

Evaluation of chlorine decay kinetics expressions for drinking water distribution systems modelling

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ABSTRACT: The decay of chlorine in drinking water involves a complex set of reactions that is usually simplified to first order kinetics in models of water quality in distribution systems. However, to be useful in optimising chlorine dosing regimes, the kinetics expression should accurately describe the shape of the chlorine decay curve for different chlorine doses and be able to simulate re-chlorination. After considering the nature of the reactions involved in chlorine decay, five simplified reaction schemes were evaluated for their suitability to describe chlorine concentration in bulk water. Each scheme was fitted to a sample of experimental data of chlorine decay in raw water obtained from Warragamba Dam (the major source of water supplied to Sydney, Australia). A scheme involving two parallel reactions of organic carbon compounds with chlorine is both necessary and sufficient to satisfy the requirements of modelling chlorine decay accurately.

INTRODUCTION

Chlorine concentration in drinking water diminishes with time. The rate of the decay in bulk water is usually described as a first order reaction [1–5]. This is done with full knowledge that it is not a real mechanism, since the reaction rate of chlorine in pure water in the dark is negligible in comparison to its reaction rate in natural waters. This indicates that chlorine is reacting with some impurities present in natural waters rather than decomposing on its own. Experiments indicate that reaction rate coefficient k (expressed as reaction rate over chlorine concentration) is a function of the initial chlorine dose and amount of chlorine already reacted with this particular water. The first order approximation is based on the assumption that chlorine reacts with organic contaminants in water, which are present in much larger quantities than chlorine. Therefore the concentration of organic contaminants is not significantly changed during the reaction with chlorine and the reaction rate is only proportional to the concentration of chlorine—the so-called pseudo-first-order reaction. This scheme for describing chlorine decay may be sufficient for some applications; namely where the chlorine dose is not varied and when a description is required only from some time after dosing. The main advantage of the first order reaction scheme is its simplicity and available analytical solution, with no need to keep track of any other concentrations but chlorine. It seems that this advantage is the decisive factor even in cases when the first order reaction does not fit the experimental data very well at all. Furthermore the same first order expression is used to describe chlorine decay in a distribution system of pipes and service reservoirs where chlorine decay is due to reaction in bulk water and reaction on the surfaces enclosing it [2,4]. It was suggested that reaction rate

on these surfaces can be correlated with the bulk reaction rate [6]. Another study by Biswas *et al.* [3], considered radial and axial mass transfer with the first order kinetics to describe chlorine decay in pipes. Here the assumption is that the first order kinetics is correct but deviation in pipes is caused by mass transfer and surface reaction. Similarly the value of the first order rate coefficient k is affected by variations in hydrodynamic conditions (laminar/turbulent flow) [7]. This deviation is possibly caused by deviation from the first order reaction kinetics. Changing of the flow pattern then changes reaction time over which reaction rate is measured and since the reaction is not of first order, the reaction rate coefficient k will seemingly change with the flow.

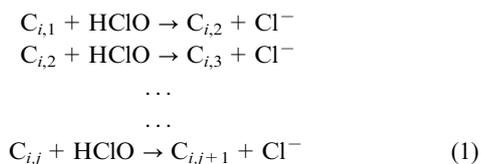
The purpose of this paper is to develop and evaluate a suitable kinetic expression, which faithfully describes chlorine decay in bulk water. Sound representation of the kinetics of chlorine decay in bulk water is considered to be a fundamental element for modelling chlorine decay in a distribution system. Thus, this paper deals with the modelling of free chlorine. Further, the nitrogenous compounds will also react with chlorine, either reducing it to chloride or forming combined chlorine. The authors have presented elsewhere [8,9] the reaction of chlorine with these nitrogenous compounds and the subsequent decomposition of combined chlorine in addition to the reaction of chlorine with organic matter. Also, if iron (in the form of ferrous ion) or manganese (as manganous ion) is present in the bulk water they will contribute to the decay of chlorine. This can be modelled in a similar way to that of organic or nitrogenous compounds. However, if surface water is used to supply the distribution system, the concentrations of nitrogenous compounds, iron and manganese will be generally small compared with that of organic compounds.

Chlorine decay is also known to be influenced by temperature. One value of activation energy (E) for all reactions can be

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used [8,9] to describe the effect of temperature. Using a value of 12 100 K for E/R estimated from experimental data obtained over the temperature range 10–25 °C, a temperature increase of 5 °C will approximately double the reaction rate. R denotes the universal gas constant. As this type of function is likely to describe chlorine decay rates over the expected operating temperature range, the effect of temperature is not considered in this paper.

Most of the chlorine reacting in water is consumed by partial oxidation of natural organic matter, while a small fraction of chlorine is consumed by the chlorination of organic compounds. The complex reaction scheme of chlorine decay can be expressed as a set of parallel and serial reactions as described by Eqn 1.



where $C_{i,j}$ is organic compound i after $j-1$ reactions with chlorine. All organic compounds $C_{i,j}$ ($i = 1, 2, \dots, n$) react simultaneously. In Equation 1, HClO is assumed to react with organic compounds as the reaction between chlorine gas and water is much faster than the reaction between chlorine and organic compounds in water and therefore chlorine gas is first converted into hypochlorous acid (HClO). Subsequently, HClO reacts with organic compounds.

Reaction rate of chlorine decay and organic carbon transformation to a more oxidised form can be described by Eqn 2:

$$r_{i,j} = -k_{i,j} [\text{Cl}] [C_{i,j}] \quad (2)$$

where $r_{i,j}$ is the reaction rate of chlorine decayed in reaction j with organic compound i , $k_{i,j}$ is the corresponding reaction rate coefficient, $[\text{Cl}]$ is the chlorine equivalent concentration of HClO, expressed in mg/L chlorine (i.e. titrated values of chlorine concentration) and $[C_{i,j}]$ is the concentration of the organic compound i after j reactions. Such a scheme, while quite complex and difficult to apply, can describe different shapes of the chlorine decay curves. It should be noted that for practical purposes the oxidation stops before reaching the final product of oxidation, carbon dioxide, so that the value of total organic carbon (TOC) is not changed significantly.

Methodology is developed in this paper to simplify the reaction scheme to the point where it cannot be reduced any further while still accurately describing chlorine decay in bulk water. Models to be evaluated are constructed and solved in AQUASIM modelling software, using the secant and simplex algorithms provided to estimate parameter values for which the model best fits the data [10].

The requirements for a model of chlorine decay in bulk water can be summarised:

- describe accurately chlorine decay profile in bulk water over time;

- describe chlorine decay curves for different initial doses;*
- describe chlorine decay curves of re-chlorination.

These features are necessary to be able to:

- model quality changes in a drinking water distribution network;
- optimise chlorine dose;
- design re-chlorination facilities;
- assess the water treatment process (in terms of stability of the produced water in relation to chlorine).

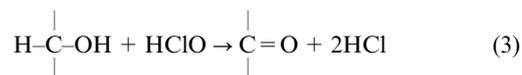
EXPERIMENTS

Chlorine stock solution was prepared by bubbling chlorine gas into demineralised water and diluting it to around 0.4 g chlorine/L. A split sample of Warragamba raw water (the major drinking water source for Sydney) was then chlorinated with the chlorine stock solution at three dosing levels (1, 2 and 4 mg/L). Brown bottles used to keep the samples during experiments were cleaned with sodium hypochlorite solution followed by rinsing with copious amounts of water having negligible chlorine demand. The samples were kept in a water bath at 25 °C. The concentration of free chlorine was measured by the amperometric method using a Wallace & Tiernan analyser. The TOC, pH and alkalinity of Warragamba raw water were 3.66 mg/L, 6.92 and 32 mg CaCO₃/L, respectively. Unfortunately these quality parameters are not an adequate basis for chlorine decay prediction, and chlorine decay experiments have to be performed to derive a predictive model.

MODELLING

First order reaction

Generally, after dosing a certain amount of chlorine, the chlorine decay curve closely approximates a first order reaction. The concentration of chlorine equivalent of organic compounds in water is usually much higher than the concentration of chlorine applied. Here the chlorine equivalent of organic compounds is understood to be an amount of chlorine which would react completely with these compounds. This definition is necessary since it is impossible to characterise the chlorine decay property of naturally occurring organic compounds in any compact way other than by direct reaction with chlorine. For example, oxidation of a hydroxy group to a ketonic group would require 5.8 mg Cl/mg of organic carbon according to Eqn 3.



With an average concentration of TOC in natural water of about 3 mg/L and assuming that all TOC has a single hydroxy

*Describe chlorine decay curves for different temperatures.

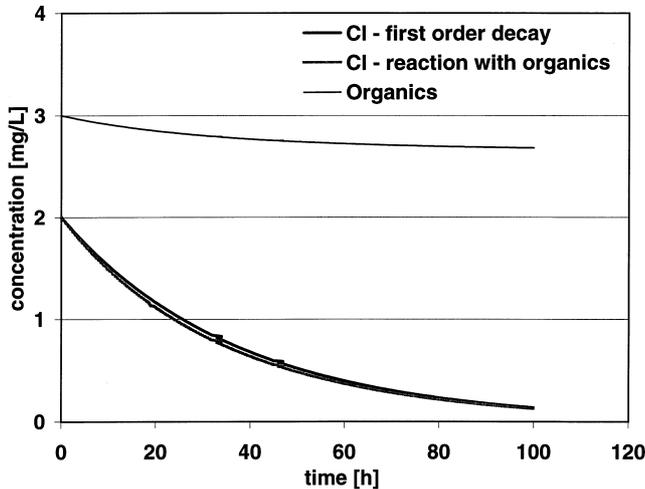


Fig 1. First order decay of chlorine compared with reaction of chlorine with organics (initial chlorine dose of 2 mg/L) and the destruction of organics (initial concentration of organic carbon = 3 mg/L) at a stoichiometric ratio of chlorine : organic carbon = 5.8 : 1.

group attached to carbon, the total oxidation of TOC to a ketonic group would require 17.4 mg Cl/L. Usually only up to 2 mg Cl/L is dosed at water treatment plants to disinfect and provide chlorine residual. Since the concentration of chlorine equivalent of organic compound would change only from 17.4 to 15.4 mg/L while the chlorine concentration changes from 2 to 0 mg/L, the pseudo-first order mechanism seems to be justified.

Figure 1 shows a comparison of a chlorine decay curve based on the first order reaction rate and that based on the reaction between chlorine and organic carbon. The first order chlorine decay is calculated according to Eqn 4 and the reaction rate of chlorine decay in reaction between chlorine and organic carbon is based on Eqn 5.

$$d[Cl]/dt = -0.027 [Cl] \tag{4}$$

$$d[Cl]/dt = -0.01 [Cl] [C_{orgC}] \tag{5}$$

where [Cl] and $[C_{orgC}]$ are the concentrations of chlorine and organic carbon, respectively.

The initial concentrations used for chlorine and organic carbon are 2 mg/L and 3 mg/L, respectively. The reaction rate coefficient of the first order equation was adjusted to fit the chlorine profile of the reaction according to Eqn 4. It can be seen that the first order reaction can ‘simulate’ the reaction with organic carbon to such an extent that it is hard to distinguish both curves. This is caused by the small relative change in organic carbon concentration due to the relatively small chlorine dose and high stoichiometric ratio (chlorine:organic carbon = 5.8:1.0). The situation would be different if either a higher initial dose of chlorine was used or carbon was only partially reactive. Then the concentration of reactive organic

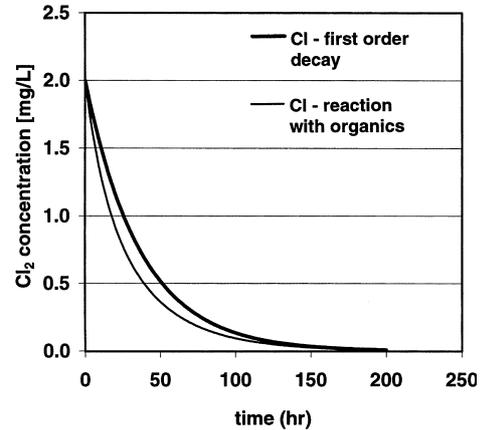


Fig 2. Comparison of depletion due to the reaction with organic carbon (organics) and first order decay of chlorine, when the organic carbon is only partially reactive (initial chlorine dose = 2 mg/L; initial concentration of organic carbon = 3 mg/L; stoichiometric ratio of chlorine : organic carbon = 1.5 : 1).

carbon would be changing during the reaction and it is then not possible to simulate the chlorine time series with the first order reaction. In practice the situation is further complicated because not all carbon is in the form of hydroxy compounds reacting at the same rate.

Figure 2 shows that the first order reaction does not match the shape of the chlorine decay curve with depletion of reducing organic carbon when the organic carbon is only partially reactive. The difference here is quite small but a more serious problem is that it is not realistic to assume that all organic compounds in water exhibit the same reaction rate. Even under these simplified assumptions the reaction rate would change significantly in subsequent re-chlorinations.

Figure 3 demonstrates that a similar discrepancy between first order decay and reaction of chlorine with an organic

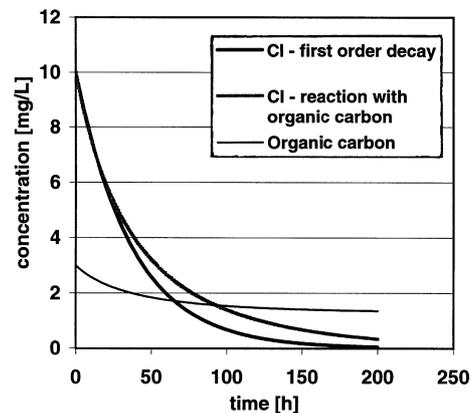


Fig 3. First order decay of chlorine compared with reaction of chlorine with organics (initial chlorine dose of 10 mg/L) and the destruction of organic carbon (initial concentration of organic carbon = 3 mg/L) at a stoichiometric ratio of chlorine : organic carbon = 5.8 : 1.

Table 1 Alternative reaction schemes of chlorine decay

No.	Reaction	Reaction rate	No. of constants
1	$\text{Cl} \rightarrow \text{Cl}^-$	$r_{\text{Cl}} = -k_1 \times C_{\text{Cl}}$	(k_1)
2	$\text{Cl} + \text{C}_{\text{orgC}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC/inert}}$	$r_{\text{Cl}} = -k_2 \times C_{\text{Cl}} \times C_{\text{orgC}}$ $r_{\text{orgC}} = r_{\text{Cl}}$	$(k_2, [\text{C}_{\text{orgC}}]_0)$
3	$\text{Cl} \rightarrow \text{Cl}^-$ $\text{Cl} + \text{C}_{\text{orgC}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC/inert}}$	$r_{\text{Cl}} = -k_1 \times C_{\text{Cl}} - k_2 \times C_{\text{Cl}} \times C_{\text{orgC}}$ $r_{\text{orgC}} = -k_2 \times C_{\text{Cl}} \times C_{\text{orgC}}$	$(k_1, k_2, [\text{C}_{\text{orgC}}]_0)$
4	$\text{Cl} + \text{C}_{\text{orgC1}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC1/inert}}$ $\text{Cl} + \text{C}_{\text{orgC2}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC2/inert}}$	$r_{\text{Cl}} = -k_1 \times C_{\text{Cl}} \times C_{\text{orgC1}} - k_2 \times C_{\text{Cl}} \times C_{\text{orgC2}}$ $r_{\text{orgC1}} = -k_1 \times C_{\text{Cl}} \times C_{\text{orgC1}}$ $r_{\text{orgC2}} = -k_2 \times C_{\text{Cl}} \times C_{\text{orgC2}}$	$(k_1, k_2, [\text{C}_{\text{orgC1}}]_0, [\text{C}_{\text{orgC2}}]_0)$
5	$\text{Cl} + \text{C}_{\text{orgC1}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC2}}$ $\text{Cl} + \text{C}_{\text{orgC2}} \rightarrow \text{Cl}^- + \text{C}_{\text{orgC2/inert}}$	$r_{\text{Cl}} = -k_1 \times C_{\text{Cl}} \times C_{\text{orgC1}} - k_2 \times C_{\text{Cl}} \times C_{\text{orgC2}}$ $r_{\text{orgC1}} = -k_1 \times C_{\text{Cl}} \times C_{\text{orgC1}}$ $r_{\text{orgC2}} = k_1 \times C_{\text{Cl}} \times C_{\text{orgC1}} - k_2 \times C_{\text{Cl}} \times C_{\text{orgC2}}$	$(k_1, k_2, [\text{C}_{\text{orgC1}}]_0)$

Where:

$C_{\text{Cl}}, r_{\text{Cl}}$ = concentration [mg/L] and reaction rate of chlorine [mg/L/h], respectively.

$C_{\text{orgC}}, C_{\text{orgC1}}, C_{\text{orgC2}}$ and $r_{\text{orgC}}, r_{\text{orgC1}}, r_{\text{orgC2}}$ = concentration [mg/L] and reaction rate of organics in [mg chlorine equivalent/L/h], respectively.

$[\text{Cl}]_0$ and $[\text{C}_{\text{orgC}}]_0, [\text{C}_{\text{orgC1}}]_0, [\text{C}_{\text{orgC2}}]_0$ = initial concentrations of chlorine and organic carbon, respectively, k_1, k_2 = reaction rate coefficients.

compound will result when a higher initial chlorine dosage (10 mg/L) is used. This effect will be apparent if more chlorine is dosed, for example, as prechlorination during treatment, or if the fraction of carbon reacting with chlorine is comparable with dosed chlorine. In practice, the situation is complicated because organic carbon is not present as a single compound but as a range of compounds with different affinity for chlorine as described by Eqns 1 and 2.

Alternative kinetic expressions†

As mentioned previously it is not practical to apply a complex

†Five basic reaction schemes describing chlorine decay in bulk water were tested:

1 First order chlorine decay reaction



2 Reaction of chlorine with organic compound



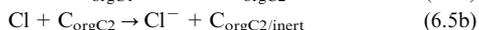
3 Combination of schemes 1 and 2



4 Reaction of chlorine with two types of organic compounds



5 Serial reaction of chlorine with organic compound which has reactive product



reaction scheme with many parameters as described by Eqns 1 and 2. Subsets of the complete reaction scheme selected on the basis of increasing complexity are shown in Table 1. Reaction rate coefficients in Table 1 are different for each reaction scheme. A typical curve with fast initial decay and slow prolonged decay was fitted by each reaction scheme, to test the ability of each scheme to describe essential characteristics of the chlorine decay curve. The results of the fitting are summarised in Table 2. The table also shows the weighted error between experimental data and model (χ^2) which can be used as a criterion of goodness of fit of a model to the experimental data [10]. The weighted error, χ^2 is defined as:

$$\chi^2(\mathbf{p}) = \sum_{i=1}^n \left[\frac{f_{\text{meas},i} - f_i(\mathbf{p})}{\sigma_{\text{meas},i}} \right]^2 \quad (6a)$$

where: $f_{\text{meas},i}$ = i th measured value; $f_i(\mathbf{p})$ = calculated value from the model, using parameter values \mathbf{p} ; $\sigma_{\text{meas},i}$ = estimated standard deviation of $f_{\text{meas},i}$.

During the fitting of the chlorine decay model to the experimental data, the parameters were adjusted by the AQUASIM software [10] until the expression 6b reached a minimum value.

$$\sum_{i=1}^n \left[[\text{Cl}]_{\text{meas},i} - [\text{Cl}]_{\text{model},i} \right]^2 \quad (6b)$$

where, $[\text{Cl}]_{\text{meas},i}$ = i th measured value of chlorine concentration; $[\text{Cl}]_{\text{model},i}$ = value of chlorine concentration calculated from the model.

Figure 4a shows the fit of the first order reaction to the typical chlorine decay data. This is an artificial decay curve based on the experience of authors with chlorine decay in drinking water which is fast initially but slows substantially with time. It is evident that the first order model does not have

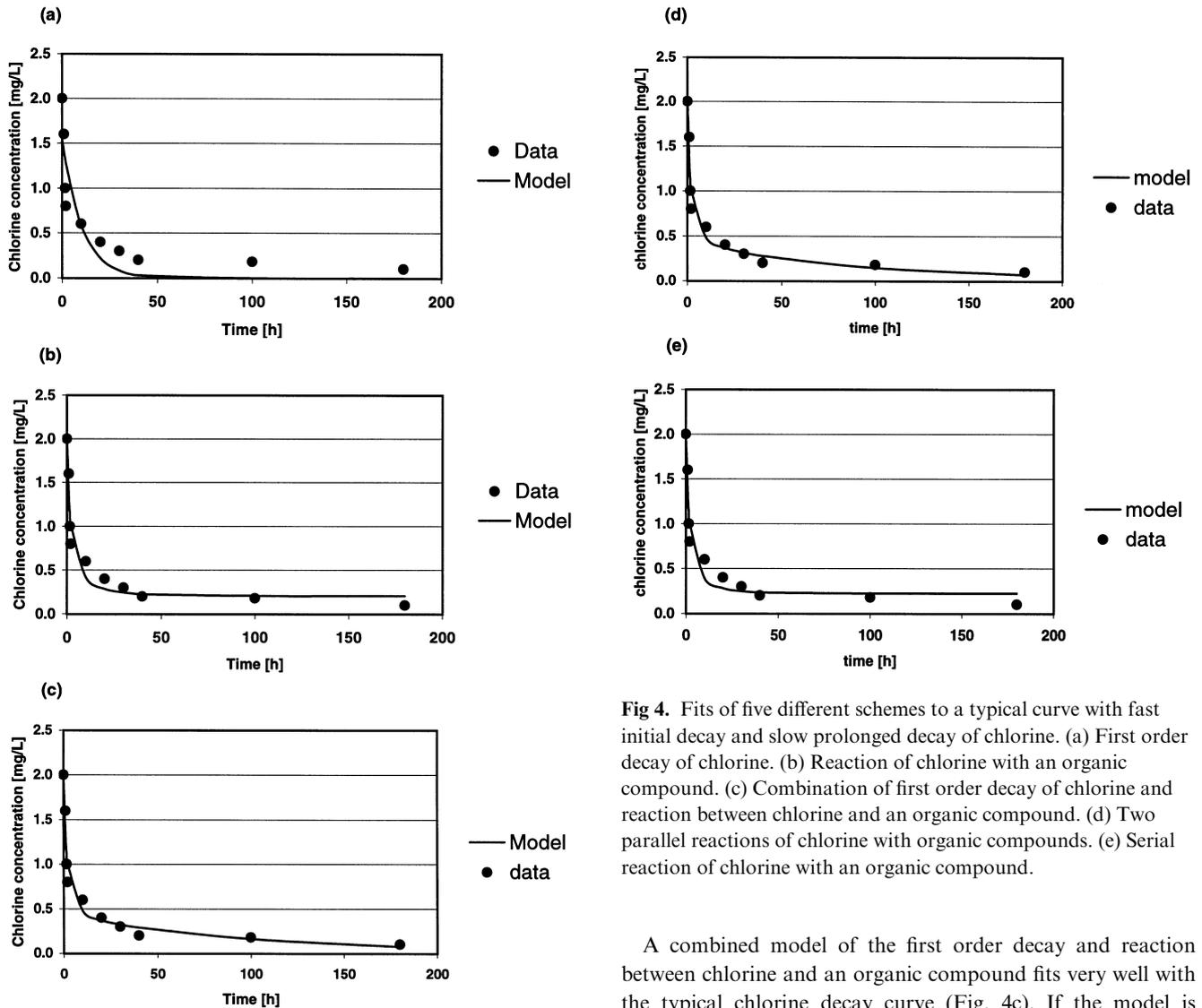


Fig 4. Fits of five different schemes to a typical curve with fast initial decay and slow prolonged decay of chlorine. (a) First order decay of chlorine. (b) Reaction of chlorine with an organic compound. (c) Combination of first order decay of chlorine and reaction between chlorine and an organic compound. (d) Two parallel reactions of chlorine with organic compounds. (e) Serial reaction of chlorine with an organic compound.

the flexibility to describe the data accurately. The fit can be matched to the beginning of the data (time < 50 h) or the end but not to the whole range of reaction time.

Figure 4b shows the fit of a model of chlorine reacting with an organic compound. It shows that a very good match between the model and data can be achieved. Unfortunately, if the initial chlorine dose were changed, the model is unlikely to maintain a similar level of accuracy. In fact the model is limited to maximum chlorine consumption equal to the initial concentration of the organic carbon chlorine equivalent $[C_{\text{org}}C]_0$ (1.81 mg/L in this case—see Table 2). This model is discussed [11–13] and applied also to the production of trihalomethanes (THM) [11]. While this model has the capacity to match any single curve of chlorine decay, it usually cannot describe multiple curves arising from varying the chlorine dose. The problem of poorly predicted initial decay was addressed by separating the chlorine demand within the first 4 h from that of the remaining period [12].

A combined model of the first order decay and reaction between chlorine and an organic compound fits very well with the typical chlorine decay curve (Fig. 4c). If the model is extrapolated over an extended time period, some inaccuracy may become apparent. This is because the first order component of the model continues to decay chlorine without diminishing the reaction rate. Experiments usually show slowing of the reaction rate of chlorine decay as contaminants are ‘exhausted’ or fast reacting contaminants are used up.

The next scheme of two parallel reactions of chlorine with organic compounds have sufficient flexibility to describe commonly encountered behaviour of chlorine in drinking water. This is demonstrated in Fig. 4d, which shows near perfect match of experimental data and this parallel model.

Figure 4e shows the results from a chlorine decay model of serial reactions. Here chlorine reacts with an organic compound, which is converted to another partially oxidised, but still reactive compound. The fit is only marginally better than the simpler reaction of chlorine with organic compound (reaction scheme 2).

The weighted error, χ^2 (Eqn 6) was found to be a minimum (0.161) for reaction scheme 4 (parallel reactions of chlorine with

Table 2 Fitting of chlorine decay curve

No.	Estimated parameters	Weighted error (χ^2)
1	$[Cl]_0 = 1.55 \text{ mg/L}$ $k_1 = 0.098 \text{ h}^{-1}$	0.723
2	$[Cl]_0 = 2.02 \text{ mg/L}$ $[C_{\text{orgC}}]_0 = 1.81 \text{ mg/L}$ $k_2 = 0.282 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.196
3	$[Cl]_0 = 2.04 \text{ mg/L}$ $[C_{\text{orgC}}]_0 = 1.57 \text{ mg/L}$ $k_1 = 0.010 \text{ h}^{-1}$ $k_2 = 0.366 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.162
4	$[Cl]_0 = 2.05 \text{ mg/L}$ $[C_{\text{orgC1}}]_0 = 1.10 \text{ mg/L}$ $[C_{\text{orgC2}}]_0 = 1.53 \text{ mg/L}$ $k_1 = 0.013 \text{ h}^{-1} \times (\text{mg/L})^{-1}$ $k_2 = 0.378 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.161
5	$[Cl]_0 = 2.03 \text{ mg/L}$ $[C_{\text{orgC1}}]_0 = 0.904 \text{ mg/L}$ $k_1 = 0.338 \text{ h}^{-1} \times (\text{mg/L})^{-1}$ $k_2 = 1.718 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.191

two organic compounds) and a maximum (0.723) for reaction scheme 1 (first order decay of chlorine).

So far the objective has been to match a model to a single chlorine decay curve. However, for practical application it is important to be able to predict consequences of different doses. The same reaction schemes (Table 1) were tested for their ability to predict the decay in a split sample of Warragamba raw water (the major drinking water source for Sydney) chlorinated at three different dosing levels (1, 2 and 4 mg/L). Figure 5a to 5e and Table 3 show the fit of different reaction schemes to the experimental data. The ordering of the schemes in terms of best fit is identical to the previous one (Table 2), but the scheme of parallel reactions of chlorine with two organic carbon compounds (reaction scheme 4) is more clearly superior to any other scheme. It is also clear that the first order reaction model is inadequate to describe the experiments (Fig. 5a). The model (reaction scheme 4) fitted to the larger number of experimental data obtained within the first 20 h of the experiments.

The Warragamba raw water contained small amounts of ammonia ($< 0.01 \text{ mg/L}$) and iron ($< 0.03 \text{ mg/L}$) and as such it is assumed that the chlorine decay was mainly due to the reaction with organic compounds. However, even if their concentration is large, the reaction of chlorine with ammonia and iron is included in the model (reaction scheme 4) as the reaction of chlorine with fast reacting compounds.

This model is just as applicable to bulk water in distribution systems as it is to raw water, for two reasons. Firstly, many water supply systems with high quality raw water do not apply conventional treatment, such as coagulation and filtration, but simply chlorinate the raw water before distribution. For

example, Warragamba raw water until recently was supplied to more than 75% of Sydney's population after disinfection alone. Most of the water supplied to Melbourne and New York is still being distributed in this way. We note that these are cities of more than 3 million inhabitants.

Secondly, treatment of raw water without biological stabilisation afterwards results in removal of less than two thirds of natural organic matter. The chlorine decay resulting from the remaining compounds in the distributed water still exhibits the same characteristics as the decay in raw water and hence still requires the same complexity of kinetic description.

Table 2 lists the initial chlorine concentration $[Cl]_0$ as one of the estimated parameters by each of the five models evaluated. In reality it is impossible to determine experimentally, the initial concentration of chlorine in natural water. The chlorine disappears so quickly after its addition to the natural water that it is impossible to conduct analysis before the initial concentration changes substantially. Thus, it is considered incorrect to fix this initial concentration and force errors in all other data points, which is a quite common approach in modelling of reaction processes. Instead, to find the initial concentration of chlorine, an identical amount of chlorine is dosed to pure water and analysed immediately, assuming that the chlorine decay is negligible in pure water. This was carried out to obtain the results shown in Table 3.

The above example demonstrates the suitability of the scheme of parallel reactions of chlorine with two organic carbon compounds (reaction scheme 4) for describing free chlorine decay. This simplified presentation is considered beneficial to compare different reaction schemes. However, reaction scheme 4 is suitable for describing free and combined chlorine decay as well as the decay of chlorine after rechlorination [8,9], but a more complex reaction scheme is necessary to describe the decay in chloraminated systems.

The parallel reaction model (reaction scheme 4) may be easily

Table 3 Fitting of chlorine decay curve to Warragamba raw water experimental data

No.	Estimated parameters	Weighted error (χ^2)
1	$k_1 = 0.094 \text{ h}^{-1}$	7.100
2	$[C_{\text{orgC}}]_0 = 1.94 \text{ mg/L}$ $k_2 = 0.132 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	1.491
3	$[C_{\text{orgC}}]_0 = 1.13 \text{ mg/L}$ $k_1 = 0.0114 \text{ h}^{-1}$ $k_2 = 0.0997 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.673
4	$[C_{\text{orgC1}}]_0 = 1.79 \text{ mg/L}$ $[C_{\text{orgC2}}]_0 = 0.626 \text{ mg/L}$ $k_1 = 0.0288 \text{ h}^{-1} \times (\text{mg/L})^{-1}$ $k_2 = 2.66 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	0.260
5	$[C_{\text{orgC1}}]_0 = 0.98 \text{ mg/L}$ $k_1 = 0.129 \text{ h}^{-1} \times (\text{mg/L})^{-1}$ $k_2 = 7400 \text{ h}^{-1} \times (\text{mg/L})^{-1}$	1.489

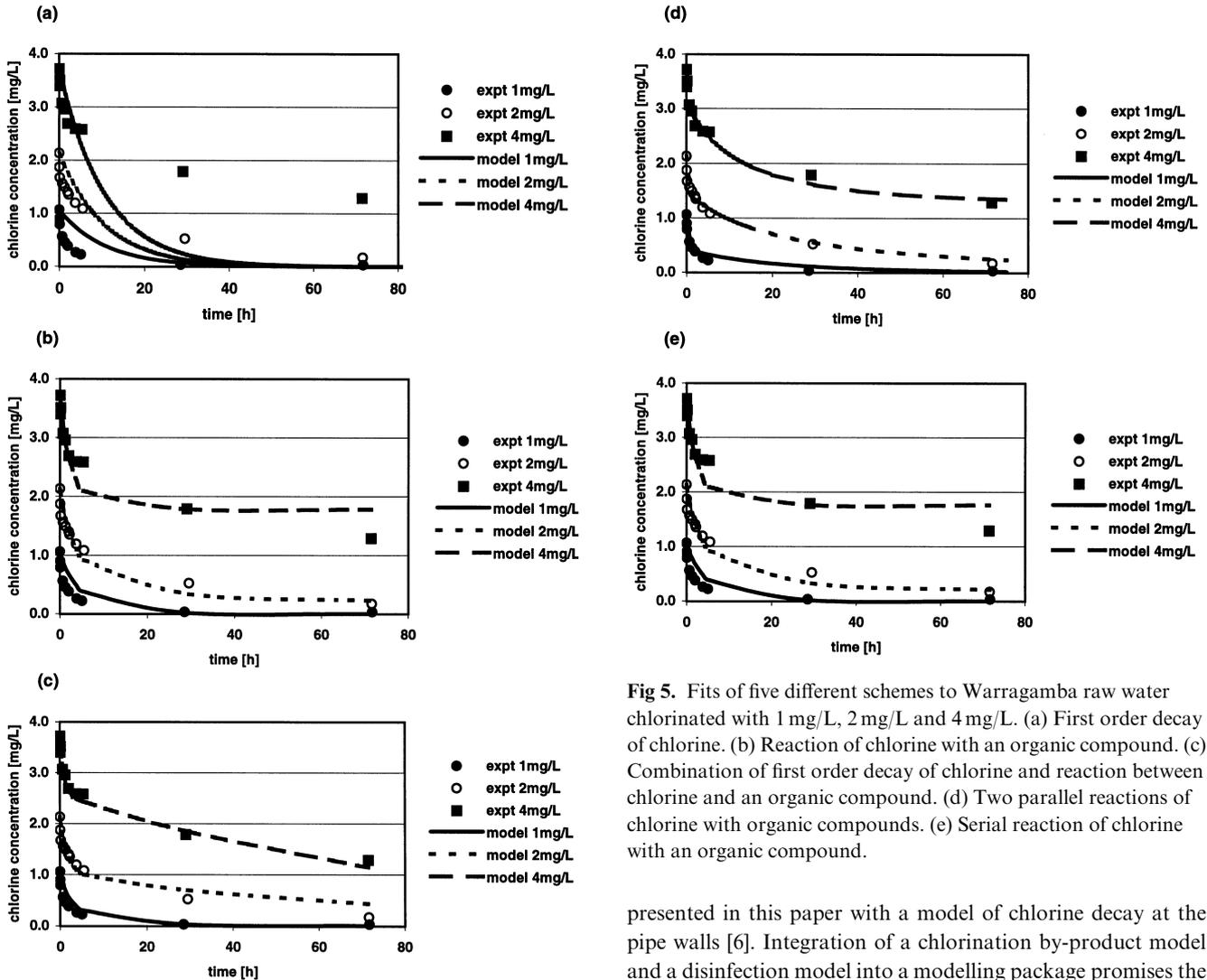


Fig 5. Fits of five different schemes to Warragamba raw water chlorinated with 1 mg/L, 2 mg/L and 4 mg/L. (a) First order decay of chlorine. (b) Reaction of chlorine with an organic compound. (c) Combination of first order decay of chlorine and reaction between chlorine and an organic compound. (d) Two parallel reactions of chlorine with organic compounds. (e) Serial reaction of chlorine with an organic compound.

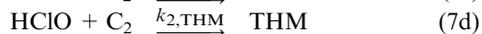
presented in this paper with a model of chlorine decay at the pipe walls [6]. Integration of a chlorination by-product model and a disinfection model into a modelling package promises the capacity to model drinking water quality more realistically than is currently possible.

CONCLUSION

The aim of this paper was to compare both currently used and some new schemes, for their ability to describe decay of chlorine in bulk drinking water. The theoretical approach based on multiple parallel and serial reactions of chlorine with a range of organic compounds present in water forms the basis for the formulation of a sequence of simplified reaction schemes.

The results were presented from optimally fitting reaction schemes to a 'typical' chlorine decay curve and to experimental data from a split sample subjected to various chlorine doses. Unfortunately the most commonly used expression, first order chlorine decay, does not match the general trend of rapid initial chlorine consumption followed by a slower reaction rate. It proved to be inadequate and does not have the capacity to model (with a single set of parameter values) the effect of

extended in the future to describe THM formation. It was suggested [11] that THMs are generated by a fraction of chlorine reacting with organic compounds and forming compounds with carbon—chlorine bonds, rather than reducing chlorine to chloride. Such a scheme is described by reactions 7a and 7b. An extended scheme to represent two parallel reactions is defined by equations 7a through 7d, below.



where: C_1 , C_2 = two groups of organic compounds; $k_{1,\text{I}}$, $k_{2,\text{I}}$ = reaction rate coefficient of chlorine oxidation of organic compounds in groups 1 and 2; $k_{1,\text{THM}}$, $k_{2,\text{THM}}$ = reaction rate coefficient of chlorine reaction with organic compounds in groups 1 and 2 to form THMs

Future work needs to be concentrated on testing the proposed link between the chlorine decay model for bulk water

different levels of chlorine dose, as can be seen from Fig. 5a. A serial scheme of an organic compound reacting with chlorine has no apparent advantage over other kinetic expressions.

Of all the tested models, that of parallel reactions of two groups of organic compounds with chlorine (reaction scheme 4 in Table 1) provides by far the best fit to the data. The model is characterised by four parameters, two initial concentrations of organic compounds reacting with chlorine and two reaction rate coefficients. The model can predict effects of changing dose, has all the prerequisites to provide an adequate description of re-chlorination and has a potential as a tool for optimisation of water treatment [8,9]. This model would also be suitable for modelling THM formation in a more flexible way.

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