Disinfectant decay and disinfection by-products formation model development: chlorination and ozonation by-products

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Abstract

Comprehensive disinfectant decay and disinfection by-product formation (D/DBP) models in chlorination and ozonation were developed to apply to various types of raw and treated waters. Comparison of several types of models, such as empirical power function models and empirical kinetic models, was provided in order to choose more robust and accurate models for the D/DBP simulations. An empirical power function model based on dissolved organic carbon and other parameters (Empirically based models for predicting chlorination and ozonation by-products: haloacetic acids, chloral hydrate, and bromate, EPA Report CX 819579, 1998) showed a strong correlation between measured and predicted trihalomethane (THM) and haloacetic acid (HAA) formation for raw waters. Internal evaluation of kinetic-based models showed good predictions for chlorine decay and THM/HAA formation, but no significant improvements were observed compared to the empirical power function model simulations. In addition, several empirical models for predicting ozone decay and bromate (ozonation disinfection by-product) formation were also evaluated and/or developed. Several attempts to develop kinetic-based and alternative models were made: (i) a two-stage model (two separate decay models) was adapted to ozone decay and (ii) an ozone demand model was developed for bromate formation. Generally, internal evaluation of kinetic-based models for ozone decay showed significant improvements, but no significant improvements for the simulation of bromate formation were observed compared to the empirical power function model simulations. Additional efforts were performed to reduce the gaps between specific models and their actual application. For instance, temperature effects and configuration of ozone contactors were considered in actual application.

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Keywords: Chlorination; THM; HAA; Ozonation; Bromate; Modeling

1. Introduction

Numerous models for disinfectant decay and disinfection by-products (D/DBPs) formation in chlorination and ozonation have been proposed in recent decades, but these models have not been sufficient in developing a comprehensive and systematic model. For chlorination and ozonation, a comprehensive model for D/DBPs should consider variation of the organic (e.g., natural
organic matter (NOM)) and inorganic (e.g., Br\textsuperscript{−}) precursors with treatment processes. Significant efforts should be focused on filling the gaps between specific models and their actual application. For example, some models, such as coagulated water trihalomethane (THM) and haloacetic acid (HAA) models, do not include temperature effects [1]. In this study, several models have also been developed for raw waters, but are of limited applicability to treated waters because of NOM variability [1]. Comparison of several types of models, such as empirical power function models and empirical kinetic models, is provided in order to choose more robust and accurate models for the D/DBP simulations in chlorination and ozonation processes.

The purpose of this paper was two fold. First, a comprehensive model was developed for predicting chlorine and ozone residual and DBP formation including THMs, HAA6, and bromate for raw and coagulated waters. Second, this research has provided D/DBP models for disinfectant/DBP simulation programs, such as the U.S. EPA water treatment plant model (WTPM) and the American Water Works Association Research Foundation (AwwaRF) integrated disinfection design framework (IDDF).

2. Materials and methods

2.1. Data bases

For the development of general D/DBP models, several databases were assembled from previous research. Tables 1 and 2 list a summary of databases used in this study. The most comprehensive bench-scale study for D/DBP was conducted by Amy et al., published in 1998 [1]. This database (hereafter referred to as the EPA 1998 database) was primarily used to develop D/DBP models. The other databases were primarily used to evaluate the models and/or develop specific complimentary models (e.g., UVA decay and short-term DBP formation). The models developed were subjected to an internal evaluation where model predictions were compared against measured data (i.e., EPA databases) upon which the model was based (calculated). The other databases were primarily used to evaluate the models and/or develop specific complimentary models (e.g., ozone decay and short-term bromate formation). The models were subjected to two different types of evaluations: (i) an internal evaluation where model predictions were compared against measured data upon which the model was based (calibrated) and (ii) an external evaluation where model prediction were compared against independent data from the literature.

2.2. Chlorination

2.2.1. Empirical power function models (multiple regression models)

Chlorination by-product models—THM & HAA: Empirical power function models are readily available for predicting chlorination DBP formation [1–3]. The model [2] has already served as the basis for the original USEPA water treatment plant model [4]. However, these models were based on high chlorine doses applied to raw/un-treated water sources. The simulation results were reported to underpredict for full-scale data [4]. Recently, Amy et al. [1] developed models (hereafter EPA 1998 models) that were based on lower chlorine doses applied to either raw/un-treated waters or chemically coagulated (conventionally treated) waters. These new models predict THMs (total and four species), HAA6 and six species, and chloral hydrate (CH), and are based on a database derived from 12 raw/un-treated waters with a subset of eight waters subjected to both alum and iron coagulation. The raw water models take the following multiple-parameter power function form:

$$\text{THM}_x = k(\text{DOC})^a(\text{Br}^–)^b(\text{Temp})^c(\text{Cl}_2)^d(\text{pH})^e(\text{time})^f,$$

where the independent parameters DOC, Br\textsuperscript{–}, Temp, Cl\textsubscript{2}, pH, and time correspond to the dissolved organic carbon (mg/L), bromide concentration (µg/L), temperature (°C), chlorine dose (mg/L), chlorination pH, and reaction time (h), respectively, and k, a, b, c, d, e, and f are empirical constants.

The strengths of the model are flexibility and applicability. This model can be applied to various water qualities (e.g., TOC or DOC and Br\textsuperscript{–}), as well as different operating conditions (e.g., pH, Cl\textsubscript{2} dose, and temperature). The major limitation of the raw/un-treated model is the questionable applicability of these models to treated waters, while the coagulated water DBP models have a limitation in application to in-plant and distribution system DBP simulations because temperature and pH are not considered as variables.

2.2.2. Modeling effort

Stepwise regression method: A multiple forward stepwise regression method was applied for the development of the empirical power function models. The multiple regression method is popular in modeling because DBP formation is well estimated from power functional equations [2]. A power function equation is a transformed equation derived from multiple linear regression. The only difference is that the input and output parameters are transformed to logarithm values.

The forward stepwise regression method is one regression method. The standard regression enters all input variables into the regression equation in one single step, while stepwise regression adds or deletes from the model at each step of the regression until the ‘best’
Table 1
Summary of databases used in model development: chlorination

(a) Bench-scale database

<table>
<thead>
<tr>
<th>Database</th>
<th>Cl\textsubscript{2} residual</th>
<th>THMs</th>
<th>HAAs</th>
<th>Other DBPs</th>
<th>Note</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 1998 [1]</td>
<td>Cl\textsubscript{2} residual</td>
<td>THM4</td>
<td>HAA6</td>
<td>N/A</td>
<td>Raw, coagulated waters, comprehensive experiments</td>
<td>Develop DBP models (THM and HAA)</td>
</tr>
<tr>
<td>EPA 1987 [2]</td>
<td>N/A</td>
<td>THM4</td>
<td>N/A</td>
<td>N/A</td>
<td>Raw waters, comprehensive experiments, short-term reaction</td>
<td>Verify short-term DBP formation</td>
</tr>
</tbody>
</table>

(b) Detailed description of bench-scale databases

<table>
<thead>
<tr>
<th>Database</th>
<th>Source</th>
<th>Description</th>
<th>Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 1998</td>
<td>‘Empirically based models for predicting chlorination and ozonation by-products’ EPA Report [1]</td>
<td>Comprehensive database for THM and HAA from 12 raw waters, eight coagulated waters, wide range of variables (DOC, UVA, Cl\textsubscript{2} dose, pH, temperature, time), THMs (four species) and HAA\textsubscript{6} (six species)</td>
<td>Comprehensive database for THMs and HAA\textsubscript{6} formation and Cl\textsubscript{2} residual</td>
<td>Coagulated water experiments were performed under one pH (\textasciitilde 7.5) and temperature (\textasciitilde 20°C)</td>
</tr>
<tr>
<td>EPA 1987</td>
<td>‘Developing models for predicting trihalomethane formation potential and kinetics’ [2]</td>
<td>Nine raw waters</td>
<td>Strength in short-term reaction periods, strength in pH and bromide variations</td>
<td>No HAAs data, high Cl\textsubscript{2}/DOC ratios</td>
</tr>
</tbody>
</table>

Temp = 10–30°C
Time = 0.1, 0.5, 1, 2, 4, 8, 24, 48, 96, and 168 h
pH = 4.6–9.8, n = 1090

N/A = not available.
### Summary of databases used in model development: ozonation

#### (a) Bench-scale database

<table>
<thead>
<tr>
<th>Database</th>
<th>O$_3$ residual</th>
<th>BrO$_3^-$</th>
<th>Other DBPs</th>
<th>Note</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 1998 [1]</td>
<td>O$_3$ residual</td>
<td>BrO$_3^-$</td>
<td>N/A</td>
<td>Raw, coagulated waters, comprehensive experiments</td>
<td>Develop DBP model (BrO$_3^-$)</td>
</tr>
<tr>
<td>WITAF 1992 [15]</td>
<td>N/A</td>
<td>BrO$_3^-$</td>
<td>Ozonation by-products (bromoform, MBAA, DBAA)</td>
<td>Limited chlorinated conditions, coagulated and ozonated waters</td>
<td>Develop UVA decay model associated with ozonation (ozone oxidation) of NOM</td>
</tr>
</tbody>
</table>

#### (b) Detailed description of bench-scale databases

<table>
<thead>
<tr>
<th>Database</th>
<th>Source</th>
<th>Description</th>
<th>Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 1998</td>
<td>‘Empirically based models for predicting chlorination and ozonation by-products’, EPA report [1]</td>
<td>10 raw waters</td>
<td>Comprehensive database for BrO$_3^-$ formation, O$_3$ residual</td>
<td>Temperature variation is not available (only 20°C)</td>
</tr>
<tr>
<td>WITAF 1992</td>
<td>‘Effect of coagulation and ozonation on the formation of disinfection by-products’ [15]</td>
<td>Source: 18 waters from USA</td>
<td>THMs and HAAs for coagulated waters</td>
<td>Ozonation apparatus is similar to semi-batch (close to CSTR)</td>
</tr>
<tr>
<td></td>
<td>Experiments: (1) coagulation, (2) ozonation</td>
<td></td>
<td></td>
<td>UVA after ozonation is available</td>
</tr>
<tr>
<td></td>
<td>DOC removal with coagulation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorination: four species of THM and five species of HAA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ozonation: BrO$_3^-$, brominated DBPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Bromoform, MBAA, DBAA)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### (c) Full-scale databases

<table>
<thead>
<tr>
<th>Database</th>
<th>O$_3$ residual</th>
<th>BrO$_3^-$</th>
<th>Other DBPs</th>
<th>Note</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEDIF/GDE</td>
<td>O$_3$ residual</td>
<td>BrO$_3^-$</td>
<td>N/A</td>
<td>Advanced treated water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(conventional + O$_3$ + BAC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(three plants)</td>
<td></td>
<td>Simulation of full-scale DBPs and disinfection decay (three plant)</td>
<td>In-plant and dist. sys. DBPs</td>
<td></td>
</tr>
</tbody>
</table>

N/A = not available, MBAA = monobromoacetic acid, DBAA = dibromoacetic acid, THM = trihalomethane, HAA = haloacetic acid, CSTR = continuous stirred-tank reactor, GDE/SEDIF = Syndicat des Eaux d’Ille de France/Generale des Eaux.
regression model is obtained. Commercial software (STATISTCA) is used for multiple stepwise regression. The main advantage of stepwise regression is that this method can sequentially select important variables automatically.

2.3. Ozonation

2.3.1. Empirical power function models (multiple regression models) for ozone decay and bromate formation

Most of the models for predicting ozone residual and bromate (BrO₅⁻) formation take empirical kinetic forms or empirical power functional forms because the complexity of natural organic matter restricts developing complete theoretically based chemical kinetic models. Siddiqui and Amy [5] developed empirical and semi-kinetic bromate formation models. These models were developed from semi-batch bench-scale experiments, and tended to be underpredictive in simulating continuous-flow full-scale and pilot-scale experiments. Ozekin [6] developed bromate formation models derived from two different reactor configurations: (i) semi-batch and (ii) true batch. In the semi-batch system, ozone was applied continuously to a batch of water to achieve a targeted applied dose. In the true-batch system, a stock solution of ozone was prepared and added to a batch of water. True batch, corresponding to a completely mixed batch (CMB) reactor, is equivalent to a plug flow reactor (PFR), while semi-batch represents deviation from PFR. Other than zero order, the concentration versus time profile of a CMB corresponds to the concentration distance profile of a PFR for the same rate constant. Compared to semi-batch models, true-batch models showed generally good simulation results in full-scale simulations. The major limitation of the Ozekin models [6] is that these models were based on a temperature of 20°C and variations in temperature cannot be directly considered.

Ozekin [6] developed ozone decay and bromate formation models from 10 different raw waters. The equations for ozone decay and bromate (BrO₅⁻, μg/L) formation are presented in Tables 3 and 4, respectively. It is noted that the ozone decay model represents ‘dissolved’ ozone residual (DO₃, mg/L). From a practical point of view, it is not easy to measure the average (dissolved) ozone residual in each chamber of an ozone contactor. If ozone residual is measured from the outlet of an ozone contactor, the type of ozone application (i.e., co-current or count-current) should be considered. According to the USEPA guidance manual [7], dissolved ozone residual under counter-current flow is taken to be half of the concentration at the outlet from the chamber (C = C₉₀/2). Otherwise, dissolved ozone residual can be assumed to be the same as the concentration at the outlet (C = C₉₀).

For the bromate formation models, equations that include an ammonia term can be applied under the condition of ammonia addition (one bromate control strategy) or a high ambient ammonia concentration, while the equations without an ammonia term can be used under low ambient ammonia concentrations. Ultraviolet absorbance (UVA) can be applied to both raw and treated waters because raw waters with low specific UVA (UVA₂₅⁴/DOC, SUVA) resemble treated waters with low SUVA derived from high SUVA raw waters. Thus, the DOC-based models can be applied to raw waters subjected to pre-ozonation, while the UVA-based models can be applied to conventionally treated waters (i.e., intermediate ozonation) and waters derived from staged ozonation.

3. Results and discussion

3.1. Chlorination

3.1.1. DOC, UVA and DOC*UVA-based models

Table 5 lists THM and HAA prediction models that were developed using the EPA databases. The \( R^2 \) values are based on log-log transforms (linearizations) of the power functions. Some models were adapted from the

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Ozone decay models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Model</td>
</tr>
<tr>
<td>DOC-based model [6]</td>
<td>[ \text{DO}_3 = 6554(\text{DOC}^{-1.64}(\text{pH}^{-4.433}(\text{O}_3)^{1.524}(t)^{-0.638}(\text{Alk})^{0.111}} ] ( R^2 = 0.67, n = 323 )</td>
</tr>
<tr>
<td>UVA-based model (developed from EPA 1998 database)</td>
<td>[ \text{DO}_3 = 45.56(\text{UVA}^{-0.719}(\text{O}_3)^{1.282}(\text{pH})^{-3.924}(\text{Alk})^{0.239}(t)^{-0.608} ] ( R^2 = 0.67, n = 213 )</td>
</tr>
</tbody>
</table>

Boundary conditions: DOC = dissolved organic carbon (mg/L): 1.1 ≤ DOC ≤ 8.4
UVA = ultraviolet absorbance at 254 nm (cm⁻¹): 0.010 ≤ UVA₂₅⁴ ≤ 0.280
pH = pH of ozonated water: 6.5 ≤ pH ≤ 8.5
Alk = alkalinity of ozonated water (mg/L as CaCO₃): 13 ≤ Alk ≤ 316
\( \text{O}_3 = \) transferred/utilized ozone (mg/L): 1.1 ≤ \( \text{O}_3 \) ≤ 10.0
\( t = \) time (min): 1 ≤ t ≤ 120
Table 4
Bromate formation models

<table>
<thead>
<tr>
<th>Name</th>
<th>Model</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>From [6]</td>
<td>[ \text{BrO}_3^- = 1.55 \times 10^{-6} \text{(DOC)}^{-1.26} \text{(pH)}^{5.82} \text{(O}_3^-)^{1.57} \text{(Br)}^{-0.73} \text{(t)}^{0.28} ]</td>
<td>Without ammonia</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.73, n = 303 )</td>
<td></td>
</tr>
<tr>
<td>Developed from [6]</td>
<td>[ \text{BrO}_3^- = 1.19 \times 10^{-7} \text{(UVA)}^{-0.623} \text{(pH)}^{5.68} \text{(O}_3^-)^{1.59} \text{(Br)}^{-0.307} \text{(t)}^{0.607} \text{(Alk)}^{-0.201} ]</td>
<td>With ammonia</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.70, n = 213 )</td>
<td></td>
</tr>
<tr>
<td>From [6]</td>
<td>[ \text{BrO}_3^- = 1.63 \times 10^{-6} \text{(DOC)}^{-1.3} \text{(pH)}^{5.79} \text{(O}_3^-)^{1.57} \text{(Br)}^{-0.73} \text{(t)}^{0.27} \text{(NH}_3^-\text{N)}^{-0.033} ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.672, n = 323 )</td>
<td></td>
</tr>
<tr>
<td>Developed from [6]</td>
<td>[ \text{BrO}_3^- = 8.71 \times 10^{-9} \text{(UVA)}^{-0.593} \text{(pH)}^{5.50} \text{(O}_3^-)^{1.279} \text{(Br)}^{-0.944} \text{(t)}^{0.337} \text{(Alk)}^{-0.167} \text{(NH}_3^-\text{N)}^{-0.051} ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.70, n = 213 )</td>
<td></td>
</tr>
</tbody>
</table>

Boundary conditions: DOC (mg/L): 1.1 ≤ DOC ≤ 8.4

- UVA at 254 nm (cm⁻¹): 0.010 ≤ UVA₂₅₄ ≤ 0.280
- pH = pH of ozonated water: 6.5 ≤ pH ≤ 8.5
- Br⁻ (µg/L): 70 ≤ Br⁻ ≤ 440
- O₃ = transferred/utilized ozone (mg/L): 1.1 ≤ O₃ ≤ 10.0
- NH₃–N = nitrogen ammonia (mg/L): 0.02 ≤ NH₃–N ≤ 3
- Alk (mg/L as CaCO₃): 13 ≤ Alk ≤ 316
- t (min): 1 ≤ t ≤ 120

other references [1,3], but several models were developed from the same database. These models use input parameters such as pH, temperature, reaction time, chlorine dose, Br⁻ concentration, DOC, UVA, and/or DOC*UVA (a two-way interaction). Total organic carbon (TOC) is assumed equivalent to DOC since DOC is generally greater than 95% of the TOC in most source waters. The coefficients represent the effect of each parameter on DBP formation. For example, the coefficient of pH for total THM (TTHM) is positive, but the coefficient of pH for HAA6 is negative. This corresponds well with TTHM and HAA6 behavior. The negative effect of pH for HAA6 formation is due to trichloroacetic acid (TCAA) formation, in that high pH induces base-catalyzed hydrolysis, thus chloroform formation prevails over TCAA formation [8]. The negative coefficient of Br⁻ on HAA6 formation indicates that higher Br⁻ concentration shifts speciation to the remaining HAA species, dichlorobromoacetic acid (DCBAA), dibromochloroacetic acid (DBCAA), and tribromooxoacetic acid (TBA), that are not part of HAA6. According to the statistical parameter (e.g., \( R^2 \)), DOC-based models (\( R^2 = 0.90 \)) show the best results, followed by DOC*UVA-based models (\( R^2 = 0.81 \)) and UVA-based models (\( R^2 = 0.70 \)) for raw water THM and HAA formation. Internal evaluation of predicted versus measured TTHM shows that the coefficient is 0.96 and the intercept is 9.96 for the raw water model (DOC-based model). A perfect simulation corresponds to an intercept of 0, a slope of 1, and an \( R^2 \) of 1.0. The DOC-based models for TTHM and HAA6 formation tend to overpredict in the lower DBP ranges, while underpredicting in the higher DBP ranges. The DOC-based model can be chosen as the models for raw water DBP predictions, and can be directly applied to the chlorination of raw waters (e.g., pre-chlorination).

3.1.2. Development of pH and temperature correction factors (coagulated waters)

The existing coagulated water DBP models have a limitation in application in DBP simulations because temperature and pH are not considered as variables (the original experiments were conducted under constant pH and temperature for the coagulated waters). Therefore, it was necessary to modify the models so that they are applicable under different pH and temperature. The pH and temperature correction factors were developed from the raw water database by using the best-fit method. Table 5 presents temperature and pH correction factors for THM and HAA formation in coagulated waters, respectively. It is noted that the pH coefficient for TCAA and HAA6 are less than unity, implying that pH has negative effects on TCAA and HAA6 formation. Temperature has a positive effect on both THM and HAA formation.

3.1.3. Development of short-term DBP formation model

Since the lower boundary condition of the EPA 1998 database is 2 h, it was necessary to develop an alternative short-term (<2 h) DBP model. The EPA 1987 database contains data for time periods as low as 0.1 h. First, the evaluation of DOC-based models for short-term ranges was conducted using the EPA 1987 database. Data satisfying the special boundary conditions were extracted; reaction times between 0.1 and 1.0 h, Cl₂/DOC ratios between 0.5 to 1.5, and a pH range of 6.5 and 7.5. The results showed that TTHM levels in the short-term ranges were underpredicted; the slope for short-term
Table 5
Summary of predictive THM and HAA models

<table>
<thead>
<tr>
<th>Name</th>
<th>Model</th>
<th>Applicable water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOC-based models [1]</strong></td>
<td>TTHM = 10^{-1.385} \cdot (DOC)^{1.098} \cdot (Cl_2)^{0.152} \cdot (Br^-)^{-0.068} \cdot (Temp)^{0.609} \cdot (pH)^{1.601} \cdot (time)^{0.263} \quad R^2 = 0.90</td>
<td>Raw waters</td>
</tr>
<tr>
<td><strong>UVA-based models [3]</strong></td>
<td>TTHM = 0.42 \cdot (UVA)^{0.482} \cdot (Cl_2)^{0.339} \cdot (Br^-)^{-0.023} \cdot (Temp)^{0.617} \cdot (pH)^{1.609} \cdot (time)^{0.261} \quad R^2 = 0.70</td>
<td>Raw waters</td>
</tr>
<tr>
<td><strong>DOC*UVA-based models [3]</strong></td>
<td>TTHM = 0.283 \cdot (DOC*UVA)^{0.421} \cdot (Cl_2)^{0.145} \cdot (Br^-)^{0.041} \cdot (Temp)^{0.614} \cdot (pH)^{1.606} \cdot (time)^{0.261} \quad R^2 = 0.81</td>
<td>Raw waters</td>
</tr>
<tr>
<td><strong>DOC-based models [1]</strong></td>
<td>TTHM = 3.296 \cdot (DOC)^{0.801} \cdot (Br^-)^{-0.223} \cdot (time)^{0.264} \quad R^2 = 0.87</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td>(developed from EPA 1998 database)</td>
<td>TTHM = 75.7 \cdot (UVA)^{0.593} \cdot (Cl_2)^{0.332} \cdot (Br^-)^{-0.066} \cdot (time)^{0.264} \quad R^2 = 0.90</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td><strong>DOC*UVA-based models (developed from</strong></td>
<td>TTHM = 23.9 \cdot (DOC*UVA)^{0.403} \cdot (Cl_2)^{0.225} \cdot (Br^-)^{-0.141} \cdot (time)^{0.264} \quad R^2 = 0.92</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td>EPA 1998 database)</td>
<td>TTHM = (TTHM_{pH=7.5, Temp=20^\circ C})*((1.156) \cdot (pH-7.5) \cdot (1.0263)^{\cdot (Temp-20)}) \quad R^2 = 0.92</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td><strong>DOC-based models [1]</strong></td>
<td>HAA6 = 9.98 \cdot (DOC)^{0.935} \cdot (Cl_2)^{0.443} \cdot (Br^-)^{-0.031} \cdot (Temp)^{0.387} \cdot (pH)^{0.655} \cdot (time)^{0.178} \quad R^2 = 0.87</td>
<td>Raw waters</td>
</tr>
<tr>
<td>(developed from EPA 1998 database)</td>
<td>HAA6 = 171.4 \cdot (UVA)^{0.584} \cdot (Cl_2)^{0.398} \cdot (Br^-)^{-0.091} \cdot (Temp)^{0.396} \cdot (pH)^{0.645} \cdot (time)^{0.178} \quad R^2 = 0.80</td>
<td>Raw waters</td>
</tr>
<tr>
<td><strong>DOC*UVA-based models (developed from</strong></td>
<td>HAA6 = 101.2 \cdot (DOC*UVA)^{0.452} \cdot (Cl_2)^{0.194} \cdot (Br^-)^{-0.0698} \cdot (Temp)^{0.346} \cdot (pH)^{0.623} \cdot (time)^{0.180} \quad R^2 = 0.85</td>
<td>Raw waters</td>
</tr>
<tr>
<td>EPA 1998 database)</td>
<td>HAA6 = 5.22 \cdot (DOC)^{0.585} \cdot (Cl_2)^{0.565} \cdot (Br^-)^{-0.031} \cdot (time)^{0.153} \quad R^2 = 0.92</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td><strong>DOC-based models [1]</strong></td>
<td>HAA6 = 63.7 \cdot (UVA)^{0.419} \cdot (Cl_2)^{0.640} \cdot (Br^-)^{-0.066} \cdot (time)^{0.161} \quad R^2 = 0.92</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td>(developed from EPA 1998 database)</td>
<td>HAA6 = 30.7 \cdot (DOC*UVA)^{0.302} \cdot (Cl_2)^{0.541} \cdot (Br^-)^{-0.012} \cdot (time)^{0.161} \quad R^2 = 0.94</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td><strong>pH and temperature correction</strong></td>
<td>HAA6 = 63.7 \cdot (UVA)^{0.419} \cdot (Cl_2)^{0.640} \cdot (Br^-)^{-0.066} \cdot (time)^{0.161} \quad R^2 = 0.92</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td><strong>DOC-based models [1]</strong></td>
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<td>Coagulated waters (alum or iron)</td>
</tr>
<tr>
<td>(developed from EPA 1998 database)</td>
<td>HAA6 = 30.7 \cdot (DOC*UVA)^{0.302} \cdot (Cl_2)^{0.541} \cdot (Br^-)^{-0.012} \cdot (time)^{0.161} \quad R^2 = 0.94</td>
<td>Coagulated waters (alum or iron)</td>
</tr>
</tbody>
</table>
TTHM measurement versus prediction was 0.77, while the slope for long-term TTHM formation was 1.01 (see Fig. 1). These results imply that DBP formation is more rapid in the short term than in the long term. The short-term TTHM prediction can be approximated by multiplying by an adjustment factor (=1.30), i.e.,

$$TTHM_{@t<2h} = 1.30TTHM_{pred},$$  \hspace{1cm} (2)$$

where TTHM$_{@t<2h}$ represents predictive TTHM formation at less than 2h, and TTHM$_{pred}$ represents predictive TTHM formation derived from the EPA 1998 models.

The second approach was to develop a separate equation for short-term TTHM formation ($t \leq 2h$). Data were extracted from the EPA 1987 database, and the equations and boundary conditions are presented in Table 6. The internal evaluation is shown in Fig. 2. The empirical models in Table 5 would be appropriate for the simulations in a plant and distribution-system DBPs characterized by a hydraulic residence time range of several hours to several days. However, the short-term DBP models (Table 6) can be applied to some special cases, such as pre-chlorination, or (free) chlorination followed by chloramination (ammonia addition), which would be characterized by a shorter hydraulic retention time (HRT) of less than 2h.

![Fig. 1. Evaluation of short-term (top) and long-term (bottom) TTHM formation: data from EPA 1987 database.](image_url)
3.1.4. Kinetic-based models

Chlorine decay and DBP formation models: Amy et al. [1] developed a two-step chlorine decay model representing rapid and slow decay (Eqs. (3)–(6)). The curve fitting indicated that the intersection point between rapid and slow decay occurred at about 5 h of reaction time. The two-step model (hereafter referred to as the EPA 1998 model) was based on the first-order decay model and generated from the bench-scale experiments using the EPA 1998 database. The EPA 1998 model consists of two equations with different time steps to predict chlorine concentration (C, mg/L) as a function of time (t, h):

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

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

\[
\ln k_1 = -0.442 + 0.889 \ln(\text{DOC}) + 0.345 \ln(7.6\text{NH}_3 - \text{N}) - 1.082 \ln(C_0) + 0.192 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right), \quad n = 129, \quad R^2 = 0.58, \]

\[
\ln k_2 = -4.82 + 1.19 \ln(\text{DOC}) + 0.102 \ln(7.6\text{NH}_3 - \text{N}) - 0.82 \ln(C_0) - 0.27 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right), \quad n = 129, \quad R^2 = 0.62. \]

Haas and Karra [9] evaluated five different chlorine decay models. They concluded that a parallel first-order decay model combined with two parallel decay models (Eq. (7)), indicating fast reaction and slow reaction, provided the best results among five different models.

\[ C = C_0[A \exp(-k_1 t) + (1-A)\exp(-k_2 t)]. \]

In adapting their model, the parameter \( A \) and the rate constants \( k_1 \) and \( k_2 \) were derived from the best-fit method using the EPA 1998 database. The parameter \( A \) should range from zero to unity. The \( k_1 \) values ranged from 0.3 to 7.9 h\(^{-1}\), but excluding large values, the remaining values for \( k_1 \) values were clustered in the range of 0.3–1.0 h\(^{-1}\). The \( k_2 \) values were around twofold smaller than \( k_1 \) values, indicating that a fast reaction site governs within short-term ranges. In an attempt to generalize an empirical relationship for predicting \( A, k_1, \) and \( k_2 \) values, a multiple stepwise regression was performed using STATISTICA software:

\[
\ln(A) = 0.168 - 0.148 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right) + 0.29 \ln(\text{UVA}) - 0.41 \ln(\text{Cl}_2) + 0.38 \ln(\text{Br}^-) + 0.0554 \ln(\text{NH}_3 - \text{N}) + 0.185 \ln(\text{Temp}), \quad n = 102, \quad R^2 = 0.75, \tag{8}
\]

\[
\ln(k_1) = 5.41 - 0.38 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right) + 0.27 \ln(\text{NH}_3 - \text{N}) - 1.12 \ln(\text{Temp}) + 0.05 \ln(\text{Br}^-) - 0.854 \ln(\text{pH}), \quad n = 102, \quad R^2 = 0.26, \tag{9}
\]

\[
\ln(k_2) = -7.13 + 0.86 \ln\left(\frac{\text{Cl}_2}{\text{DOC}}\right) + 2.63 \ln(\text{DOC}) - 2.55 \ln(\text{Cl}_2) + 0.62 \ln(\text{SUVA}) + 0.16 \ln(\text{Br}^-) + 0.48 \ln(\text{NH}_3 - \text{N}) + 1.03 \ln(\text{Temp}), \quad n = 102, \quad R^2 = 0.85, \tag{10}
\]

where DOC = dissolved organic carbon (mg/L): 1.2 ≤ DOC ≤ 10.6, UVA = UV absorbance at 254 nm (cm\(^{-1}\)): 0.010 ≤ UVA ≤ 0.318, SUVA = specific UVA (= UV\(_{254}/\text{DOC}\)) (L/mg-m): 0.83 ≤ SUVA ≤ 6.6, NH\(_3\)–N = ammonia concentration (mg/L as N): 0.065 ≤ NH\(_3\)–N ≤ 0.69, Cl\(_2\) = applied chlorine dose (mg/L): 1.51 ≤ Cl\(_2\) ≤ 33.55, Br\(^-\) = bromide concentration (mg/L): 7 ≤ Br\(^-\) ≤ 600, Temp = temperature (°C): 15 ≤ Temp ≤ 25, pH: 6.5 ≤ pH ≤ 8.5, \( t \) = reaction time (h): 2 ≤ \( t \) ≤ 168, \( A \) = parameter: 0.23 ≤ \( A \) ≤ 0.97 (theoretically 0 ≤ \( A \) ≤ 1), \( k_1 \) = rate constant for the fast reaction (h\(^{-1}\)): 0.30 ≤ \( k_1 \) ≤ 7.29, \( k_2 \) = rate constant for the slow reaction (h\(^{-1}\)): 0.0015 ≤ \( k_2 \) ≤ 0.0708.

The parameter \( A \) may be interpreted as the ratio of the rate of formation of the rapidly decomposing species to that of the slowly decomposing species. Values of the parameter \( A \) appear to be highly dependent on the Cl\(_2\)/DOC ratio, and a lower Cl\(_2\)/DOC ratio induces greater values. This implies that the applied Cl\(_2\) dose is rapidly consumed in the fast reaction under the lower Cl\(_2\)/DOC ratio. A greater parameter variability occurs in the case of \( k_1 \). The lack of data sets in the short-term ranges would result in a poor correlation in estimating \( k_1 \) values. In the two-phase model, the first phase represents fast decay and the second phase represents...
slow decay. The two-phase model consists of one
equation, and hence, the model appears to be suitable
to describe the behavior of Cl₂ decay over the entire
range of contact times. In addition, the kinetic-based
model contains no discontinuity. The EPA model
requires the estimation of two parameters (k₁, k₂), while
two-phase model requires three parameters in predicting
chlorine residuals. This implies that the two-phase
model would induce less accuracy in chlorine residual
predictions. Overall, internal evaluation of the two-
phase model and the EPA 1998 model shows that the
two-phase model better predicted chlorine residuals
compared to the EPA 1998 model (Fig. 3).

A sensitivity analysis was conducted under the
conditions that one parameter was varied while the
other parameters were held constant. The median values
of A, k₁, k₂ were chosen as the baseline. The results of
the sensitivity analysis show that parameter A exhibits
the relatively more significant effect on chlorine resi-
duals than the other parameters (k₁ and k₂) (Fig. 4).
Chlorine residuals decreased with increasing A, k₁, and
k₂ values. During the first 10 h, k₁ governs the changes of
chlorine residuals, while k₂ governs the changes of
chlorine residuals after 10 h.

Chlorination DBP formation model: Generally, THM
and HAA initially form fast during the first several
hours, and then slow down as the time frame progresses
from hours to days [1]. Thus, it is possible to describe
the reaction according to two phases; one with a fast
reaction, and another with a slow reaction. Second-
order kinetics can be adapted for THM and HAA
formation, representing the fast reacting site and the slow
reacting site:

\[
\frac{dTTHM}{dt} = k_1[Cl_2][F_1*DOC] + k_2[Cl_2][F_2*DOC],
\]

where [F₁*DOC] and [F₂*DOC] represent the fast-
reacting site, and the slow-reacting site in NOM,
respectively. To simplify the equation, we assume that
these sites are relatively constant with reaction time.
Thus, Eq. (11) can be expressed by pseudo-first-order
kinetics:

\[
\frac{dTTHM}{dt} = k_{1a}[Cl_2] + k_{2b}[Cl_2],
\]

where \(k_{1a} = K_1[F_1*DOC]\) and \(k_{2b} = K_2[F_2*DOC]\). Sub-
stituting Eq. (12) into Eq. (11) yields:

\[
\frac{dTTHM}{dt} = k_{1a}[Cl_2]A \exp(-k_1t) + (1-A)\exp(-k_2t) + k_{2b}[Cl_2]A \exp(-k_1t) + (1-A)\exp(-k_2t).
\]

Assuming that the first term is governed by a fast
reaction, and the second term is governed by a slow
reaction, then the slow reaction in the first term and the
fast reaction in the second term can be ignored. Thus,
Eq. (13) can be represented as follows:

\[
\frac{d[TTHM]}{dt} = k_{1a}[Cl_2]A \exp(-k_1t) \\
+ k_{2b}[Cl_2](1-A)\exp(-k_2t).
\]

Integrating Eq. (14) yields:

\[
[TTHM] = [Cl_2]\{k_{1a}A/(-k_1)(\exp(-k_1t) - 1) \\
+ k_{2b}(1-A)/(-k_2)(\exp(-k_2t) - 1)\}
\]

\[
= [Cl_2]\{A_{TTHM}(1 - \exp(-k_1t)) \\
+ B_{TTHM}(1 - \exp(-k_2t))\},
\]

where \(A_{TTHM} = k_{1a}A/k_1\), and \(B_{TTHM} = k_{2b}(1-A)/k_2\).

It should be noted that the kinetic coefficients \((k_1\) and \(k_2\)) are the same as the kinetic coefficients determined in the chlorine decay model. An attempt was made to test the model using the EPA 1998 database. Fig. 5 demonstrates the two-phase model simulations for chlorine decay, TTHM formation, and HAA6 formation. All simulations were successful in predicting chlorine decay, TTHM, and HAA6 formation. This implies that chlorine decay can be considered as a mirror image to THM and HAA formation. In order to develop equations for general use, \(A_{TTHM}\) and \(B_{TTHM}\) were determined from a multiple stepwise regression.

\[
\ln(A_{TTHM}) = -2.11 - 0.87 \ln\left(\frac{Cl_2}{DOC}\right) \\
- 0.41 \ln(NH_3-N) + 0.21 \ln(Cl_2) \\
+ 1.98 \ln(pH), \quad n = 101, \quad R^2 = 0.71,
\]

\[
\ln(B_{TTHM}) = 1.46 - 1.11 \ln(SUVA) + 0.67 \ln\left(\frac{Cl_2}{DOC}\right) \\
+ 0.27 \ln(UVA) + 0.093 \ln(Br^-) \\
+ 1.41 \ln(pH) + 0.13 \ln(NH_3-N), \quad n = 101, \quad R^2 = 0.35.
\]

The same approach was applied to develop the HAA6 prediction models:

\[
[HAA6] = [Cl_2]\{A_{HAA6}(1 - \exp(-k_1t)) \\
+ B_{HAA6}(1 - \exp(-k_2t))\},
\]

\[
\ln(A_{HAA6}) = 3.25 + 0.86 \ln\left(\frac{Cl_2}{DOC}\right) + 0.066 \ln(UVA) \\
- 0.14 \ln(Br^-) - 0.17 \ln(NH_3-N) \\
+ 0.25 \ln(SUVA), \quad n = 66, \quad R^2 = 0.79,
\]

Fig. 5. Two-phase model simulations for chlorine decay (top), TTHM formation (middle), and HAA6 formation (bottom): data adapted from EPA 1998 database.

Fig. 6. Internal evaluation of kinetic-based model and power function model (DOC based) using EPA 1998 database (top: TTHM formation, bottom: HAA6 formation).
\[
\ln(B_{\text{HAA6}}) = 4.37 + 1.11 \ln(C_2) - 0.30 \ln(\text{UVA}) - 2.47 \ln(\text{pH}), \quad n = 66, \quad R^2 = 0.46. \quad (20)
\]

The internal evaluation using the parameters estimated from Eqs. (16)–(20) showed good predictions for TTHM and HAA6; however, no significant improvement was observed when compared to the empirical power function model simulations (Fig. 6). It should be noted that all parameters for DBP formation (i.e., \(A_{\text{TTHM}}, B_{\text{TTHM}}, A_{\text{HAA6}}, \text{ and } B_{\text{HAA6}}\)) are not a function of temperature, but rate constants \((k_1 \text{ and } k_2)\) for the \(\text{Cl}_2\) decay are a function of temperature. The pH parameter shows positive effects on TTHM formation, but negative effects on HAA6 formation. The parameters for DBP formation \((A_{\text{TTHM}}, B_{\text{TTHM}}, A_{\text{HAA6}}, \text{ and } B_{\text{HAA6}})\) represent the amounts of reaction sites, either fast or slow, while rate constants \((k_1 \text{ and } k_2)\) represent the rate of reactions.

### 3.2. Ozonation

#### 3.2.1. Development of temperature correction factors

As mentioned earlier, the ozone decay and bromate formation models developed from the study [1] were conducted under a temperature of 20°C. Therefore, a temperature correction was needed in order to apply the models to actual systems. Dissolved ozone is more stable at lower temperature, and increasing the temperature increases the reaction rate (decay) constant. Bromate formation increases with increasing temperature. Siddiqui et al. [10] proposed a temperature correction equation as follows:

\[
[\text{BrO}_3^3]_{\text{at temp} T} = [\text{BrO}_3^3]_{\text{at temp} 20^\circ C}(1.043)^{T-15}, \quad (21)
\]

where \([\text{BrO}_3^3]_{\text{at temp} 20^\circ C} = \text{bromate ion concentration at } 20^\circ C \text{ and } T = \text{temperature (°C)}\).

Eq. (21) has a limitation in predicting temperature effects on bromate formation because the exponent is based on 15°C (bromate formation models were developed based on 20°C). Therefore, other temperature correction factors were developed from a full-scale database (Syndicat des Eaux d’Île de France and Generale des Eaux (SEDF/GDE) database) shown in Table 2. Eqs. (22) and (23) represent the temperature correction for ozone residual and bromate formation, respectively.

Temperature correction for ozone decay model

\[
[\text{DO}_3^3]_{\text{at temp} T} = [\text{DO}_3^3]_{\text{at temp} 20^\circ C}(0.927)^{T-20}, \quad (22)
\]

where \([\text{DO}_3^3]_{\text{at temp} 20^\circ C} = \text{dissolved ozone at } 20^\circ C\).

Temperature correction for bromate model

\[
[\text{BrO}_3^3]_{\text{at temp} T} = [\text{BrO}_3^3]_{\text{at temp} 20^\circ C}(1.035)^{T-20}, \quad (23)
\]

where \(T = \text{temperature; } 2^\circ C \leq T \leq 24^\circ C\).

The implications of these factors are a 53% ozone residual decrease with every 10°C increase and a 41% bromate increase with every 10°C increase. A simulation of temperature effects is shown in Fig. 7. An evaluation of temperature correction factors is presented in Tables 7 and 8 using the Ozekin [6] and Siddiqui and Amy [5] data. Temperature effects on ozone residual and bromate formation vary with source and experimental conditions, suggesting that other factors, such as natural organic matter characteristics and different kinetics, are involved in ozone decay and bromate formation. While the prediction of temperature effects on ozone decay and bromate formation varied, the estimation was considered acceptable.

Until now, most facilities are operating ozonation processes on an ozone dose basis. Thus, ozone doses are relatively constant throughout seasons. The temperature correction factors show significant discrepancies in ozone residuals and bromate formation with temperature. It is important to note that ozone residual affects contact time (CT) values. Fig. 8 illustrates a simulation of CT versus bromate formation for a plug flow reactor (PFR) under different temperatures. According to the simulation results, higher CT values can be achieved at lower temperatures when the same bromate formation is expected (Table 9). Log inactivation of Giardia also increases with decreasing temperature, but the increments are less than the increments of CT values because of lower increases of \(k\) (kinetic coefficient for microorganism inactivation) values with increasing temperature. The ozone doses corresponding to 10 μg/L of bromate formation were 3.4, 2.7, and 2.4 mg/L at 10°C, 20°C, and 25°C, respectively. Therefore, higher ozone doses can be used at lower temperature to obtain higher CT values for the same bromate formation (10 μg/L).

#### 3.2.2. Development of model for ozone oxidation of NOM

Relatively little DOC removal occurs with ozonation [11], and no significant change in DOC is observed
It is assumed that no reduction of DOC is expected from ozonation, a conservative assumption with respect to chlorination DBP predictions. However, ozone reduces UV absorbance significantly, and UVA reduction increases with ozone doses up to more than 70% at an O$_3$/DOC ratio of 3 mg/mg, as observed in a bench-scale experiments [14]. UVA exponentially decreases with increasing O$_3$/DOC ratios. A UVA decay model was developed from the WITAF 1992 database [15]. This model has relevance to a contactor with multiple ozone application points and overresponding NOM transformation. The database was established from experiments that were conducted under the same reaction time (hydraulic retention time (HRT) = 11.7 min). To compensate for this limitation of the same reaction time, ozone demand (ozone dose minus ozone residual) was considered as an input parameter because ozone demand is dependent upon the reaction

### Table 7
Evaluation of temperature correction factor for ozone residual

<table>
<thead>
<tr>
<th>Source waters</th>
<th>Temperature (°C)</th>
<th>Measured ozone residual (mg/L)</th>
<th>Difference based on 20°C (%)</th>
<th>Simulation from Eq. (22) (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
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<td>15</td>
<td>1.3</td>
<td>+8</td>
<td>+46</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.8</td>
<td>−33</td>
<td>−32</td>
<td></td>
</tr>
<tr>
<td>Florida USA</td>
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<td>+42</td>
<td>+46</td>
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<td>20</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
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<td>0</td>
<td></td>
</tr>
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<td>25</td>
<td>1.8</td>
<td>−18</td>
<td>−32</td>
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<td></td>
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<td>−40</td>
<td>−32</td>
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</table>

### Table 8
Evaluation of temperature correction factor for bromate formation

<table>
<thead>
<tr>
<th>Source waters</th>
<th>Temperature (°C)</th>
<th>Measured BrO$_3$ (µg/L)</th>
<th>Difference based on 20°C (%)</th>
<th>Simulation from Eq. (3) (%)</th>
<th>Source</th>
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<tbody>
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<td>16</td>
<td>+60</td>
<td>+19</td>
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</table>
The equation and boundary conditions are presented as follows:

\[ UVA = 0.796(UVA_0)^{1.091}(O_3 - O_{3\text{res}})^{-0.167} \]
\[ \times \left( \frac{O_3}{DOC} \right)^{0.194} (\text{Alk})^{0.059} \]

where \( O_3 \) = transferred ozone dose (mg/L): 0.41 \( \leq O_3 \) \( \leq 23.65 \), \( O_{3\text{res}} \) = ozone residual (mg/L): 0.05 \( \leq O_{3\text{res}} \) \( \leq 3.11 \), \( \text{Alk} \) = alkalinity (mg/L as CaCO₃): 10 \( \leq \text{Alk} \) \( \leq 475 \), pH: 5.5 \( \leq \text{pH} \) \( \leq 8.4 \), DOC = dissolved organic carbon (mg/L): 0.6 \( \leq \text{DOC} \) \( \leq 40.0 \), \( O_3/\text{DOC} \) = ozone dose/DOC ratio: 0.43 \( \leq O_3/\text{DOC} \) \( \leq 2.30 \), \( UVA_0 \) = UV absorbance at 254 nm for the influent waters (cm⁻¹): 0.019 \( \leq UVA_0 \) \( \leq 1.398 \), and \( UVA \) = UV absorbance at 254 nm for the effluent waters (cm⁻¹): 0.011 \( \leq UVA \) \( \leq 0.866 \).

Fig. 9 shows the internal evaluation of the UVA decay model, and Fig. 10 shows an external validation based on other researchers' data. The external validation demonstrates that the UVA decay model showed good precision \( (R^2 = 0.88) \), but poor accuracy (slope = 1.58), i.e., UVA for ozonated waters tended to be overpredicted. More data are needed to evaluate the accuracy of the model over wider boundary conditions.

### 3.2.3. Multiple ozonation (staged ozonation)

An ozone contactor is usually comprised of multiple cells, and these cells can be either ozone application cells or residence/reaction cells. When ozone is applied to multiple cells (staged or split ozonation), bromate formation is different than single-stage ozonation because of the different NOM characteristics and \( \text{Br}^- \) concentrations between the influent water and already ozone-reacted water from prior cells. In the case of staged ozonation, a step-wise analysis of each ozonation step can be applied. The UVA-based model is more appropriate for this case because UVA is reduced with ozonation. In addition to the changes of NOM properties, \( \text{Br}^- \) varies between different cells because it is incorporated into brominated ozonation by-products in the prior cells. Bromide concentration, NOM variations, and different ozone doses should be considered systemically in evaluation of staged ozonation. Fig. 11 shows a schematic diagram of bromate simulation for staged ozonation. The \( \text{Br}^- \) remaining in a subsequent cell is...
estimated from the following equations;

\[
(Br^-)_t = (Br^-)_0 - BrO_3^- \quad \text{as} \quad Br^- - TOBr = (Br^-)_0 - 0.625(\text{BrO}_3^-) - TOBr. \quad (25)
\]

TOBr (total organic bromine) formation due to ozonation can be estimated from the following equation [16].

\[
\text{TOBr} = (Br)^{1.68}(\text{DOC})^{-0.652}(O_3)^{1.1}(\text{pH})^{-3.62}(\text{TIC})^{-0.168} \times (\text{NH}_3-N)^{0.085}(\text{H}_2\text{O}_2)^{-2.25},
\]

\[
 n = 98, \quad R^2 = 0.98. \quad (26)
\]

The main limitation of the above model (Eq. (26)) is that it can be used only when hydrogen peroxide is applied (zero concentration of H\textsubscript{2}O\textsubscript{2} cannot be input to the model). An alternative model can be used, which was developed from Siddiqui and Amy [5].

\[
\text{TOBr} = 0.9(\text{DOC})^{-1.07}(\text{pH})^{-1.05}(O_3)^{0.766}(Br^-)^{1.53} \times (\text{Temp})^{1.08}(\theta)^{0.847}, \quad n = 70, \quad R^2 = 0.95. \quad (27)
\]

where TOBr = total organic bromine (µg/L), DOC (mg/L): 3 < DOC ≤ 7, pH: 6.5 ≤ pH ≤ 8.5, TIC = total inorganic carbon (mg/L as C), NH\textsubscript{3}-N = ammonia concentration (mg/L), O\textsubscript{3} = transferred ozone dose (mg/L): 1.5 ≤ O\textsubscript{3} ≤ 17.5, Br\textsuperscript{−} (mg/L): 0.25 ≤ Br\textsuperscript{−} ≤ 1.5, Temp = reaction temperature (°C): 20 ≤ Temp ≤ 30, and θ = ozonation temperature (°C): 20 ≤ θ ≤ 30.

Assuming that reaction temperature and ozonation temperature are the same, then the equation is as follows:

\[
\text{TOBr} = 0.9(\text{DOC})^{-1.07}(\text{pH})^{-1.05}(O_3)^{0.766}(\text{Br}^-)^{1.53} \times (\text{Temp})^{1.07}. \quad (28)
\]

It should be noted that the units for bromide concentration are mg/L in Eqs. (27) and (28). This model was developed based on the ultimate TOBr formation (a reaction time of 24 h). TOBr formation may form rapidly and remain relatively constant after initial rapid formation occurs [17]. Therefore, Eq. (28) can be used under normal operating conditions where reaction time ranges from several minutes to hours, while Eq. (27) can be used when hydrogen peroxide is applied. The limitation of the Siddiqui and Amy equation [5], Eq. (28), is that ammonia effects are not included in the model. A recalibrated model could potentially be developed combining these two databases, but the databases are not currently available.

### 3.2.4. Application

The models described in the previous sections can be applied to the direct simulation of disinfectant and DBP predictions. These models are powerful in assessing the effects of operating conditions such as changing pH and disinfectant doses. The comprehensive modeling
approach can be used in more complicated situations. For example, the effect of staged ozonation can be simulated from comprehensive models, as illustrated by the example in Table 10. Under the given conditions, scenario A (100% ozone applied at the first cell) yields the highest bromate formation, while scenario D (50%;25%;25% split) yields the lowest bromate formation [16]. Thus, a 29% bromate reduction would be achieved from split ozonation. The simulation results, considering the effects of UVA and Br⁻ due to staged ozonation, exhibited that bromate formation for staged ozonation follows the same trend as measured values, although overprediction was observed in all scenarios (Table 10).

3.2.5. Kinetic-based models

Ozone decay models: Ozone decay in NOM-free water follows first-order kinetics. However, ozone decay in the presence of NOM yields very rapid decomposition during the initial stages (e.g., 1 min), followed by a slower decomposition [18]. The presence of NOM results in an initial rapid ozone consumption. Thus, a two-staged model is proposed in describing ozone decay [18]. Ozone decay occurs very rapidly during the first minute, but there are little data for times of less than 1 min. Thus, a pseudo-zero-order reaction is assumed over the first minute of reaction, and a pseudo-first-order reaction is proposed for the slow reaction:

$$ C = C_0 - k_1 t \quad (0 \leq t \leq 1 \text{ min}), $$

$$ C = C_1 \exp(-k_2(t - 1)) \quad (t > 1 \text{ min}). $$

From the boundary condition, Eq. (29) is equal to Eq. (30) at 1 min:

$$ C_0 - k_1 = C_1. $$

Thus, Eq. (30) can be expressed as follows:

$$ C = (C_0 - k_1) \exp(-k_2(t - 1)) = (C_0 - \Delta) \exp(-k_2(t - 1)), $$

where $\Delta$ represents the ozone consumption during the first minute of the reaction (ozone demand).

Table 10
Simulation of stage ozonation (water qualities: DOC = 2.4 mg/L, UVA₂₅₄ = 0.082 cm⁻¹, alkalinity = 78 mg/L, Br⁻ = 500 µg/L, pH = 7.6, and temperature = 12°C)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Ozone dose (mg/L)</th>
<th>Percent ozone split</th>
<th>Simulated BrO₃⁻</th>
<th>Measured BrO₃⁻</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
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<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>B</td>
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<td>75</td>
<td>25</td>
<td>0</td>
<td></td>
</tr>
<tr>
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<td>75</td>
<td>0</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>E</td>
<td>1.6</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 12. Internal evaluation of kinetic-based model and power function model (UVA based) for ozone residual (EPA 1998 database).

The ozone demand ($\Delta$) and the rate constant ($k_2$) were determined using a best-fit method, and general equations were derived from stepwise regression (an extensive tabulation of $\Delta$ ($= k_1$)).

$$ \ln(\Delta) = -0.795 + 0.618 \ln(UVA) + 0.596 \ln(O_3) - 0.092 \ln(Alk) + 1.41 \ln(pH) - 0.071 \ln(Br^{-}) - 0.0237 \ln(NH_3-N), $$

$$ n = 84, \quad R^2 = 0.96, $$

(32)

$$ \ln(k_2) = 0.771 + 2.2 \ln(UVA) - 0.364 \ln(Alk) + 5.44 \ln(pH) - 2.10 \ln(SUVA) - 1.07 \ln(O_3) - 0.545 \ln(Br^{-}), $$

$$ n = 61, \quad R^2 = 0.79, $$

(33)

where DOC (mg/L): 1.1 ≤ DOC ≤ 8.4, UVA at 254 nm (cm⁻¹): 0.010 ≤ UVA₂₅₄ ≤ 0.280, pH of influent water: 6.5 ≤ pH ≤ 8.5, alkalinity of influent water (mg/L as CaCO₃): 13 ≤ Alk ≤ 316, Br⁻ (µg/L): 70 ≤ Br⁻ ≤ 440, O₃ = transferred/utilized ozone dose (mg/L): 1.1 ≤ O₃ ≤ 10.0, and $t$ (min): 1 ≤ $t$ ≤ 120.

Fig. 12 illustrates the internal evaluation of the two-staged model for ozone decay/residual. Compared to the UVA-based model, the two-staged model predictions were significantly improved with respect to $R^2$. 

![Graph showing simulation of stage ozonation](image-url)
Bromate formation model (ozone demand model): An ozone demand model for bromate formation is based on the concept that ozone consumption is linearly correlated with bromate formation. The suggested experimental results can be used for developing an ozone demand model in the following form:

$$\text{BrO}_3^- / C_{03} = a \left[ \frac{O_3 \text{ dose}}{C_{03} \text{ residual}} \right]$$

The parameter $a$ was derived from the EPA 1998 database.

$$\ln(a) = \frac{6.96 - 2.30 \ln(DOC) + 0.822 \ln(\text{Br}^-)}{0.981 \ln(O_3) + 2.96 \ln(pH)} - 0.101 \ln(NH_3-N), \quad n = 85, \quad R^2 = 0.77.$$  

The internal evaluation of the ozone demand model, illustrated in Fig. 13, did not significantly improve predictions when compared to the UVA-based model simulations.

4. Conclusions

In this study, several empirical models for predicting disinfectant (in this study chlorine and ozone) decay and disinfection by-product formation were evaluated and/or developed. An empirical power function model based on DOC parameters (EPA 1998 model) showed a strong correlation between measured and predicted THM and HAA formation for raw waters. pH and temperature correction factors were developed for coagulated water DBP (THM and HAA) models. Thus, THM and HAA predictions for coagulated waters can be made over ranges of pH and temperature variations.

An attempt to develop kinetic-based was made. Chlorine decay, and TTHM and HAA6 formation can be refined using a two-phase model (i.e., fast reaction plus slow reaction). Generally, internal evaluation of kinetic-based models showed good predictions, but no significant improvements were observed compared to the empirical power function model simulations. However, the important aspects of kinetic-based models are (i) it is possible to conduct mass balances about reactors if the ideal reactor configuration is known and (ii) the models are easily adjusted to site-specific cases when site-specific rate constants are determined.

Ozone decay and bromate formation equations, valid only at a temperature of 20°C, were developed, with O$_3$ decay being a function of O$_3$ dose, DOC/UVA, pH, alkalinity, and time, and bromate formation being a function of O$_3$ dose, DOC/UVA, bromide concentration, pH, ammonia, and time. In adapting these equations to the comprehensive model, several modifications and adjustments were made. First, the models were recalibrated in terms of UVA to permit their use in intermediate ozonation. Second, a temperature correction factor was developed. Third, a UVA reduction algorithm was developed to reflect changes in water quality (e.g., NOM) after ozonation. Fourth, a step-wise protocol was developed to permit an assessment of staged ozonation. This last modification involved the use of the UVA reduction algorithm to predict the effluent UVA from a given stage serving as the influent to the next stage. It was also necessary to develop a bromide consumption algorithm, where the bromide incorporated into bromate within a given stage is subtracted from the influent bromide to reflect the bromide entering a second stage.

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References


