Modeling disinfection by-products: coupling hydraulic and chemical models
K. Ghebremichael, A. Gebremeskel, N. Trifunovic and G. Amy

ABSTRACT
There are established chemical models that can predict disinfectant decay and DBPs formation with respect to various water quality parameters and reaction time (water age). While models such as EPANET are powerful tools in hydraulic simulations, they have limited use in simulating water quality, containing only a basic chlorine decay subroutine. This paper presents a study on the use of a link that was developed to couple the external water quality models and the hydraulic model of EPANET 2. The coupled model has been applied to a hypothetical distribution system under steady and non-steady conditions. Simulations have taken the form of sensitivity analyses to probe operational strategies such as modified treatment as well as optimized secondary disinfection in order to maintain sufficient chlorine residual at critical points within the distribution system. Simulations have also been performed to compare the relative rates of formation of THMs vs HAAs as well as individual species. Of particular interest is optimization of chlorine dose to minimize residual chlorine under non-steady-state conditions.

Key words | chemical and hydraulic models, distribution network, EPANET2, HAAs, THMs

INTRODUCTION
DBPs are formed by the reactions between disinfectants and natural organic matter (NOM) and inorganic substances such as bromide (Br\(^{-}\)) in water (Maes et al. 1988; Sadiq & Rodriguez 2004). Although chemical disinfection is crucial to control microbiological risks, potential chemical risks are of concern (Clark & Sivagesean 2002). Drinking water disinfection, therefore, poses the dilemma of a risk trade off. It is, therefore, important to optimize disinfection such that chemical risks are minimized and this is where models have significant merit. The formation of DBPs in the distribution system is affected by a number of water quality parameters and operating conditions: pH, temperature, water age, chlorine residual, natural organic matter (NOM) and Br\(^{-}\) concentrations. Assessment of the effect of each parameter on the formation of DBPs is complex and the use of models to predict effects of water quality and operational variation is important.

Water quality models are used to predict chemical and biological changes in the network, their distribution and risks (Nyarko 1998). Moreover, they can be used as decision support tools for operational control during the treatment process and chlorine boosting schedules. There are established hydraulic models developed for water distribution systems such as EPANET 2, however, they have limited value in simulating water quality apart from chlorine decay simulation. According to Rosman (1998), EPANET 2 uses a first order saturation growth kinetics to model the growth of THMs and assumes that the rate of formation of THMs is proportional to the difference between a limiting (maximum) value and the current value. The approach fails to account for the effect of chlorine level on THMs formation and the maximum concentration of DBPs should be predetermined (Rosman 1998). Moreover, the EPANET 2 water quality model does not consider water quality parameters for predicting THM growth and chlorine decay.

There are established chemical models that can predict the formation of regulated DBPs, as a function of precursor..
concentrations, water quality, disinfectant dose and reaction time. Amy et al. (1998) developed statistically based empirical models (USEPA chemical models) that were based on low chlorine doses applied to either raw/untreated waters or chemically coagulated (conventionally treated) waters. The USEPA chemical models also include first order chlorine decay models which represent rapid and slow decay. The USEPA treated/coagulated water models do not include the pH and temperature parameters in predicting DBPs, hence correction factors have been developed to adjust the results of the model (Sohn et al. 2004).

Due to the limitations of EPANET 2 for water quality modeling it is important to couple/link it with external models, which have more robust water quality features. In this study the two models have been linked externally, that is, output from the hydraulic model has been used to run the chemical models subroutines to simulate water quality information in extended time period. The above approach has been applied to a hypothetical distribution system and used to compare the relative rates of formation of various DBPs species (THMs and HAAs).

The main objective of this study was to create a link between EPANET 2 and USEPA chemical models in order to assess water quality of extended coverage and duration. The specific objectives were: to predict DBPs formation and chlorine decay in a distribution system under steady and non-steady conditions, to assess how water quality parameters affect the formation of DBPs, to prepare isopleths for DBPs species (THMs and HAAs).

Raw water DBPs models

\[
[TTHM] = 10^{-1.385\times[DOC]^{0.098}[Cl_2]^{0.152}[Br^-]^{0.068}} \\
\times [\text{temp}]^{0.609}[\text{pH}]^{1.601}[t]^{0.263}
\] (1)

\[
[THAA] = 9.98[DOC]^{0.935}[Cl_2]^{0.445}[Br^-]^{-0.051} \\
\times [\text{temp}]^{0.387}[\text{pH}]^{-0.655}[t]^{0.178}
\] (2)

Coagulated (alum) water models for temperature 20°C and pH = 7.5

\[
[THAA] = 7.05[DOC]^{0.581}[Cl_2]^{0.529}[Br^-]^{-0.080}[t]^{0.159}
\] (3)

\[
[TTHM] = 10^{0.651}[DOC]^{0.752}[Cl_2]^{0.246}[Br^-]^{-0.185}[t]^{0.258}
\] (4)

**MATERIALS AND METHODS**

This study was based on modeling of hydraulic and water quality aspects of a distribution system. It involved writing C++ codes for linking the USEPA chemical models and EPANET 2 using the toolkit functions. Water age from EPANET 2 and water quality parameters as well as chlorine dose were used as input variables for the chemical models. The developed program was applied on a sample network (Figure 1). The Hazen-Williams coefficients for all pipes was 130. A time pattern with demand multipliers has also been considered (Table 1). The output is comprised of water age (h), chlorine residuals (mg/L), TTHM (µg/L), THAA (µg/L), and the respective species (µg/L). The DBPs prediction models (Amy et al. 1998) included the raw and alum coagulated water models for total THMs, total HAAs, and their species (Equation 1–4). The pH and temperature correction factors were also incorporated in the coagulated alum water models (Equations 5 and 6, Sohn et al. 2004). Units of TTHM, THAA and Br⁻ concentrations were in µg/L, temperature in °C, chlorine dose and DOC in mg/L, and time in hrs.

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**Table 1 | Water demand multipliers**

<table>
<thead>
<tr>
<th>Period (hrs)</th>
<th>0–4</th>
<th>4–8</th>
<th>8–12</th>
<th>12–16</th>
<th>16–20</th>
<th>20–24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplier</td>
<td>0.6</td>
<td>1.0</td>
<td>1.2</td>
<td>1.3</td>
<td>1.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 1 | Layout of the sample network.
Temperature and pH correction factors

\[
\text{TTHM} = \left( \text{TTHM}_{@pH = 7.5, \text{Temp} = 20^\circ C} \right) \times (1.156^{(pH - 7.5)}(1.0263)^{(	ext{Temp} - 20)})
\]

\[
\text{THAA} = \left( \text{THAA}_{@pH = 7.5, \text{Temp} = 20^\circ C} \right) \times (0.932^{(pH - 7.5)}(1.021)^{(	ext{Temp} - 20)})
\]

Chlorine decay models

The chlorine decay models are described in two steps (Equations 7–10): The fast chlorine decay model is defined as:

\[
C_1 = C_0 \exp(-k_1 t), \quad 0 \leq t \leq 5 \text{h}
\]

where \(C_1\) is the predicted chlorine residual in mg/L, \(C_0\) is the initial chlorine concentration, and \(k_1\) is the first order reaction rate constant in hr\(^{-1}\).

The following is the empirical relationship for predicting \(k_1\):

\[
\ln(K_1) = 0.442 + 0.889 \ln(\text{DOC})
+ 0.345 \ln(7.6(\text{NH}_3 - \text{N})) - 1.082 \ln(C_0)
+ 0.192 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right)
\]

where \(\text{DOC}\) is in mg/L, \(\text{Cl}_2\) is in mg/L and \(\text{NH}_3 - \text{N}\) is in mg/L as N.

The slow chlorine decay model is defined as

\[
C_2 = C_0 \exp[5(k_2 - k_1)]\exp(-k_2 t), \quad 5 \leq t \leq 168 \text{ hours}
\]

\(k_2\) can be estimated from the following empirical expression:

\[
\ln(K_2) = -4.817 + 1.187 \ln(\text{DOC})
+ 0.102 \ln(7.6(\text{NH}_3 - \text{N})) - 0.821 \ln(C_0)
- 0.271 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right)
\]

RESULTS AND DISCUSSIONS

Three scenarios, steady and non-steady conditions, have been considered to assess DBPs formation and chlorine decay in the distribution network.

Scenario 1—Steady-state condition

This is a steady state condition where the demand and the source chlorine concentrations were considered to be constant. In this scenario, three methods (listed below) were used to predict DBPs and chlorine residuals in a network and a chlorine dose of 2 mg/L were assumed. i) DBPs and chlorine residuals prediction by the standard internal algorithm of EPANET 2, ii) DBPs and chlorine residuals prediction by USEPA chemical models where weighted average water ages were calculated manually and iii) DBPs and chlorine residuals prediction by the linked EPANET 2 and USEPA chemical model, where water age was obtained from EPANET 2 simulation.

Predicting THMs growth using the first (EPANET 2) method does not give accurate results. One needs to know, beforehand, the limiting (maximum) THM concentrations. For estimating the chlorine decay in the bulk solution and at the pipe wall, values of bulk and wall coefficients were assumed based on literature \((\text{USEPA 2002; Rossman 2000})\).

In this case bulk and wall coefficients of 1 m/d and 1.5 m/d were assumed, respectively. In the second and third methods USEPA chemical models were used for average water quality condition with pH 7.5, temperature 20°C, DOC 2 mg/L, \(\text{Br^-} 100 \mu \text{g/L}\) and \(\text{Cl}_2/\text{DOC}\) ratio of 1.0. The predicted THM and chlorine residual values for all methods are shown in Figure 2.

It is observed that both the THMs and the chlorine residual values for the second and third methods, which use USEPA chemical models, were similar. This indicates that
water age estimation by EPANET 2 is based on weighted average calculation (since the manual calculation of water age was based on weighted average calculation). The chlorine residual estimated by EPANET 2 was significantly different from the result of USEPA chemical model (Figure 2). This might be due to the difference in the assumptions for predicting the chlorine decay and also due to the absence of real bulk and wall coefficients data. Finally it could be stated that scenario 1 is useful for predicting THMs and chlorine residuals under steady conditions. Figure 2 also shows that as the water travels to the furthest nodes (node 4), an increase in THMs formation and increased chlorine decay were observed. At the furthest node chlorine residual was below 0.2 mg/L and THMs concentration was above 40 μg/L.

Scenario 2—Non-steady-state condition with variable demand and constant chlorine dosage

This is an un-optimized situation where constant chlorine concentration is dosed without considering the THMs formation in the distribution system. This is a situation, which occurs in real distribution networks. Under this scenario a constant chlorine dose of 2 mg/L and a time pattern on nodal demand were considered. The results indicated that (not shown) the formation of THMs and chlorine residual follow the demand pattern. Accordingly as the water demand decreased the THMs formation increased and chlorine residual decreased. This can be explained by the increase in water age as the demand decreased. The reverse was observed as demand increased.

Scenario 3—Non-steady-state condition with varying demand and chlorine dosage

This is an optimized situation where the chlorine dose is adjusted in order to control the THMs formation in the distribution systems. Initially the THMs and chlorine residuals were predicted by considering chlorine concentration of 2 mg/L. However in this scenario the maximum THM formation was set not to exceed 40 μg/L, which is the maximum THM formation recommended by USA stage II DBPs rule. Hence the program gives a warning (alerts) to adjust the chlorine concentration at the source if the THM formation exceeds 40 μg/L in the network. Figure 3 Shows the THMs, chlorine dose and chlorine residual for non-steady state condition at the furthest node (node 4). Average water quality conditions were: pH 7.5, temperature 20°C, DOC 2mg/L, Br⁻ 100 μg/L, and for a minimum chlorine dose of 1.1mg/L. The curves indicate the time lag between the chlorine addition at the treatment plant and the concentration of chlorine residual and THM at node 4. For the first 14 h, the chlorine residual and THM at node 4 were zero. Once the chlorinated water reaches this node it will maintain certain amount of chlorine residual and THM depending on the chlorine dose.

In this scenario the maximum THM level was maintained at about 40 μg/L and the chlorine residual was set to remain constant at 0.1 mg/L by adjusting the demand through time. When the THM tends to go beyond the maximum limit, the chlorine dose is adjusted (reduced) automatically. The chlorine dose variation predicated by the model is very essential to have chlorine dose schedule to maintain the THM level below the maximum value. The results indicate that the required chlorine dose varies between 2 mg/L and 1.1 mg/L at different times as shown in Figure 3. When the chlorine dose was 1.1 mg/L, the chlorine residual at node 4 became 0.1 mg/L (which is lower than 0.2 mg/L). This suggests the need to boost the chlorine residual levels at this node to maintain the minimum residual requirement for effective disinfection.

The non-steady-state scenarios are useful to investigate the formation of THMs and chlorine residuals in a distribution system under varying conditions. Moreover, scenario 3 is very helpful for the operators to monitor the...
chlorine dose at the treatment plant and to schedule chlorine boosting in the distribution system in order to maintain minimum residual and limit THMs level.

**Effect of water quality parameters and treatment conditions**

Sensitivity analyses were performed for scenario 2 to understand the effects of individual water quality parameters (pH, temperature, Br\textsuperscript{−}, and DOC), treatment conditions (chlorine dose and DOC) and hydraulic condition (water age) on the formation of DBPs. In general temperature has positive effect on the formation of both TTHM and THAAs (Xie 2004). The higher the temperature the higher the reactivity and hence higher rate of production of end products (DBPs). The effect of pH on DBPs formation varies depending on the type of DBPs considered (TTHM and THAA). As shown in Figure 4 a higher pH results in a higher level of TTHM but a lower level of THAA. This is explained by the fact that HAAs species such as TCAA (the most predominant HAAs species) undergo hydrolysis reactions especially at higher pH to form TTHM. Up to pH of 6.5, the concentration of THAA is higher beyond which the concentration of TTHM becomes higher. And the trend indicates that the total DBPs (TTHM and THAA) increases with pH. Since HAAs (particularly DCAA and TCAA) have higher cancer risk factors, maintaining high pH may help reduce cancer risks. On the other hand low pH favors effective disinfection by chlorine (as a result of higher HOCl formation). Optimum pH that is ideal for all the treatment processes may not be easy to attain. Considering all these issues, the best option would be to reduce DBP precursors, that is, reduce the DOC concentration before chlorination.

In general increasing DOC levels in chlorinated water increases the formation of DBPs. However treatment processes such as coagulation followed by sedimentation and/or filtration not only reduce the amount of organic precursors, but also induces changes in precursors characteristics. For example, the specific UV absorbance (SUVA) of the treated water reduces and its reactivity, hence DBPs formation, is lowered. The prediction provided by raw water model (not shown) corresponds to over prediction compared to coagulated water models (Amy et al. 1998), this is because the raw water model does not incorporate the change in precursors reactivity by pre treatment processes such as coagulation, sedimentation and filtration.

Bromide ion has a positive effect on the formation of TTHM while reducing the THAA formation. This is because higher Br\textsuperscript{−} concentration shifts speciation to dichlorobromoacetic acid (DCBAA), dibromochloroacetic acid (DBCAA), and tribromochloroacetic acid (TBAA), which are not part of HAA6 (Sohn et al. 2004). It is stated in Amy et al. (1998) that the ratio of Br\textsuperscript{−}/DOC is the parameter most influential in controlling THM and HAA speciation. As the ratio increase, a shift to the more bromo-substituted species occurs. Formation of brominated THMs species (CHBr\textsubscript{3}) and HAAs species (DBAA) increased with increasing Br\textsuperscript{−}/DOC ratio.

Increasing chlorine dose increases the formation of both TTHM and THAA (Figure 5a). At higher chlorine dosages the formation of HAAs is favored over THMs. In the case of water age, this study indicate that the formation of TTHM, THAA, and their species continuously increased with increase in water age and that THMs were dominant over HAAs (Figure 5b). This may be explained by the fact that some chlorinated DBPs such as HAAs may degrade in extremities of distribution systems (AWWA 2002).

**Isopleths for DBPs and cancer risks**

Isopleths for THMs and chlorine residual are plotted for scenario 2 considering average water quality conditions (Figure 6). The results indicate that DBPs formation are higher as the water travels further from the source. On the other hand chlorine concentration decreases towards the furthest nodes. In assessing the chemical risks...
contributions associated with DBPs, TCAA has a higher chemical risk contribution in the network due to its higher concentration compared to the other DBPs (Table 2) and CHBr₃ has the lowest risk contribution. Total chemical risk is highest at node 4, which represents the highest water age. In order to minimize the higher chemical risks at some points in the network (due to high DBPs formation) either alternative disinfectants like

### Table 2: Total and individual chemical risks in the distribution system

<table>
<thead>
<tr>
<th>DBPs</th>
<th>Chemical risk factors (per ug/L)</th>
<th>Chemical risk contributions of DBPs at each node</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>$1.7 \times 10^{-7}$</td>
<td>$2.55 \times 10^{-6}$</td>
</tr>
<tr>
<td>CHBrCl₂</td>
<td>$1.7 \times 10^{-6}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>CHBr₂Cl</td>
<td>$2.4 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>CHBr₃</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$2 \times 10^{-8}$</td>
</tr>
<tr>
<td>DCAA</td>
<td>$3.0 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>TCAA</td>
<td>$2.4 \times 10^{-6}$</td>
<td>$2.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Total</td>
<td>$7.3 \times 10^{-5}$</td>
<td>$8.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

*The risk factors are only representative values.*
chloramines can be used or, based on water quality modeling, to provide chlorine-boosting schedules.

CONCLUSIONS

Since the water quality model in EPANET 2 does not have water quality parameter features for predicting THM growth and chlorine decay, an external link was developed (in C++ programming language) to couple/link the USEPA chemical models and EPANET 2 hydraulic model. The linked model was applied on a sample network to predict the formations of DBPs and chlorine decay under steady and non-steady-state conditions. The following conclusions can be drawn from this study:

- Creating a link between DBPs models and hydraulic models (EPANET 2) is very useful for having a direct simulation of DBPs formations in the distribution networks for extended time periods.
- The model is very useful for optimizing the chlorine dosage and to prepare chlorine dose schedule so that the DBPs formation in the distribution system does not exceed the maximum concentration limits.
- The model can be used to select location of booster chlorination points to maintain the minimum required chlorine residual in the network.

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REFERENCES


