Modeling formation and control of disinfection byproducts in chlorinated drinking waters
Edward McBean, Zoe Zhu and Wen Zeng

ABSTRACT

While disinfection of drinking water reduces the risks of pathogenic infection, threats to human health due to the formation of disinfection byproducts (DBPs) may arise due to natural organic precursors. Regression-based models characterizing the formation of DBPs are derived from data for 28 conventional water treatment plants in Ontario. DBPs are shown to be correlated statistically with dissolved organic carbon, pre-and post-chlorination dosages, pH and temperature. Using backward elimination nonlinear regression, a set of mathematical functions are obtained ($R^2 = 0.62$ to 0.79) for an array of DBPs. The models are used to guide decision-makers in the selection and operation of drinking water treatment processes to decrease DBP formation, indicating that a shift from emphasis on pre-chlorination to post-chlorination has the most effect on DBP formation.

Key words | DBPs, disinfection byproducts, drinking water disinfection, drinking water treatment plants, human health risk

INTRODUCTION

A variety of chemical and physical agents have been employed to destroy pathogenic microorganisms in drinking water. Chlorine has been the primary drinking water disinfectant for more than 90 years. Averill (1852), for example, proposed chlorine disinfection of human wastes as a public health measure against epidemics such as typhoid and cholera. Chlorine disinfection dramatically reduced the incidence of typhoid (Hooker 1913). Chlorine is the least expensive of the disinfectant options, but also has high oxidizing potential, thereby providing a chlorine residual throughout the distribution system and hence protection against microbial recontamination.

An increase in chemical agents in raw water sources has added to the challenge in disinfection processes (Watkinson 2006). Concerns also include viruses (e.g. hepatitis) (e.g. Melnick et al. 1978; Nasser 1994), protozoans (e.g. Brown et al. 1992; Leland et al. 1993). With the increasing concern for removing and inactivating some of the more resistant pathogens such as Giardia and Cryptosporidium, large chlorine doses are needed but simultaneously, water utilities must minimize the formation of disinfection byproducts (DBPs).

Disinfection processes are influenced by different physico-chemical and biological factors and the disinfection efficiency, Ct, can be characterised by a combination of dose and contact time (Gates 1998) and also characterised by percentage percentage inactivation. Water at a higher pH may also require a higher chlorine dose to maintain a consistent level of microbial inactivation before entering the distribution system to comply with the Surface Water Treatment Rule (SWTR). However, changes to pH to control DBPs should be carefully considered to prevent a decrease in corrosion control effectiveness in the distribution system and to avoid possible lead and copper corrosion problems (US EPA 2007). Table 1 compares the disinfection efficiency of chlorine disinfectants under varying conditions of temperature, pH, contact time and dose (after Sadiq & Rodriguez (2004)). Generally, the

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inactivation of organisms increases with increasing Ct. The pH has different effects on different disinfectants but, in general, at lower pH, chlorine is more effective against organisms than in alkaline conditions. Further, Ct required for inactivating microorganisms is lower in warm water than in cold water thus requiring higher chlorine dosages in winter than in summer conditions.

One of the challenges also is to maintain adequate chlorine residuals within the distribution system. The disinfectant residuals deplete rapidly when the water temperature is high, which explains the difficulty of maintaining minimum residual levels in large distribution systems during summer periods. Also, microbial activity within the distribution systems is higher in warm than in cold waters (Arora et al. 1997) resulting in the need for higher disinfectant doses in winter than in summer conditions.

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Table 1 Percent of inactivation of various organisms under varying disinfection conditions

<table>
<thead>
<tr>
<th>Disinfectants</th>
<th>Conc. (mg/l)</th>
<th>Organism (Group)</th>
<th>Contact time (min)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Percentage of Inactivation</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>2.0</td>
<td>V. cholerae (B)</td>
<td>30</td>
<td>7.0</td>
<td>20</td>
<td>&gt;99.99</td>
<td>Clark et al. (1994a,b)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Coliform (B)</td>
<td>2</td>
<td>7.0</td>
<td>5</td>
<td>&gt;99.99</td>
<td>Berman et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>E. coli (B)</td>
<td>2</td>
<td>7.0</td>
<td>5</td>
<td>&gt;99.999</td>
<td>Rice et al. (1999a)</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>C. jejuni (B)</td>
<td>1</td>
<td>6.0</td>
<td>4</td>
<td>&gt;99.99</td>
<td>Blaser et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>A. butzleri (B)</td>
<td>1</td>
<td>7.1</td>
<td>5</td>
<td>&gt;99.999</td>
<td>Rice et al. (1999b)</td>
</tr>
<tr>
<td></td>
<td>0.6–2.5</td>
<td>Polio virus (V)</td>
<td>0.7–2.4</td>
<td></td>
<td>5</td>
<td>&gt;99</td>
<td>Hoff (1986)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Rota virus (V)</td>
<td>0.25</td>
<td>6.0</td>
<td>5</td>
<td>&gt;99.99</td>
<td>Berman &amp; Hoff (1984)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Rota virus (V)</td>
<td>1.5</td>
<td>10.0</td>
<td>5</td>
<td>=99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>MS2 coliphage (V)</td>
<td>1</td>
<td>7.0</td>
<td>5</td>
<td>=99.99</td>
<td>Berman et al. (1992)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>G. lamblia (P)</td>
<td>10</td>
<td>6–7</td>
<td>25</td>
<td>=99</td>
<td>Clark et al. (1989)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>G. lamblia (P)</td>
<td>10</td>
<td>6.0</td>
<td>15</td>
<td>=99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>G. lamblia (P)</td>
<td>60</td>
<td>6–7</td>
<td>5</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>E. intestinalis (P)</td>
<td>8–16</td>
<td></td>
<td></td>
<td>=99</td>
<td>Rice et al. (1999c)</td>
</tr>
<tr>
<td>Mono-chloramines</td>
<td>1.0</td>
<td>C. jejuni (B)</td>
<td>15</td>
<td>8.0</td>
<td>5</td>
<td>&gt;99</td>
<td>Blaser et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>Rota virus (V)</td>
<td>360</td>
<td>8.5</td>
<td>5</td>
<td>=99</td>
<td>Berman &amp; Hoff (1984)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>MS2 coliphage (V)</td>
<td>1</td>
<td>7.0</td>
<td>5</td>
<td>=99</td>
<td>Berman et al. (1992)</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>C. parvum (P)</td>
<td>90</td>
<td>5</td>
<td></td>
<td>=90</td>
<td>Korich et al. (1990)</td>
</tr>
<tr>
<td>Chlorine-dioxide</td>
<td>0.5</td>
<td>Rota virus (V)</td>
<td>-1</td>
<td>6.0</td>
<td>5</td>
<td>&gt;99</td>
<td>Berman &amp; Hoff (1984)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Rota virus (V)</td>
<td>0.25</td>
<td>10.0</td>
<td>5</td>
<td>&gt;99</td>
<td></td>
</tr>
</tbody>
</table>

Source: Sadiq & Rodriguez (2004); Legends: B, Bacteria; V, Viruses; P, Protozoa.

inactivation of organisms increases with increasing Ct. The pH has different effects on different disinfectants but, in general, at lower pH, chlorine is more effective against organisms than in alkaline conditions. Further, Ct required for inactivating microorganisms is lower in warm water than in cold water thus requiring higher chlorine dosages in winter than in summer conditions.

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Since the discovery of total trihalomethanes (TTHMs) in drinking water in the 1970s, hundreds of specific compounds have been identified as drinking water DBPs (Richardson 1998). In the United States, stringent DBP regulations have been promulgated, placing limits on TTHMs and the sum of five species of haloacetic acids (HAA₅). Some DBPs are carcinogenic, mutagenic, or possibly teratogenic (Simmon & Tardiff 1978). Natural organic matter (NOM) is the organic precursor. US EPA guidelines for DBPs are 0.080 mg/L for TTHMs and 0.060 mg/L for HAA₅ (US EPA 2002). For systems that conduct monitoring yearly or less frequently, each sample is considered the locational running annual average (LRAA) for that monitoring location. However, if any single sample has a TTHM or HAA₅ concentration greater than the MCL, the system does not incur a violation immediately. Instead, the system must begin increased monitoring (US EPA 2007).

It is clear from the above that many interrelated conditions influence the formation of TTHMs and HAAs. To provide prediction capabilities under different environmental conditions, this paper describes regression-based
models for DBP formation developed from field data for a series of water treatment systems using surface water as the raw water source. Further, examples indicating how the models can be used by decision-makers to provide insights on opportunities to minimize DBP formation levels are described.

**FACTORS INFLUENCING DBP FORMATION**

The major halogenated DBPs (i.e. TTHMs and HAAs) are chemically stable, so they accumulate in disinfected waters and their concentrations increase with reaction time so long as a disinfectant residual exists. However, many halogenated DBPs are chemically unstable and are subject to hydrolysis or further oxidation. There is a reaction time during which the concentrations reach a maximum.

Chlorination dose has a variable impact on DBP formation. If the treatment system has an excess of disinfectant that is precursor-limited, small changes in the chlorine dose often only have minor effects on DBP formation. However, if the treatment system is under disinfectant-limited conditions, changes in disinfectant dose will have a large effect. As a general rule, disinfectant dose plays a greater role in DBP formation during primary disinfection than during secondary disinfection because primary disinfectants are usually added in amounts well below the long-term demand. Therefore, the disinfectant is the limiting reactant.

The relationship between disinfectant dose and DBP formation can be illustrated with a simple kinetic model. Figure 1 shows the results of a kinetic simulation for the simple second-order reaction as follows: $A + B \rightarrow C$, where $A$ represents the NOM precursor material, $B$ is the disinfectant, $C$ is the particular DBP, and $k$ is the second-order rate constant (AWWA 1999). The three curves in Figure 1 are the result of the calculation for three different combinations of $k$ and reaction time $t$.

Halogenated DBP formation, by an approximation, is proportional to the Total Organic Carbon (TOC) concentration at the point of chlorination. A number of investigators have found that TTHM formation has increased with increasing soluble organic content, reporting a first-order reaction with respect to Dissolved Organic Carbon (DOC) (e.g. Stevens et al. 1976; Trussell & Umphres 1978; Babcock & Singer 1979). The precursors of DBP formation are NOM, such as humic and fulvic acids. These natural organic DBP precursors can be subdivided into a hydrophobic fraction of primarily humic material and a hydrophilic fraction of primarily fulvic material. Babcock & Singer (1979) also found that the relative contribution to TTHM production of the humic fraction is greater than that of the fulvic fraction since it reacts more readily with chlorine. The NOMs in the water can be estimated by measuring surrogate parameters, including those of TOC and DOC, UV light absorbency at 254 nanometer (nm) wavelength (UV-254), specific UV absorbance, and TTHM formation potential. Additional details on NOM assessment are provided in US EPA (1999).

The rate of formation of DBPs, increases with increasing temperature. However, the high temperatures also accelerate depletion of chlorine residual and DBPs degrade more quickly. Reactive DBPs would undergo abiotic reactions with bases or active chlorine at a faster rate. For this reason, temperature increases may actually cause a decrease in the concentration of certain DBPs, such that the effects are unclear.

The pH effects on DBP formation vary for different byproducts (Singer et al. 1995). Many DBPs (HAAs, Trichlorophenol, haloacetonitriles, etc.) decrease in concentration with increasing pH, with the important exception being the TTHMs. It is probably base-catalyzed hydrolysis mechanisms which have the greatest overall...
effect on DBP formation. More specifically, many DBPs are decomposed by base-catalyzed hydrolysis. These compounds are less prevalent in waters with high pH and they tend to decrease in concentration at longer residence times (see Type 1 in Table 2). The TTHMs increase at high pH because many hydrolysis reactions actually lead to TTHM formation (Type 2 in Table 2). Other byproducts are themselves unaffected by base hydrolysis (e.g. the HAAs), but their formation pathways may be altered at high pH, resulting in lower production rates at high pH (Type 3 in Table 2).

Disinfection of source water containing the bromide ion may lead to the formation of brominated DBPs. Increases in the ratios of the bromide ion to the chlorine dose, and the ratio of the bromide ion to the DOC concentration, results in a shift in TTHMs and HAAs speciation to the more bromine-substituted species (Krasner et al. 1989; Black et al. 1996).

Sadiq & Rodriguez (2004) have summarized a number of predictive models for TTHMs and HAAs. While the models derived from laboratory data have demonstrated good predictive characteristics of TTHMs (e.g. Amy et al. 1987, 1998; Adin et al. 1991; Chang et al. 1996; Rathbun 1996a,b; Clark & Sivaganesan 1998; Rodriguez et al. 2000), the models developed from field conditions have much lower accuracy of prediction of TTHMs (e.g. Golfinopoulos & Arhonditsis 2002). As well, the same situation holds true for HAAs where the models derived from laboratory conditions (e.g. Clark & Sivaganesan 1998) are substantially better at prediction than those derived from field conditions (e.g. Villanueva et al. 2003) although the number of predictive models for HAAs is much smaller than the number derived for TTHMs.

DATA EMPLOYED IN DEVELOPMENT OF THE PREDICTIVE MODELS IN THIS RESEARCH

Water quality data including DBP concentrations collected from twenty-eight water treatment plants operating in Ontario over a two-year period were selected for purposes of this investigation. The data were provided by the Drinking Water Surveillance Program (DWSP) of the Ontario Ministry of the Environment (MOE).

Table 3 summarizes average and standard deviations of raw water and chlorination dosages for the twenty-eight water treatment plants. A total of 180 individual water samples were employed in the analyses which follow.
STATISTICAL PREDICTIVE MODELS FOR DBP FORMATION

Simple correlation structure

The correlation matrix between the variables employed herein is provided in Table 4. These summarized results indicate the high degree of correlation between DOC concentrations and raw water and treated water with TTHMs (0.76 and 0.78) and HAAs (0.81 and 0.81); clearly, DOC is very important in determining DBP formation.

Tables 5a and 5b summarize the percentages of the TTHMs and HAAs consisting of the individual subspecies. The tables show that the chlorinated DBPs are dominant, ranging from 70 to 90% of TTHMs and HAAs and the brominated DBPs range from 10 to 30%. These findings demonstrate the ratio of brominated DBP/chlorinated DBPs are low for Ontario conditions, indicating that Bromine concentrations are low and the bromide effect on DBP formation is relatively minor.

Stepwise regression with backward elimination method

When the number of predictors is too large to allow for explicit or implicit examination of all possible subsets, several alternative selection procedures generally will identify good models. The simplest such procedure is the backward elimination (BE) method.

The BE method begins with regression using all variables, and subsequently reduces the number of variables in the equation until a decision is reached on the equation to use. It is an economical approach in the sense that it examines only the “best” regressions containing a certain number of variables. The steps in the procedure are:

1. A regression equation containing all variables is computed.
2. The $P$-value of the $t$-test is calculated for every predictor variable treated as if it was the last variable to enter the regression equation.
3. The lowest $P$-value of each variable, say $P_L$, is compared with a pre-selected significance level $P_0$, say 0.05.
   a. If $P_L < P_0$, remove the variable $X_L$ from consideration and re-compute the regression equation in the remaining variable.
   b. If $P_L > P_0$, adopt the regression equation as calculated.

| Dissolved organic carbon (DOC) of raw water (mg/L) | 3.57 | 2.10 |
| pH of raw water | 8.05 | 0.40 |
| Average temperature of raw water (°C) | 11.0 | 2.63 |
| Total chlorine dosage (mg/L) | 2.47 | 0.94 |

Notes: Statistics for Delhi, Goderich, Tecumseh, Union, Wallaceburg, Windsor, Amherstburg, Belleville, Oshawa, Picton, Port Hope, Burlington, Owen Sound, Thunder Bay, Whitby, South Glengarry, Elgin Primary, Nanticoke, St. Catharines, Casselman, Pembroke, Renfrew, Rockland, Kenora, Redrock, Huntsville, Sudbury, and Trenton.

Table 4 | Correlation table of the variables in regression model (log-transformed)

<table>
<thead>
<tr>
<th>DOCraw</th>
<th>DOCtreated</th>
<th>Pre-Cl2 dose</th>
<th>Post-Cl2 dose</th>
<th>Total Cl2 dose</th>
<th>Temperature</th>
<th>pHraw</th>
<th>pHtreated</th>
<th>TTHMs</th>
<th>HAAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOCraw</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOCtreated</td>
<td>0.91</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-Cl2 dose</td>
<td>0.15</td>
<td>0.18</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-Cl2 dose</td>
<td>0.39</td>
<td>0.32</td>
<td>-0.15</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Cl2 dose</td>
<td>0.46</td>
<td>0.45</td>
<td>0.73</td>
<td>0.47</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>-0.09</td>
<td>-0.09</td>
<td>-0.03</td>
<td>0.14</td>
<td>0.04</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pHraw</td>
<td>-0.34</td>
<td>-0.20</td>
<td>-0.15</td>
<td>-0.08</td>
<td>-0.13</td>
<td>0.05</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pHtreated</td>
<td>-0.45</td>
<td>-0.36</td>
<td>-0.08</td>
<td>-0.24</td>
<td>-0.23</td>
<td>-0.11</td>
<td>0.28</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>TTHMs</td>
<td>0.76</td>
<td>0.78</td>
<td>0.30</td>
<td>0.42</td>
<td>0.57</td>
<td>0.17</td>
<td>-0.28</td>
<td>-0.37</td>
<td>1.00</td>
</tr>
<tr>
<td>HAAs</td>
<td>0.81</td>
<td>0.81</td>
<td>0.26</td>
<td>0.35</td>
<td>0.51</td>
<td>-0.10</td>
<td>-0.37</td>
<td>-0.41</td>
<td>0.82</td>
</tr>
</tbody>
</table>
This is an appropriate procedure, especially for the purpose of seeing all the variables in the equation in order “not to miss anything” (Draper & Smith 1981 and Tyagi et al. 1996). It also can prevent regression equations from relying too heavily on the automatic selection preformed by the computer, so as to generate comparable results to ordinary least squares regression for the statistical modeling of water quality constituents, in which high interparameter correlations exist.

Non-linear regressions were conducted by logtransforming the data, comparable to Amy et al. (1987, 1998), Watson (1993), Ozekin (1994), Chang et al. (1996), Rathbun (1996a,b), Huixian et al. (1997), Rodriguez et al. (2000), respectively. The resulting equations for TTHMs, HAAs, chloroform, and trichloro acetic acid are as follows:

(1) Regression results for TTHMs formation model

The predictive model for TTHMs takes the following form:

\[
\text{TTHMs} = 10^{0.715 \times (\text{DOC}_{\text{raw}})^{0.322} \times (\text{DOC}_{\text{treated}})^{0.761} \\
	 \times (\text{Pre} - \text{Cl}_2)^{0.206} \times (\text{Post} - \text{Cl}_2)^{0.184} \times (\text{Temp})^{0.204}}
\]

(1)

where the independent parameters DOC\text{raw}, DOC\text{treated}, Pre-Cl\text{2}, Post-Cl\text{2}, and Temp correspond to the dissolved organic carbon (mg/L) in the raw and treated water, pre- and post-chlorine dose (mg/L), and temperature (°C), with all variables statistically significant at 95%.

The predicted versus observed TTHMs from this equation are illustrated in Figure 2. Considering the large number of observations (n = 180) generated from a number of different treatment plants, this model accounts for much of the variation in TTHM concentrations of the independent model parameters.

(2) Regression results for HAAs formation model

The model for HAAs reflecting the statistically significant variables is:

\[
\text{HAAs} = 10^{5.333 \times (\text{DOC}_{\text{raw}})^{0.380} \times (\text{DOC}_{\text{treated}})^{0.774} \\
	 \times (\text{Pre} - \text{Cl}_2)^{0.102} \times (\text{pH}_{\text{raw}})^{-2.599}}
\]

\[
(2)
\]

Predicted value vs observed value of TTHM with log transformed data

\[
y = 0.7303x + 0.3542
\]

\[
R^2 = 0.7303
\]

Figure 2 | Scatterplot of TTHMs (µg/L) Observed vs Predicted (log data).

Predicted value vs observed value of HAAs in logtransformed data

\[
y = 0.7215x + 0.4005
\]

\[
R^2 = 0.7215
\]

Figure 3 | Scatterplot of HAAs (µg/L) Observed vs Predicted (log data).
where the independent parameters DOC$_{raw}$, DOC$_{treated}$, Pre-Cl$_2$, and pH$_{raw}$ correspond to the dissolved organic carbon (mg/L) in the raw and treated water, pre-chlorine dose (mg/L), and pH in the raw water. All of the parameters in Equation (2) are statistically significant and the model has an $R^2$ of 0.72 as shown in Figure 3.

(3) Regression results for subspecies of TTHMs and HAAs

Formalities with respect to Equations (1) and (2) and for a series of other subsets of TTHMs and HAAs are summarized in Table 6. The fit for all of the equations is seen to be robust.

### PROCEDURES TO REDUCE DBP LEVELS

(a) Shift in locations of chlorine doses

An approach to decrease DBP formation is to consider shifting from prechlorination to post-chlorination because of the acknowledged relationships of TTHMs and HAAs with DOC. This approach has value because the water treatment processes decrease the DOC concentrations (e.g. at Delhi, Ontario, the mean DOC in the raw water is 5.04 mg/L whereas the mean DOC in the treated water is 2.54 mg/L). The systems model for TTHMs, (1), confirms this since the exponent in pre-chlorination is 0.206 whereas for post-chlorination, the exponent is 0.184. Retaining the same total chlorine dose but applying more of the chlorine at a later point in the treatment sequence (i.e. increase post-chlorination) results in lower TTHM formation. The results of the analysis are listed in Table 7; the total chlorination levels remain the same but with the change in chlorine levels, the TTHMs and HAAs decrease as the shift is made to higher post-chlorination (see Figure 4). The shaded portions of Table 7 indicate where the TTHMs and HAAs exceed the US EPA guidelines. As depicted in Figure 5, reductions of 62% and 39% for TTHMs and HAAs, respectively, are obtained through shifting the dosages of chlorine for different locations.

(b) Reduced chlorine dosage

An alternative possible strategy is to use [1] and [2] to estimate the change in DBP formation concentrations with

### Table 6 | Summary results of the regression analyses

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Model</th>
<th>Correlation coefficient</th>
<th>Model statistical significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTHMs</td>
<td>TTHMs = $10^{0.715} \times (\text{DOC}<em>{\text{raw}})^{0.322} \times (\text{DOC}</em>{\text{treated}})^{1.761} \times (\text{Pre-Cl}_2)^{0.206}$</td>
<td>0.86</td>
<td>$P &lt; 0.0005$</td>
</tr>
<tr>
<td>HAAs</td>
<td>HAAs = $10^{0.33} \times (\text{DOC}<em>{\text{raw}})^{0.380} \times (\text{DOC}</em>{\text{treated}})^{0.774} \times (\text{Pre-Cl}_2)^{0.102} \times (\text{pH})^{-2.599}$</td>
<td>0.85</td>
<td>$P &lt; 0.0005$</td>
</tr>
<tr>
<td>HAAs$_5$</td>
<td>HAAs$<em>5$ = $10^{3.758} \times (\text{DOC}</em>{\text{raw}})^{0.343} \times (\text{DOC}_{\text{treated}})^{0.876} \times (\text{Pre-Cl}_2)^{0.515}$</td>
<td>0.86</td>
<td>$P &lt; 0.0005$</td>
</tr>
<tr>
<td>Dichloroacetic</td>
<td>Dichloroacetic = $10^{4.044} \times (\text{DOC}<em>{\text{raw}})^{0.357} \times (\text{DOC}</em>{\text{treated}})^{0.711} \times (\text{Pre-Cl}_2)^{0.108}$</td>
<td>0.79</td>
<td>$P &lt; 0.0005$</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Chloroform = $10^{3.283} \times (\text{DOC}<em>{\text{raw}})^{0.534} \times (\text{DOC}</em>{\text{treated}})^{1.154} \times (\text{Pre-Cl}_2)^{0.212}$</td>
<td>0.89</td>
<td>$P &lt; 0.0005$</td>
</tr>
</tbody>
</table>

### Table 7 | Changes of TTHMs and HAAs in response to shifts in pre- and post-chlorination

<table>
<thead>
<tr>
<th>Pre-chlorine levels</th>
<th>Post-chlorine levels</th>
<th>TTHMs</th>
<th>HAAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1000</td>
<td>2.7000</td>
<td>0.0838</td>
<td>0.0776</td>
</tr>
<tr>
<td>0.5500</td>
<td>3.2500</td>
<td>0.0720</td>
<td>0.0723</td>
</tr>
<tr>
<td>0.2750</td>
<td>3.5250</td>
<td>0.0633</td>
<td>0.0674</td>
</tr>
<tr>
<td>0.1375</td>
<td>3.6625</td>
<td>0.0553</td>
<td>0.0628</td>
</tr>
<tr>
<td>0.0688</td>
<td>3.7313</td>
<td>0.0481</td>
<td>0.0585</td>
</tr>
<tr>
<td>0.0344</td>
<td>3.7656</td>
<td>0.0418</td>
<td>0.0545</td>
</tr>
<tr>
<td>0.0172</td>
<td>3.7828</td>
<td>0.0362</td>
<td>0.0508</td>
</tr>
<tr>
<td>0.0086</td>
<td>3.7914</td>
<td>0.0314</td>
<td>0.0473</td>
</tr>
</tbody>
</table>

Notes: All values in mg/L; Shaded areas indicate concentrations of TTHMs and HAAs which exceed US EPA guidelines.
reduced chlorination levels. The results listed in Table 8 demonstrate how the DBPs decrease in magnitude in response to decreased chlorine levels. With reductions of chlorine, TTHMs and HAAs concentrations lower than the US EPA guidelines can be obtained.

(c) Reduced DOC in raw water

The implication of reduced DOC in the source (raw) water on HAAs formation, for different pre-chlorine dosage, is depicted in Figure 6, as an example, demonstrating the substantial effect of lower DBP concentrations can be achieved by use of coagulation/flocculation. Clearly, the influence of the implementation of coagulation/flocculation can be an important option to reduce DBP formation whole avoiding the consequences of low disinfection actions.

(d) Cautionary notes

It is emphasized that the value of systems models is to explore potential options. However, while useful, other aspects must also be considered, including:

(i) there must always be caution used when using systems models to extrapolate. Are the results still valid with the extrapolation?

(ii) while reducing chlorination levels may reduce DBP formation, the functioning of the chlorine disinfection will at some point not be accomplished and not meet stipulated guidelines. For example, prechlorination prior to coagulation may be being used to reduce biofouling in the filters and to oxidize iron and manganese. Hence the strategy of reducing chlorine dosages to reduce DBP formation must be evaluated for its other ramifications.
CONCLUSION

An array of predictive models has been developed to characterize DBP formation in water treatment plants using surface water, for facilities in Ontario. These predictive models are shown to be improved over other predictive models. The models were used for decision support to investigate the potential to control DBP formation, for example, by shifting from pre-chlorination to post-chlorination, and reducing chlorine dosage, to reduce DBP formation concentrations or employ the enhanced coagulation to reduce the natural organic carbon to control the DBP formation.

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