

## Modelling disinfection by-products in contact tanks

Guichan Zhang, Binliang Lin and Roger A. Falconer

### ABSTRACT

Numerical modelling has been extensively used in the field of environmental engineering as an efficient method for predicting the fate of contaminants. For chlorine disinfection contact tanks, current numerical models predict the disinfection processes as well as first-order functions for chlorine demand. In recent years, the study of the formation of Disinfection By-Products (i.e. DBPs) in drinking water has been a cause for public concern. Since both chemical analyses and monitoring of DBPs are very expensive and not yet widely available, the establishment of an efficient numerical model has become *a priori* for the analysis of DBPs. This study includes a second-order kinetic representation for chlorine consumption in the disinfection processes and incorporates this representation in a numerical model to predict the formation of DBPs. The model has been refined to predict the chlorine demand in the disinfection process and the distribution of the main DBPs in contact tanks, including primarily total trihalomethanes (TTHMs), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA).

**Key words** | contact tank, disinfection processes, chlorine, disinfection by-products (DBPs), numerical modelling, hydrodynamic modelling

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### INTRODUCTION

Chlorine disinfection, which was first adopted for water purification some 80 years ago, is still regarded as the most effective method of prophylaxis against epidemics. However, as chlorine is a strong oxidant, it reacts with Natural Organic Materials (i.e. NOMs) in water and produces Disinfection By-Products (DBPs) whilst sterilising organisms. Since the discovery of total trihalomethanes (TTHMs) in 1974 (Bellar *et al.* 1974), hundreds of halogenated DBPs have been identified in drinking water. Trihalomethanes (THMs) were identified as carcinogens and the first class of halogenated DBPs produced by chlorination, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were subsequently identified as the second major class of DBPs in treated water (Philip 1994). The Safe Drinking Water Act of the United States also includes bromodichloromethane ( $\text{CHBrCl}_2$ ), dichloroacetic acid (DCAA) and bromate ( $\text{BrO}_3^-$ ) as possible carcinogens. Recent carcinogenic risk research indicates that the carcinogenic order of organic halides is:  $\text{DCAA} >$

$\text{CHBrCl}_2 > \text{CHCl}_3$ . The toxicity of bromodichloromethane is stronger than chloroform, and dichloroacetic acid is regarded as being a more potent carcinogen than any of the THMs (Philip 1994).

The UK Water Supply Regulation, which was promulgated in 1991, is based on the European Union Directive 80/778/EEC and the World Health Organisation (WHO) guideline for drinking water quality (Johnson *et al.* 1997). It states that disinfection for drinking water should have 30 min contact time at a  $\text{pH} < 8$ , with a minimum free chlorine residual of  $0.5 \text{ mg l}^{-1}$ . Likewise, the limiting concentration of total trihalomethanes (TTHMs) should be  $100 \mu\text{g l}^{-1}$ . In recent years poor raw water quality has resulted in an increase in the chlorine dose required in order to comply with the free chlorine requirement, which has resulted in an increase in the formation of disinfection by-products in treated water. Since the influence of halogenated organics on human health has caused public concern, the European Union is now considering reducing

the limiting concentration of TTHMs to  $40 \mu\text{g l}^{-1}$  (Stevenson 1995). With the improvement in analytical analysis, more and more halogenated organics have been recognised in drinking water. Hence, the current regulations of water disinfection, which are more concerned with sterilising organisms, may not any longer be regarded as sufficient for protecting human health. Thus, in order to lay the scientific foundation to a new regulation that contains individual DBPs more detailed investigations are necessary.

Some alternative oxidants and disinfectants have been used in drinking water disinfection, such as ozone, chlorine dioxide, chloramines and UV light. However, all of these alternative disinfectants have some health risks due to the formation of other DBPs. The key DBPs of concern for alternative oxidation are that ozone disinfection produces  $\text{BrO}_3^-$ , chlorine dioxide disinfection produces  $\text{ClO}_2^-$  and chloramines produce CNCl. Likewise, UV light is not regarded as a reliable disinfectant for giardia and cryptosporidium cysts (Philip 1994). It is therefore expected that chlorine will continue to be used as the main disinfectant for the foreseeable future. At the same time the tightening of regulations and the raising of drinking water standards have both led to more serious requirements for predicting and controlling DBPs in the water treatment process.

The analysis and monitoring of DBPs are complicated tasks that need precise and expensive devices, as well as a considerable amount of pre-treatment sample processing. Many countries still cannot use DPBs as indicators for routine monitoring of drinking water quality. With the rapid progress of modern computer technology, the use of numerical models to predict the DBPs produced in the disinfecting process is increasingly becoming a more useful means of monitoring water quality. Numerical models, which have the advantage of low cost, portability and short running time, have become a key part of the analytical methods in the field of environmental monitoring and management, including analysing the distribution of DBPs.

This study has focused on the DBPs of most public concern and has established models to assess drinking water quality. Based upon an existing first-order model for simulating the disinfection processes in contact tanks,

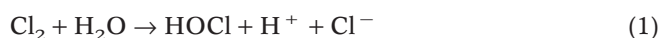
this study involves the development of a second-order model for predicting the key DBP concentrations in tanks including total trihalomethanes (TTHMs), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA).

## CHLORINE DECAY AND DISINFECTION PROCESSES

### Chlorine decay and consumption

When chlorine is added to water several reactions take place that influence the chlorine consumption, including: (i) chlorine decay, which leads to the production of hypochlorous acid (HOCl) and hypochlorite ions ( $\text{OCl}^-$ ), with the HOCl being a disinfecting agent and the  $\text{OCl}^-$  not being a disinfectant; (ii) hypochlorous acid (HOCl) then rapidly penetrates the microbial cells and kills off the micro-organisms, which form part of the disinfection process; and (iii) chlorine reacts with both organic and inorganic chemicals (e.g., ammonia, humic materials, ferrous iron, bromide ions, etc.) to produce DBPs.

Once the chlorine has dissolved into the water, two types of reactions then take place. The chlorine first reacts with the water, which can be described by a first-order kinetic model to give:



$$dC/dt = -kC \quad (2)$$

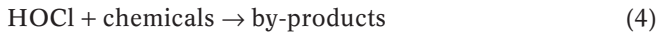
where  $C$  = chlorine concentration ( $\text{mg l}^{-1}$ );  $k$  = first-order decay coefficient ( $\text{min}^{-1}$ ); and  $t$  = time in minutes. Integrating equation (2) gives:

$$C = C_0 e^{-kt} \quad (3)$$

where  $C_0$  = initial chlorine concentration ( $\text{mg l}^{-1}$ ).

Most of the current disinfection models have been developed on the basis of solving equations (1) and (2), as chlorine decay is regarded as the dominant reaction occurring in the disinfection process. Although chlorine

decay only dominates at the beginning of a fast reaction, the HOCl then generally reacts with the chemicals to form DBPs, giving:



or



where  $A$  and  $B$  = chlorine and reacting materials and  $P$  = disinfecting by-products. The rate of this reaction is given by:

$$\begin{aligned} dC_A/dt &= -k_A C_A C_B \text{ or } dC_B/dt \\ &= -k_B C_A C_B \text{ or } dC_P/dt = k_P C_A C_B \end{aligned} \quad (6)$$

where  $k_A/a = k_B/b = k_P/p$ ,  $C_A$ ,  $C_B$  and  $C_P$  = concentrations of  $A$ ,  $B$  and  $P$  ( $\text{mg l}^{-1}$ ),  $t$  = time in minutes,  $k_A$ ,  $k_B$  and  $k_P$  = first-order decay coefficient of  $A$ ,  $B$  and  $P$  ( $1 \text{ mg}^{-1} \text{ min}^{-1}$ ).

By combining equations (1), (4) and (5), i.e. by combining the chlorine decay with the reaction between the HOCl and chemicals, Robert (1998) has given a second-order model for predicting chlorine consumption in the disinfection process as follows:

$$C = \frac{C_0 (1-R)}{1 - R e^{-ut}} \quad (7)$$

where  $R$  (dimensionless) and  $u$  ( $\text{min}^{-1}$ ) are coefficients given by

$$R = \frac{aC_{B0}}{bC_{A0}}, \quad u = \left( \frac{bC_{A0}}{a} - C_{B0} \right) k_A$$

and they were estimated using the modified Gauss-Newton method. In this paper, the estimated values for  $R$  and  $u$  are:  $R = 1.02$ ,  $u = -0.0025$ .

Differentiating equation (7) then gives:

$$\frac{dC}{dt} = -\frac{C_0 (1-R) R e^{-ut}}{(1 - R e^{-ut})^2} \quad (8)$$

## Disinfection

The main purpose of disinfection is to sterilise bacteria and viruses in the drinking water. This reaction is assumed to be a first-order reaction. The resulting relationship can be described as follows:

$$N = N_0 e^{-kt} \quad (9)$$

where  $N_0$  and  $N$  = number of microbes at contact time 0 and  $t$  respectively, where  $t$  = disinfection contact time (h), and  $k$  = microbial decay coefficient ( $\text{h}^{-1}$ ).

A similar formula has been proposed by Chick (1908) to describe the relationship between the rate of disinfection and concentration of disinfectant, which is usually given as:

$$N = N_0 e^{-k' c^n t} \quad (10)$$

where  $n$  = empirical coefficient (which is approximately 1 for chlorine disinfection). The decay rate  $k'$  is a complicated function that depends upon the disinfection condition, such as microbe type, chemical composition of the water, temperature, disinfectant type and the pH value.

Different countries and different water treatment regulations may lead to different organisms being chosen as the main indicators of bacterial pollution. In the UK *Escherichia coli* (*E. coli*) organisms are chosen as the indicator for bacterial pollution. In the USA, the surface water treatment rule uses *Giardia lamblia* (*G. lamblia*). For *E. coli*, Haas (Stevenson 1995) gives  $k'$  as  $0.19 \text{ l mg}^{-1} \text{ s}^{-1}$  under the condition of  $5^\circ\text{C}$  and a pH 8.5 of  $0.4 \text{ mg min l}^{-1}$  CT value. For *G. lamblia*,  $k'$  is given as  $18.4 \text{ l mg}^{-1} \text{ h}^{-1}$  at  $25^\circ\text{C}$  and a pH 7.0 of  $0.25 \text{ mg h l}^{-1}$  CT value (Johnson 1997). The differential form of equation (10) can be written as:

$$dN/dt = -k' C^n N. \quad (11)$$

## Disinfection by-products formation

As a result of the complicated methods of analysis for DBPs, some other items, such as total organic carbon

(TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm ( $UV_{254}$ ), etc., have been used as surrogates for predicting DBPs. Since there are many factors influencing the formation of halogenated DBPs, such as pH, contact time, temperature, season, organic concentration, chlorine dose and residual, and bromide concentration, none of the substituted parameters can be used alone to give the exact prediction of the concentration of DBPs in treated water. The United States Environmental Protection Agency (USEPA) have now used DBP predictive equations, which incorporate various governing factors, to assess the impact of specific parameters on water quality (Philip 1994). The following equations are taken from the USEPA's Water Treatment Plant Simulation Program for TTHMs, DCAA and TCAA:

$$TTHM = 0.00309[(TOC)(UV_{254})]^{0.440}(Cl_2)^{0.409}(T)^{1.06} \times (pH - 2.6)^{0.715}(Br + 1)^{0.036}(t)^{0.265} \quad (12)$$

$$DCAA = 0.605(TOC)^{0.291}(UV_{254})^{0.726}(Cl_2)^{0.480}(T)^{0.665} \times (Br + 1)^{-0.568}(t)^{0.239} \quad (13)$$

$$TCAA = 87.182(TOC)^{0.355}(UV_{254})^{0.901}(Cl_2)^{0.881} \times (pH - 2.6)^{-1.732}(Br + 1)^{-0.679}(t)^{0.264} \quad (14)$$

where  $TTHM$  = total trihalomethanes concentration ( $mg\ l^{-1}$ ),  $DCAA$  = dichloroacetic acid concentration ( $\mu g\ l^{-1}$ ),  $TCAA$  = trichloroacetic acid concentration ( $\mu g\ l^{-1}$ ),  $TOC$  = total organic carbon concentration ( $mg\ l^{-1}$ ),  $UV_{254}$  = ultraviolet absorbance at 254 nm ( $cm^{-1}$ ),  $Cl_2$  = chlorine dose ( $mg\ l^{-1}$ ),  $T$  = temperature ( $^{\circ}C$ ), and  $Br$  = bromide ion concentration ( $mg\ l^{-1}$ ). Equations (12)–(14) can be reduced to the simpler form of:

$$DBP = mt^n \quad (15)$$

where  $DBP$  is a surrogate for TTHMs, DCAA or TCAA, and  $n$  expresses the various exponents of  $t$  in equations (12)–(14) respectively. The differential form of equation (15) can be written as:

$$d(DBP)/dt = nmt^{n-1}. \quad (16)$$

## NUMERICAL MODEL

The numerical model DIVAST (Depth Integrated Velocities And Solute Transport) developed by Falconer (Falconer and Liu 1988) is a finite difference model for predicting time varying water elevations, depth averaged velocity components and solute concentration distributions in a nearly horizontal flow field.

The depth integrated transport equation used to predict the depth averaged solute concentration distributions (Falconer 1993) is given as follows:

$$\frac{\partial \Phi H}{\partial t} + \left[ \frac{\partial \Phi U H}{\partial x} + \frac{\partial \Phi V H}{\partial y} \right] - \frac{\partial}{\partial x} \left[ H D_{xx} \frac{\partial \Phi}{\partial x} + H D_{xy} \frac{\partial \Phi}{\partial y} \right] - \frac{\partial}{\partial y} \left[ H D_{yx} \frac{\partial \Phi}{\partial x} + H D_{yy} \frac{\partial \Phi}{\partial y} \right] + H(\Phi_c + \Phi_k) = 0 \quad (17)$$

where  $\Phi$  = depth averaged solute concentration (chlorine, microbe or DBPs) per unit volume,  $\Phi_c$  = volume input,  $\Phi_k$  = decay or kinetic transformation rate,  $H$  = water depth,  $U, V$  = depth averaged velocity components in  $x$  and  $y$  directions respectively, and  $D_{xx}, D_{xy}, D_{yx}, D_{yy}$  = depth averaged dispersion-diffusion coefficients in  $x, y$  directions respectively (in  $m^2\ s^{-1}$ ), which have been shown to be of the following form:

$$D_{xx} = \frac{(k_l p^2 + k_t q^2) \sqrt{g}}{C \sqrt{p^2 + q^2}} \quad (18)$$

$$D_{xy} = D_{yx} = \frac{(k_l - k_t) p q \sqrt{g}}{C \sqrt{p^2 + q^2}} \quad (19)$$

$$D_{yy} = \frac{(k_l q^2 + k_t p^2) \sqrt{g}}{C \sqrt{p^2 + q^2}} \quad (20)$$

where  $k_l$  and  $k_t$  are the depth averaged longitudinal dispersion and lateral turbulent diffusion constants respectively, and  $p$  and  $q$  are the unit width discharges in the  $x, y$  directions respectively.

### Disinfection model

When equations (8) and (11) are substituted into equation (17), the disinfection model for chlorine concentration and organisms can be written as:

$$\begin{aligned} & \frac{\partial CH}{\partial t} + \frac{\partial CUH}{\partial x} + \frac{\partial CVH}{\partial y} - \frac{\partial}{\partial x} \left[ HD_{xx} \frac{\partial C}{\partial x} + HD_{xy} \frac{\partial C}{\partial y} \right] \\ & - \frac{\partial}{\partial y} \left[ HD_{yx} \frac{\partial C}{\partial x} + HD_{yy} \frac{\partial C}{\partial y} \right] - \frac{C_0(1-R)Re^{-ut}}{(1-Re^{-ut})^2} H = 0 \end{aligned} \quad (21)$$

$$\begin{aligned} & \frac{\partial NH}{\partial t} + \frac{\partial NUH}{\partial x} + \frac{\partial NVH}{\partial y} - \frac{\partial}{\partial x} \left[ HD_{xx} \frac{\partial N}{\partial x} + HD_{xy} \frac{\partial N}{\partial y} \right] \\ & - \frac{\partial}{\partial y} \left[ HD_{yx} \frac{\partial N}{\partial x} + HD_{yy} \frac{\partial N}{\partial y} \right] - k'CNH = 0. \end{aligned} \quad (22)$$

### Disinfection by-products model

Likewise, for the prediction of disinfection by-product concentration distributions produced in a contact tank these can be predicted using the following equation, obtained by combining equations (16) and (17):

$$\begin{aligned} & \frac{\partial (DBP)H}{\partial t} + \frac{\partial (DBP)UH}{\partial x} + \frac{\partial (DBP)VH}{\partial y} - \frac{\partial}{\partial x} \left[ HD_{xx} \frac{\partial (DBP)}{\partial x} \right. \\ & \left. + HD_{yy} \frac{\partial (DBP)}{\partial y} \right] - \frac{\partial}{\partial y} \left[ HD_{yx} \frac{\partial (DBP)}{\partial x} + HD_{yy} \frac{\partial (DBP)}{\partial y} \right] \\ & + nmt^{n-1}H = 0. \end{aligned} \quad (23)$$

### SIMULATION CONDITION

The simulation tank used in this study was based on a laboratory model tank which simulated a prototype chlorine contact tank located in West Yorkshire and operated by the Western Division of Yorkshire Water plc. The model tank, for which detailed measurements of velocity and tracer concentration distributions existed, was a 1:8 scale model of the existing Embassy chlorine contact tank. The rectangular tank was 94 cm in width, 60 cm in depth and 200 cm in length, as shown in Figure 1. The main flow and water quality parameters are shown in Tables 1 and 2

respectively. The theoretical retention time within the original prototype tank was 35 minutes. The parameter  $n$  used in the calculations was:  $n=0.265$  for TTHM,  $n=0.239$  for DCAA and  $n=0.264$  for TCAA (see equations (12), (13) and (14)).

## RESULTS AND DISCUSSION

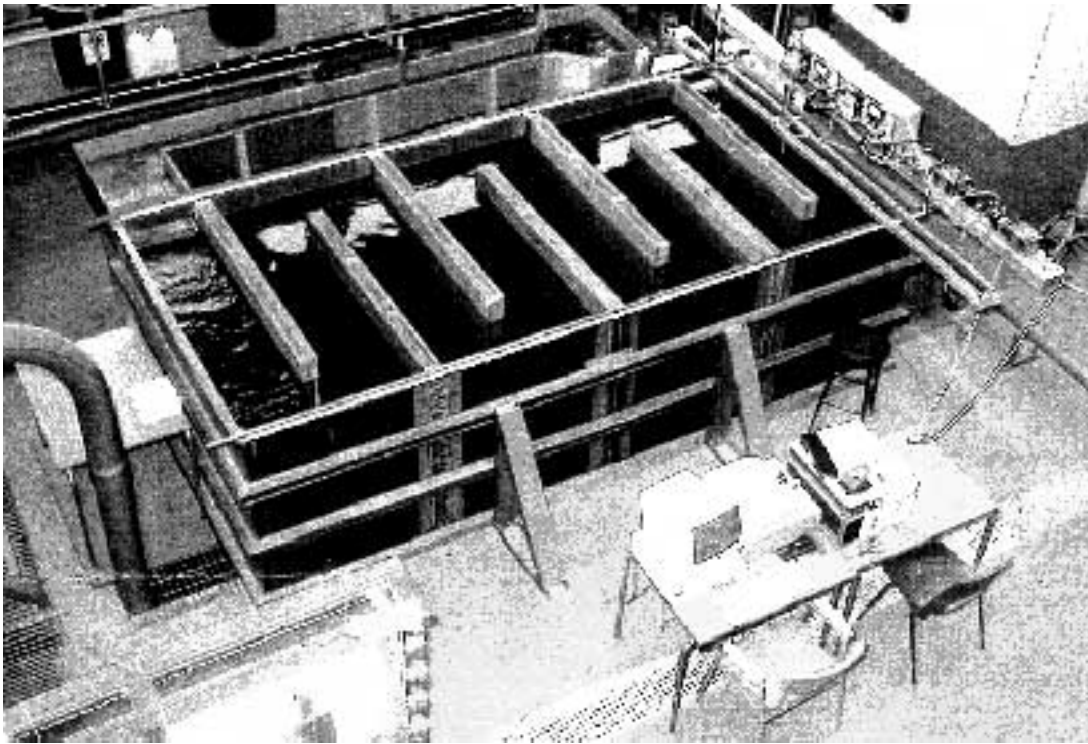
### Velocity distribution

A previous study has extensively compared the predicted velocity fields obtained using the numerical model described above with the experimental measurements, with the results showing that the model predictions were close to the measured data (Wang 1995). A typical illustration of the predicted velocity field is given in Figure 2.

### Concentration distribution

The model described above was then used to simulate the formation of disinfection by-products in the model tank for two controlled conditions. In the first test case 5 mg l<sup>-1</sup> of chlorine was added continuously at the inlet of the simulation tank until the free chlorine residual at the outlet was almost 0.5 mg l<sup>-1</sup> in the tank. For this case the DBP concentration could be determined at the outflow of the tank and after the retention time. The predictions for each controlled by-product could then be compared with the regulation for the UK and those by-products failing to meet the regulations could be identified. Strategies could then be adopted to guarantee that the required treated effluent standards were met. For the second test, chlorine was added in the contact tank only at the start of the simulation time. The results of Wang (1995) showed that the stable time for chlorine injection was 0.6 s, so that injection of chlorine was ceased after this time. In this test it was possible to predict how the DBPs spread through the tank during the simulation period. The main objective of this test was to investigate the reaction of chlorine with organisms within the water column, thus to improve our understanding of the DBPs' formation processes. These types of test are also used in laboratory experimental study





**Figure 1** | Model contact tank.

**Table 1** | Flow parameters of model contact tank

Parameters	Value
Design flow ( $\text{l s}^{-1}$ )	1.170
Water depth (mm)	536.0
Tank capacity ( $\text{m}^3$ )	0.878
Mean velocity ( $\text{mm s}^{-1}$ )	10.4
Theoretical retention time (min)	12.5

**Table 2** | Water quality parameters for contact tank

Parameters	Value
Chlorine dose ( $\text{mg l}^{-1}$ )	5.0
Total organic carbon (TOC) ( $\text{mg l}^{-1}$ )	4.48
Ultraviolet absorbance at 254 nm ( $\text{cm}^{-1}$ )	0.06
Water temperature ( $^{\circ}\text{C}$ )	18
Water pH value	7.0
Bromide ion concentration ( $\text{mg l}^{-1}$ )	0.036

of disinfection processes. The reason for choosing 0.6 s as the chlorine releasing time was mainly due to computational grounds, i.e. two full steps (time step = 0.3 s) were used, and it was also believed to be a realistic time for the releasing mechanisms to operate.

### Free chlorine at outlet kept at $0.5 \text{ mg l}^{-1}$

Figures 3–5 show the predicted concentration distributions of TTHMs, DCAA and TCAA for a fixed free chlorine level at the outlet. The variation in the

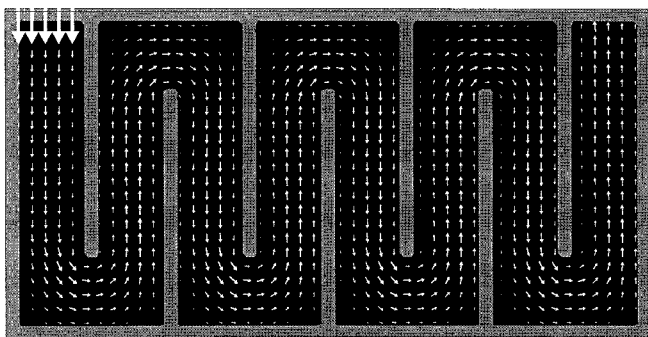


Figure 2 | Velocity in disinfection contact tank.

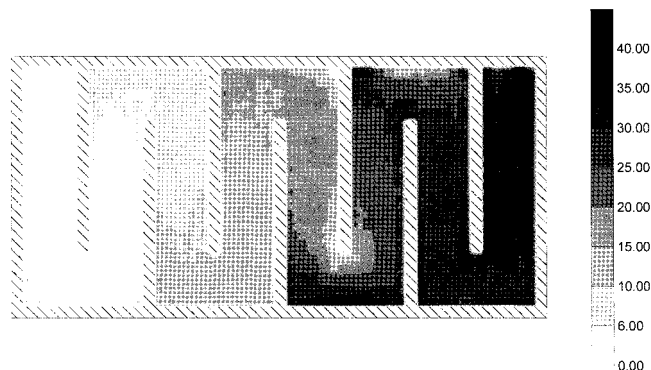


Figure 4 | Predicted DCAA concentration (in  $\mu\text{g l}^{-1} \times 100$ ).

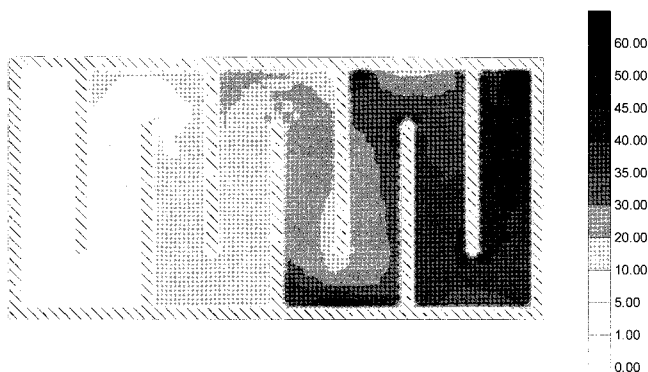


Figure 3 | Predicted TTHMs concentration (in  $\mu\text{g l}^{-1}$ ).



Figure 5 | Predicted TCAA concentration (in  $\mu\text{g l}^{-1} \times 1,000$ ).

corresponding range of concentrations at the outlet of the tank for these three DBPs are listed in Table 3 below.

Disinfection efficiency was also studied by comparing the outlet/inlet bacterial concentrations. Since the free chlorine within the contact tank were always above  $0.5 \text{ mg l}^{-1}$ , the bacterial concentrations reduced rapidly within the contact tank. It has been found that the ratio of outlet concentration to the inlet concentration was less than  $10^{-7}$  for both *E. coli* and *G. lamblia*.

#### Chlorine added at start of simulation for 0.6 s

Table 4 shows the variation in the chlorine concentration with time from 0.03 to 5.0 min. From the results it is clear that the chlorine concentration level decreases rapidly after stopping the injection of  $5 \text{ mg l}^{-1}$  chlorine for 0.6 s only. Initially, the chlorine concentration in the contact

Table 3 | Concentration of DBPs at outlet of model tank

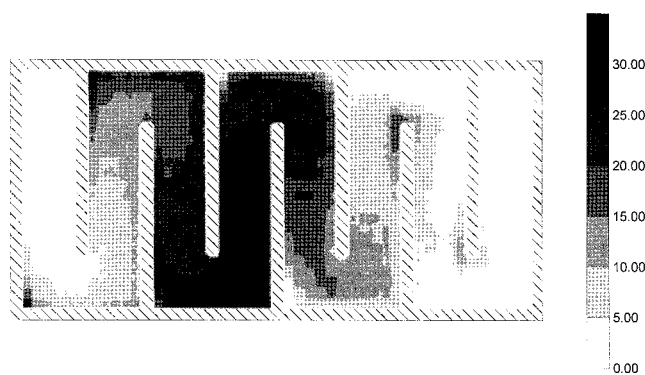
Disinfection by-product	Range of concentration
TTHMs	$34\text{--}56 \mu\text{g l}^{-1}$
DCAA	$0.26\text{--}0.43 \mu\text{g l}^{-1}$
TCAA	$0.25\text{--}0.41 \mu\text{g l}^{-1}$

tank decreased from  $5 \text{ mg l}^{-1}$  to about  $0.07 \text{ mg l}^{-1}$  in a very short period of time, i.e. 0.03 min or 1.8 s, and to  $0.013 \text{ mg l}^{-1}$  in 0.1 min or 6.0 s, as shown in Table 4. The chlorine concentration was predicted to be below  $0.001 \text{ mg l}^{-1}$  after 5 min.

As mentioned above, this consumption of chlorine was caused by decay and reacting with organics and inorganics in the water column.

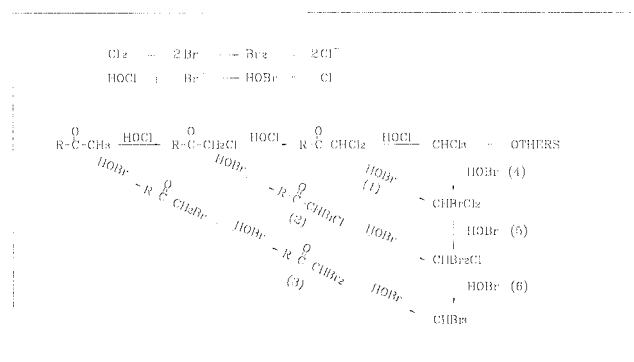
**Table 4** | Maximum chlorine concentration between 0.03–5.0 min

Time (min)	Chlorine concentration (mg l <sup>-1</sup> )
0.03	0.068
0.07	0.06
0.1	0.013
5.0	0.001

**Figure 6** | TTHMs concentration (in µg l<sup>-1</sup>) after simulation time of 5.0 min.

When 5 mg l<sup>-1</sup> of chlorine was injected into the tank for a simulation time of 0.6 s, the concentration of TTHMs was about 1.20 µg l<sup>-1</sup>. This concentration kept increasing after chlorine injection had stopped, and after a simulation time of 0.03 min or 1.8 s the TTHMs concentration had increased to 0.0047 mg l<sup>-1</sup>, while the chlorine concentration had decreased from 5 mg l<sup>-1</sup> to about 0.068 mg l<sup>-1</sup>, as shown in Table 4. The TTHMs concentration then reached its maximum value of about 20 µg l<sup>-1</sup> before decreasing again (see Figure 6).

These results indicate that TTHMs are formed gradually, and a certain reaction time is required for the formation of TTHMs. There are two types of reaction for the formation of DBPs existing in disinfection tanks. One is the reaction between HOCl and organics, as shown in equation (4), and the other is the reaction between chlorine and organics or inorganics. Chlorine is a very strong oxidant and it can react with some materials like Br<sup>-</sup>, which might influence the DBPs concentration. In

**Figure 7** | Potential formation of THM-Br.

the reaction to form TTHMs, chlorine reacts with organics in the water column to form THM-Cl. At the same time, the chlorine oxidises Br<sup>-</sup> to HOBr or Br<sub>2</sub>, and then both HOCl and HOBr react with the precursors of THMs, so that more THM-Br is produced. THM-Br is produced in a manner as shown in Figure 7.

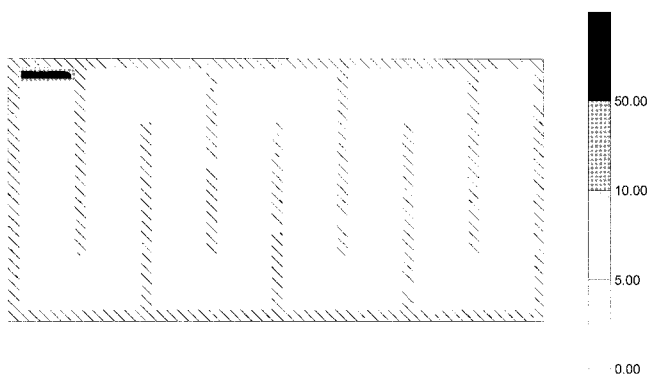
The results show that chlorine decay dominates at the beginning of the disinfection processes in the tank, and this reaction finishes quickly. The reaction between the chlorine—or HOCl—and its substitutes, including organics and inorganics, then plays a very important role in the formation of TTHMs. The formation reaction of DBPs is still continuous, even if chlorine injection has stopped. These results indicate that the formation of DBPs relies on the second-order consumption of chlorine.

For DCAA and TCAA the same change occurs as for TTHMs, but the maximum concentrations occur at different times. As shown in Figures 8 and 9, DCAA reaches the maximum concentration of about 0.045–0.06 µg l<sup>-1</sup> after a simulation time of 0.07 min (Figure 8), and TCAA about 0.0075 µg l<sup>-1</sup> after a simulation time of 1.0 min (Figure 9). Table 5 summarises the maximum concentration for chlorine and DBPs and the variation tendency of DBPs in the disinfection process.

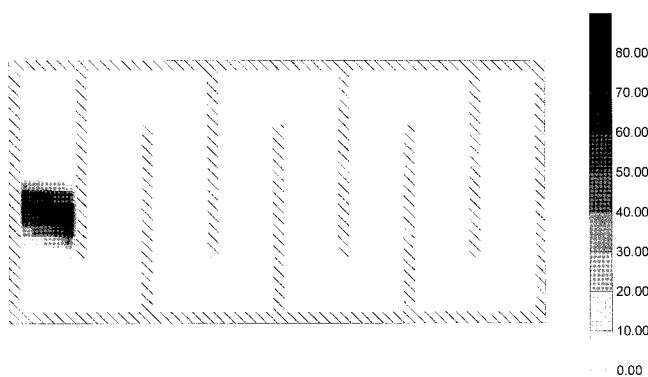
## CONCLUSION

In this study, a 2D numerical model has been established to predict the formation of DBPs during the chlorine





**Figure 8** | DCAA concentration (in  $\mu\text{g l}^{-1} \times 1,000$ ) after simulation time of 0.07 min.



**Figure 9** | TCAA concentration (in  $\mu\text{g l}^{-1} \times 10,000$ ) after simulation time of 0.07 min.

disinfection processes. The model deploys the advective-diffusion and chemical reaction equations to simulate chlorine decay, bacteria kill and the formation of three types of DBPs, i.e. TTHMs, DCAA and TCAA. The formation of DBPs is based on the chlorine second-order consumption. Two predictions at different controlled conditions show that:

- (i) If the chlorine residual concentration at the outlet of the tank is to be maintained at a certain level, then it is possible to predict the concentration of the DBPs at the outflow.
- (ii) If chlorine injection occurs at the inlet of the tank only for a very short time interval, then the model can predict the variation of DBPs along the tank. The concentration of DBPs change individually,

**Table 5** | Maximum concentration and reaching time of chlorine and DBPs

Item	Max. concentration	Reaching time
Chlorine	$5.0 \text{ mg l}^{-1}$	0.01 min
TTHMs	Above $20 \mu\text{g l}^{-1}$	1.0 min
DCAA	$0.045\text{--}0.06 \mu\text{g l}^{-1}$	0.07 min
TCAA	Above $0.0075 \mu\text{g l}^{-1}$	1.0 min

although they may still increase for a certain time even when chlorine injection has stopped.

Research is now continuing at the Environmental Water Management Research Centre, at Cardiff School of Engineering, in extending this model to three dimensions for a non-hydrostatic vertical pressure distribution.

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## NOTATION

The following symbols are used in this paper:

DBPs	disinfection by-products
TTHM	total trihalomethane
$\text{CHBrCl}_2$	bromodichloromethane
DCAA	dichloroacetic acid
TCAA	trichloroacetic acid
HOCl	hypochlorous acid
$\text{OCl}^-$	hypochlorite ion

$\text{Cl}_2$	chlorine concentration;
$k$	chlorine first-order decay constant
$A, B$	reacting substances
$a, b$	coefficient of reacting substances $A, B$ respectively
$P$	products of reaction between $A$ and $B$
$p$	coefficient of products
$k_a$	reaction rate constant of $A$
$k_b$	reaction rate constant of $B$
$k_p$	reaction rate constant of products $P$
$R$	dimensionless constant
$u$	second-order reaction rate constant
$\Phi$	depth averaged solute concentration per unit volume
$\Phi_c$	surface input
$\Phi_k$	decay or kinetic transformation rate
$D_{xx}, D_{yy}$	depth averaged dispersion-diffusion coefficient in $x, y$ direction respectively
$D_{yx}, D_{xy}$	depth averaged longitudinal dispersion constant
$k_t$	lateral turbulent diffusion constant
$N_0, N$	number of microbes at contact time 0 and $t$ respectively
$k'$	microbial decay coefficient
<i>E. coli</i>	<i>Escherichia coli</i> organisms
<i>G. lamblia</i>	<i>Giardia lamblia</i> organisms
TOC	total organic carbon
DOC	dissolved organic carbon

$\text{UV}_{254}$	ultraviolet absorbance at 254 nm
USEPA	United State Environmental Protection Agency
$\text{Br}^-$	bromide ion concentration

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