Accounting for the influence of initial chlorine concentration, TOC, iron and temperature when modelling chlorine decay in water supply

Paula Vieira, Sérgio T. Coelho and Dália Loureiro

ABSTRACT

Degradation of water quality in supply and distribution systems is one of the foremost problems that water companies are faced with. It is everyday practice in many countries to maintain a residual quantity of a disinfectant such as chlorine throughout the system, in order to ensure the safety of distributed water. However, the chlorine added at the water treatment plant disappears as it travels to the consumer tap, due to reactions in the bulk of the flow and at the pipe walls. This paper analyses the influence on free chlorine bulk decay of several water quality parameters, such as temperature, initial chlorine dosage, organic matter and iron content. The performance of five alternative kinetic models for describing the disinfectant behaviour is also assessed, considering both static and steady-state flow conditions. For the conditions tested, a parallel pseudo-first order model provided the best results.

Although, in practice, parallel first order kinetic models fit experimental data better than the classic first order model, most water quality modelling software still relies on the latter as a base choice. The paper discusses practical conditions that may influence model selection for network simulation purposes, and the relevance of the associated errors.

Key words | chlorine, decay, kinetics, modelling, water distribution

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INTRODUCTION

Degradation of water quality in supply and distribution systems has an impact on public health, on public acceptance of the final product and on the cost of making water reach the customer's tap. Water transport and distribution systems are, from the viewpoint of water quality, akin to large reactors where chemical and biological reactions take place, both in the bulk of the supplied water and at the interface between water and system components such as pipes, fittings and storage tanks.

Distribution of pathogen-free water for human consumption is, in this respect, the chief objective of water suppliers. Disinfection has been a widespread treatment practice in trying to achieve this goal, by destroying pathogenic organisms and preventing waterborne contamination. The most widely used disinfectant is chlorine. The

maintenance of a residual quantity of chlorine throughout the system, in order to ensure the microbiological safety of distributed water, is a current practice in many countries worldwide. The purpose of this chlorine residual is the prevention of regrowth of micro-organisms that have escaped treatment or entered the distribution system itself due to external contamination caused by pipe breakage, maintenance works, negative pressure-driven intrusion, incursion of insects, birds and rodents in storage tanks, and other causes.

The residual chlorine concentration added to the treated water at the entrance of a transport and distribution system does not remain constant during the transport to the consumer tap; it gradually lowers as chlorine reacts in the bulk phase of the water and at the wall

interface of pipes and tanks. Decay may lead to the total disappearance of the disinfectant, thus increasing the probability of microbiological contamination. The effect becomes more relevant in network zones with high water travel times, such as network ends with low consumption. This paper reports on laboratory research on the influence of several water quality parameters, such as temperature, chlorine dosage, organic and iron content on the rates of chlorine bulk decay. The performance of five alternative kinetic models for describing these reactions is also assessed, considering both static and steady-state flow conditions.

The study of water quality changes in distribution systems can clearly benefit from the use of computer-based mathematical models. Besides requiring a rigorous calibration of the underlying hydraulic model, the use of such water quality models demands an accurate determination of the kinetics of the modelled constituent (if non-conservative, as is the case with chlorine), by means of field and laboratory studies performed on the very same water that flows in the system.

The classic kinetic model used to describe chlorine bulk reactions, included in most water quality modelling software, is a first order exponential decay model. However, in practice, a parallel first order model (a two phase decay characterized by two decay constants: k'_1 associated with an initial fast decay and k'_2 associated with a second slower decay) provides a better fit of laboratory decay tests. If—given the modelling software's limitations or other circumstances—the first order model must be used, it is important to be able to evaluate the magnitude and significance of the errors associated with the results, in view of the purpose intended and taking into account the errors associated with the analytical methods deployed for the determination of chlorine concentrations. Based on the previous analysis of the influence of water quality characteristics on the chlorine decay, this paper also discusses practical conditions for the application of first order/parallel first order models in distribution networks.

As the reactive behaviour of combined chlorine (e.g. chloramines) is different from free chlorine, it should be noted that this paper only addresses the second form of the disinfectant.

CHLORINE DECAY

The chemical species that result from chlorine dissolution in water participate in several reactions with compounds of organic and of inorganic nature. These reactions are usually grouped into two components, relating to the decay within the water body (bulk decay) and to the decay that occurs through contact with the container wall (wall decay).

In the bulk of the flow, chlorine reacts with easily oxidizable inorganic species present in the treated water, such as ammonia, iron, manganese, sulfides, nitrites and cyanides, as well as with less reactive compounds such as organic compounds (aminoacides, proteins, phenolic forms, etc.) resulting from natural organic matter, from treatment by-products or from system contamination. Table 1 summarizes the inorganic chemistry of such processes.

Although still to be fully understood, most common chlorine reactions with organic matter include substitution (hydrogen by chlorine), oxidation (total to CO_2 or only partial) and addition to multiple bonds. According to Kastl *et al.* (1999), partial oxidation is the main component of chlorine consumption, if compared with the chlorination of organic compounds. In general, more reactive compounds with chlorine have aromatic rings with at least one donor group or are nitrogen compounds or aliphatic compounds with oxygen atoms (Jadas-Hécart *et al.* 1992). The absence of those structures in organic compounds will lead to a lower reactivity, as in the case of lipids and carbohydrates. Given the contents of common distribution water with respect to such organic and inorganic species, it can be argued that the most relevant factors for bulk water quality studies are organic matter, iron and manganese.

Apart from bulk consumption, chlorine also decays due to interaction with pipe and tank walls and fittings. This wall decay, which includes reactions with the wall material itself (for example, due to corrosion phenomena), with adhering biofilms and with accumulated sediments, is mostly a function of pipe characteristics: material, inner coating, age, diameter and presence of attached biomass. The present paper addresses only the bulk component of the decay.

Table 1 | Chlorine reactions with inorganic compounds in the bulk of supplied water (based on Sawyer & McCarty 1978 and White 1999)

	Reactions
Iron	
In water supply, iron usually occurs naturally in groundwaters or can be a product of the degradation of metallic materials from the distribution system. Chlorine reaction with this species consists of the oxidation of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}). In general, the first one is present in water in the form of bicarbonate, which is slightly soluble and the second one, depending on the hydroxide content, may hydrolyse quickly to ferric hydroxide, which precipitates as a red solid. The reaction, which is extremely rapid in solution, proceeds over a wide range of pH (4–10), the optimum value being pH$\geq$7. Both free and combined chlorine can react this way. If iron is in an organic form, the velocity is considerably lower.	Global reaction (omitting the formation of ferric ion): $2\ Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)$ $\rightarrow 2\ Fe(OH)_3 + CaCl_2 + 6\ CO_2$
Manganese	
Free chlorine oxidizes manganese compounds that precipitate as manganese dioxides. This type of reaction is not important if the disinfectant is chloramine or other form of combined residual. The reaction, which is slow (2 to 4 hours to reach completion), proceeds over a range of pH 7 to 10, the optimum being the higher values. If manganese is in an organic form, the velocity is even lower.	$MnSO_4 + Cl_2 + 4\ NaOH$ $\rightarrow MnO_2\downarrow + 2\ NaCl + Na_2SO_4 + 2\ H_2O$
Nitrites	
Free chlorine oxidizes nitrites present in the distributed water to nitrates.	$HOCl + NO_2^- \rightarrow NO_3^- + HCl$
Hydrogen sulfide	
Hydrogen sulfide gas, usually present in groundwaters, reacts instantaneously with chlorine to form sulfur or sulfate. In the first case, sulfur precipitates as colloidal white particles. At pH below 6.4 all sulfides are converted into sulfates (complete oxidation), at pH 7 30% of the sulfides present are completely oxidized to sulfur and at pH between 9 and 10 this fraction equals 50%.	Sulfur precipitation: $H_2S + Cl_2 \rightarrow S\downarrow + 2\ HCl$ Complete oxidation: $H_2S + 4\ Cl_2 + H_2O \rightarrow H_2SO_4 + 8\ HCl$
Cyanides	
At pH > 8.5, chlorine reacts with cyanides giving origin to cyanates. Complete decomposition of cyanides to gaseous nitrogen can occur between pH 8.5 and 9.5. In this case the carbon atom is converted to bicarbonates.	Conversion to cyanates: $2\ Cl_2 + 4\ OH^- + 2CN^- \rightarrow 3\ CNO^- + 4\ Cl^- + 2\ H_2O$ Formation of nitrogen gas: $5\ Cl_2 + 10\ OH^- + 2CN^- \rightarrow 2\ HCO_3^- + N_2\uparrow + 4\ H_2O$

MODELLING OF CHLORINE DECAY KINETICS

Studies carried out during the last decade in several countries concerning chlorine disappearance in drinking water, have proposed several models to describe the decay kinetics of this disinfectant. Since knowledge is limited on the chemical kinetics of the chlorine reactions in distribution systems, modelling has been based on the consideration of the following global reaction:

$$Cl + Reac \rightarrow Products$$
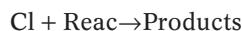
where Cl represents the chlorine species and Reac refers to all species that can potentially react with it. This reaction comprises all the reactions with which chlorine

Table 2 │ Kinetic laws proposed for describing chlorine decay

Model	Differential equation ($dC/dt=$)	Integrated equation	Adjustable parameters
First order	$-k'C$	$C = C_0 \times \exp(-k't)$	k'
Second order	$-k'CC_R$	$C = \dfrac{C_0(1-R)}{1-R \times exp(-ut)}$	R, u
n^{th} order	$-k'C^n$	$C = \left(k't(n-1) + \left(\dfrac{1}{C_0}\right)^{(n-1)} \right)^{-\frac{1}{n-1}}$	k', n
Limited first order	$-k'(C-C^*)$	$C = C^* + (C_0 - C^*)\exp(-k't)$	k', C^*
Parallel first order	$-k'_1 C_1, -k'_2 C_2$ where $C_{1,0} = C_0 x$ $C_{2,0} = C_0(1-x)$	$C = C_0 x \exp(-k'_1 t) + C_0(1-x)\exp(-k'_2 t)$	k'_1, k'_2, x

can participate in drinking water, each characterized by an individual mechanism and kinetics. Due to this complexity and to the fact that the exact composition of Reac remains unknown, the models developed have adopted a 'black box' approach: single reactions that lead to chlorine decay are not taken in consideration separately, but as a whole with a global velocity and global kinetics law representing the fate of the disinfectant.

From the theory of chemical kinetics, it is known that the general rate law for these reactions is expressed by Equation (1)

$$dC/dt = -k \cdot C^n \cdot [\text{Reac}]^m \qquad (1)$$

where C is the chlorine concentration, [Reac] is the concentration of the species that react with chlorine, dC/dt is the rate of reaction, k is the kinetic constant or rate constant of the reaction, n is the order of the reaction with respect to chlorine and m is the order of the reaction with respect to Reac. For a given reaction, k, n and m are independent of the concentrations of the species that participate in the reaction (either chlorine or Reac). n and m are characteristic of a specific reaction but k varies with temperature. In practice, if it is assumed that Reac is in excess over chlorine and, thus, its concentration is almost constant and remains unchanged during the course of the reaction (i.e. [Reac] = [Reac]$_0$), the previous

equation expresses a pseudo-first order rate law of the type:

$$dC/dt = -k' \cdot C^n \qquad (2)$$

where k' is the apparent rate constant. As $k' = k \cdot [\text{Reac}]^m$ (k being the true rate constant of Equation (1)) k' will depend on the concentration of the species reacting with chlorine.

The classic kinetic model for describing chlorine reactions included in most network analysis water quality models is a first order model with respect to chlorine (Haas & Karra 1984; Biswas &Clark 1993; Rossman 1993; Rossman *et al.* 1994; Chambers *et al.* 1995; Vasconcelos *et al.* 1997). A law of this kind means that the reaction velocity is proportional to the concentration of the reactant, the constant of proportionality being the decay constant k' (see Table 2). This model thus represents chlorine concentration as decaying exponentially over time.

In order to upgrade this simplistic first order description of chlorine decay, other studies proposed the kinetic laws presented in Table 2. An nth order kinetic law (Haas & Karra 1984) means that the reaction velocity is proportional to the nth power of chlorine concentration. The limited first order model (Haas & Karra 1984) assumes that a fraction of the initial chlorine concentration, C^*, remains unchanged and only the remainder, $C_0 - C^*$,

decays exponentially according to a first order law. A parallel first order rate law (Haas & Karra 1984) assumes two components to the reaction, each decaying according to a first order law: a fraction x of the initial concentration, xC_0, decays exponentially with a rate constant k'_1 and the remainder, $(1 - x)C_0$, decays also exponentially but with a different rate constant k'_2. A second order model (Clark 1998) with respect to chlorine and all other reactants that contribute to its consumption, Reac, assumes that the velocity of the reaction is proportional to the concentrations of both species.

Although other models that also account for the concentration of organic compounds have been suggested (e.g. Kastl *et al.* 1999), only simple models that require solely the monitoring of chlorine concentration were selected for the present work.

MATERIALS AND METHODS: DETERMINATION OF CHLORINE BULK DECAY CONSTANTS

Since bulk decay is by definition a function of water quality characteristics only, and not influenced by the pipe's characteristics, the decay constants relative to this component of chlorine decay were determined in the laboratory by means of bottle tests. The experiments were performed on water samples taken from a ground source that supplies the city of Almada (Portugal), population 50,000. Chlorination is the only treatment applied to this water and the free residual chlorine concentration entering the distribution system is approximately 0.5–0.6 mg l^{-1}. Water samples for bottle tests were collected at the pumping station, just upstream of chlorination, and rapidly transported, in cooled conditions, to the laboratory.

In a total of 42 experiments, three series of bottle tests were carried out with the aim of evaluating the influence of several variables on the bulk chlorine decay. The initial conditions of each test series are shown in Table 3. In order to study the effect of initial chlorine dosage and of temperature, in series 1, tests were carried out on water samples spiked only with chlorine, in concentrations ranging from 0.1 mg l^{-1} to 4.0 mg l^{-1}. A temperature range of 15 to 25°C was simultaneously investigated.

In series 2, in order to study the effect of the organic content (measured as total organic carbon, TOC), tests were run by adding an organic compound that simulates organic matter. For this series, ran at an intermediate temperature of 15°C, two chlorine concentrations were selected: a high value, 2 mg l^{-1}, and a low value, 0.2 mg l^{-1}. Finally, the influence of iron content was evaluated in series 3, by adding an iron compound to the sample water (which had previously been spiked with chlorine) in the range 0.02–1.5 mg l^{-1}. Once more, an intermediate temperature was chosen (15°C), as well as an intermediate value of chlorine concentration: 1 mg l^{-1}.

In water supply systems, two situations may occur in practice: (a) chlorine is in excess over the reactive compounds that can react with it; or (b) the reactive compounds are in excess over chlorine. Kastl *et al.* (1999) have shown that case (b) is the most frequent in distribution networks. As the prime objective of this work was to address chlorine modelling in distribution networks, the tested ranges of concentrations were selected in order to be representative of real conditions found in such networks, i.e. situation (b).

Chlorine was added as a dilute solution, prepared from a 5% sodium hypochlorite commercial solution (Panreac). Organic material was simulated with indulin (Westvaco), which has a molecular structure similar to humic substances present in source waters. The desired iron concentration was obtained from the dilution of a 1,010 mg l^{-1} commercial standard (Aldrich). A calibrated glass thermometer was used to measure all temperatures. A titrimetric method using DPD as an indicator and ferrous ammonium sulfate as titrant (*Standard Methods* 1995) was used for the residual chlorine determinations. Only free chlorine was measured. TOC analyses were performed using the combustion/infrared method in a Dohrman equipment.

To perform each bottle test (Figure 1), a large volume of spiked water (5 l) was prepared by mixing the water collected in the distribution system with sodium hypochlorite, indulin (only in test series 2) and iron (only in test series 3). Then, this mixture was split into several 300 ml dark glass bottles (Winkler type), completely filled (no headspace) and tightly closed. These bottles were stored in an incubator and, after predefined time steps, were opened and the free residual chlorine was

Table 3 | Experimental conditions of bottle tests

Test series	Test no.	Organic content added to the water (mg l^{-1} TOC)	Iron (mg l^{-1} Fe)	Initial residual chlorine (C_0) (mg l^{-1})	Temperature (°C)
1	1.2.1			0.1	15
	1.2.2			0.2	15
	1.2.3			0.5	15
	1.2.4			1.0	15
	1.2.5			1.5	15
	1.2.6			2.0	15
	1.2.7			3.0	15
	1.2.8			4.0	15
	1.3.1			0.1	20
	1.3.2			0.2	20
	1.3.3			0.5	20
	1.3.4			1.0	20
	1.3.5			1.5	20
	1.3.6			2.0	20
	1.3.7			3.0	20
	1.3.8			4.0	20
	1.4.1			0.1	25
	1.4.2			0.2	25
	1.4.3			0.5	25
	1.4.4			1.0	25
	1.4.5			1.5	25
	1.4.6			2.0	25
	1.4.7			3.0	25
	1.4.8			4.0	25
2	2.1.1	1		0.2	15
	2.1.2	2		0.2	15

Table 3 | *continued*

Test series	Test no.	Organic content added to the water (mg l^{-1} TOC)	Iron (mg l^{-1} Fe)	Initial residual chlorine (C_0) (mg l^{-1})	Temperature (°C)
	2.1.3	5		0.2	15
	2.1.4	7		0.2	15
	2.1.5	10		0.2	15
	2.2.1	1		2.0	15
	2.2.2	2		2.0	15
	2.2.3	5		2.0	15
	2.2.4	7		2.0	15
	2.2.5	10		2.0	15
3	3.1.1		0.02	1.0	15
	3.1.2		0.05	1.0	15
	3.1.3		0.1	1.0	15
	3.1.4		0.3	1.0	15
	3.1.5		0.5	1.0	15
	3.1.6		0.8	1.0	15
	3.1.7		1.0	1.0	15
	3.1.8		1.5	1.0	15

determined. The decay coefficient was estimated by fitting of experimental values (free chlorine residuals vs. time elapsed since the beginning of the test) with the kinetic models for chlorine decay from Table 2.

RESULTS AND DISCUSSION

Kinetic model for chlorine bulk decay

Typical results from a bottle test are presented in Figure 2. As expected, free chlorine disappeared with time as a result of reacting with other species present in the water.
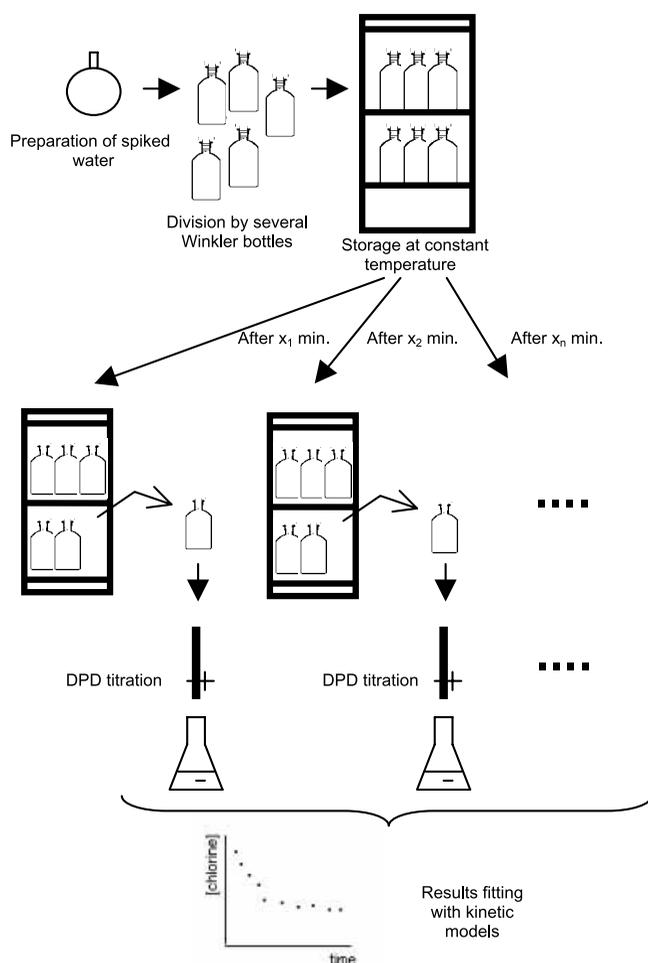
Figure 1 │ Methodology for the determination of bulk decay constant.

In all tests, a fast initial decay was observed, corresponding to the reaction of the more reactive species such as iron (II) and highly reactive organic compounds. This phase lasted for about 15 min for the lower initial chlorine concentrations studied, and 3 h for the higher concentrations. When TOC was added, this value was as low as 3 min. Chlorine consumption in this phase shows a wide variation from 3%, in the case of high initial disinfectant concentrations (~4 mg l^{-1}), to 80%, for low chlorine concentrations (~0.2 mg l^{-1}).

A second, slow and more prolonged decay followed. Now, chlorine is consumed by less reactive compounds such as some organic species (humic substances and proteins) and these reactions took, in some cases, more than 1 month to reach completion. Several authors have already

reported this two-phase decay behaviour (Qualls & Jonhson 1983; Jadas-Hécart *et al*. 1992; Kiéné *et al*. 1998; Wen Lu & Kiéné 1999), although the duration of each phase varies significantly from study to study, due to the dependency on water characteristics. In addition to decay due to reactions with other compounds, and if the time frame allows it, chlorine self-decomposition may take place, though at a much lower rate than the other reactions. This reaction may become significant in the second slow phase of the decay, and after long contact times, in which case the overall decay constant might also be explained by the decay constant of chlorine self-decomposition.

The main objective of performing bottle tests is the determination of bulk decay constants that give a measure of the rapidity of reactions between a disinfectant and all chemicals present in the water that can react with it. In the present work, those coefficients were determined by fitting experimental bottle test results with the five kinetic models (integrated form) listed in Table 2, using non-linear least-squares regression. Typical profiles obtained this way can be seen in Figure 2.

In general, the parallel first order model provided the best fit, with correlation coefficients (r^2) between 0.810 and 0.999. In 74% of the cases this was the most satisfactory model, followed by the nth order model that yielded the best fit in 13% of the cases. Parallel first order decay seemed to be the second most adequate in 44% of the experiments. In only a few tests (20%) did the classic first order model best fit the experimental profiles (correlation coefficients between 0.550 and 0.950), although in the remaining cases the marginal difference from the best models was not significant, justifying the reasonable results obtained in water quality modelling using this simple rate law. Figure 2 also shows that the shape of a parallel first order adjusts more easily to the characteristic curvature of experimental data than others. These results are confirmed by additional research carried out on a 200 m test rig, under steady-state flow conditions, filled with water from the public supply network, then rechlorinated in controlled laboratory conditions to an initial disinfectant concentration of 1.61 mg l^{-1} and tested for a range of Reynolds numbers typical in real water supply systems (0 to 35,000). In these tests, organic matter was also added to achieve an initial concentration of 5 mg l^{-1} TOC.
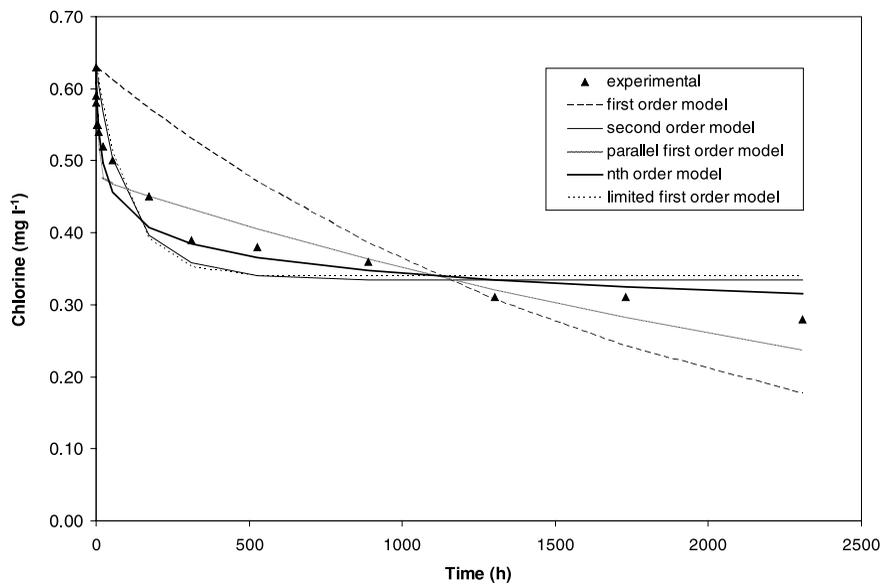
Figure 2 | Fitting of experimental results from a bottle test with alternative kinetic models: typical curves (results from test 1.2.3: C_0=0.63 mg l^{-1}, T=14.6°C; no addition of organic matter or iron).
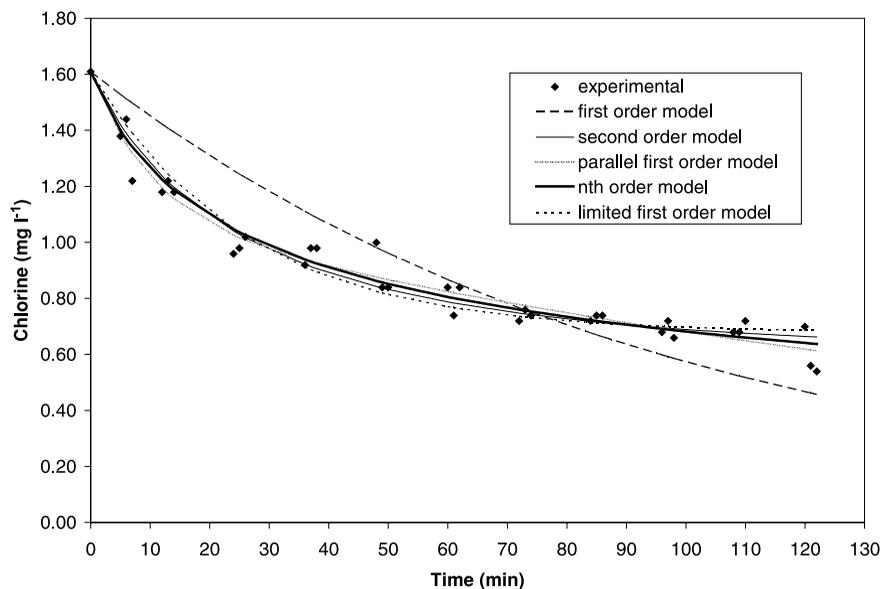
Figure 3 | Fitting of experimental results from a chlorine decay test in steady-state flow conditions: typical curves (C_0=1.61 mg l^{-1}, TOC=5 mg l^{-1}; no addition of iron; flow rate=1.5 l s^{-1}).

Figure 3 illustrates the fitting of the experimental values of chlorine decay, with the same five kinetic models (Table 2), for the maximum steady-state flow value, $Q = 1.5 \, l \, s^{-1}$, corresponding to a Reynolds number equal to 3,500 (similar curves were obtained for all the other flows). Please note that the time scale used in Figure 3 is different to that of Figure 2. For the range of tested Reynolds numbers, results showed that the first order

model allows a poor fitting of experimental values, giving, on average, r^2 values below 0.6. The remainder of the models allow, on average, r^2 values above 0.9. Also as in static conditions (bottle tests) the parallel first order model and the nth order model provided a good fit of experimental data, with average r^2 values above 0.95. Details of this research can be found elsewhere (Loureiro 2003).

Another important advantage of the parallel model relates to the fact that most water quality modelling software only allows the use of a simple first order model while it is more correct to input a value of a decay constant obtained with a parallel fitting (for example, k'_2 if travel times in the system to be modelled are, clearly, on the second decay phase) than one obtained from a first order fitting.

INFLUENCE OF WATER QUALITY ON CHLORINE DECAY

Determination of decay constants by bottle testing is unquestionably the reference method, but also the most expensive and time consuming. Availability of mathematical relationships between decay constants and the factors affecting them, would be of help in obtaining those coefficients in a more expedite way and based only on water quality data already collected in routine monitoring programmes carried out by water companies. In order to apply this procedure, it is essential to know the exact dependence of the constants on each of those variables, this study being done for each distribution system. Figures 4 to 7 show how, in the present work, the bulk decay constant varied with the four parameters mentioned earlier: initial chlorine concentration, temperature, organic and iron content. The existence of possible correlation between this constant and those variables was evaluated using the decay constants obtained with the parallel first order model, as this was the equation that best described chlorine behaviour in the present system.

As already reported by some authors (Fang Hua *et al.* 1999; Powell *et al.* 2000) for a simple first order model, it can be seen that the initial chlorine concentration influences the rate of disappearance of the disinfectant: higher
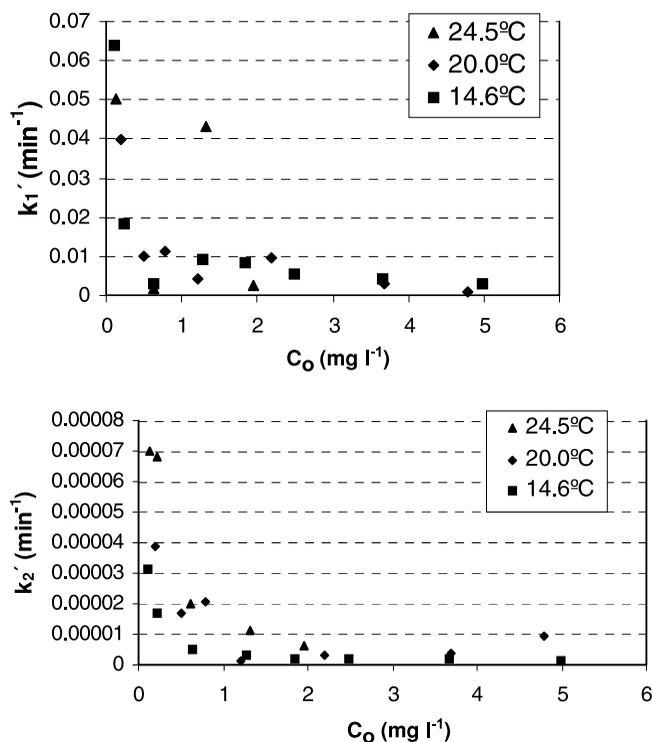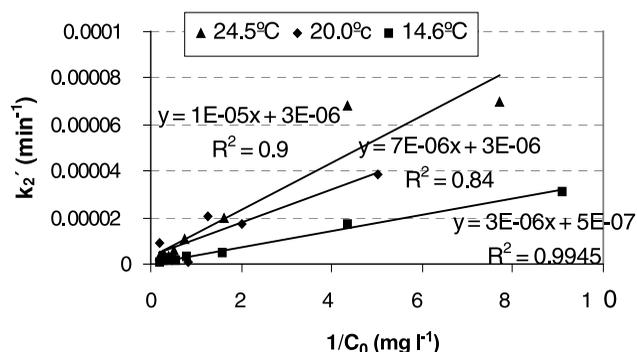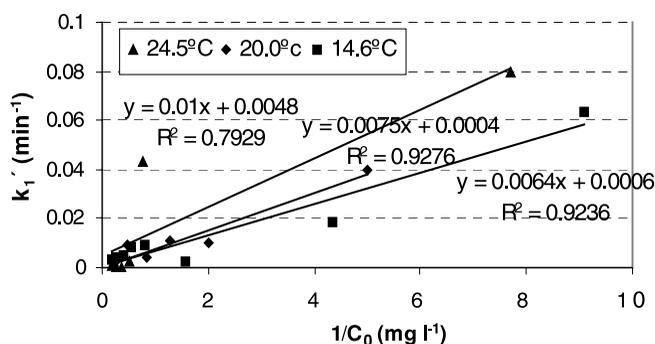

Figure 4 | Influence of initial chlorine concentration, C_0, on bulk decay constants (results from test series 1; T=14.6°C, 20.0°C, 24.5°C; no addition of organic matter or iron).

C_0 values corresponded to slow decays, that is, lower k'_1 and k'_2 values (Figure 4). This variation suggested an inverse relation of the type k_{bulk} vs. $1/C_0$. Indeed it was found that, within experimental limits, k_{bulk} correlates well with $1/C_0$ (correlation coefficients>0.79) (Figure 5).

As a 'true' kinetic constant for a specific chemical reaction is only a function of temperature, the fact that, in the present work, the decay constants vary with the concentration of initial chlorine suggests that different reactions occur for low and high doses as already reported by some authors. For example, UKWIR (1998) argues that the number of available reactive sites (or reactants) varies as a function of the initial dose: the most reactive sites (or reactants) are available even for low doses whereas the less reactive are only available at high doses.

Once again, the self-decomposition of chlorine might be playing a role as a remaining reaction, especially in the case of high C_0.

Figure 5 | Bulk decay constants as a function of the inverse of initial chlorine concentration, $1/C_0$ (results from test series 1; $T=14.6°C$, $20.0°C$, $24.5°C$; no addition of organic matter or iron).
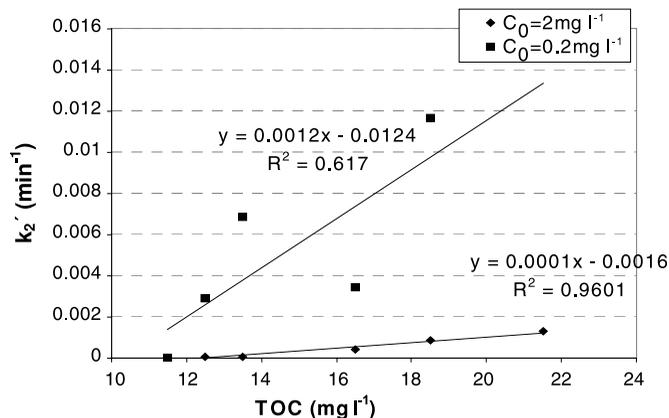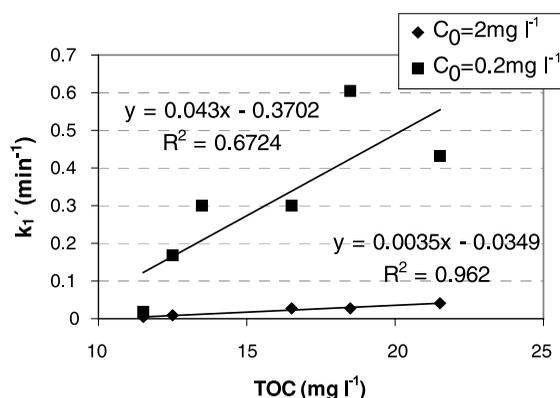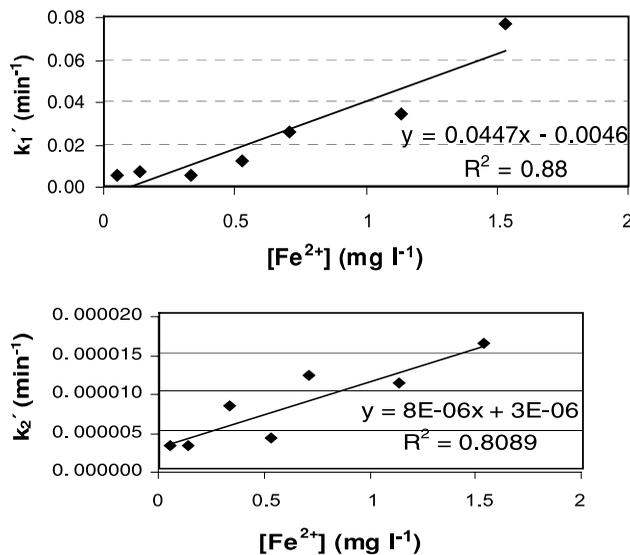

Figure 6 | Influence of TOC on bulk decay constants (results from test series 2; $T=15.0°C$; $C_0=0.2$ and 2 mg l^{-1}; no addition of iron).

Arrhenius's law expresses the change in kinetic constants with temperature and, for most chemical reactions, that coefficient increases with increased temperature. In the present work, results from test series number 1 also show that trend in the case of chlorine decay.

Organic and iron contents were also found to influence chlorine decay. Figures 6 and 7 present the linear relationships between TOC or iron (II) concentration and kinetic constants. As can be seen, good correlation coefficients were obtained in these cases (>0.81). Correlation was poorer in the case of an initial chlorine concentration of 0.2 mg l^{-1}, due to the difficulty in quickly analysing the chlorine in this excessively rapid experiment. It is interesting to note that k'_2 dependence on TOC is stronger (greater slopes) than that of k'_1 (Figure 6), a fact that might denote the importance of reactions of organic compounds in the second phase of the decay. The situation reverses with iron (Figure 7) as its reactions are faster and, therefore, more important in the initial phase of chlorine decay.

In the second stage, organically bound iron can still be reacting slowly with chlorine (White 1999), which means that not all of this metal has reacted in the first stage and explains the fact that k'_2 still has a little variation.

Following the explanation given in a previous section of this paper, the fact that a variation of the kinetic constants with the concentration of reactants (organics and iron) was found, suggests that, in the studied range of concentrations, the reaction has a parallel pseudo-first order and not a parallel first order as initially assumed. Therefore, the decay constants are not true rate constants k, but apparent rate constants k' where $k' = k[\text{organics}]$, in the case of the variation with TOC and $k' = k[\text{iron}]$, in the case of the variation with iron. As, for a given reaction and a given temperature, k has a constant value, as the concentrations of organics or iron vary k' also varies.

Figure 7 | Influence of iron concentration on bulk decay constants (results from test series 3; T=15.0°C; C_0=1 mg l^{-1}; no addition of organic matter).

Finally, taking in account the expression proposed by Kiéné *et al.* (1998) for the relationship between the kinetic constant, temperature and TOC:

$$k' = a \times TOC \times exp\left(\frac{-b}{T}\right) \qquad (3)$$

(where k': kinetic constant, min^{-1}; TOC: total organic carbon, mg l^{-1}; T: temperature, K), and considering the inverse dependency on C_0, a correlation of the type:

$$k' = a \times TOC \times exp\left(\frac{-b}{T}\right) \times \frac{c}{C_0} \qquad (4)$$

has been tested in the present work. The following empirical relationships have been obtained with reasonably good correlation coefficients (R = 0.887 in the case of k'_1 and R = 0.751 in the case of k'_2):

$$k_1' = 0.01344 \times TOC \times exp\left(\frac{848}{T}\right) \times \frac{0.01375}{C_o} \qquad (5)$$

$$k_2' = 0.00209 \times TOC \times exp\left(\frac{848}{T}\right) \times \frac{4.839}{C_o} \qquad (6)$$

CONDITIONS FOR FIRST ORDER MODEL USE

As already mentioned, most water quality modelling software only allows the use of a simple first order model to describe the bulk decay of chlorine. In this situation, the user has to input the value of one decay constant that, in practice, should be obtained from a laboratory decay test fitted with a parallel first order model. The main question that arises from this procedure is, when may a first order model be used with minor errors?

Figure 8 proposes a methodology to determine whether a simple first order model can be used in water quality simulation in distribution systems. The first step is to compare the range of water travel times in the system to be modelled (obtained from a hydraulic model) with the chlorine decay curve (obtained from a bottle test performed in the laboratory with the water that supplies the system to be modelled). If system travel times correspond, clearly, to the second phase of the decay test, then the behaviour of chlorine can be described solely by k'_2 as this is the decay constant that characterizes this phase. In these conditions, the use of a simple first order model has minor errors associated. On the other hand, if the range of water travel times comprises both the first and the second laboratory decay phases, then a thorough evaluation has to be made. In a parallel first order model, if either the first ($C_0 \cdot x \cdot exp(-k'_1 \cdot t)$) or the second member ($C_0 \cdot (1-x) \cdot exp(-k'_2 \cdot t)$) of the equation

$$C = C_0 \cdot x \cdot exp(-k'_1 \cdot t + C_0 \cdot (1-x) \cdot exp(-k'_2 \cdot t)$$

is negligible, the expression becomes a simple first order model, with a kinetic constant equal to k'_2, in the first case, or equal to k'_1, in the second case. The fraction of initial chlorine that reacts by a fast mechanism, x, influences this predominance of the first or the second phase of the decay: for very low or very high values of x, the first order model can be used for practical purposes with minor error. Figure 9, which depicts chlorine decay curves for several conditions, helps us to understand this statement. As can be seen, for high x values (Figure 9a), the total decay curve approaches the decay curve of the first order model with coefficient k'_1. For low x values (Figure 9b), the total decay now comes closer to the k'_2 model. Finally,
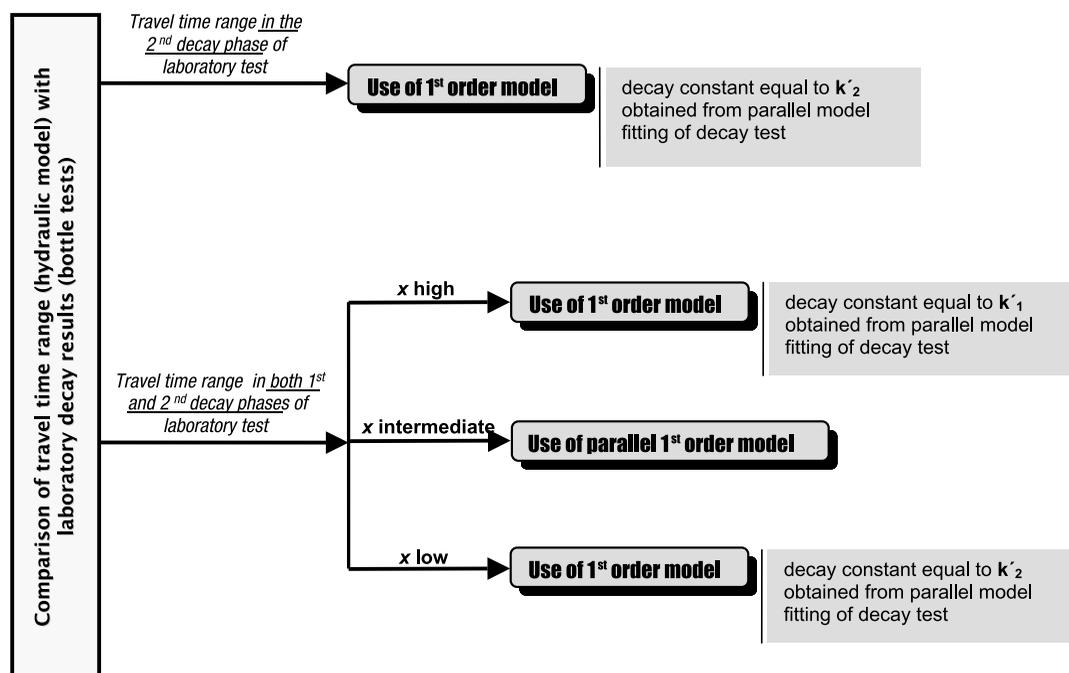
Figure 8 | Decision diagram for first order/parallel first order kinetic model use in water quality modelling.

if x assumes an intermediate value (Figure 9c), then, for quality modelling purposes, a software that enables the use of the parallel first order model must be chosen as the error associated with describing the total decay with a simple first order model may not be negligible.

Furthermore, conditions for first order model application can be set, based upon the variation of fraction x with water quality parameters or, in other words, we can define which ranges of water characteristics determine the use of a simple first order model or a parallel. Figures 10 to 12 present the influence of chlorine, organic (as TOC) and iron concentrations on the variable x. x values were obtained from the parallel first model fitting of the bottle tests previously described in the 'Materials and methods' section.

In the total of 42 experiments, x varied from about 0.05 to 0.9. Figure 10 shows a decrease of x with initial disinfectant concentration, this behaviour being more pronounced at very low C_0. At high concentrations (above 1.5 mg l^{-1}) there is only a slight dependency on chlorine concentration and x becomes extremely low (below 0.1). There is a clear increase of the fraction of chlorine rapidly reacting with increased iron content of the water (Figure

11). Concerning TOC, x can assume very high values (above 0.9) only if chlorine concentration is low and organic content is high (Figure 12).

In summary, water characteristics that lead to high x values are (notice the grey area on Figure 12): low chlorine concentrations (<0.2 mg l^{-1}), especially together with high TOC (>15 mg l^{-1}) and high iron content (although, probably not commonly found in drinking water).

Water characteristics corresponding to low x values are (notice the grey areas on Figures 10 and 11): high chlorine concentrations (>1.5 mg l^{-1}) and low iron content (<0.01 mg l^{-1}).

So, the first order kinetic model should be used carefully if chlorine concentrations are too low or too high and if iron content is too low.

CONCLUSIONS

The changes in water quality that take place throughout the distribution networks are still an underrated question from the point of view of preventive action. In routine
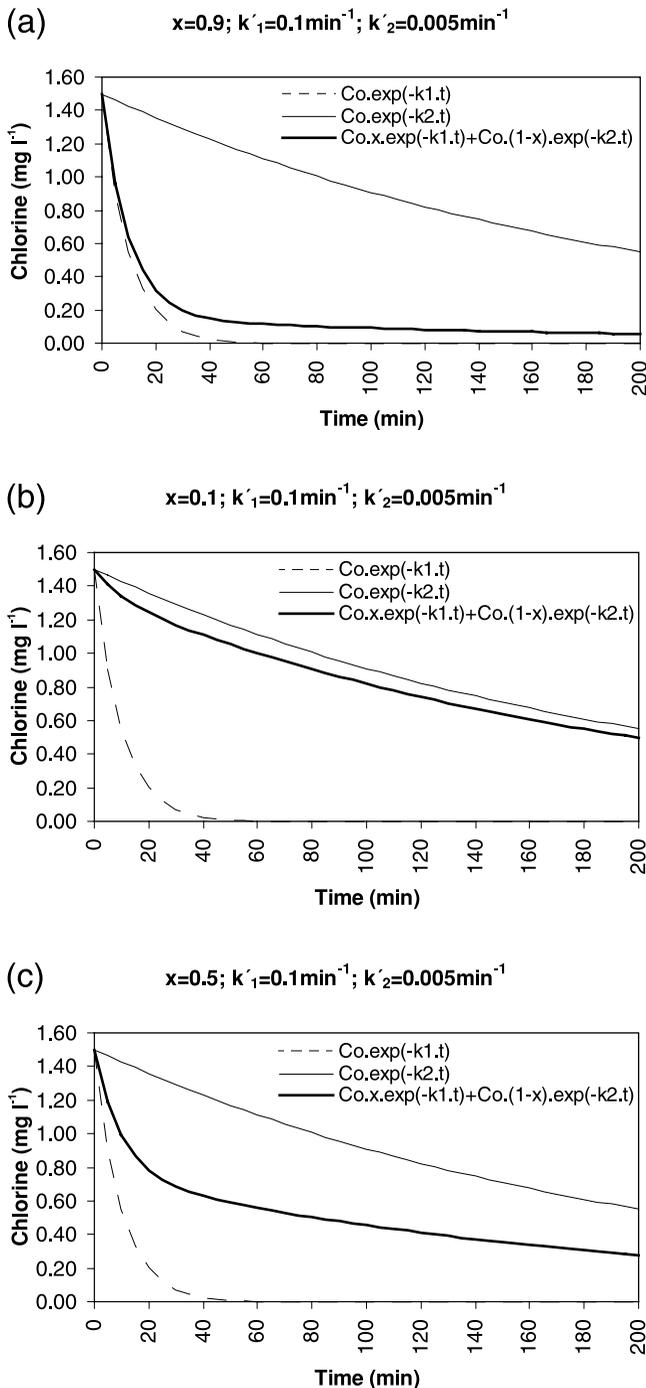
(a)

(b)

(c)

Figure 9 | Examples of chlorine decay curves for several x, k'_1 and k'_2 conditions.

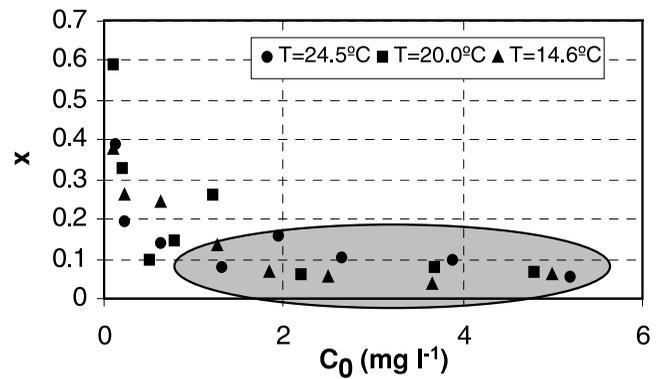**Figure 10** | Influence of initial chlorine concentration on the fraction x (results from test series 1; $T = 14.6°C$, $20.0°C$, $24.5°C$; no addition of organic matter or iron).

Improved understanding of the kinetics associated with changes in water quality taking place in the distribution systems, and particularly those regarding residual chlorine, will afford water supply managers better fulfilment of regulatory requirements, as well as customer satisfaction.

The reported research has led, among others, to the following main conclusions:

- In the bulk of supply water, chlorine decay is characterized by two phases: an initial fast phase where fast reactions occur, followed by a second, slower phase where less reactive species react with the disinfectant. The first, fast phase is relevant not only at the entrance of a distribution system, but
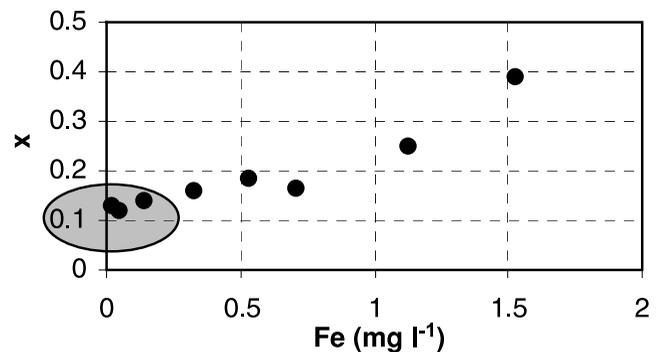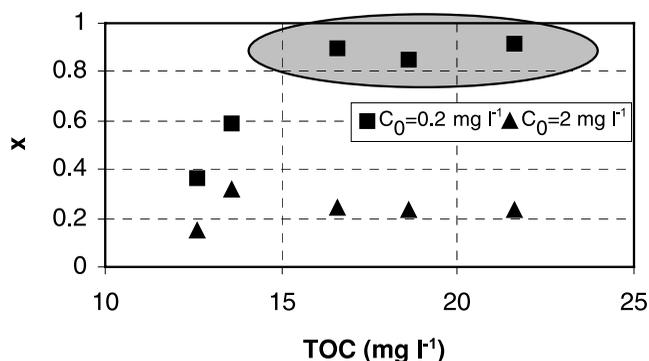
water quality management of supply systems, it is the treatment stage that traditionally absorbs most of the technical and financial resources.

Figure 11 | Influence of iron concentration on the fraction x (results from test series 3; $T = 15.0°C$; $C_0 = 1$ mg l^{-1}; no addition of organic matter).

Figure 12 | Influence of organic content on the fraction *x* (results from test series 2; T=15.0°C; C_0=0.2 and 2 mg l^{-1}; no addition of iron).

also at points where rechlorination or contamination take place.

- For the range of concentrations tested—which is representative of conditions found in water distribution networks—a parallel first order model was the best approach in reproducing the two phase decay behaviour, as opposed to the first order model frequently employed in water quality modelling. This conclusion applied both to laboratory static conditions and to tests carried out in a loop system with steady state flow conditions similar to those found in real distribution systems. This first order model is, in fact, a pseudo-first order model as the experimental rate constants were found to depend on the reactants' concentrations.

- The quality of the supplied water, namely chlorine dosage, temperature, iron concentration and organic content, influences the rate of chlorine bulk decay; therefore, specific laboratory determination of the decay parameters for each particular distribution system and water to be modelled should not be overlooked.

- For a given distribution system, correlations between decay parameters and water characteristics may be obtained from experimental data and later used to predict decay parameters from routine quality control carried out on that same system. Once more, it should be emphasized that such relationships are system-specific.

- Since most water quality modelling software still relies heavily on first order kinetic laws, it is important to evaluate the errors associated with the choice of this model over the one proposed here (parallel first order). If the travel times in the distribution system clearly correspond to the second phase of the decay curve, then those errors are minor. On the other hand, if the travel times comprise both phases, then the errors incurred by the use of a simple first order model increase with the following conditions: too low or too high initial chlorine dosage and too low iron content of the water.

- There is a need for continued research on improved decay models for chlorine reactions to be incorporated in water quality network models.

ACKNOWLEDGEMENTS

NOTATION

k	(true) rate constant
k', k'_1, k'_2	apparent rate constants
C	chlorine concentration
C_0	chlorine concentration
[Reac]	concentration of the species that can react with chlorine
[Reac]$_0$	initial concentration of the species that can react with chlorine
[Fe^{2+}]	iron concentration
C^*	limiting chlorine concentration

n, m	reaction order
x	fraction of initial chlorine that decays with a rate constant k'_1 according to the parallel first order model
t	time
R, u	adjustable parameters from second order model

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