Chlorine decay under steady and unsteady-state hydraulic conditions

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Abstract

This paper describes a simulation framework for the scale-adaptive hydraulic and chlorine decay modelling under steady and unsteady-state flows. Bulk flow and pipe wall reaction coefficients are replaced with steady and unsteady-state reaction coefficients. An unsteady decay coefficient is defined which depends upon the absolute value of shear stress and the rate of change of shear stress for quasi-unsteady and unsteady-state flows. A preliminary experimental and analytical investigation was carried out in a water transmission main. The results were used to model monochloramine decay and these demonstrate that the dynamic hydraulic conditions have a significant impact on water quality deterioration and the rapid loss of disinfectant residual.

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1. Background

Understanding the spatial and temporal variability of chlorine and monochloramine in water transmission and distribution networks is critical for managing the water quality, detecting and responding to contamination events (Yang et al. 2008) and complying with various regulatory requirements. The loss of disinfectant residual in water supply systems poses a public health risk while excessive levels may produce taste and odour problems, accelerate pipe corrosion and enhance the formation of trihalomethanes, haloacetic acids and chlorophenols (Vasconcelos et

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The parameters and processes that influence the water quality changes are complex. Pipe material, age, water temperature, pH, corrosion and biofilm formations modify the chemical and biological reactions that take place in the bulk fluid and on the pipe wall.

A critical factor governing the decay of residual disinfectant within transmission and distribution pipes is the hydraulic conditions. Although it is assumed that water supply systems operate under steady or nearly steady hydraulic conditions, this assumption is frequently violated due to routine demand changes, planned or accidental operational changes, pump scheduling, pressure management activities and occasional failures (Fig. 1). Consequently, the operational conditions vary between steady, quasi-unsteady and unsteady-state flows.

![Fig. 1. Continuously acquired pressure using InfraSenseTS (SR 128S/s): (a) pressure transients in a distribution system caused by a large industrial user over a period of 24 hours, (b). a detail of a captured transient event.](image)

Experimental studies have shown that chlorine demand and in particular the wall demand is flow dependent. However, there has been little evidence of the impact of the dynamic hydraulic conditions on chlorine decay (Woodward et al. 1995; Clark & Haught 2005). Gradual to fast changes in hydraulic conditions generate fluctuations in the velocity profile that increase shear stress and energy dissipation (Brunone et al. 2000, Brunone and Berni, 2010). The resulting dispersive and transport forces can change the water quality by influencing the mechanisms of particle deposition, biofilm formation, shear-induced biofilm detachment, internal corrosion and particle resuspension (Clark et al. 1993). The rates of chemical reactions are also affected by the greater mixing and transport of chemicals between the pipe wall and the bulk flow (LeChevallier et al. 1988; Clark et al. 2010).

An accelerated decay of chlorine residual caused by resuspended sediments and corrosion scales during increased flow velocity was demonstrated by Gauthier et al. (1998) and Sarin et al. (2004). When deposits are mobilised by hydraulic disturbances, the chlorine demand may become extremely high and lead to the rapid depletion of chlorine residual as up to 80% of total suspended solids are organic matter including pathogens and microbiological organisms (Gauthier et al. 1998, Camper et al. 2003).

The inadequacy of current telemetry systems to continuously monitor the dynamic hydraulic conditions in operational water networks, combined with the lack of accurate and reliable in-pipe water quality sensors have precluded investigations into the deterioration of water quality under unsteady flows. Various approaches have been proposed that model chlorine propagation based on the assumption of steady-state flows (e.g., Vasconcelos et al. 1997; Uber 2009) or transient conditions (Fernandes & Karney 2004) with limited experimental research. Long-term field investigations with high spatial and temporal resolution data for studying the kinetics of disinfectant decay in operational systems have been non-existent.
2. Scale adaptive hydraulic and chlorine decay modelling

2.1. Outline

In order to investigate experimentally and analytically the impact of the unsteadiness of flow conditions on the temporal and spatial variability in water quality and the mechanisms of deterioration, a simulation framework which enables scale-adaptive hydraulic and chlorine decay modelling for a wide range of flow conditions has been proposed (Fig. 2a). This framework is supported by novel instrumentation technologies for continuous high-frequency time-synchronised monitoring (Stoianov and Hoskins, 2012). The InfraSense ultra-low-power remote telemetry units (RTU) continuously capture the dynamic hydraulic conditions with a sampling rate of 128S/s and time synchronization of 5ms. Acquired raw data and classified events are stored for up to six months in a rotating memory buffer. In this way, periods of steady, quasi-unsteady and unsteady-state flows are automatically identified and the data are available for further analysis and calibration with user defined time resolution for retrospective time intervals (Fig. 2b&c).

Fig. 2. Continuous monitoring and scale adaptive modelling framework enabled by the InfraSenseTS telemetry system

This paper uses the term unsteady-state to describe fast-occurring transient events in which the effects of the fluid inertia and/or elasticity of the fluid and pipe are an essential factor in the flow behaviour. The term quasi-unsteady flow (sometimes also referred to as quasi-steady flow) is used to describe unsteady flow in which the inertial or elastic terms have a negligible influence on the flow behaviour. For the purpose of this study we have integrated the InfraSense RTUs with reagent and membrane-free, in-pipe water quality sensors (IntellisondeTM, Intellitect Water Ltd, UK).
2.2. Kinetics of chlorine decay

The kinetics of chlorine decay is a topic of extensive research (Vasconcelos et al. 1997; Brown et al. 2011). Existing water quality models simulate chlorine propagation assuming a steady-state flow or a sequence of steady-state flow snapshots over an extended period of time. The overall disinfectant decay can be modelled as a single decay coefficient which is flow dependent and a function of residence time (Clark & Haught 2005). Woodward et al. (1995) conducted experiments under laminar and turbulent flows and derived an empirical formulation which correlates a single decay coefficient with flow rate \( K = 0.222 \cdot Q^{0.6} + 0.002 \). Another approach uses a decay coefficient which takes into account the reactions in the bulk and at the pipe wall (Rossman et al. 1994):

\[
K = K_b + K_w
\]

where \( K_b \) and \( K_w \) are the bulk and wall reaction rate constants, respectively. \( K_b \) is a function of temperature, initial disinfectant concentration and organic content in the water, and it is determined by laboratory bottle tests. \( K_w \) depends on the pipe characteristics and the rate of mass transfer of disinfectant to the wall and is defined as:

\[
K_w = \frac{k_w k_f}{R_h (k_w + k_f)}
\]

where \( k_f \) is a flow dependent mass transfer coefficient and \( R_h \) is the hydraulic radius. \( k_w \) is the wall reaction rate constant and it is inversely proportional to the Hazen-Williams roughness (Vasconcelos et al. 1997). The coefficient \( k_f \) is a function of the Sherwood number to incorporate the flow rate, pipe diameter and length, kinematic viscosity and molecular diffusivity. \( k_w \) takes into account the flow rate but not its acceleration and deceleration.

The impact of flow velocity on the loss of chlorine residual in unlined metallic pipes could be significant (Powell, 2000, Clark and Haught, 2005). Clark et al. (2010) demonstrated that in old unlined metal pipes the loss of chlorine residual increases with velocity. Chlorine residual transport models commonly use first order kinetics. Experimental results from bench-scale reactors built from old cast/ductile iron mains show that first-order reaction kinetics represents well the observed changes in chlorine concentration (Digiano and Zhang, 2005). Alternative approaches were also investigated including a wall reaction limited model, a zero-order reaction limited model and a mass transfer limited model as outlined by Clark and Haught (2005). Fernandes & Karney (2004) developed a transient one dimensional (1D) water quality model to investigate the impact of inertia and compressibility on the disinfectant transport and the changes in chlorine concentration. Naser et al. (2004) extended this transient water quality model to a 2D model to include the unsteady shear stress. In summary, very few water quality models take into consideration the changes in disinfectant decay due to the cross-sectional variations in flow velocity during unsteady-state flows which result in increased shear forces.

The approach proposed in this paper incorporates the physical phenomenon that quasi-unsteady and unsteady-state flows generate large dispersive and transport forces which affect the chlorine decay by influencing the mechanisms of particle deposition, biofilm formation, shear-induced biofilm detachment and particle suspension. The proposed chlorine decay model includes the impact of detached biofilms and re-suspended deposits caused by unsteady flows on changes in chlorine demand.

2.3. Steady and unsteady-state decay coefficients

The application of a single modelling approach to cover all hydraulic conditions and network systems frequently results in significant discrepancies between observed and simulated data. The proposed scale adaptive
simulation framework (Fig. 3) approximates quasi-unsteady flow conditions with extended period simulation analysis (EPS) with a short time step rather than using rigid water column analysis. A 1D transient water quality model with a shear stress dependent decay coefficient was developed to simulate the disinfectant transport under unsteady-state flow conditions. The unsteady model integrates the mass transport with a hydraulic transient solver.

The analyses of the hydraulic conditions (Fig. 2) are coupled with varying decay coefficients which take into account the change in shear stress and the rate of change of shear stress (Fig. 3). Three definitions of disinfectant decay coefficients are investigated: i) a single and constant coefficient; ii) a bulk and wall coefficient, and, iii) a new coefficient that differentiates between quasi-unsteady and unsteady-state flow conditions.

Experimental studies have been performed to determine mathematical expressions describing biofilm-sediments detachment rates (Abe et al. 2012). The PODDS model proposed by Boxall and Saul (2005) links particle mobilisation to the excess fluid shear stress during hydraulic changes, i.e., the difference between the applied shear stress at the wall and the steady state shear stress under which biofilms are grown and conditioned. The PODDS model does not consider the rate of change of flow, i.e. the rate of change of shear stress, when modelling the particle re-suspension. It is assumed that the rate of change in shear stress is a critical factor for the shear-induced detachment of biofilms and resuspension of sediments. This implies that small-amplitude but fast-occurring hydraulic instabilities (Fig. 1) might have significant impact both on chlorine residual and discoloration. Abe et al. (2012) showed that the biomass detachment rate correlate neither with the increase in shear stress during detachment nor with the ratio of shear stress, i.e. the underlying assumption used for the PODDS model. This is most likely due to the viscoelastic behaviour of biofilms, which has been neglected in detachment models so far. This hypothesis is extended here to biofilm-sediment formations which might also behave viscoelastically. In pipes, the sediments are analogous to colloids and the biofilm acts as cross-linked polymer gel. This perspective might be beneficial for understanding the dynamics of these formations under unsteady flow, where they behave as elastic solids over short time periods but linear viscoelastic fluids over longer time scales. Contrary to the elastic behaviour where the strain of a material is linearly proportional to the applied stress, viscoelastic materials exhibit time-dependent strain. If a load is applied slowly, the stiffness decreases and the biofilm-sediment formation is able to store the applied energy. The hypothesis is also supported by experimental results provided by Stoodley et al. (2001) who demonstrated that biofilm detachment is linked to a rapid increase in shear stress.

In this study, $K = K_u + K_{as}$, where $K_u$ is the total decay coefficient during steady hydraulic conditions and $K_{as}$ describes the additional chlorine demand due to the particle resuspension resulting from the flow dynamics as
defined in equation (3). $K_{\text{us}}$ is a function of the absolute change of steady shear stress and the rate of change of shear stress. Under unsteady-state flows, the rate of change of shear stress is determined by the value of the unsteady shear stress. The latter is calculated using the transient hydraulic model, and it accounts for the rate of change and magnitude of flow velocity and cross-sectional variations in a velocity profile during unsteady-state flow conditions. Both of these processes cause particle mobilization.

$$
K_{\text{us}} = \begin{cases} 
K_{\text{us}(q_{\text{us}})} = K_w \left[ |\Delta \tau|, \left| \frac{d\tau}{dt} \right| \right] & \text{quasi-unsteady} \\
K_{\text{us}(\tau_{\text{us}})} = K_w \left[ |\Delta \tau|, \tau_{\text{us}} \right] & \text{unsteady-state}
\end{cases}
$$

The coefficient $K_{\text{us}}$ is calibrated with experimental data obtained during steady-state flow conditions and represents both the bulk and wall decay processes. The additional $K_{\text{us}}$ term describes the disinfectant decay due to biofilm re-suspension and enhanced mixing associated with the change of shear stress and the rate of change of shear stress for quasi-unsteady flows; and, to the change of shear stress and the unsteady-state shear stress developed during unsteady-state flows.

3. Experimental investigation

An experimental investigation was carried out in a 105 year old water transmission pipeline which transports continuous flow of 50,112 m$^3$/d (580 l/s). The pipeline is an unlined cast iron main which has an internal diameter of 1,220 mm and a total length of 21,905 m (Fig. 4).

A pumping station (Fig. 4b) with six fixed-speed pumps delivers water to five water transmission mains, one of which was used in this study. Unlined cast iron pipes tend to have a higher probability of corrosion which results in encrustation, tuberculation, deterioration in water quality and the potential for increased bacteriological growth and biofilms. High-frequency hydraulic data including flow at 1S/s and pressure at 128S/s with time synchronization of 5ms were collected at the three sites labelled F&P and the water quality data were collected at the two sites labelled WQ (Fig. 4a,d). The F&P sites (Fig. 4a,c) included an InfraSense RTU and an insertion type electromagnetic flow meter (ABB Aquaprobe V2). Flow, pressure and water quality data were also acquired at the pumping station. The WQ labelled sites (Fig. 4a,d) included a multi-parameter, in-pipe water quality probe (Intellisonde) and an InfraSense RTU. The acquired water quality data included pH, total chlorine, free chlorine, DO, conductivity, temperature, turbidity and 'apparent' colour, i.e., colour from both dissolved and suspended components. Bio-fouling and deposition of calcium carbonate caused by the electrochemical reactions significantly affected the performance of the sensors during the trial. Frequent sensor calibrations were carried out to improve and ensure the quality of the acquired data (Aisopou et al. 2012). The piezometric head and flow data for a 1-hr period which captures a naturally occurring unsteady flow event are plotted in Fig. 5.

The observed rapid flow changes were caused by the upstream pumps switching off at t~1000s followed by switching the pumps on at t~2400 s. As the pumps were switched off, flow reversal occurred between J1 and F&P3 due to the demand at J1 and J2 and the longitudinal profile of the transmission main (Fig. 4a). This is illustrated by the piezometric head in Fig. 5d. The flow reversal was measured as zero by the flow meter at site F&P3 as the output signal was not scaled for negative values (reverse flows). Flow data acquired from the pumping station (the inlet of the transmission main, F&P1 and WQ2 show that no flow reversal occurred between the pumping station and WQ2 which is the pipe section used in this study. The positive flow measured during the pumps shut down period between the pumping station and WQ2 is maintained by the combined action of the surge protection and pressure equalisation schemes which are used to minimise the impact of pump trips and the resulting pressure surges and flow reversals. For example, a 1524mm pipeline provides additional flow into the manifold when the
pumps switch off via a set of infusion valves (Fig. 4b). Any potential water blending or contamination resulting from that additional flow was carefully considered and it was concluded that it would have no impact on the presented results due to the low flow velocity and time it takes to reach WQ2.

Fig. 4. Experimental case study: (a). Longitudinal profile of the water transmission main; (b). Pumping station layout; (c) F&P measurement site: InfraSense & Aquaprove v2; (d) WQ site: Intellisonde WQ probe and InfraSense.

Fig. 5. Dynamic hydraulic behaviour caused by upstream pumps switching off and on: (a) high-frequency pressure; (b) flow; and details of the propagation of the pressure wave are shown in (c) and (d).

Colour, pH and monochloramine obtained from the water quality probes at the pumping station and WQ2 site during the captured fast hydraulic changes are shown in Fig. 6. Poor performance of the turbidity sensors at both WQ1 & WQ2 limited the use of turbidity data. The water quality data used in the presented analysis were acquired
from the pumping station and WQ2. The data from WQ1 was used to benchmark the performance of the in-pipe electrochemical sensors with the reagent-based sensors installed in the pumping station. While the accuracy of the reagent-free water quality sensors gradually deteriorated, their repeatability and good dynamic response combined with frequent grab sampling allowed for a reasonable estimation of the water quality changes occurring in the studied section of the transmission main. The acquired water quality data can be summarized as following (Fig. 6) (i) little temporal variability during steady-state flow conditions; (ii) the observed increase in ‘apparent’ colour (Fig. 6d) was attributed to the re-suspension of sediments caused by the rapid changes in flow velocity similar to observations made by Hoven and Vreeburg (1992) and Boxall and Saul (2005). The magnitude of this increase is within the range of 20° Hazen for WQ2 which indicates a medium to high level of sediments (biofilms and corrosion tubercles); (iii) the rapid changes in flow velocity (Fig. 6b) correspond to significant changes in monochloramine (Fig. 6f); and (iv) changes in the pH (Fig. 6h) correlate with the observed increase in colour.

Three formulations of the monochloramine decay coefficient were applied: i) a single coefficient, $K$; ii) a combined bulk and wall coefficient, $K = K_b + K_w$; iii) the proposed unsteady-state coefficient, $K = K_{us} + K_{us}$ (Fig. 7). When the pumps were off, the flow velocity was considerably reduced which resulted in decreasing the
concentration of monochloramine within 0.02mg/l. This change in concentration is insignificant in comparison to the monochloramine decay following the increase in flow velocity. The maximum monochloramine decay captured at WQ2 following the rapid increase in flow velocity was in excess of 0.2mg/l. Neither the constant decay coefficient nor the combined bulk and wall coefficient managed to accurately model the observed loss in residual monochloramine concentration. A most likely explanation for these observations is that while the combined bulk and wall coefficient takes into account the impact of flow velocity on the monochloramine decay rate, these do not consider the increased disinfectant decay rate caused by the detachment of biofilms and resuspended sediments following the rapid changes in flow velocity.

Fig. 7. Observed and simulated monochloramine concentrations at site WQ2. The simulated concentrations are obtained using: i) constant decay coefficient $K$, ii) combined bulk and wall coefficient, $K=K_b+K_w$, iii) unsteady-state coefficient, $K=K_{ss}+K_{us}$ when $K_{us}$ is applied to a section of the pipe and to the whole pipe. The dotted line shows the occurrences of the quasi-unsteady-state flows.

The U-shape data of monochloramine concentrations confirms that enhanced decay reactions do not occur along the complete pipeline system, but rather in discrete locations based on the size and position of slugs of resuspended material. Therefore, the length of pipe for which $K_{us}$ is applied and the duration depend on the size of the mobilised slug and the flow rate. Furthermore, the value of $K_{us}$ is site and time dependent as the migration of sediments and the conditioning of biofilms might change following a hydraulic disturbance. The calibration process is facilitated by the availability of continuous hydraulic and water quality data from which specific events can be retrospectively extracted. Fig. 7 compares the modelled monochloramine concentration during and after the rapid change in flow velocity for cases when the unsteady-state decay coefficient is applied within the whole pipe and at a discrete location, i.e. 700m upstream of WQ2. The application of a higher reaction rate within the whole pipe results in low monochloramine concentrations over a long time period. This comparison circumstantiates the assumption that the particle mobilisation occurred within a discrete section.

4. Conclusions

The mechanisms that lead to the loss of disinfectant residual in transmission and distribution systems remain little understood. This preliminary study provides a unique insight into the impact of the unsteady flow conditions on the kinetics and decay of chlorine disinfectants by integrating novel instrumentation technologies for continuous high-frequency time-synchronised monitoring with scale adaptive modelling of the hydraulic conditions and their impact on the loss of disinfectant residual.

Based on the acquired hydraulic and water quality data and published studies, it is hypothesised that the change of shear stress, the rate of change of shear stress and the unsteady shear stress are main factors affecting biofilm-
sediment re-suspension (particularly in metallic pipes). Consequently, the proposed unsteady decay coefficient accounts for these phenomena. For quasi-unsteady flows, it considers the change of shear stress and the rate of change of shear stress; while for transient flows the unsteady decay coefficient depends upon the change of shear stress and the unsteady shear stress. The precise mechanisms remain unclear and further research is required to better understand the unsteady turbulent flow behaviour and its impact on the formation and transport of slugs of resuspended material.

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