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Evaluation of Chlorine Decay in Drinking Water Systems for Different Flow Conditions: From Theory to Practice

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Abstract An intensive study was developed to assess the influence of different flow conditions in the chlorine decay of drinking water systems based on a series of experiments tested on a loop pipe linked to the Lisbon water distribution system. Water samples and chlorine measurements were taken under three distinct flow conditions: (1) *steady-state regimes*; (2) *combined flow situations*—an initial steady-state period, followed by successive transient events and a new steady-state period; (3) *isolated flow tests*—steady-state flow regimes and transient flow regimes performed independently. All the tests were replicated for a typical range of Reynolds numbers in real water distribution systems. More specifically, pressure and velocity variations associated with hydraulic transients or water hammer conditions may degrade water quality. The series of results obtained in steady-state flow conditions confirmed the

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rate of chlorine decay increases with the Reynolds number and provided evidence that hydraulic transients have a slowing-down effect on chlorine decay rates.

Keywords Drinking systems · Chlorine residual · Hydraulic transients · Kinetic model · Water quality

1 Introduction

Drinking water systems are essential to every modern society. These infrastructures are exposed to a number of risks, notably involving unexpected material and technological failure of hydraulic and hydromechanical system components, such as leakage occurrence, ruptures in pipes, tanks, malfunction of level regulators, automatic controllers, valves, pumps start-up/stoppages, booster chlorination and surge protection devices. But all these components are needed to achieve the required quality and quantity of the water supplied to the population. These systems must be considered critical in terms of social and economic aspects, and their vulnerability should be a matter of present and future concern.

In water distribution systems the water travels through a complex pipe system where its quality is changed by a series of physical, chemical and biological processes. It is recognized that the sanitation service has direct repercussions on the health of the population, especially in the supply of treated water. Thus, in order to control the water quality, putting hygienic habits into practice and preventing diseases, the treatment and transportation of water includes its disinfection. At this stage a minimum level of residual disinfectant must be guaranteed so as to protect water quality in the distribution system. Chlorine and chlorine compounds are the substances most commonly used in water treatment plants. One characteristic of chlorine is its residual disinfection potential, which prevents the growth of microorganisms throughout the network, which may either remain after treatment or be introduced by contamination because of pipe breaks, maintenance of the network, problems with negative pressure, or the entry of animals and contaminants in the reservoirs (Vieira et al. 2004).

The chlorine is not a conservative substance. Thus, the consumption of its residual depends on factors such as reactivity with water, pipe wall material, hydraulic flow regimes, duration of residence, control of pH, temperature and the presence of organic matter, microorganisms and biofilms, corrosion of pipe walls and so forth. Two components can be considered for chlorine decay: reactions that occur at the pipe walls and those that occur in the middle of the flow (Clark et al. 1993).

Water quality can thus be influenced by the decay of chlorine-based residual, bacterial regrowth, temperature, disinfectant residual and the presence of assimilable organic carbon. The decay of chlorine residual throughout the networks is a prime concern of all water supply managers. The disinfectant is quite important not only as a barrier against pathogenic microorganisms, but also as an overall indicator of water quality. Once it leaves the treatment plant, chlorine is subject to several chemical reactions, decaying along the distribution system.

The decay of chlorine can be influenced by several factors whose effects have not been fully characterized: (1) physical characteristics of the network and system components (Clark et al. 1993; Holt et al. 1998; Hallam et al. 2002)—dead-end sections, tank geometry, pipe material and age; (2) water quality parameters (Powell et al. 2000a; Hallam et al. 2003; Vieira et al. 2004)—temperature, initial chlorine concentration, organic matter, iron content and number of rechlorinations; (3) system operation and maintenance—storage capacity of tanks, real water losses, intermittent operation; (4) and hydraulic conditions (LeChevalier 1990; Menaia et al. 2002), flow conditions and pressure variation. All these effects are superimposed on the hydraulic transport mechanisms that are usually assumed to be either steady or nearly steady, but may not be. One potential water quality degradation process that has been almost completely neglected in the modelling literature is the impact of transient flow conditions. In fact, it is possible that water quality could be degraded not only by increasing the risk of pipe failure due to significant pressure variation, but also by the formation of biofilms, corrosion and/or tuberculation on the pipe wall, more susceptible to transport by high flow velocities.

Considering the effect of flow conditions on chlorine residual, Menaia et al. (2002) showed that the consumption of bulk chlorine residual depends on flow velocities and pipe diameters, for steady-state flow conditions. Other authors have suggested that transient flow regimes may have a direct effect on water quality beyond that caused by the associated structural deterioration of the pipes or negative pressures (LeChevalier 1990; Brunone et al. 1999, 2000). A transient flow regime is characterized by the temporal variation of pressure and flow throughout the water supply system, due to local disturbances. These may include valve manoeuvres, pump trip-off and start-up or an accidental burst pipe, which induce reverse flow and completely different velocity profiles from those in steady-state flow conditions (Ramos et al. 2003). It has been suggested that these flow conditions could lead to a more efficient flow mixing or cause the detachment of biofilm or scaling products (LeChevalier 1990; Brunone et al. 2000). Fernandes and Karney (2000, 2002) have suggested that the inertia and compressibility effects during transient events may lead to changes in chlorine concentrations. In reality, system operation may sometimes change suddenly, creating new hydraulic conditions. Pumps have an on/off cycle, valves are sometimes opened or closed, pipes may break suddenly, and although water is withdrawn more or less continuously from the system, it happens at varying rates. This situation can create an interaction, which should not be neglected, due to the connection between fluid properties (water density and compressibility) and the governing constraint of mass conservation. Since water is only slightly compressible, even a small change in density can produce a significant change in pressure. Elastic effects are manifested through the mechanism of pressure wave propagation, which convey changes in the delivery conditions. It is through the pressure waves that the large values of fluid momentum are adjusted. In fact, it is the truly steady conditions that are rare and short-lived; pipe systems are dynamic and inertia and compressibility effects become important every time a new action occurs or is induced.

Among the motivations for the present study of the effect of transient flows on chlorine decay are: i) recent research into the influence of steady-state flow conditions on chlorine residual decay; ii) possible relations between transient flow characteristics and water quality problems; iii) the little experimental evidence for such relationships. This paper thus aims to provide a set of experimental results that relate the decay of chlorine to the occurrence of transient events. The experimental set-up was developed to simulate transient pressure flow conditions, induced by typical hydromechanical manoeuvres. Some results relative to the decay of chlorine in steady-state flow conditions are also presented and a comparative analysis is presented.

2 Methodology and Objectives

Water quality modelling is based on the hydraulic conditions in the system to evaluate flow paths in the pipeline system, the mixing from different sources, the dilution of contaminants and the travel/detention times. Steady-state models have traditionally been used, but more recently a complete one-dimensional transient model has been coupled to a chemical transport model (Fernandes and Karney 1999). After a brief description of the theory associated with the chlorine decay modelling process, extensive experimental work is presented to show an interesting and innovative analysis of how transient flow regimes can influence the decay of chlorine residual compared with the decay observed in steady-state flow conditions, for the same initial Reynolds numbers (Ramos et al. 2001; Loureiro 2003). The steady-state test is designed to characterize the decay of chlorine under steady-state flow conditions and provide a database to evaluate the decay of chlorine during transient events. The transient tests were developed to analyze if transient flow regimes could influence the decay of chlorine decay.

Each test involved a preliminary procedure intended to establish the hydraulic flow conditions, viz., the steady-state flow regime, and to add chlorine and humates. Humates are the most common form of organic matter present in finished water and are therefore the main factor in chlorine decay. The compounds were added to the system at an upstream sampling point, using a peristaltic pump. After the preliminary procedure, three tests were carried out in order to monitor the chlorine concentration during different flow regimes. The steady-state flow conditions were established based on typical Reynolds numbers in real water supply systems. To monitor the required chlorine concentrations at each test time water samples were analysed using the DPD ferrous titrimetric method (APHA 1998).

3 Chlorine Decay Modelling

3.1 Dynamic Models

Valve manoeuvres, pump trip-offs and start-ups and accidental burst pipes are typical events that generate the transient flows considered during the design of pipe systems. Even though knowledge of the type of actions that induce stronger effects on the pressure variation is useful, the correct prediction of pressure wave propagation, especially the damping effect, is not always properly accounted for, and this influences the system's re-operation, advanced model calibration and dynamic behaviour of the system response. Any disturbance induced in the flow propagates at an elastic wave speed (c) that will strongly influence the dynamic response in the pipeline. Pressure transients are usually described by the water hammer equations of the continuity and momentum. The basic differential equations of fixed pipes and unsteady pressurised flows can be further simplified to a hyperbolic system of equations which can be presented in matrix form as follows (Ramos 1995; Ramos et al. 2009):

$$\frac{\partial U}{\partial t} + \frac{\partial F(U)}{\partial x} = D(U) \tag{1}$$

yielding the following vectors:

$$U = \begin{bmatrix} H \\ Q \end{bmatrix} \quad F(U) = \begin{bmatrix} \dfrac{c^2}{g\,A} Q \\ g\,A\,H \end{bmatrix} \quad D(U) = \begin{bmatrix} 0 \\ -\dfrac{J\,g\,A}{Q^2} Q\,|Q| \end{bmatrix} \tag{2}$$

where $x =$ distance along the pipe axis (m); $t =$ time (s); $A =$ cross-section flow area (m^2); $Q =$ discharge (m^3/s); $H =$ piezometric head (m); $J =$ hydraulic gradient (−); $g =$ gravitational acceleration ($m\ s^{-2}$); $c =$ wave speed (m/s).

Based on the same principle, the dynamic evaluation models of the chlorine decay simulate the spatial distribution of chemicals throughout the pipe system, as well as the changes in the network's behaviour, such as varying water levels inside the reservoirs, the start-ups and trip-off of pumps, variation of flow regimes in pipes and rapid changes in demand. These models are based on 1D-dimensional flow, a steady state regime in the network, instantaneous and complete mixing in nodes, insignificant longitudinal dispersion, with a single chemical with one or more sources of contaminations and the kinetics of the first order decay that occur in the flow and in the wall pipe region. They are based on the mass conservation laws.

The primary water quality processes within a pipe are advection, diffusion and dispersion, chemical reactions, biological reactions, interactions at the inner pipe surface and external sources and sinks. These processes can include the simultaneous transport of multiple substances and their interactions. The mass transport of a single chemical, herein described for chlorine decay, is the 1-D advection-dispersion-reaction equation (ADR), and without source and sink terms, represented by

$$\underbrace{\frac{\partial C_i(x,t)}{\partial \mathrm{t}} + V_i \frac{\partial C_i(x,t)}{\partial x}}_{\text{advection}} + \underbrace{D\frac{\partial^2 C_i(x,t)}{\partial x^2}}_{\text{dispertion}} + \underbrace{R\left[C_i(x,t)\right]}_{\text{chemical and biologic reactions}} = 0 \tag{3}$$

in which i—pipe branch; Ci(x,t) is the substance concentration at a point; Vj is the average pipe velocity in the pipe i; D is the longitudinal dispersion coefficient; R [Ci(x,t)] is the rate reaction.

Fernandes and Karney (1999, 2000, 2002) present the finite difference method applied to the advection equation with reaction (Eq. 3) to find the solution, taking into account the basic grid used for the hydraulic simulation by the Method of Characteristics (MOC). There is a mismatch in the time scales between the advection and the water hammer effect and these researchers propose a procedure based on an accumulation of the mass flux over a number of hydraulic steps to appropriately extend the water quality time step. It is assumed that the disinfectant concentration source is constant and known for C(0,t), and the initial condition C(x,0) is also assumed to be known. Thus, the mass balance equation for the defined control volume can be written as (Fernandes and Karney 1999):

$$V\frac{\partial C}{\partial t} = (J_{in} - J_{out})\,A - KV\overline{C} \tag{4}$$

where $\overline{C}$ is the average concentration in the control volume, based on the concentrations for the grid points of a given control volume $\left(C_{x-1}^{t}, C_{x-1}^{t+1}, C_{x}^{t}, C_{x}^{t+1}\right)$; A = cross sectional area; J_{in} = flux of mass entering the control volume; J_{out} = flux of mass that is leaving the control volume; and K = chemical reaction sink.

3.2 Kinetic Models

Clark et al. (1993) and Vieira et al. (2004) developed models to represent the decay of chlorine residual in distribution systems. They usually consider two components: one related to the flow and another related to the region next to the pipe walls. The loss of chlorine residual in pipe networks is a function of many factors, including the speed of the flow, the residence time, the pipes' diameter, the bulk decay and the wall decay, in the region close to the pipe wall, which make it hard to maintain optimal residual disinfection in water distribution systems. Regarding the model with a combination of effects in the flow and in the region of the wall, it is common to adopt first-order kinetic modelling to estimate the chlorine decay (Tamminen et al. 2008). The performance of the water quality models is sensitive to the values of kinetic constants, so the determination of these values is fundamental to representing real systems.

For the study of kinetic constants, the chlorine residual monitoring and laboratory analyses must be developed. It is widely accepted that chlorine in distribution systems decays due to reactions with compounds contained within the bulk water (bulk decay) or due to reactions at the pipe wall (wall decay) (Powell et al. 2000a, b; Hallam et al. 2002). In order to model bulk decay, which is the subject of this study, several models have been proposed to find bulk kinetic decay constants. Table 1 summarises some kinetic models used to simulate bulk chlorine decay. The kinetic model usually employed to model bulk chlorine decay within network modelling packages is the first order model (Rossman 2000). Other authors consider that the parallel first order model better reproduces chlorine decay behaviour and provides a more general approach (Vieira et al. 2004).

Available constants for bulk and wall chlorine decay are typically determined under static conditions or inferred from differential network measurements (Clark 1998; Powell et al. 2000b). Due to differences in pipe diameters, and particularly to variations in flow velocity, turbulent mixing varies greatly in space and time in water distribution systems. Such variations may lead to changes in the chlorine residual decay rates, which are not accounted for in currently available chlorine models such as EPANET (Rossman 2000) or Piccolo, despite the fact that velocity and diameter values are available throughout the simulations.

Table 1 Chlorine decay kinetics models

Model	Differential equation	Integrated equation	Adjustable parameters
First order	$dC/dt = -kC$	$C = C_0 exp\,(kt)$	k
Second order	$dC/dt = -kCC_R$	$C = \dfrac{C_0\,(1-R)}{1-Re\,xp\,(-ut)}$	R, u
nth order	$dC/dt = -kC^n$	$C = \left(kt\,(n-1) + \left(\dfrac{1}{C_0}\right)^{(n-1)}\right)^{-\frac{1}{n-1}}$	k, n
Limited first order	$dC/dt = -k(C - C^*)$	$C = C* + (C_0 - C*)\,exp\,(-kt)$	k, C^*
Parallel first order	$dC/dt = -k_1C_1$, $dC/dt = -k_2C_2$ $C_{1,0} = C_0\,x$ $C_{2,0} = C_0\,(1-x)$	$C = C_0x\,exp\,(-k_1t) + C_0\,(1-x)\,exp\,(-k_2t)$	k_1, k_2, x

4 Experimental Procedure

4.1 Experimental Set-Up

The experimental set-up comprised a single pipe loop system with a total length of 200 m (Fig. 1). The pipe material was polyethylene (HDPE), with a nominal diameter of 50 mm (2″). The system was equipped with several valves (i.e., isolation valves and a check valve) and a variable speed pump. A ball valve immediately upstream of the pump was used for generating fast transients.

A peristaltic pump was used for adding chemicals to the system water at an upstream sampling point. A flow meter and five pressure transducers were installed in the system in order to monitor flow and piezometric head during steady-state and unsteady-state flow conditions, respectively. Water samples could be collected

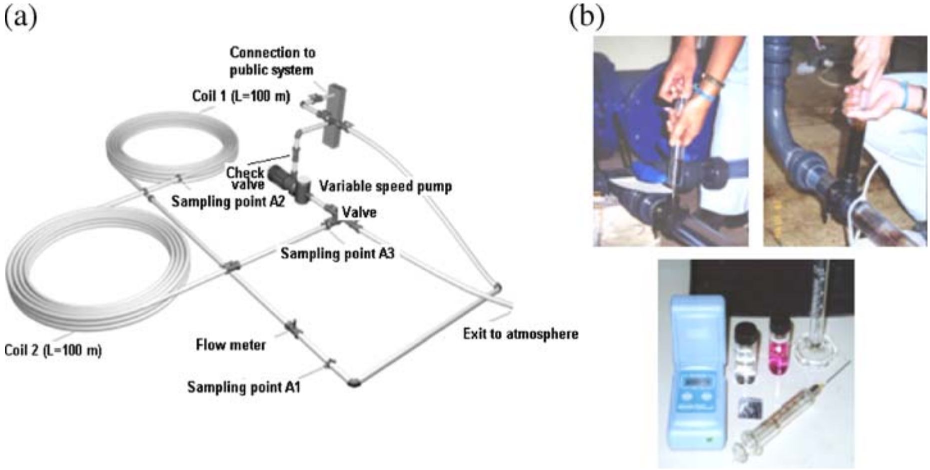


Fig. 1 **a** Pipe loop system; **b** experimental procedures in the analysis of chlorine residual decay—water sample, addition of organic matter, portable meter

throughout the system at three sample points: A1—downstream of the variable speed pump; A2—at the midway point along the loop; A3—upstream of the manoeuvre valve. Sampling was carried out through ϕ 13 mm ports sealed with butyl rubber stoppers, using a hypodermic syringe. As a principle, sampling was always conducted in duplicate throughout the study, having values of chlorine representative of the system, at each time step (Ramos et al. 2001; Ramos and Loureiro 2002; Loureiro 2003).

Table 2 summarizes some design options (and their objectives) considered in order to properly monitor hydraulic and water quality parameters.

4.2 Preliminary Procedure

This extensive experimental campaign at the IST Hydraulic Lab was developed in a specific pipe rig (Fig. 1) connected to the public water distribution system (Ramos et al. 2001; Loureiro 2003). The system was filled with water from the public supply network. Before each test, any trapped air was thoroughly eliminated and the required steady-state flow regime was established through the appropriate setting of the variable speed pump. Chlorine and organic matter were added to the system in order to adequately control initial experimental conditions, using a peristaltic pump. The use of a peristaltic pump allows a better distribution of compounds through the system. Chlorine was added to test water as a sodium hypochlorite solution (5% active chlorine, Panreac), in order to start each test with a stable initial concentration of 1.5 mg/L. After the addition and homogenization of chlorine, organic matter was added to the system. To simulate the organic content of the water, humates (humic acid, sodium salt, Aldrich) were added to make up a total organic carbon (TOC) concentration of around 5 mg/L.

Table 2 Design options and physical characteristics

Design option	Applications/ objectives
Flow circulation—loop system	Necessary to reach equilibrium conditions To establish uniform water quality along the system after the preliminary procedure To analyse the same water over a long period To evaluate chemical processes which may have long reaction rates
Pipe configuration—circular	Circular configuration, with a diameter of 2 m in order to minimize pipe fittings
Pipe diameter—2″	To allow a representative range of Reynolds numbers from distribution systems
Pipe length—200 m	To allow a proper travel time according to experimental procedure
Pipe, valves and pump material—plastic	To decrease the decay of chlorine with pipe, valves and pump material (Holt et al. 1998; Hallam et al. 2002; Menaia et al. 2002) For easy and compatible connections between elements
PVC transparent pipe branches	To confirm the elimination of the air trapped in the systems when the system is filled
No pipe movements	Assuring pipe loop-system stability and minimizes interactions between the fluid and the structure during transient events
Pipe gradient	Enables the elimination of air trapped in the pipe system

In order to study the capacity response to distribute chlorine and organic matter uniformly through the system, determine the number of water samples and quantify the importance of wall demand in the global decay, preliminary tests were performed. It was confirmed experimentally that chlorine and organic matter were really distributed uniformly throughout the pipe system very rapidly and the wall demand was insignificant.

4.3 Steady-State Flow Test

To perform the steady-state test, a set of three water samples (corresponding to one third of the flow cycle throughout the system) was taken at the same section (sampling point A3) and analysed (every 10 min for a 2-h period. The goal was to have representative data about the concentration of chlorine in the test water throughout the system, during the test period. The steady-state tests were carried out with the same flow velocity used during the preliminary procedure to add chlorine and organic matter. The tests described were replicated considering a range of Reynolds numbers in steady-state flow conditions between ≈ 0 and 34,699.

4.4 Combined Flow Test

Three types of flow conditions were considered to study the decay of chlorine residual: (1) a first stage with a total duration of one hour under steady-state flow conditions; (2) a second with a total duration of twenty minutes under unsteady-state flow conditions; (3) a third stage with a total duration of forty minutes under steady-state flow conditions with the same flow velocity as the first stage. In the first stage, the experimental procedure was similar to that used in the steady-state test. The second stage consisted of successive transient flow events, caused by fast closing manoeuvres of an isolation valve (ball valve). Water samples were taken at the sampling point A3 and analysed periodically (5 min).

The tests described were replicated for a range of Reynolds numbers in steady-state flow conditions between 13,880 and 34,699. The range of Reynolds numbers tested was selected based on a study developed to analyze typical ranges in water supply systems which lead, for average flow conditions, to a range of Reynolds numbers between 10,000 and 100,000 and a flow regime corresponding to transition turbulent flow (Ramos et al. 2001; Loureiro 2003). The pressure under steady- and unsteady-state flow conditions was measured using transducers located at three pipe sections (A1, A2 and A3).

4.5 Isolated Flow Test

The goal of this test was to confirm the results obtained in the tests with combined flow regimes using a different procedure, for the same range of Reynolds numbers. In this test, steady-state flow conditions and transient conditions were tested separately. After the preliminary procedure, a steady-state test was performed with a total duration of 60 min. A set of three water samples was collected every 10 min at sampling point A3.

After the steady-state test, the water in the system was completely drained, and the system was refilled with new water supplied by the public system. Following another preliminary procedure, an unsteady-state test was performed with the same initial steady-state flow, as in the corresponding steady-state flow test, and with the same total duration (60 min). Transient flow regime was caused by the successive rapid closing and opening of an isolation valve during the period of test. Water samples were taken at sampling point A3 and analysed periodically (5 min). The tests described were replicated considering a range of Reynolds numbers in steady-state flow conditions between 13,880 and 34,699.

5 Results and Discussion

5.1 Hydraulic Test

Figure 2 illustrates the variation of piezometric head caused by a fast closure manoeuvre of a ball valve (average duration of 0.07 s), placed downstream of the pipe, at three sampling points (A1, A2 and A3). The steady-state flow discharge was 1.5 l/s, corresponding to $V = 1.03$ m/s and $Re = 34{,}699$ and the maximum overpressure (Joukowsky overpressure) was $\Delta H\text{max} = 30.5$ m. It is shown that the pressure response at the sampling point A1 is the reverse of that observed at sampling points A2 and A3, in terms of extreme pressure values. This behaviour is due to the occurrence of positive and negative pressure waves caused respectively downstream and upstream of the manoeuvre valve in the loop-pipe system. The Transient test replicated successive transient events similar to the one illustrated in Fig. 2 for twenty minutes between two steady-state flow regimes with the same flow discharge.

5.2 Steady-State Flow Test

The decay of chlorine is characterized by a first phase, with a high decay rate and a short duration, followed by a second phase with a slower rate (Figs. 3 and 4). In order

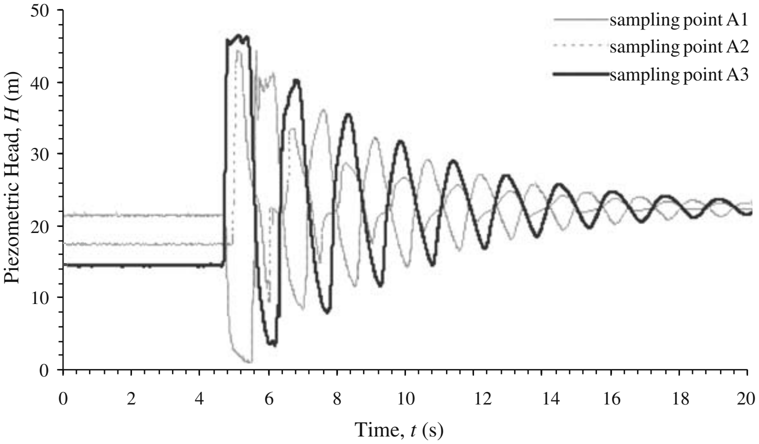


Fig. 2 Experimental measurements of piezometric head time history at sampling points A1, A2 and A3

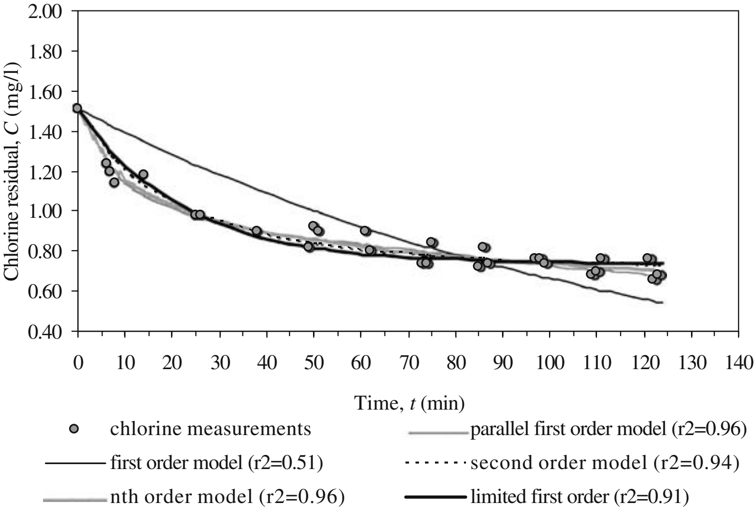


Fig. 3 Model fitting to chlorine measurements using five different kinetic models ($Q_0 = 1.0$ l/s)

to model the behaviour of chlorine residual in steady-state flow conditions, the fitting of kinetic models presented in Table 1 was assessed. Figures 3 and 4 illustrate the fitting of the kinetic models presented as well as the correlation values (r^2) obtained, for Q = 1.0 l/s and Q = 1.5 l/s (similar curves were obtained for all the other flows). For the range of Reynolds numbers tested (0 to 34699), the first order model does not predict the decay of chlorine observed with enough accuracy, providing r^2 below 0.8. The remaining models provided r^2 values above 0.9. The parallel first order model

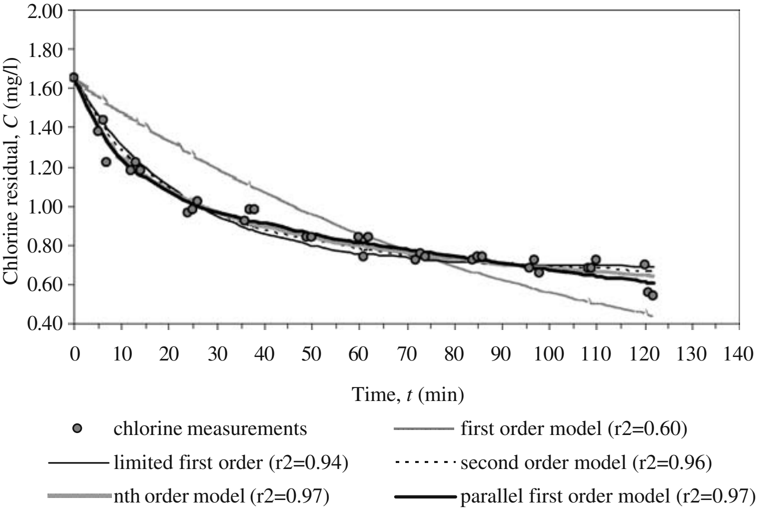


Fig. 4 Model fitting to chlorine measurements using five different kinetic models ($Q_0 = 1.5$ l/s)

and the nth order model provided the best fit to experimental data, with r^2 values above 0.95.

Using the parallel first order model, the decay of chlorine is characterized by the weighted sum of two first order models, which allows characterization of the initial fast decay phase by a kinetic constant k_1 and the second slower decay phase by a kinetic constant k_2. In view of the fact that all the tests involve both phases of decay, the parallel first order model was adopted to obtain the kinetic constants—k_1 and k_2, necessary to compare the results obtained in steady-state tests with the results obtained in the combined flow tests and the isolated flow tests.

Figure 5 illustrates the fitting between the experimental values of chlorine residual and the parallel first order model, for different steady-state flow values—$Q_0 = 0.6$, 1.0 and 1.5 l/s. Furthermore, the results point out that the decay of chlorine residual depends on Reynolds number. Under steady-state flow conditions, the increase of Reynolds number induces an additional turbulence, which will promote the reaction between the components. The results obtained confirm recent research by Menaia et al. (2002), which has shown a direct influence of steady-state flow conditions on the chlorine decay rate. The fact that the parallel first order model was used in this research, as opposed to the simple first order model used in Menaia et al. (2002), allows extra flexibility in analysing the results.

In order to further characterize the correlation between chlorine decay and flow velocity, Figures 6 and 7 show the variation of the kinetic constants of k_1 and k_2 as a function of the Reynolds number. Linear dependency models were fitted to the resulting values, showing significant correlation. Thus, for the conditions tested, there seems to be substantial evidence of a direct correlation between the flow velocity, or flow turbulence (*Re* is directly proportional to V, for constant D), and the chlorine decay constants. It is also a convenient scale-up parameter. For the parameter x, there seems to be no sufficient evidence of a correlation between the Reynolds number, as the values of x show little change across the full range of velocities, having an average value of 0.32 (obtained based on these values:0.366; 0.293; 0.308; 0.364; 0.277). The Reynolds number is defined as $\mathrm{Re} = V.D/\nu$ (with V being flow velocity [m/s], D the internal pipe diameter [m] and ν the kinematic viscosity [$\mathrm{m}^2\ \mathrm{s}^{-1}$]), and is a dimensionless measure of hydrodynamic turbulence.

5.3 Combined Flow Test

The goal of this test was to compare a steady-state test (whose the procedure and results have been given previously) with a combined flow test, based on the same initial steady-state flow conditions (Q_0) during the first hour of test, in order to evaluate the effect of transient flow conditions on chlorine decay. The combined flow test is characterized by a flow regime in steady-state conditions during the first hour, followed by twenty minutes of transient flow conditions and finally by 40 min again in steady-state flow conditions. The last stage of the test had the same flow conditions as the first hour of test.

In order to evaluate the effect of transient flow conditions on chlorine decay, the parallel first order model was fitted to the initial first hour only in both tests (steady-state test and combined test), which corresponds to steady-state flow conditions.

Figures 8, 9, 10, 11, and 12 illustrate the variation of chlorine concentration during the combined flow tests, as well as the curve fitting using the parallel first order model

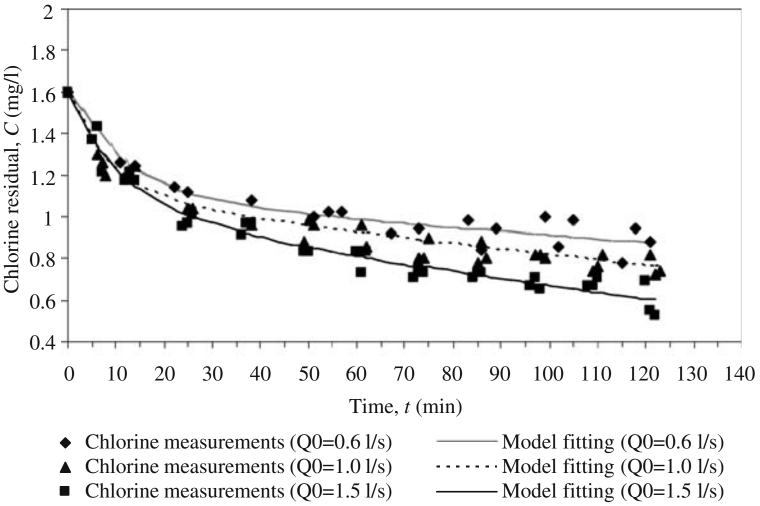


Fig. 5 Chlorine decay tests at different steady-state flow velocities, with parallel 1st order model fitting

Fig. 6 Variation of k_1 with Reynolds number

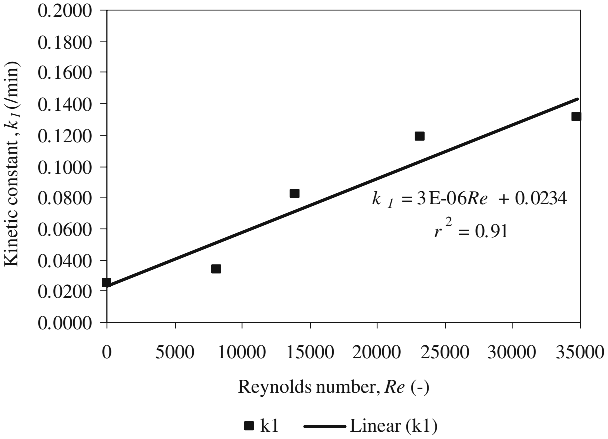
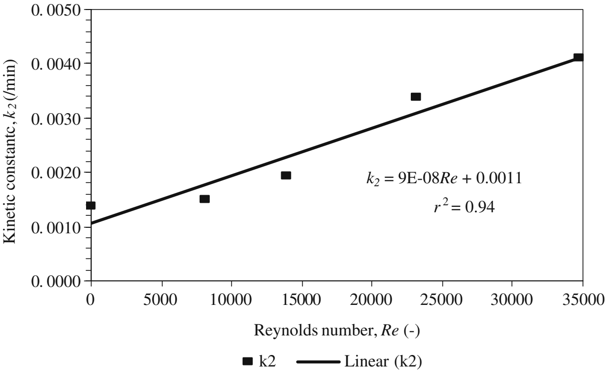


Fig. 7 Variation of k_2 with Reynolds number



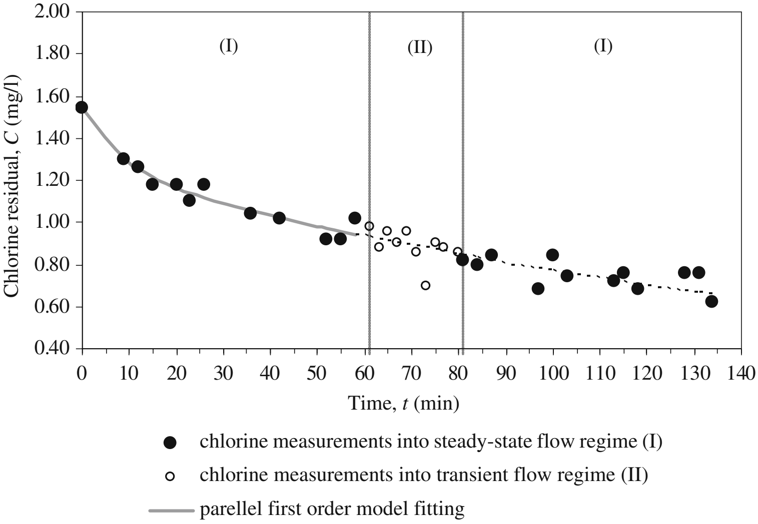


Fig. 8 Chlorine decay for combined flow test with model fitted for initial 60 min only ($Q_0 = 0.6$ l/s)

for the first hour of test, for $Q_0 = 0.6$, 1.0 and 1.5 l/s, respectively. Figures 9, 11 and 13 show the parallel first order model for the first hour of test, for steady-state flow test, for $Q_0 = 0.6$, 1.0 and 1.5 l/s, respectively. It can be seen that the model allows a good fitting to experimental data during the first hour for both types of tests, giving r^2 above 0.94.

Figures 9, 11 and 13 show that, in steady-state conditions, the parallel first order model allows the decay of chlorine during the second hour of test to be predicted with sufficient accuracy. To support the hypothesis that the sample of errors between experimental data and the model, during the second hour, belongs to the same

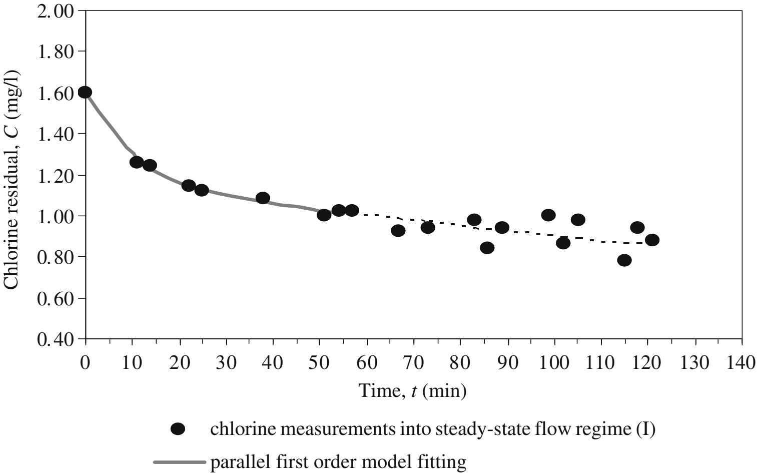


Fig. 9 Chlorine decay for steady-state flow test with model fitted for initial 60 min only ($Q_0 = 0.6$ l/s)

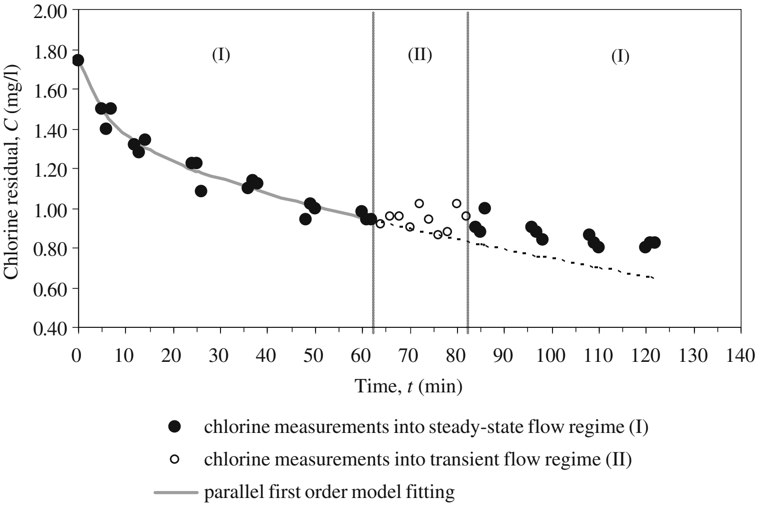


Fig. 10 Chlorine decay for combined flow test with model fitted for initial 60 min only ($Q_0 = 1.0$ l/s)

population as the errors obtained during the first hour, the Kolmogorov–Smirnov test was performed. According to Table 3, and considering that the null hypothesis is that both error samples come from identical populations, it is shown that this hypothesis can be accepted for the values of flow tested, in steady-state flow conditions. This methodology is used to predict the chlorine residual with the support of a kinetic model by comparing the chlorine decay during the second hour observed in a corresponding transient test (i.e., with the same initial steady-state flow discharge) (Table 4).

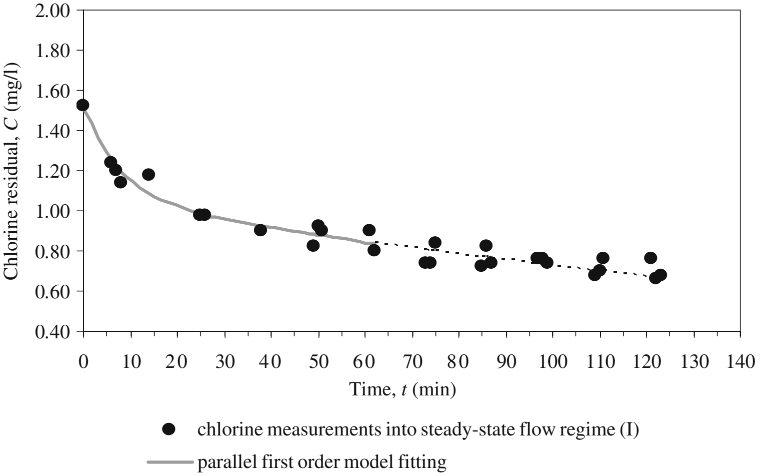


Fig. 11 Chlorine decay for steady-state flow test with model fitted for initial 60 min only ($Q_0 = 1.0$ l/s)

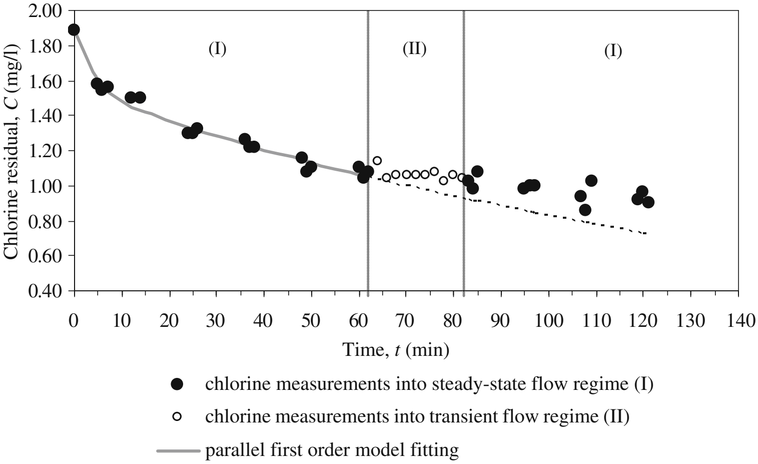


Fig. 12 Chlorine decay for combined flow test with model fitted for initial 60 min only ($Q_0 = 1.5$ l/s)

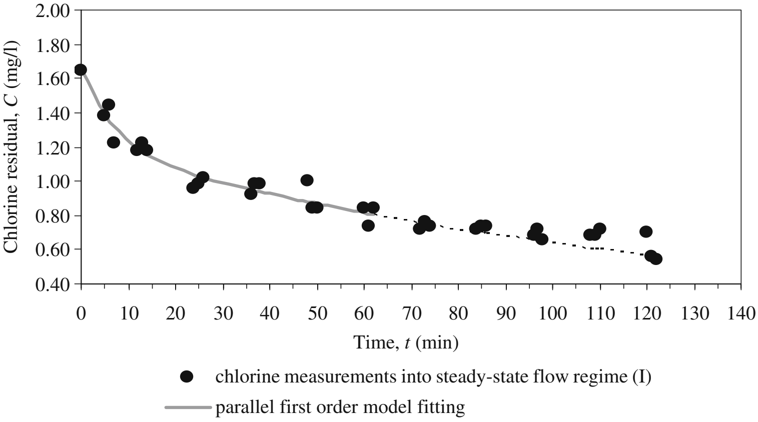


Fig. 13 Chlorine decay for steady-state flow test with model fitted for initial 60 min only ($Q_0 = 1.5$ l/s)

Table 3 Kolmogorov–Smirnov test for Q = 0.6, 1.00 and 1.50 l/s

Q (l/s)	Steady-state test		Combined flow test	
	$T_1 = \max\|S_1(x) - S_2(x)\|$	$w_{0.95}^{(a)}$	$T_1 = \max\|S_1(x) - S_2(x)\|$	$w_{0.95}^{(a)}$
0.60	0.5	0.6	0.29	0.49
1.00	0.4	0.5	0.77	0.43
1.50	0.2	0.5	0.95	0.43

$w_{0.95}^{(a)}$ has to be greater than $T_1 = \max|S_1(x) - S_2(x)|$ for the success of the Kolmogorov–Smirnov test at the level of significance of 95%. Where $S_1(x)$ and $S_2(x)$ are empirical distribution functions of the errors between experimental data and the model in the first hour and the second hour, respectively

Table 4 Parallel first-order model fitting for the first hour only for the steady-state and combined flow test

Q (l/s)	Steady-state test				Combined flow test			
	x (–)	k_1 (min^{-1})	k_2 (min^{-1})	r^2	x (–)	k_1 (min^{-1})	k_2 (min^{-1})	r^2
0.60	0.270	0.1056	0.00260	1.00	0.191	0.1150	0.00480	0.95
1.00	0.274	0.1653	0.00466	0.95	0.208	0.1608	0.00621	0.96
1.50	0.302	0.1087	0.00521	0.94	0.160	0.3343	0.00680	0.98

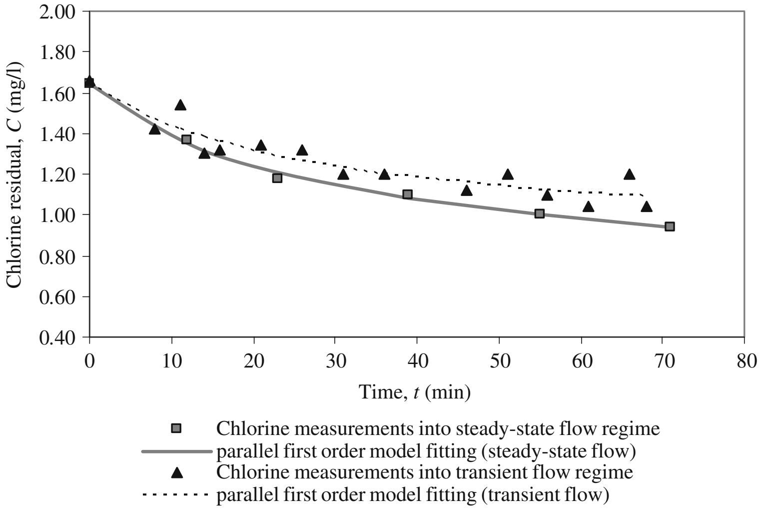


Fig. 14 Isolated flow test for $Q_0 = 0.6$ l/s ($k_1 = 0.96\, k_{01}, k_2 = 0.64\, k_{02}$)

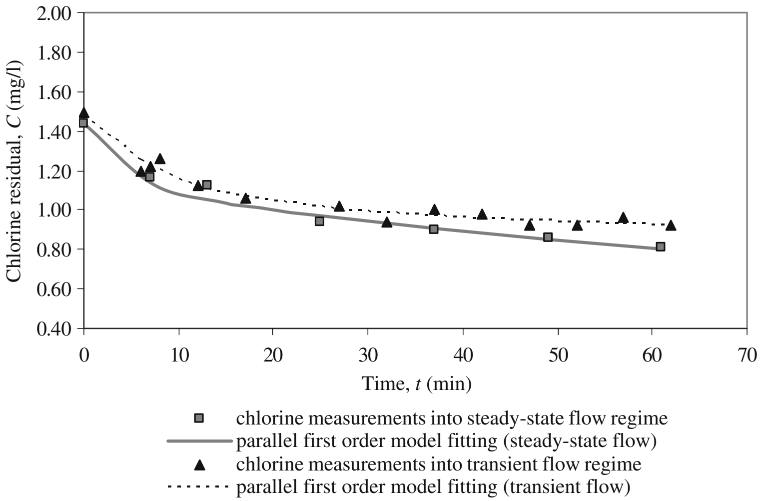


Fig. 15 Isolated flow test for $Q_0 = 1.0$ l/s ($k_1 = 0.94\, k_{01}, k_2 = 0.38\, k_{02}$)

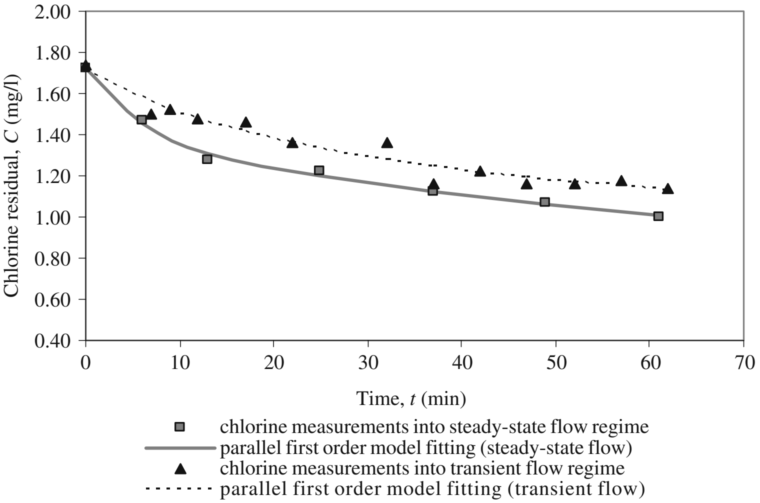


Fig. 16 Isolated flow test for $Q_0 = 1.5$ l/s ($k_1 = 0.4\, k_{01}, k_2 = 0.63\, k_{02}$)

Figures 8, 10, and 12 show that the model underestimates the concentration of chlorine during the second hour. The occurrence of transient events indicates a slowing of the experimental decay rates as compared to the prediction given by the model (Loureiro 2003). However, for lower Reynolds numbers (Q = 0.6 l/s) the effect of transient events was not very significant. The observations are confirmed by the results of the Kolmogorov-Smirnov test, where the null hypothesis is rejected for Q = 1.00 and 1.50 l/s.

Although the characteristic of the water is variable from test to test the results obtained in the combined flow test confirm that, in steady-state flow conditions, the decay of chlorine increases with the Reynolds number.

5.4 Isolated Flow Test

The parallel first order model was fitted to average values of chlorine obtained every 10 min, in steady-state flow conditions, and to the values of chlorine obtained every 5 min, in transient flow conditions. Figures 14, 15 and 16 show the results for the isolated flow test for $Q_0 = 0.6, 1.0$ and 1.5 l/s. It is shown that the kinetic constants k_1 and k_2 decrease in transient flow conditions compared with the kinetic constants k_{01} and k_{02} in steady-state flow conditions.

6 Conclusions

Although hydraulic transients may promote some additional local mixing and consequently increase chemical reactions, particularly in regions of high shear stress, they occur in very short bursts and, in the case of valve closure manoeuvres, lead to significant decreases in the average flow (Reynolds number) at each instant and section of the system. Therefore, in contrast with the results observed for steady-state flow conditions (steady-state test), where chlorine decay increases with the increase in the Reynolds number, a lowering of the decay rates may be expected during the tested transient events, and this was confirmed by the results obtained. The transients are quite important and occur frequently in any water pipe system several times a day. They induce strong pressure fluctuations and consequently wall-shear stress and high levels of turbulence. However there are different types of turbulences: by velocity increasing or by flow-stoppage. This study bring here the influence of flow-stoppage with safe results in terms of water quality, but on contrary in terms of hydraulic behaviour that can put in risk the all system by ruptures or leaks occurrence.

The results of the research described lead to the following main conclusions:

- The decay of chlorine during steady-state flow conditions is characterized by an initial phase with a high decay rate followed by a second phase with a slower decay rate.
- The parallel first-order model allows a proper description of chlorine decay during steady-state flow conditions without the occurrence of transient events.
- The kinetic constants k_1 and k_2 increase with the Reynolds number in steady-state flow conditions, confirming the research of Menaia et al. (2002).
- The parameter x of the parallel first-order model is not significantly influenced by the Reynolds number.
- The occurrence of transient flow conditions, caused by rapid closing manoeuvres, changes the chlorine decay rate. During transient flow conditions, the decay rate decreased compared with the results obtained during an equivalent period under steady-state flow conditions (Ramos et al. 2001; Loureiro 2003).
- The effect of transient events on chlorine decay, compared with the decay during steady-state flow conditions, is more relevant for higher initial Reynolds numbers (Loureiro 2003).

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