. Reactive aldicarb experiments

The experiment apparatus for aldicarb consisted of a 7.62-cm inside diameter, 426.8-m-long straight ductile iron pipe in a configuration similar to that of the tracer experiments (Fig. 1b). The ductile iron pipe, fiberglass-lined inside for negligible wall demand, was long enough that two sensor stations could be used to quantify water quality changes along its length. In the experiments ($Q_p = 83.21$ L/min and $Re = 25,000$), a volume of 50-L aldicarb solution was injected into the pipe through a port 24.4 m upstream from the sensor station #1 (Fig. 1b). Calculated initial aldicarb concentration was 0.2, 1.1 and 2.2 mg/L in the “slug” after assumed
complete mixing. At two sensor stations, a side water stream approximately 0.5 L/min was diverted from the pipe to measure free chlorine, total chlorine and chloride concentration using ATI model A15 sensors and Hach CL-17 total chlorine analyzer.

Measured free chlorine and total chlorine concentrations are shown in the time-series concentration ($c$–$t$) plots in Fig. 3. Experimental data are given in Szabo and Hall (2006). Clearly the chlorine residual loss shows a U-shaped curve pattern with a slightly wider opening at the top than at the bottom. This curve geometry is little changed between the two sensor stations in a 311-m flow distance, and is consistent among all three initial aldicarb concentrations. The depth of residual loss curve $D_c$, which is defined as the concentration difference between the background and the curve’s flat bottom (Fig. 4), is 8–10%, 43–45% and 87–88% for the initial aldicarb concentrations of 0.2, 1.1 and 2.2 mg/L, respectively (Table 2). Measured $D_c$ values and the initial aldicarb concentrations are linearly correlated.

The chlorine and chloride measurement results lead to the suggestion that the reactive contaminant propagated from the “slug” into the bulk phase and simultaneously reacted with chlorine producing a residual loss at the contaminant–water interface. Consequently, chlorine residual concentration varied continuously at both upstream and downstream sides of the “slug”, forming the characteristic U-shaped pattern (Fig. 4). Furthermore, average width of the residual loss curve remained similar within the measurement error among the experiments of different initial aldicarb concentrations and for the two sensor stations spaced 311 m apart (Table 2). In the free chlorine c–t plots, for example, the average opening and bottom width is $20.3 \pm 0.9$ min ($m \pm 1\sigma$, $n = 6$) in units of water flow time. Another geometric measurement is the curve width $19.8 \pm 0.3$ min ($m \pm 1\sigma$, $n = 6$) at the 50% residual loss (Table 2). Both measurements are statistically identical to the 20-min duration of contaminant injection, strongly suggesting that the contaminant “slug” experienced no significant dispersion during the 335.4-m flow distance. This is in contrast to the greater degrees of dispersion observed in the non-reactive tracer experiments (Fig. 2).

Even in the same aldicarb experiments, chloride as the reaction product with a noticeable concentration increase from the “slug” into the bulk phase and simultaneously reacted with chlorine producing a residual loss at the contaminant–water interface. Consequently, chlorine residual concentration varied continuously at both upstream and downstream sides of the “slug”, forming the characteristic U-shaped pattern (Fig. 4). Furthermore, average width of the residual loss curve remained similar within the measurement error among the experiments of different initial aldicarb concentrations and for the two sensor stations spaced 311 m apart (Table 2). In the free chlorine c–t plots, for example, the average opening and bottom width is $20.3 \pm 0.9$ min ($m \pm 1\sigma$, $n = 6$) in units of water flow time. Another geometric measurement is the curve width $19.8 \pm 0.3$ min ($m \pm 1\sigma$, $n = 6$) at the 50% residual loss (Table 2). Both measurements are statistically identical to the 20-min duration of contaminant injection, strongly suggesting that the contaminant “slug” experienced no significant dispersion during the 335.4-m flow distance. This is in contrast to the greater degrees of dispersion observed in the non-reactive tracer experiments (Fig. 2). Even in the same aldicarb experiments, chloride as the reaction product with a noticeable concentration increase...
exhibits a different c–t curve geometry than the reactant chlorine. An extended dispersion tail (Levenspiel, 1972) is noticeable for \( t^* > 21.5 \) min at the 24.4-m sensor station and is more pronounced for \( t^* > 42.2 \) min at the 335.4-m station, especially in the 2.2 mg/L experiments (Fig. 3).

### 3. Modeling

In addition to the experimental work described above, the differences between non-reactive sodium fluoride and...
fast-reacting aldicarb were further examined using a one-dimensional CDR model modified from Danckwerts equations.

3.1. Fast-reacting contaminant “slug” transport in water pipe

Chlorine concentration \( C(x', r', \theta', t') \) in a water pipe follows the mass conservation equation:

\[
\nabla C' + u'(x', r', \theta') \cdot \nabla_x C = -\nabla_x D_{\text{eff}} C' - R(C', t'),
\]

where \( D_{\text{eff}} \) is the effective chlorine dispersion coefficient in water; \( R(C', t') \) is the rate of chlorine decay including both bulk demand and wall demand. The velocity scalar \( u'(x', r', \theta') \) represents the transverse velocity field as a function of axial distance \( x' \), radial distance \( r' \) and azimuth angle \( \theta' \) in a cylinder coordinate system (Fig. 5a). In the simplest term, Eq. (3) describes the chlorine decay rate \( \frac{dc}{dt} \) as a function of convection \( \nabla_x C' \), longitudinal and radial dispersion \( \nabla_x \nabla_x C' \), chlorine bulk demand and wall demand \( R(C', t') \).

The parameters \( P_{LD} \) and \( P_{TD} \) are axial and transverse Péclet numbers, respectively. Dimensionless radial distance \( r' \), axial distance \( x' \), time \( t' \) and concentration \( C' \) are the dimensionless equivalents normalized against pipe radius \( r_o' \), pipe length of interest \( n_s' \), characteristic convection time \( t_c' \) and chlorine concentration at a reference pipe location \( C_r ' \).
Fig. 4 – Progressive chlorine residual loss at initial aldicarb concentrations 0.2, 1.1 and 2.2 mg/L. Average chlorine concentration and one standard derivation ($\bar{m} \pm 1\sigma$) are marked for the chlorine ($Cl_f$) and total chlorine ($Cl_t$) measurements. Note that the U-shape chlorine residue loss is consistent at all initial aldicarb concentrations and persistent in the flow between two sensor stations of 311-m distance.
respectively. Scaling factor ($n_s$) allows flow modeling for a pipe length of interest in units of pipe radius; $n_s = 2$ for the characteristic pipe length. The first term on the right-hand side of Eq. (4) measures radial diffusion in transverse. Its constant is the ratio of characteristic time between convection and radial diffusion (Chakraborty and Balakotaiah, 2002):

$$t_{c} = \frac{n_s D_{eff}}{u_r r_0}$$

\[6\]

### Table 2 – Observed geometry of the free chlorine residual loss curve in the aldicarb pipe flow experiments

<table>
<thead>
<tr>
<th>Chlorine loss curve parameter</th>
<th>Residual loss curve geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x^* = 24.4$ m</td>
</tr>
<tr>
<td></td>
<td>0.2 mg/L 1.1 mg/L 2.2 mg/L</td>
</tr>
<tr>
<td>Opening width $\Delta x^*$ (min)</td>
<td>23 24 29</td>
</tr>
<tr>
<td>Bottom width $\Delta r_1^*$ (min)</td>
<td>16 16 15</td>
</tr>
<tr>
<td>Average width $(\Delta x^<em>+\Delta r_1^</em>)/2$ (min)</td>
<td>19.5 20.0 22.0</td>
</tr>
<tr>
<td>50% residual loss curve width (min)</td>
<td>19.2 19.6 19.9</td>
</tr>
<tr>
<td>Residual loss curve depth ($h_r$)</td>
<td>0.08 0.45 0.88</td>
</tr>
<tr>
<td>Slug width at injection ($t^* = 0$)</td>
<td>20 20 20</td>
</tr>
</tbody>
</table>

Note: All widths can be converted to equivalent pipe length by multiplying average flow velocity 30.5 cm/s.

Fig. 5 – Schematic diagrams for a contaminant “slug” introduced into a drinking water pipe: (A) a contaminant “slug” in transport between the two paired sensor stations, (B) the CDR process of a reactive contaminant “slug” reacting with chlorine in the bulk phase and (C) non-reactive contaminant or tracer dispersion in pipe flow. Dashed line—initial chlorine level $C_0$. Other symbols are defined in the nomenclature.
This constant can be sufficiently small to neglect the radial diffusion term in Eq. (4) for turbulent pipe flows in a paired configuration of online sensor stations (Fig. 5a) that Yang et al. (2007) described in adaptive contaminant monitoring. Using the dimensionless transverse-averaged flow velocity \( u_x \), for \( u_x, v, w \), a dimensionless bulk averaged flow velocity \( \bar{u}_x \) and a decay rate term \( \bar{W}(c, t) \) for wall demand, Eq. (4) becomes a modified one-dimensional Danckwerts equation for chlorine in water pipes:

\[
\frac{\partial \bar{c}}{\partial t} + \frac{\partial \bar{c}}{\partial x} = \frac{1}{n_r^2 Pe_D} \left( \frac{\partial^2 \bar{c}}{\partial x^2} \right) - k_b \bar{c} - \bar{W}(c, t),
\]

where \( k_b = \frac{(n_r^2 r_s)^2}{\bar{u_x}} k'_0 \).

The governing equation (7) is valid to describe mass transport in long and narrow pipes for which longitudinal dispersion is fully developed (Taylor, 1953, 1954). This condition is satisfied in the aldicarb experiments with the setup of two sensor monitoring stations (Fig. 5a). When the axial Pe´clet number \( Pe_x = n_r^2 Pe_D \) is sufficiently large, longitudinal dispersion becomes negligible and subsequent simplifications yield the governing equations of Rossman et al. (1994) for the EPANet model (Rossman, 2002). The condition prevails in a distribution network except for laminar and stagnant flow regions such as distribution network dead ends. Furthermore, Clark and Haught (2005) evaluated the wall demand in Eq. (7) and compared the wall reaction limited model of Rossman et al. (1994) with the mass transfer-limited wall reaction kinetics; however, because of the condition under which these experiments were conducted, wall reaction was not considered for the fiberglass-lined pipe interior.

3.1.1. Physical model

Fig. 5b shows a reactive contaminant “slug” introduced instantaneously into a flowing straight water pipe. Chlorine transport in this situation can be described using the modified one-dimensional Danckwerts equation. The instantaneous contaminant introduction would simulate a line break, back siphonage and even intentional sabotage. Contaminant back siphoning from pipe breaks, for example, usually lasts for \(< 10 \)s before the negative transient pressure dissipates (AWWA, 2004). Following the introduction, a contaminant “slug” moves along the bulk phase, propagates by molecular diffusion and longitudinal dispersion, and reacts with chloride disinfectants in the water. Simultaneously chlorine-contaminant fast reactions can rapidly reduce and even deplete chlorine residuals inside of the “slug”, producing a chlorine concentration gradient from bulk phase toward the contamination. The resultant chlorine mass flux is in opposite direction to that of reactive contaminants at the contaminant–water interface (Fig. 5b).

3.1.2. Chlorine decay inside of a contaminant “slug”

In general, the instantaneous introduction of a reactive contaminant “slug” into chlorinated drinking water can lead to changes in both chlorine bulk demand and wall demand. The new bulk demand in the contaminant “slug” after assumed instant complete mixing is described by the generalized reactions:

\[
a[A] + q_{1}[Cl] \rightarrow p_1[P_1],
\]

\[
b[B] + q_{2}[Cl] \rightarrow p_2[P_2],
\]

in which \([A]\) and \([B]\) are fast- and slow-reacting contaminants that react with chlorine \([Cl]\) to produce the reaction products \([P_1]\) and \([P_2]\) at the rate \( k'_1 \) and \( k'_2 \), respectively, which yields two second-order equations (Clark and Sivaganesan, 2002). Assuming negligible wall demand or \( W(c, t) \approx 0 \) for fiberglass-lined pipe, chlorine residual decay in the “slug” is given by:

\[
c = f_m \left[ \frac{(1 - R_1)}{1 - R_1 e^{-1 - x / R'_1}} \right] + (1 - f_m) \left[ \frac{(1 - R_2)}{1 - R_2 e^{-1 - x / R'_2}} \right] - \bar{W}(c, t),
\]

\[
c \approx f_m \left[ \frac{(1 - R_1)}{1 - R_1 e^{-1 - x / R'_1}} \right] + (1 - f_m) \left[ \frac{(1 - R_2)}{1 - R_2 e^{-1 - x / R'_2}} \right].
\]

In Eq. (8), parameters \( k_b, k'_s \) and \( k'_f \) are dimensionless kinetic constants for the residual pre-mixing bulk demand, slow- and fast-reacting contaminants, respectively; \( k'_s = k'_f + k'_b \) is the overall slow chlorine reaction rate in the “slug”; \( f_m \) is molar fraction of the chlorine consumption by the fast-reacting contaminants, while \((1-f_m)\) denotes all other chlorine consumptions by slow reactions. \( R_1 \) and \( R_2 \) are empirical dimensionless parameters as defined in Clark et al. (2001).

3.1.3. Chlorine reaction at contaminant–water interfaces

The chlorine residual concentration profile at the contaminant–water interface determines the extent and geometry of chlorine residual loss recorded at the sensor stations in Fig. 5b. Taking \( u_x = 1 \) for turbulent pipe flows (Lu et al., 1993) and using transverse-averaged concentration \( \bar{c} \), Eq. (7) becomes:

\[
\frac{\partial \bar{c}}{\partial t} + \frac{\partial \bar{c}}{\partial x} = \frac{1}{n_r^2 Pe_D} \left( \frac{\partial^2 \bar{c}}{\partial x^2} \right) - k_b \bar{c} - \bar{W}(c, t),
\]

with boundary and initial conditions:

\[
\bar{c}(x, t) = 1 \quad \text{at} \ t > 0
\]

\[
\bar{c}(x, 0) = 0 \quad \text{at} \ x = 0.
\]

\[
\bar{c} \equiv f_m \left[ \frac{(1 - R_1)}{1 - R_1 e^{-1 - x / R'_1}} \right] + (1 - f_m) \left[ \frac{(1 - R_2)}{1 - R_2 e^{-1 - x / R'_2}} \right]
\]

at \( \left( u_x t - \frac{h}{2} \right) \leq x \leq \left( u_x t + \frac{h}{2} \right) \)

and

\[
\bar{c}_o = \begin{cases} f(c_{x=x_0}) & \text{at} \ t = 0. \\ 1 & \text{at} \end{cases}
\]

\( f(c_{x=x_0}) \) is a chlorine concentration input function at sensor station \#1 (Fig. 5a); \( f(c_{x=x_0}) = 1 \) for the contaminant introduced at this location. Boundary conditions in the contaminant “slug” \( (u_x t - h/2) \leq x \leq (u_x t + h/2) \) are given in Eqs. (10) and (11); the dimensionless “slug” length \( h = h' / r_s \) changes with time in response to the contaminant front propagation or contraction. In this study, the model was solved using an explicit numerical scheme of forward time and center space with moving boundary conditions. Similar numerical computation techniques can be found in program BIO-1D for contaminant transport simulation in groundwater.
3.2 Non-reactive contaminant “slug” transport in water pipes

In contrast to the previous analysis for fast-reacting contaminants, conservative contaminants have no reactivity with chlorine. Longitudinal dispersion is the controlling factor over their mass transport. Between these two extremes are contaminants exhibiting slow-reacting kinetics, for which modifications to the model in Eq. (12) are required. A familiar example of non-reactive solutes is the conservative tracer sodium fluoride (Fig. 5c) often used in pipe flow testing (e.g., Taylor, 1953, 1954; Aries, 1956; Ekambara and Joshi, 2004). When $k_b = 0$ and $W(c, t) = 0$, the CDR governing equation in Eq. (9) is simplified to

$$\frac{\partial C}{\partial t} + \frac{\partial (v C)}{\partial x} = \frac{1}{\kappa_0 D} \left( \frac{\partial^2 C}{\partial x^2} \right),$$

which is identical to that of Levenspiel (1972) for tracer transport in pipe flows. When the contaminant or a tracer moves in the form of “slugs” (Fig. 5c), the exit age ($t^*$) can be solved explicitly from Eqs. (13) and (14) of Levenspiel (1972). Li (2000) found these equations conform to tracer experiment results under a wide range of flow conditions in a long water pipe.

$$E^* = \frac{1}{2 \sqrt{\pi Pe_{c_1}^{-1}}} \exp \left\{ - \frac{(1 - t^*)^2}{4 Pe_{c_1}^{-1}} \right\}, \quad Pe_{c_1} \leq 100. \quad (14)$$

The simplified CDR model was calibrated in comparison with the Levenspiel’s (1972) analytical solution and against the tracer experimental results in Table 1. Using the model parameters in Table 3, both the numerical modeling (Eq. (12)) and the analytical solutions (Eq. (13)) generate E-curves consistent with the tracer experimental results (Fig. 2). The two models are consistent with each other except for the area at the E-curve peak where the numerical model slightly over-estimated.

4. Discussions

4.1 Chlorine decay in a contaminant “slug”

Mason et al. (1990) outlined the reactive pathways and proposed the reaction kinetics for aldicarb oxidation in chlorinated drinking water. In chlorine oxidation, the aldicarb carbamate structure and its thio function group are transformed to yield the intermittent products aldicarb-sulphone and aldicarb-sulphoxide. The initial fast oxidation is followed by slow reaction of more recalcitrant intermittent compounds at a rate several orders of magnitude smaller. Extrapolated from the experimental results of Mason et al. (1990), the aldicarb-chlorine fast reaction should have followed a kinetic
order of 1.78 at pH = 7.0 for the initial chlorine 0.90 mg/L in
the aldicarb experiments of this study.

4.1.1. Quasi-steady-state chlorine decay
As shown in Figs. 3 and 4, chlorine residual loss within the
contaminant “slug” displayed no significant change between
the two sensor stations in a 311-m flow distance. It follows
that residual loss in the “slug” must have reached a quasi-
 steady state before the water reached the 22.4-m sensor
station at a 1.4-min hydraulic retention time.

The quasi-steady-state condition is further evident in
comparing the aldicarb pipe flow experiments with the
aldicarb bench-scale studies of Haught et al. (2005). In the
bench-scale study, concentrated aldicarb solution was added
to a glass beaker reactor and mixed well with tap water. Initial
aldicarb concentration was 0.2–2.2 mg/L after mixing (Haught
et al., 2005). Measured chlorine residual concentrations
normalized against the initial concentration at $t^* = 0$ were
used to calculate the residual loss produced by the aldicarb-
induced bulk demand; wall demand was negligible for the
pre-cleaned glass beaker. The results showed a strong linear
relationship between chlorine residual loss and initial aldi-
carb concentration (Fig. 6).

In the pipe flow experiments, the chlorine residual loss
within the aldicarb “slug” exhibits the same linear relation-
ship as in the bench-scale testing (Fig. 6). This agreement
strongly suggests that in the pipe flow experiments chlorine
residual loss within the “slug” is primarily the result of bulk
demand in aldicarb oxidation, and also reinforces the notion
that complete mixing and quasi-steady-state chlorine decay
in the “slug” must have occurred during its transport from the
injection port to the first sensor station.

4.1.2. Chlorine decay kinetics and boundary conditions
The CDR model boundary condition in Eq. (10) relies on the
competitive second-order chlorine decay kinetics of Clark and
Gang et al. (2003) and Warton et al. (2006) described a first-
order kinetic model for drinking water, which may be
applicable to approximate the residual loss in the multi-step
successive oxidation of aldicarb:

$$\dot{c} = f_m e^{-k_1 t} + (1 - f_m) e^{-k_2 + k_b x}.$$  \hspace{1cm} (15)

Fig. 7 shows a comparison between the second-order and
first-order kinetics models. Also plotted are chlorine loss ($\Delta c$)
observed at the 22.4- and 335.4-m sensor stations in the
aldicarb pipe flow experiments. Both chlorine decay models
approximated the observed residual loss using modeling
parameters in Table 3, and also predicted the same quasi-
steady-state chlorine decay in the extended time. They differ
in the period immediately following introduction of the
aldicarb “slug” (Fig. 7). Furthermore, the second-order kinetic
model in Eq. (10) provides additional information on the
nature of reactive contaminants in the “slug”. The second-
order model parameters ($f_m$, $k_1$, and $k_2$) are related to water
quality parameters such as total organic carbon, UVA, pH,
initial chlorine concentration and temperature (Clark et al.,
2001). Therefore, the second-order kinetic model was selected
to represent the CDR model boundary condition in Eq. (10). It
should be noted, however, that the second-order competitive
model examined in this study for aldicarb-chlorine reaction
may not work as well for some other contaminants. This
variance should be considered in model definition.

4.2. Residual loss curve geometry and control variables
Fig. 8 shows experimental data for the 24.4-m sensor station
($x = 320$) and the CDR modeling results at initial aldicarb
concentrations of 0.2, 1.1 and 2.2 mg/L. Numerical simulation
is based on Eqs. (9)–(11) and the model parameters in Table 3.
relations between the residual loss curve geometry (width, depth and slope), contaminant reaction rate constant and chlorine longitudinal dispersivity.

The influence of contaminant reactivity on the residual loss curve geometry is assessed by using $k_f' = 0.05$ and $0.3 \text{ s}^{-1}$ in the CDR model (Table 3). The experimental results by Mason et al. (1990) revealed a logarithmic relationship between observed reaction rate of aldicarb oxidation and the initial chlorine concentration. Extrapolation from their results yielded a pseudo-first-order constant of $0.02-0.18 \text{ s}^{-1}$ for the $0.2-2.2 \text{ mg/L}$ initial aldicarb concentrations of this study. In another approach, model fitting using Eq. (8) to the experimental residual loss data yielded $k_f' = 0.05 \text{ s}^{-1}$ that falls into the range $0.02-0.18 \text{ s}^{-1}$ based on Mason et al. (1990). Thus $k_f' = 0.05 \text{ s}^{-1}$ was selected for the CDR model simulations producing the residual loss curves consistent with experimental results for all initial aldicarb concentrations (Fig. 8a–c).

When the constant increases to $0.3 \text{ s}^{-1}$, model-calculated residual loss at a quasi-steady state is rapidly established within $t < 50$ or $t' = 0.5 \text{ min}$ and the loss curve slope is steepened (Fig. 8c). In this comparison, the larger value $k_f' = 0.3 \text{ s}^{-1}$ is the first-order decay constant that Brosillon et al. (2006) reported for glyphosate, a fast-reacting herbicide of the same chemical class. For the fast-reacting contaminants—aldicarb and glyphosate, their chlorine reactivity controls the degree of chlorine decay within the “slug” which serves as CDR model boundary condition in Eq. (10) and therefore can significantly affect the geometry of a residual loss curve. This effect remains significant, and the U-shaped chlorine residual loss curve can persist in a straight pipe when mechanical mixing is absent and the rate of chlorine-contaminant reaction inside of the “slug” exceeds longitudinal dispersion flux of the solute (chlorine or aldicarb), namely $k_i c > (1/n_x^2\text{Pe}) (\partial^2 c/\partial x^2)$ in Eq. (9).

Compared to reactivity, the longitudinal dispersion has relatively small effect on the chlorine residual loss curve geometry. The modeled curve geometry has small change when effective dispersivity increases from $33$ to $1400 \text{ cm}^2/\text{s}$ (Fig. 8e). However, the effect of longitudinal dispersion becomes important for less reactive contaminants; the most extreme is the non-reactive contaminants or tracers. For the latter, the dispersion curve geometry is directly related to the effective dispersion coefficient of the solute and to the pipe flow Péclet number (Aries, 1956; Levenspiel, 1972; Ekambare and Joshi, 2004). Evidently in this study, substantial longitudinal dispersion was observed in the sodium fluoride tracer experiments (Fig. 2). Even in the aldicarb experiments, chlorine as the reaction product also displayed an asymmetric dispersion profile spreading beyond the zone of chlorine residual loss (Fig. 3).

4.3. Implications for real-time contaminant detection

The non-reactive sodium fluoride in the tracer experiments showed a large concentration decrease over 97 times in a 112.2-m turbulent flow distance. In general, the longitudinal dispersion can lead to a large reduction in concentration making it difficult to measure the target compounds in real-time field applications. This often results in false negative detections (US EPA, 2005; Klise and McKenna, 2006). However,
many studies (e.g., Donohue and Lipscomb, 2002) have pointed to the fact that health risk from contaminant exposure depends on both the concentration and mass intake. In the sodium fluoride experiments, Li (2000) reported that the entire tracer mass was conserved in less than 7–13 min of the pipe flow or 484–900 L of water column (Table 1). If the chemical was highly toxic, risk from the small volume of contaminated water could not be underestimated.

The chlorine residual loss curve and its geometry potentially offer a more reliable detection marker for a reactive contaminant “slug” in drinking water. This potential relies on a close relationship between the residual loss, chloride concentration increase, and the contaminants reactivity as examined in the aldicarb experiments and corresponding CDR modeling. The concentration changes can be detected using real-time chlorine and chloride sensors, and the

Fig. 9 – Experimental and CDR modeling results showing the use of first- and second-order concentration time derivatives to mark the front edge of an incoming contaminant “slug”. These two variables can better detect the edge than the absolute concentration measurements, even at the low aldicarb concentration 0.2 mg/L. CDR model parameters are given in Table 3.
relationships can be quantified in an adaptive monitoring scheme of Yang et al. (2007) that requires an accurate characterization of the chlorine loss curve geometry, particularly at the leading edge of a contaminant “slug”. For this purpose, first- and second-order concentration derivatives ($\Delta c/\Delta t, \Delta^2 c/\Delta t^2$) are better monitoring parameters than the absolute chlorine concentrations in detecting the aldicarb “slug”, even at the low contaminant concentration (Fig. 9).

5. Conclusions

Experimental testing and numerical simulation using a CDR model have quantified the transport of non-reactive sodium fluoride and reactive pesticide aldicarb in the pilot-scale drinking water pipes under turbulent flow conditions. Major conclusions are:

- When instantaneously introduced into turbulent flow of a straight pipe, reactive contaminants can move in a discrete “slug” bounded by a reactive interface where the contaminants are oxidized by chlorine in the bulk phase. Longitudinal dispersion forces the “slug” propagating into the uncontaminated bulk phase, while the propagation is counteracted and inhibited by aldicarb-chlorine fast reactions. This CDR process is considered to have produced the characteristic U-shaped curves in the chlorine residual concentration as consistently observed in the aldicarb pipe flow experiments.
- In examination of the CDR process, a modified one-dimensional Danckwerts model reproduced the observed chlorine profiles across the reactive aldicarb “slug”. Quantitative analysis shows that the geometry (width, depth and slope) of a residual loss curve is a function of the fast-reaction kinetic constant ($k_j$), molar fraction of fast and slow reactions ($f_m$) and the axial Pécelt number ($Pe_a$).
- In the aldicarb experiment using a fiberglass-lined water pipe, the quasi-steady-state condition in the residual loss was established within the “slug” in less than 1.3 min. The chlorine decay in the “slug”, which serves as the boundary condition in the CDR model, can be described by the competitive second-order kinetic model of Clark and Sivaganesan (2002) at no or negligible chlorine wall demand. For the fast-reacting aldicarb, rapidly developed chlorine decay controlled the geometry of observed residual loss curve. This generic relationship can be potentially explored to identify the chemical and kinetic properties of a reactive contaminant.
- In the sodium fluoride tracer experiments, determined exit ages are consistent with E-curves generated by both the Levenspiel’s (1972) analytical model and the numerical CDR model in Eq. (13) when wall demand and bulk demand are set to zero. Both the experimental and modeling results show that a significant degree of dispersion is responsible for >97 times of tracer concentration decrease in the 112.2-m flow distance, yielding potential difficulties in direct measurement of the target concentrations.

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