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WATER TREATMENT PLANT MODEL
USER'S MANUAL

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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VERSION 2.2, AUGUST 2005

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The WTP Model, version 2.2 was developed for the United States Environmental Protection Agency (USEPA) by:

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The guidance provided herein may be of educational value to a wide variety of individuals in the water treatment industry, but each individual must adapt the results to fit their own practice. The USEPA and its contractors shall not be liable for any direct, indirect, consequential, or incidental damages resulting from the use of the WTP Model.

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FORWARD

This *User's Manual* for version 2.2.1 of the WTP Model has been prepared to provide users with a basic understanding of:

1) program setup and operation, and

2) the underlying assumptions and predictive equations used by the WTP Model

It is not to be construed that the results from the WTP Model will necessarily be applicable to individual raw water quality and treatment effects on a site-specific basis. This model does *not* replace sound engineering judgment for an individual application.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES, CONT'D.

LIST OF FIGURES

LIST OF FIGURES, CONT'D

LIST OF ABBREVIATIONS

Item	Description
BAC	Biologically-active carbon
BAF	Biologically-active filtration
BCAA	Bromochloroacetic acid
BDCAA	Bromodichloroacetic acid
BDCM	Bromodichloromethane
BDOC	Biodegradable dissolved organic carbon
CDBAA	Chlorodibromoacetic acid
CDBM	Chlorodibromomethane
CDWO	Center for Drinking Water Optimization

CHBr$_3$ Bromoform

LIST OF ABBREVIATIONS, CONT'D.

Item	**Description**
CHCl$_3$	Chloroform
Cl$_2$	Chlorine dose or residual
CT	Concentration $\times$ Time
DBAA	Dibromoacetic acid
DBCM	Dibromochloromethane
DBP	Disinfection by-product
DCAA	Dichloroacetic acid
D/DBPR	Disinfectants/Disinfection By-products Rule
DBCAA	Dibromochloroacetic acid
DCAA	Dichloroacetic acid
DOC	Dissolved organic carbon
F	F-statistic for significance of a correlation
GAC	Granular activated carbon
GWUDI	Groundwater under the direct influence of surface water
HAA	Haloacetic acid
HAA5	Sum of 5 selected HAA species
HAA6	Sum of 6 selected HAA species
HAA9	Sum of 9 selected HAA species
ICR	Information Collection Rule
IESWTR	Interim Enhanced Surface Water Treatment Rule
LT1ESWTR	Long-term 1 Enhanced Surface Water Treatment Rule
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MF/UF	Microfiltration/ultrafiltration
MG	Million gallons
MGD	Million gallons per day
mg/L	Milligrams per liter
n	Number of data points
NF	Nanofiltration
R^2, R^2_{adj}	Correlation coefficient, adjusted correlation coefficient

RM   Rapid mix

LIST OF ABBREVIATIONS, CONT'D.

Item	Description
SEE	Standard error of the estimate
SWTR	Surface Water Treatment Rule
THM	Trihalomethane
TOC	Total organic carbon
TOX	Total organic halides
TBAA	Tribromoacetic acid
TCAA	Trichloroacetic acid
Temp	Temperature of water
TTHM	Total trihalomethanes
UFC	Uniform (DBP) formation conditions
USEPA	United States Environmental Protection Agency
UV	Ultraviolet (disinfection)
UVA	Ultraviolet light absorbance at wavelength of 254 nanometers
WTP	Water treatment plant
WQ	Water quality

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1. INTRODUCTION

1.1 BACKGROUND

The United States Environmental Protection Agency (USEPA) Water Treatment Plant (WTP) Model (versions 1.0 to 1.55) was originally developed in 1992 and used to support the Disinfectant/Disinfection By-product (D/DBP) regulatory negotiation process in 1993-1994 (Roberson et al., 1995). The original model and its verification were discussed by Harrington et al. (1992).

The 1992 version of the WTP Model predicted the impact of water treatment processes on (1) water quality parameters affecting disinfectant residual decay and disinfection by-product (DBP) formation, and (2) the actual disinfectant residuals and DBP concentrations themselves. However, by 1998, just before the Stage 2 D/DBP Rule regulatory negotiation process, it became clear that the 1992 WTP Model needed to be updated. Many of the original predictive algorithms were outdated, while other key algorithms, water quality parameters, and treatment processes were simply not included.

The 1992 WTP Model has been updated for the USEPA by the Center for Drinking Water Optimization (CDWO) at the University of Colorado and University of Cincinnati, Malcolm Pirnie, Inc., and Schmueser Gordon Meyer, Inc. to create WTP Model, version 2.2. The objectives were to modify existing model algorithms to reflect the expansion in understanding and available data relative to DBP formation and treatment processes since 1992. Furthermore, the objectives were to extend the WTP Model with new algorithms for advanced treatment processes and alternative disinfectants. All model algorithms included in version 2.2 are described in **Chapter 5** of this *User's Manual*.

The WTP Model initially was developed to assist utilities in achieving total system optimization (TSO), an approach by which *existing* treatment processes within a plant can be utilized to help utilities meet both the required levels of disinfection and DBPs regulated under USEPA's various microbial/DBP rules. The revised WTP Model can also be used to:

- assist utilities in identifying and screening new treatment technologies to assist in meeting these regulations,
- assist utilities in evaluating the possible effects of source water or treatment process operations on DBP formation, and

- assist regulatory agencies, including USEPA, in assessing the potential impact of new regulations on treatment requirements over a large group of plants.

The WTP Model is not intended to be a replacement for treatability testing to evaluate the effectiveness of various processes on disinfectant decay and DBP formation in specific water supplies. However, it does provide a useful tool for evaluating the potential effect of different unit processes on compliance with many of the new and forthcoming regulations. Users of the program should be familiar with water treatment plant design and operation, as well as procedures and methodologies used to disinfect water and control DBP formation. The WTP Model, like any computer program, cannot and should not replace sound engineering judgment, and careful selection of inputs and interpretation of outputs is required. Furthermore, the validity of the output is primarily a function of the extent and quality of plant-specific data input and the extent to which an individual application can be accurately simulated by predictive equations that are based upon the central tendency of observations made for a broad set of waters and treatment conditions.

1.2   WTP MODELING APPROACH

The WTP Model uses the following approach (outlined below in order) to estimate water quality parameters during treatment:

- Prediction of basic inorganic parameters (pH, alkalinity, hardness) as affected by chemical addition;
- Prediction of natural organic matter (NOM) removal/changes as affected by treatment;
- Prediction of disinfectant decay based upon applied doses, demands exerted by NOM and inorganic material, water detention times and temperatures, and treatment processes;
- Inactivation of *Giardia*, *Cryptosporidium*, and viruses based upon the predicted values of the above-noted parameters as well as water detention times and temperatures, treatment basin baffling characteristics, and USEPA-published CT tables;
- Prediction of DBP formation based upon water detention times/temperatures and the predicted values of the above-noted parameters within the treatment plant and the distribution system.

The WTP Model simulates DBP formation under given treatment conditions and permits the user to evaluate the effects of treatment changes on the projected disinfectant decay and DBP formation. By using the model under different treatment scenarios, the user can gain an understanding of how the input variables affect disinfection and DBP formation. It must be stressed that the model is largely

empirical in nature. It is NOT intended to be used as the sole tool for decisions regarding "full-scale" implementation of treatment strategies for individual water systems.

Figure 1-1 illustrates the WTP Model process schematic including selected model inputs and outputs (note the treatment train shown is an example - the model accommodates simulation of user-definable treatment trains built from a list of available unit processes. The WTP Model, version 2.2 includes the treatment processes and disinfection options shown in **Table 1-1**. The model simulates the formation of the following DBPs:

- Trihalomethanes (THMs) – four individual species and their sum (TTHM)
- Haloacetic acids (HAAs) – nine individual species and the total of five (HAA5), six (HAA6) and nine (HAA9) species
- Total organic halogen (TOX)
- Bromate
- Chlorite
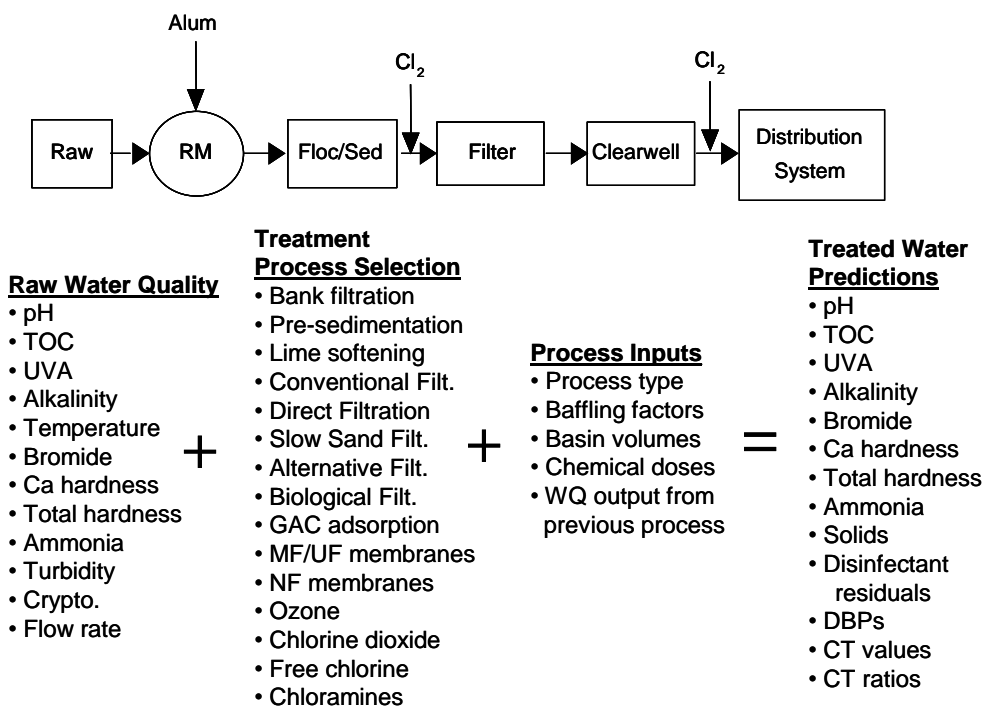
Figure 1-1 Water Treatment Plant Model Schematic

1.3   MANUAL PURPOSE AND ORGANIZATION

This manual is intended to provide guidance to the WTP Model user in the following areas:

- Utilizing the WTP Model computer program - navigating the various screens, etc.
- Selecting inputs and interpreting outputs
- Understanding the WTP Model's basis, the predictive algorithms

In addition to this introductory chapter, this User's Manual contains four other chapters:

- **Chapter 2** describes how to set up and run the model and explains menu components.
- **Chapter 3** describes how to run the WTP Model and how to input the required data. A model of a typical treatment plant is developed as an example, data input options are outlined, and a general description of how to use the program is provided.
- **Chapter 4** provides guidance for interpretation of the output from the WTP Model program.
- **Chapter 5** describes the equations used in the program.

Table 1-1 WTP Model Treatment Processes and Disinfectant Options

Treatment Processes
Bank Filtration
Pre-sedimentation
Alum, Ferric Coagulation; Lime Softening
Flocculation/Sedimentation
Filtration (rapid-rate, slow sand, diatom. earth, cartridges and bags)
Biological Treatment
• Ozone-BAF or BAC (bio.-active granular or carbon media filters)
• Slow Sand Filtration
Granular Activated Carbon (GAC) Adsorption (with reactivation)
Microfiltration/Ultrafiltration Membrane Treatment
Nanofiltration Membrane Treatment
Disinfectants
Free Chlorine, Chloramines, Chlorine Dioxide, Ozone, UV Light

2.   GETTING STARTED

Chapter 2 contains information on installing and using the WTP Model, version 2.2.1. Please note that the WTP Model user interface application only runs on **Windows computers**.

2.1   INSTALLING THE WTP MODEL AND GETTING STARTED

To install the WTP Model user interface, open the Windows Installer Package called "WTPModelSetup.msi". Follow the installation instructions—the default settings should work well for most users. To run the WTP Model user interface, open the "WTP Model" shortcut located on the desktop or in the file directory where the software is stored (e.g., in the Program Files directory in the C: drive). If the software opens successfully, you should see the start-up window shown in **Figure 2-1**. To simulate a treatment plant, the user must first specify a project, either by creating a new project or opening an existing one.
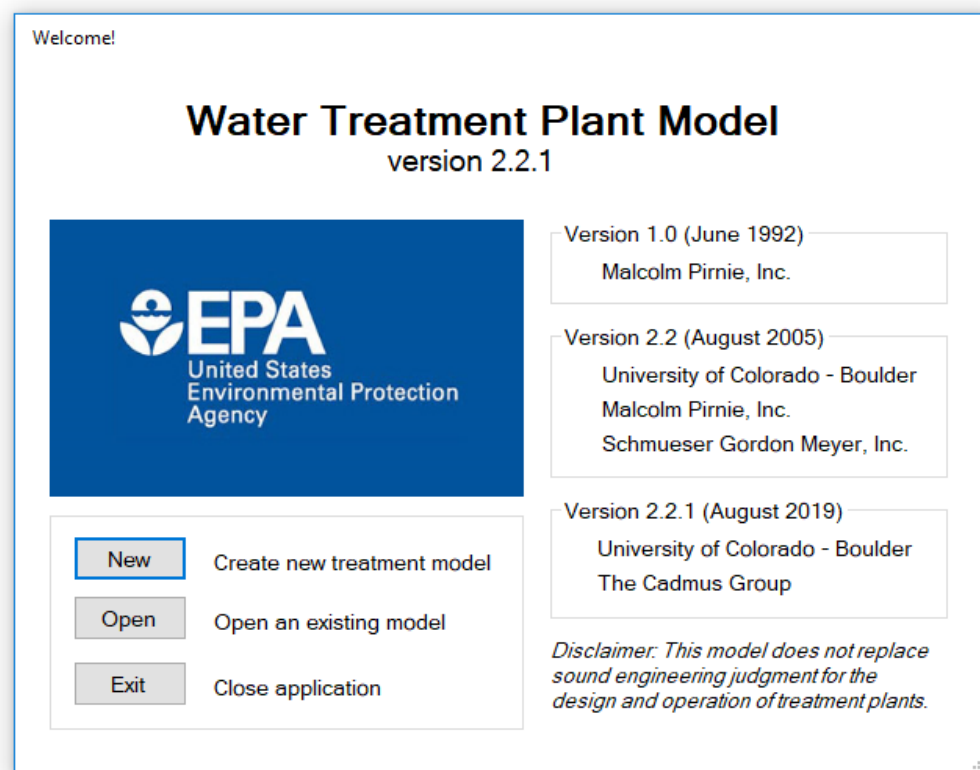
Figure 2-1 Start-up window of the WTP Model

2.2   MAIN MENU COMPONENTS

2.2.1   Main Window
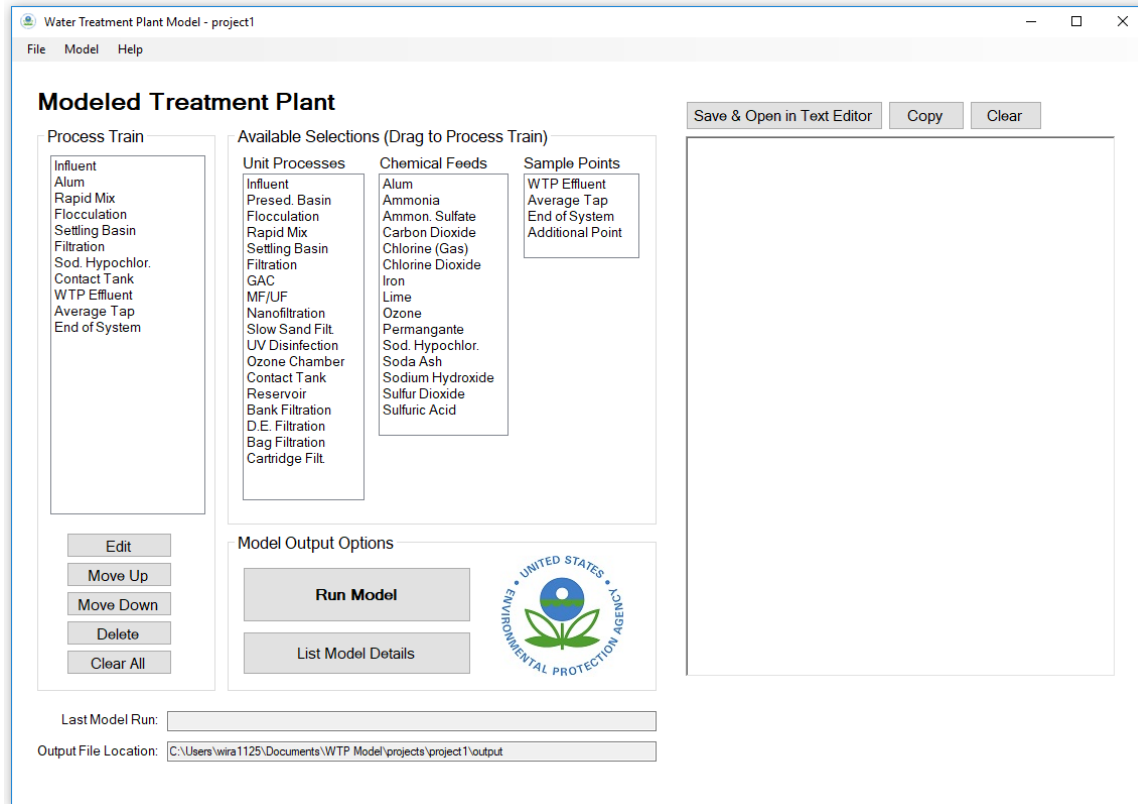
Figure 2-2 Main window for the WTP Model

Menus

File - the *File* pull-down menu, located at the left end of the upper toolbar contains the following options:

- *New* – The user must specify a WTP Model project to run simulations. This option is used to create a new project.

  To create a new project, click File → New. A dialog will appear with the name of the project. Click OK to exit the dialog and return to the home screen.

- *Open…* – The user must specify a WTP Model project to run simulations. Selecting this option the user can open an existing project.

If you have already created a project and want to resume work, click File → Open... A folder browser dialog (Figure 2-3) will appear. By default, all files generated by the user interface application are in a folder called *WTP Model* within the user's *Documents* folder. Within *WTP Model* is the *projects* folder, which contains the WTP Model project folders.

If a project exists, it should be in *projects*. To open a project, <u>click on the project folder</u> (as shown in Figure 2-3) and then press "OK". On the home screen, the project name should be displayed in the top left corner.

- *Save* – Save current treatment plant configuration.
- *Save As...* – Save project with a new name.
- *Rename Project* – Rename the current project.
- *Exit* – Close and exit the user interface application.
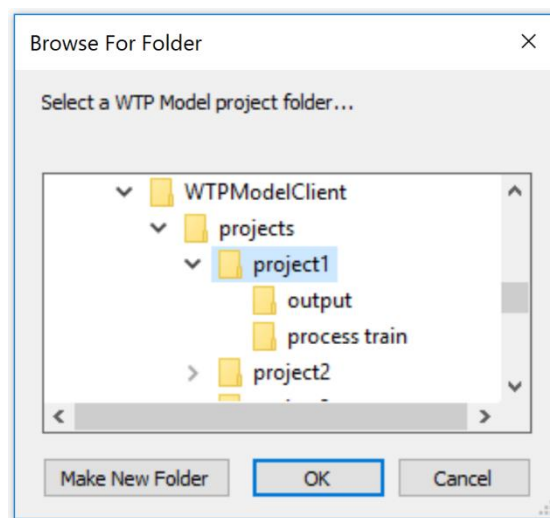
Figure 2-3 Folder browser dialog for opening existing WTP Model projects

<u>Model</u> - the *Model* pull-down menu, located to the right of the *File* pull-down menu contains the following options:

- *List Details* – Display a list of the input data for each unit process, chemical feed, and sample point in the process train.
- *Run* – This selection will run the model and display output data in eleven different summary tables.

Help - the Help pull-down menu, located to the right of the *File* pull-down menu contains the following options:

- *WTP Model Manual* – Open the Water Treatment Plant Model manual.

In **Chapter 3**, we discuss the model inputs, process train parameters, and constructing a treatment train in more detail.

3.   MODEL OUTLINE AND USE

Chapter 3 describes how to simulate a water treatment plant using the WTP Model program. The emphasis of this chapter is on input data. **Chapter 4** focuses on output data.

3.1   SIMULATING THE TREATMENT PLANT

Before the model can be executed, a simulated version of the treatment plant process train must be developed. In addition, input data for the plant to be simulated must be collected and entered into the WTP Model program. A conceptual schematic of the model inputs/outputs and process calculation subroutines is shown in **Figure 3-1**. The overall program algorithm (steps the program follows) for a simulated process train is shown in **Figure 3-2**.
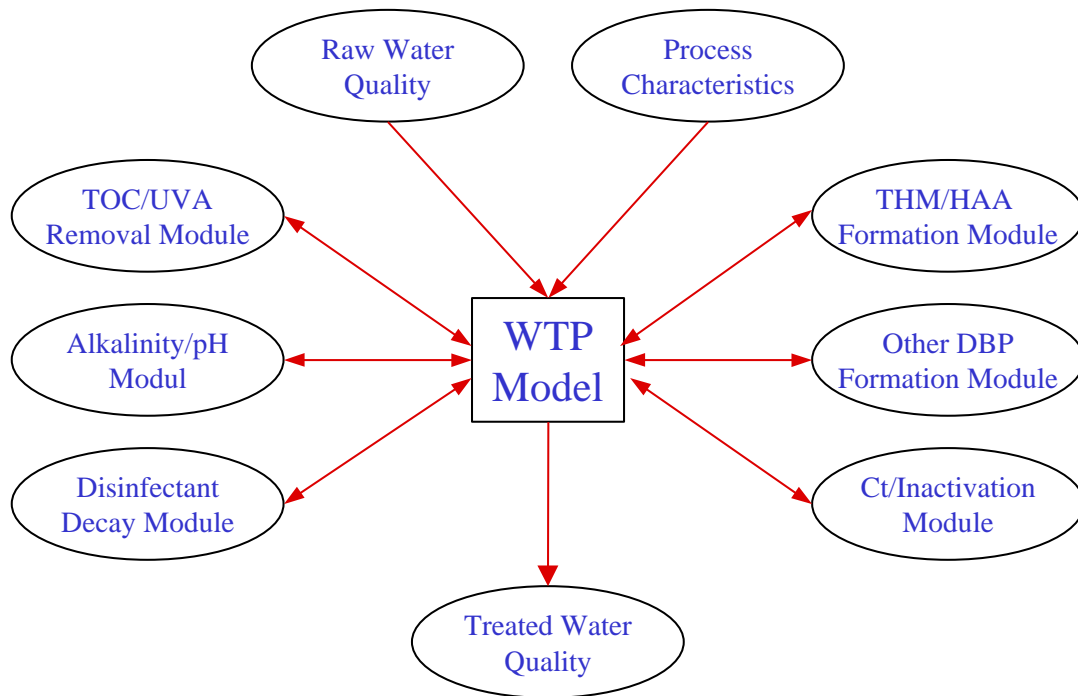
Figure 3-1 Interaction of the WTP Model Component Parts

These procedures and illustrative figures provide some direction on the operation of WTP. Main menu options not specifically explained here are described in **Chapter 2**.

User Constructs Process Train

• Selects and orders process elements

• Inputs parameter values

Model Performs Initial Calculations

• Characterizes process train as conventional-type, direct filtration-type, biotreatment-type, etc. (based on type and order of user-selected units)

• Calculates log inactivation requirements for pathogens (based on plant type and user input values)

Model Simulates a Single Process Element

Chem. Addition Point

Unit Process

Sample Point

Model Calculates (as applicable)…

•UVA oxidation

• Ammonia consumption

• pH/alkalinity changes

• Calcium/magnesium precipitation

Model Calculates (as applicable)…

• Unit process detention time

• TOC/UVA removal

• Inorganic parameter changes (incl. pH/alk.)

• Disinfectant residual decay and pathogen inactivation achieved

• DBP formation

Model Calculates (as applicable)…

• Free chlorine or chloramine decay

• pH/alkalinity

• DBP formation

Model Saves Process Effluent Water Quality

• Serves as influent water quality to the next process element

Last Unit?

YES

NO – Proceed to next process element

Model Generates Ouput

End

Figure 3-2 Overall Algorithm for WTP Simulation

Version 2.2.1 of the WTP Model computer program is interactive and menu-driven. The main menu functions permit the user to direct the program to:

- Create an input file;

- Modify an input file;

- Save input/output files;

- Perform water treatment plant simulation run;

The WTP Model requires the following types of input data:

- Source water type (surface water or groundwater)

- Organic raw water quality parameters

    - Total organic carbon (TOC)

    - Ultraviolet absorbance at 254 nm (UVA)

- Inorganic raw water quality parameters

    - pH

    - Bromide concentration

    - Alkalinity concentration

    - Total and calcium hardness concentration

    - Ammonia-nitrogen concentration

- Water treatment process characteristics

    - Types and sequence of unit processes

    - Unit process (hydraulic) baffling factors and volumes

    - Plant flow rates - average and peak-hour

    - Unit process-specific input parameters

    - Location and magnitude of chemical dosages

- Distribution system sampling location detention times

- Other input parameters

    - Raw water turbidity (required if user is interested in sludge generation estimates)

    - Source water *Cryptosporidium* concentration

    - Groundwater virus disinfection requirements (if applicable)

    - Average and minimum water temperature

Many of the input parameters required by the WTP Model are straightforward and readily available. However, the model user may not be familiar with all the inputs, and some parameters deserve additional explanation. **Tables 3-1** through **3-13** list the WTP Model's inputs for the "Influent" unit

process, all the unit processes in the "Unit Processes" list box, and the "Lime" item in the "Chemical Feeds" list box on the main window. Input values for the other chemicals in the "Chemical Feeds" list box, and the items in the "Sample Points" list box are self-explanatory.

Table 3-1 includes recommended bounds for the ranges of raw water quality input parameters. These recommended limits were developed with consideration given to the ranges of these parameters observed in the data sets used to develop the WTP Model's major predictive algorithms for a conventional plant using alum or iron coagulation and free chlorine as the disinfectant. The user is free to enter input values outside these ranges; however, the user should be aware that it is anticipated that the predictive accuracy of the model will decrease in such cases. For situations where the actual raw water quality to be simulated is outside the bounds shown in **Table 3-1**, the user should consider the parameter ranges applicable to the individual predictive algorithms (listed with the algorithm descriptions in **Chapter 5**) to be simulated for the specific modeling run; these algorithms also should be consulted when simulating a plant that uses alternative (to free chlorine) disinfectants, lime softening, or advanced processes, such as granular activated carbon, ozone-biofiltration, or membrane treatment. A review of the limitations of the predictive algorithms for such processes allows the user to consider input range, and other, limitations specific to a given application of the model.

The WTP Model output file contains information for all the input parameters such as the raw water quality and the treatment plant process characteristics. In addition, the output contains the following calculated parameters at the end of each process element:

- Unit process and cumulative process train detention time
- Organic and inorganic water quality parameters
- Disinfectant residual concentrations
- DBP concentrations
- CT achieved and inactivation ratios for viruses, *Giardia*, and *Cryptosporidium*
- Solids concentrations

Table 3-1 "Influent" Input Parameters

Input Parameter	Units	Recommended Range[1]	Notes
pH	std. units	6.5 - 8.5	Common parameter; critical to many calcs.
Influent Temperature	Deg. C	3 - 25	Note the units! Value is used as water temp. for all calcs. except worst-case CT predictions.
Minimum Temperature	Deg. C	3 - 25	Note the units! Value is used only for worst-case (max. flow/min. temp.) CT calculations
Total Organic Carbon	mg/L	1.5 - 15	If available, use dissolved organic carbon (DOC) value here.
UV Absorbance at 254 nm	1/cm	0.020 - 0.750	i.e. "UV," "UVA," or "UV_{254}"; critical parameter for many key calculations
Bromide	mg/L	0.020 - 0.300	Note units! Value is important for DBP calcs.
Alkalinity	mg/L as $CaCO_3$	Parameters not as critical to predictive algorithms for TOC removal, chlorine decay, or TTHM/ HAA5 formation.	Common parameter. Used in pH, softening, O_3 residual, bromate, and enhanced coag. calcs.
Calcium Hardness	mg/L as $CaCO_3$		$=2.6 \times Ca^{2+}$ concentration in mg/L; an accurate input is critical only if softening is simulated.
Total Hardness	mg/L as $CaCO_3$		Accurate input value is critical only if softening is simulated.
Ammonia	mg/L as N		Note units. Used in breakpoint chlorination and pH calculations.
Turbidity	NTU		Only used in calculation of sludge generation estimates
Peak Flow	mgd		Peak hourly flow rate; used only in predicting worst-case CT conditions
Plant Flow	mgd		Flow rate used in all DBP formation calculations.
Surface Water by SWTR	True/ False		Defines source as a surface water (or GWUDI) or groundwater; affects disinfection required
Source Water Crypto. Conc.	oocysts/ Liter		Used to determine *Crypto.* disinfection requirements for surface water plants
LT2 Rule Watershed Control Program Credit?	True/ False		Determines whether a surface water plant with filtration will receive 0.5-logs of *Cryptosporidium* removal credit for a watershed control program meeting proposed LT2 criteria
If GW System, Is Virus Disinfection Req'd?	True/ False		Determines whether virus disinfection is required of a groundwater source (allows simulation under proposed GW Rule scenario)
Virus Disinfection for GW, if Req'd	logs		Total disinfection credit required for viruses if the source is groundwater

1. This column contains the limits for input parameters that represent a condition in which the bounds of the predictive algorithms are met for simulation of alum/ferric TOC removal, free chlorine decay, and TTHM/HAA5 formation in a conventional plant using free chlorine as a primary and secondary disinfectant with no alternative disinfectants or advanced treatment processes. User is advised to consult individual algorithm discussions in **Chapter 5** for more info.

Table 3-2 General Unit Process Input Parameters

Input Parameter	Units	Notes
Volume[1]	MG	Basin water volume through which the "Peak Flow" and "Plant Flow" (as defined in the "Influent" unit process data entry dialogue box) pass
Ratio of T50/Detention Time[2]	--	Baffling factor equal to the ratio of the mean residence time as typically estimated via tracer testing (T_{50}) and the theoretical detention time (volume/flow rate). Used to calculate mean detention time.
Ratio of T10/Detention Time[2]	--	Baffling factor equal to the ratio of T_{10} as typically estimated via tracer testing or basin baffling design features. Used to calculate CT achieved values and to simulate basin mixing conditions for chemical reaction calcs.
1. Input applies to all Unit Processes, except any type of filtration process, "GAC," and "UV Disinfection."		
2. Input applies to all Unit Processes, except "GAC," "MF/UF," "Nanofiltration," "UV Disinfection," "Bag Filtration," and "Cartridge Filtration."		

Table 3-3 "Filtration" Unit Process Input Parameters

Input Parameter	Units	Notes
Volume	MG	Total volume of granular media filter process. This value is also used to calculate the empty bed contact time of the filter with the assumption that 50% of the volume is filter media and 50% is water.
Chlorinated Backwash Water?	True/ False	Used by WTP Model for determining only whether or not a filter is to be considered bio-active. If "TRUE," filter will not be considered bio-active even if other conditions indicate so.
Filter Media (Anthracite/Sand or GAC)	S or G	Used by WTP Model to calculate only organics removal rate by a biofilter. A higher removal rate is assumed for GAC media versus anthracite/sand media.
Giardia (Virus and Crypto.) Removal Credit-Conv. Filters	logs	These three inputs assign removal credits for pathogen disinfection for the "Filtration" unit process <u>if</u> it is the <u>primary</u> filtration step <u>and</u> part of a <u>conventional</u> filtration process sequence that includes coagulant addition followed by "Rapid Mix," "Flocculation," and "Settling Basin" unit processes all prior to "Filtration."
Giardia (Virus and Crypto.) Removal Credit-Direct Filters	logs	These three inputs assign removal credits for pathogen disinfection for the "Filtration" unit process <u>if</u> it is the <u>primary</u> filtration step <u>and</u> part of a <u>direct</u> filtration process sequence that includes coagulant addition followed by a "Rapid Mix" and "Settling Basin" prior to "Filtration."
CFE Turb. Meets LT2 Toolbox Criteria?	True/ False	This is the proposed LT2 Toolbox Combined Filter Effluent (CFE) turbidity performance credit for *Cryptosporidium*. When "True," WTP Model assigns an additional 0.5-log *Cryptosporidium* removal credit if the "Filtration" process is the <u>primary</u> filtration step in conventional or direct filtration train and the "IFE Turb…." input is "False." Proposed LT2 Toolbox criteria included a CFE turbidity limit of 0.15 ntu.
IFE Turb. Meets LT2 Toolbox Criteria?	True/ False	This is the proposed LT2 Toolbox Individual Filter Effluent (IFE) turbidity performance credit for *Cryptosporidium*. When "True," WTP Model assigns an additional 1.0-log *Cryptosporidium* removal credit if the "Filtration" process is the <u>primary</u> filtration step in conventional or direct filtration train. Proposed LT2 Toolbox criteria included an IFE turbidity limit of 0.10 ntu.
Crypto. Credit as 2nd Stage Filt.	logs	*Cryptosporidium* removal credit assigned if the "Filtration" process is serving as a 2nd stage filter per the proposed LT2 Toolbox criteria.

Table 3-4 "GAC"[1] Unit Process Input Parameters

Input Parameter	Units	Notes
Empty Bed Contact Time (at 'Plant Flow')	min-utes	Equals GAC media volume (available to flow, on average) divided by 'Plant Flow' from the "Influent" unit process dialogue box. Note units.
Reactivation Frequency	days	Average interval for replacement or reactivation of the GAC.
GAC Contacting System (Single/Blended)	S or B	Enter "S" for a system with all the GAC at the same point in its TOC breakthrough curve at any point in time. Enter "B" for a set of GAC contactors run in parallel with staggered reactivation times.
TOC Breakthrough for Single Unit (Max/Average)	M or A	Used by WTP Model to calculate only the effluent TOC from the GAC process if "S" is selected for the above input. Enter "M" if want the maximum TOC (occurs just prior to reactivation), or "A" if want the average TOC for the breakthrough curve.
Crypto. Removal Credit as 2nd Stage	logs	*Cryptosporidium* removal credit assigned if the "GAC" process is serving as a 2nd stage filter per the proposed LT2 Toolbox criteria.
1. "GAC" stands for "granular activated carbon" adsorption. This unit process is intended for modeling post-filter GAC adsorbers that employ reactivation of spent carbon.		

Table 3-5 "MF/UF"[1] Unit Process Input Parameters

Input Parameter	Units	Notes
Percent Recovery	%	Percent of water recovered through process (i.e. not wasted)
Giardia (Virus and Crypto.) Removal Credit as 1st Stage	logs	These three inputs assign removal credits for pathogen disinfection for the "MF/UF" unit process <u>if</u> it is the <u>primary</u> filtration step. The values are typically established by State primacy agencies.
Crypto. Removal Credit as 2nd Stage	logs	*Cryptosporidium* removal credit assigned if the "MF/UF" process is serving as a 2nd stage filter per the proposed LT2 Toolbox criteria.
1. "MF/UF" stands for microfiltration/ultrafiltration, which refers to that class of membrane treatment technologies generally removing only particles, not dissolved constituents.		

Table 3-6 "Nanofiltration" Unit Process Input Parameters

Input Parameter	Units	Notes
Molecular Weight Cut-off	gm/mol	Generally defines the size of the pores of the NF membrane. Value should be obtained from the membrane manufacturer.
Percent recovery	%	Percent of water recovered through process (i.e. not wasted)
Giardia (and virus) Removal Credit as 1st Stage	logs	These two inputs define the removal credit assigned if the "Nanofiltration" process is the primary filtration step and 100% of the flow is treated. The values of the credits are typically established by State primacy agencies.
Crypto. Removal Credit	logs	The *Cryptosporidium* removal credit assigned if the "Nanofiltration" process is the primary or 2nd stage filtration step and 100% of the flow is treated. The value of the credit is typically set by State primacy agencies.
TOC Removal by NF	%	Base input on actual performance or test data.
UVA Removal by NF (<= TOC Rem.)	%	Base input on actual performance or test data. Model will not allow entry of a value that is greater than that entered for TOC removal.
Bromide Removal by NF	%	Base input on actual performance or test data.
Fraction of Flow Treated by NF	%	WTP Model predictions assume a split-stream treatment configuration (portion of flow will bypass the NF membranes and be blended back with the NF-treated water).
1. "Nanofiltration" is a membrane treatment process that typically removes a significant percentage of natural organic matter and divalent cations.		

Table 3-7 "Slow Sand Filt." Unit Process Input Parameters

Input Parameter	Units	Notes
Liquid Volume	MG	Average water volume for a granular media filter process. This is roughly the total basin volume contacted by water minus the volume occupied by filter media particles.
TOC Removal (various temp. ranges)	%	These three inputs set the amount of TOC removal that the WTP Model will calculate through a slow sand filter for various water temperatures as long as disinfectant residuals on the filter are all less than 0.1 mg/L.
Giardia (Virus and Crypto.) Removal Credit as 1st Stage	logs	These three inputs assign removal credits for pathogen disinfection for the "Slow Sand Filt." unit process <u>if</u> it is the <u>primary</u> filtration step.
Crypto. Removal Credit as 2nd Stage	logs	*Cryptosporidium* removal credit assigned if the "Slow Sand Filt." process is serving as a 2nd stage filter per the proposed LT2 Toolbox criteria.

Table 3-8 "UV Disinfection" Unit Process Input Parameters

Input Parameter	Units	Notes
Giardia (virus and *Crypto.*) Inactivation Credit	logs	These three inputs define the inactivation credit assigned for these pathogens for the "UV Disinfection" unit process.

Table 3-9 "Bank Filtration" Unit Process Input Parameters

Input Parameter	Units	Notes
Eligible for LT2 Toolbox Crypto. Credit?	True/ False	If True, WTP Model will assign *Cryptosporidium* removal credit due to "Bank Filtration" based on the remaining inputs.
Distance from Wells to Surface Water	feet	Used as basis to determine which value of *Cryptosporidium* removal credit to assign. If distance is less than 25 feet, no credit will be assigned.
Crypto. Removal Credit: (two different distance ranges)	logs	These two inputs define the amount of Cryptosporidium removal credit to be assigned based on the horizontal distance between the withdrawal wells and surface water source per the proposed LT2 Toolbox criteria.

Table 3-10 "D.E. Filtration" Unit Process Input Parameters

Input Parameter	Units	Notes
Liquid Volume	MG	Average water volume for a granular media filter process. This is roughly the total basin volume contacted by water minus the volume occupied by filter media particles.
Giardia (Virus and Crypto.) Removal Credit as 1ˢᵗ Stage	logs	These three inputs assign removal credits for pathogen disinfection for the "D.E. Filtration" unit process <u>if</u> it is the <u>primary</u> filtration step. The values are typically established by State primacy agencies.
Crypto. Removal Credit as 2ⁿᵈ Stage	logs	*Cryptosporidium* removal credit assigned if the "D.E. Filtration" process is serving as a 2ⁿᵈ stage filter per the proposed LT2 Toolbox criteria.
1. "D.E. Filtration" stands for diatomaceous earth filtration.		

Table 3-11 "Bag Filtration" Unit Process Input Parameters

Input Parameter	Units	Notes
Giardia (Virus and Crypto.) Removal Credit as 1ˢᵗ Stage	logs	These three inputs assign removal credits for pathogen disinfection for the "Bag Filtration" unit process <u>if</u> it is the <u>primary</u> filtration step. The values are typically established by State primacy agencies.
Crypto. Removal Credit as 2ⁿᵈ Stage	logs	*Cryptosporidium* removal credit assigned if the "Bag Filtration" process is serving as a 2ⁿᵈ stage filter per the proposed LT2 Toolbox criteria.

Table 3-12 "Cartridge Filt." Unit Process Input Parameters

Input Parameter	Units	Notes
Giardia (Virus and Crypto.) Removal Credit as 1st Stage	logs	These three inputs assign removal credits for pathogen disinfection for the "Cartridge Filtration" unit process <u>if</u> it is the <u>primary</u> filtration step. The values are typically established by State primacy agencies.
Crypto. Removal Credit as 2nd Stage	logs	*Cryptosporidium* removal credit assigned if the "Cartridge Filtration" process is serving as a 2nd stage filter per the proposed LT2 Toolbox criteria.

Table 3-13 "Lime" Chemical Feed Input Parameters

Input Parameter	Units	Notes
Lime Dose	mg/L as $Ca(OH)_2$	--
For pH adjustment (P) or Softening (S)	P or S	If "P" is entered, the WTP Model will not enter into any precipitation calculations. If "S" is entered the WTP Model will simulate precipitation of calcium and magnesium.

3.2 CREATING A PROCESS TRAIN

This section outlines how to create a process train, enter process parameters, and run the model. A typical process train for a conventional treatment plant is developed as an example. A unit process flow diagram for the example is shown in **Figure 3-3**. This information is needed to create the process train and enter data. To better understand the development of this process train, it is recommended that the unit process components of the process train be arranged in a sequential block diagram, as illustrated in **Figure 3-4**. **Figure 3-5** presents a summary of input parameters and raw water quality data as shown in the program's "Process Train Data Table" output listing. **Figure 3-6** summarizes selected input parameters (such as pathogen removal requirements and process hydraulics), as given in Table 2 of the WTP Model output.
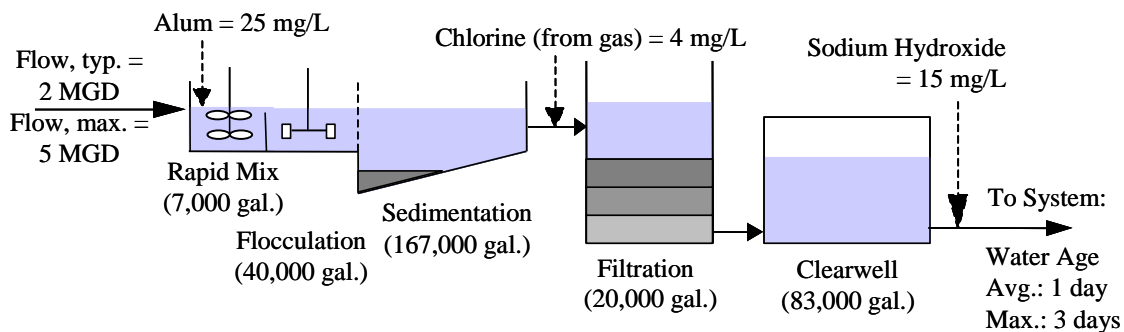
Figure 3-3 Flow Schematic for Example Process Train

```
         ┌─────────────┐
         │  Influent   │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │    Alum     │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │  Rapid Mix  │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │ Flocculation│
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │Sedimentation│
         │    Basin    │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │  Chlorine   │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │  Filtration │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │ Contact Tank│
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │   Sodium    │
         │  Hydroxide  │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │ WTP Effluent│
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │ Average Tap │
         └─────────────┘
                │
                ▼
         ┌─────────────┐
         │End of System│
         └─────────────┘
```
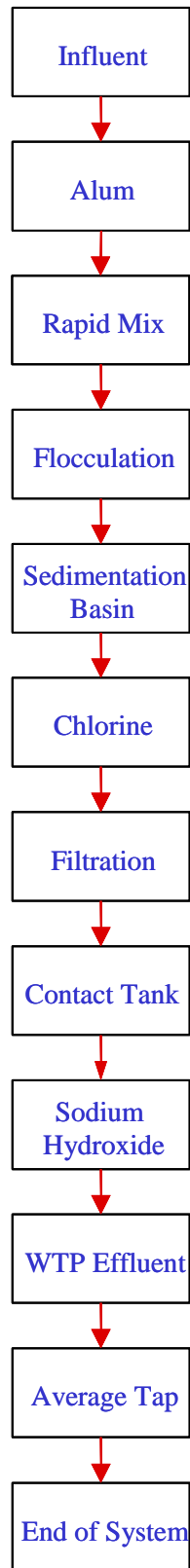
Figure 3-4 Block Diagram of Example WTP Model Process Train

```
Process train data for i:\2002\2002-276\20\win\test.wtp
Influent
        pH ....................................... 8.0
        Influent Temperature ..................... 20.0  (Celsius)
        Minimum Temperature ...................... 5.0   (Celsius)
        Total Organic Carbon ..................... 3.0   (mg/L)
        UV Absorbance at 254nm ................... 0.060(1/cm)
        Bromide .................................. 0.050(mg/L)
        Alkalinity ............................... 100   (mg/L as CaCO3)
        Calcium Hardness ......................... 100   (mg/L as CaCO3)
        Total Hardness ........................... 120   (mg/L as CaCO3)
        Ammonia .................................. 0.01 (mg/L as N)
        Turbidity ................................ 5.0   (NTU)
        Peak Flow ................................ 5.000 (MGD)
        Plant Flow ............................... 2.000 (MGD)
        Surface Water by SWTR .................... TRUE   (TRUE/FALSE)
        Source Water Crypto. Concentration ....... 0.000 (oocysts/Liter)
        LT2 Rule Watershed Control Prog. Credit? . FALSE  (TRUE/FALSE)
        If GW System, Is Virus Disinfection Req'd?  FALSE (TRUE/FALSE)
        Virus Disinfection for GW, if Req'd ...... 4.0 (logs)
Alum
        Alum Dose ................................ 25.0 (mg/L, Al2(SO4)3*14H2O)
Rapid Mix
        Volume of Basin .......................... 0.0070(MG)
        Ratio of T50/Detention Time .............. 1.00 (ratio)
        Ratio of T10/Detention Time .............. 0.10 (ratio)
Flocculation
        Volume of Basin .......................... 0.0400(MG)
        Ratio of T50/Detention Time .............. 1.00 (ratio)
        Ratio of T10/Detention Time .............. 0.10 (ratio)
Settling Basin
        Volume of Basin .......................... 0.1670(MG)
        Ratio of T50/Detention Time .............. 1.00 (ratio)
        Ratio of T10/Detention Time .............. 0.30 (ratio)
Chlorine (Gas)
        Chlorine Dose ............................ 4.0   (mg/L as Cl2)
Filtration
        Volume of Filter.......................... 1.0000(MG)
        Ratio of T50/Detention Time .............. 0.50 (ratio)
        Ratio of T10/Detention Time .............. 0.03 (ratio)
        Chlorinated Backwash Water? .............. TRUE   (TRUE/FALSE)
        Filter Media (Anthracite/Sand or GAC) .... A/S    (S or G)
        Giardia Removal Credit - Conv. Filters ... 2.5 (logs)
        Virus Removal Credit - Conv. Filters ..... 2.0 (logs)
        Crypto. Removal Credit - Conv. Filters ... 3.0 (logs)
        Giardia Removal Credit - Direct Filters .. 2.0 (logs)
        Virus Removal Credit - Direct Filters .... 1.0 (logs)
        Crypto. Removal Credit - Direct Filters .. 3.0 (logs)
        CFE Turb. Meets LT2 Toolbox Criteria? .... FALSE  (TRUE/FALSE)
        IFE Turb. Meets LT2 Toolbox Criteria? .... FALSE  (TRUE/FALSE)
        Crypto. Credit as 2nd Stage Filt. ........ 0.5 (logs)
Contact Tank
        Volume of Basin .......................... 0.0830(MG)
        Ratio of T50/Detention Time .............. 1.00 (ratio)
        Ratio of T10/Detention Time .............. 0.50 (ratio)
Sodium Hydroxide
        Sodium Hydroxide Dose .................... 15.0   (mg/L as NaOH)
WTP Effluent
Average Tap
        Average Residence Time (For Average Flow)    1.0  (Days)
End of System
         Maximum Residence Time (For Average Flow) 3.0   (Days)
```

Figure 3-5 Process Train Data Table for WTP Model

```
                              Table 2
                     Selected Input Parameters
-----------------------------------------------------------------
Parameter                               Value  Units
-----------------------------------------------------------------
TEMPERATURES
     Average                             20.0  (deg. C)
     Minimum                             5.0  (deg. C)
PLANT FLOW RATES
     Average                            2.000  (mgd)
     Peak Hourly                        5.000  (mgd)

DISINFECTION INPUTS/CALCULATED VALUES
Surface Water Plant?                    TRUE
Giardia: Total Disinfection Credit Required  3.0  (logs)
Giardia: Credit Achieved (other than by CT)  2.5  (logs)
Giardia: Inactivation Credit by CT Required  0.5  (logs)

Virus: Total Disinfection Credit Required  4.0  (logs)
Virus: Credit Achieved (other than by CT)  2.0  (logs)
Virus: Inactivation Credit by CT Required  2.0  (logs)

Crypto.: Total Disinfection Credit Required  3.0  (logs)
Crypto.: Credit Achieved (other than by CT)  3.0  (logs)
Crypto.: Inactivation Credit by CT Required  0.0  (logs)


DISINFECT. CREDITS (not incl. CT): Giardia   Virus      Crypto
(in order of appearance)
Filtration                         2.5       2.0        3.0
CHEMICAL DOSES
(in order of appearance)
Alum                                    25.0  (mg/L as Al2(SO4)3*14H2O)
Chlorine (Gas)                          4.0  (mg/L as Cl2)
Sodium Hydroxide                        15.0  (mg/L as NaOH)

PROCESS HYDRAULIC PARAMETERS:    T10/Tth   T50/Tth   VOL. (MG)
(in order of appearance)
Rapid Mix                          0.1       1.0       0.0070
Flocculation                       0.1       1.0       0.0400
Settling Basin                     0.3       1.0       0.1670
Filtration                         0.0       0.5       1.0000
Contact Tank                       0.5       1.0       1.0000
```

Figure 3-6 WTP Model Output Table 2 – Selected Input Parameters

To properly simulate a water treatment process, the WTP Model expects that process trains are constructed following some simple rules. Be sure to follow these rules carefully to obtain predictions of treated water quality that are relevant to the type of plant intended to be modeled. These rules are:

- **In every process train always include a "WTP Effluent" sample point at the effluent point of the plant.** For the WTP Model, the effluent point is the point downstream of which no more units of type "Unit Process" or "Chemical Feed" will occur. This is typically the location that

marks the transition from the treatment process to the distribution system. In an actual treatment plant it would be the point right after the final clearwell or pump wetwell, or, if a final chemical feed point occurs as water leaves the last basin, it would be the point directly downstream of this final chemical feed point. The WTP Model needs to know where this transition point occurs so as to properly predict plant effluent water quality, to invoke the proper predictive algorithms, and to keep track of the proper residence time (a.ka. "water age") to be used for distribution system disinfectant decay and DBP formation algorithms.

- **Never include units of type "Unit Process" or "Chemical Feed" downstream of the "WTP Effluent" sample point.** Erroneous water quality predictions for distribution system sample points may occur if this is done.

- **Include a "Rapid Mix" in the process train as the first unit of type "Unit Process" following any coagulant or lime (for softening) chemical feed points.** That is, after any "Alum," "Iron," or "Lime" (where lime is used for softening, not just pH adjustment) chemical feed points, but before the next unit of type "Unit Process," always include a "Rapid Mix" unit process if you intend for the addition of the chemical(s) to result in coagulation. The "Rapid Mix" needs to be added even if there is not a true rapid mix basin at the actual facility being represented. That is, the physical plant may use an in-line static mixer, a series of bends and fittings, a throttled valve, or a hydraulic jump to cause mixing; however, within the WTP Model, this point of mixing should be represented with a "Rapid Mix" unit process. The user can input a very small volume if the actual mixing process has a very short contact time. The reason that a "Rapid Mix" unit process needs to be included after coagulants is that the WTP Model needs to know where coagulation is occurring in the treatment plant so that it can simulate TOC and UVA reduction due to coagulation at that point. The WTP Model also uses the location of the rapid mix relative to other unit processes to make determinations about the type of treatment plant being simulated and invoke the appropriate predictive algorithms. For example, if there is a "Chlorine" chemical feed point just upstream of the "Rapid Mix" unit process, the WTP Model knows that the plant is of the pre-chlorination type, and it will use the proper DBP formation algorithms to predict in-plant DBP levels.

- **Include one or more "Ozone Chambers" as the first units of type "Unit Process" to follow an "Ozone" chemical feed point.** Treatment plants that use ozone for primary disinfection or even just oxidation are typically designed with dedicated contact chambers to provide contact

time between the ozone and the water. The WTP Model relies upon this type of configuration to properly predict bromate formation, ozone residual decay, and ozone CT (and associated log inactivation credits). The WTP Model assumes that ozone residual will NOT persist outside of dedicated "Ozone Chambers," so the user will not see any ozone residual predicted in the effluent of any other type of unit process. Note that the WTP Model does not assign any ozone CT credit to the first "Ozone Chamber" in the process train since it is assumed that this chamber is an ozone application chamber in which mass transfer of the ozone is occurring. In treatment plant design, this is typically the first tank containing ozone diffusers, and it often has a shorter detention time, more mixing (due to the turbulence caused by the ozone gas bubbles), and a less predictable ozone residual profile than the ozone contact tanks to follow.

- **If intending to simulate an biofiltration plant with either biologically active filter or GAC contactor be sure the conditions in the "Biofiltration eligibility" section are met**

3.2.1 How to Build a Process Train

The list on the left titled "Process Train", contains the components of a treatment plant that are being simulated. For a new project, this list will be populated with a conventional treatment plant with default values. To add other components to the train, the user can drag and drop "Unit Processes", "Chemical Feeds", and "Sample Points", onto the list of "Process Train". At a minimum, the user must include the following selections to run the WTP Model: "Influent" information and the "WTP Effluent", "Average Tap", and "End of System" sampling points. A full list of "Available Selections" are described in Table 3-2.

Table 3-1 Available Unit Process, Chemical Feed, and Sample Point Selections

Unit Processes	Chemical Feeds	Sample Points
Presed. Basin	Alum	WTP Effluent
Rapid Mix	Ammonia Sulfate	Average Tap
Flocculation	Ammonia	End of System
Settling Basin	Carbon Dioxide	Additional Point
Filtration	Chlorine (Gas)	
GAC	Chlorine Dioxide	
MF/UF	Iron	
Nanofiltration	Lime	
Slow Sand Filtration	Ozone	

UV Disinfection	Permanganate
Ozone Chamber	Sodium Hydroxide
Contact Tank	Sodium Hypochlorite
Reservoir	Soda Ash
Bank Filtration	Sulfur Dioxide
D.E. Filtration	Sulfuric Acid
Bag Filtration	
Cartridge Filtration	

The order of "Process Train" components is significant. The "Influent" process must be at the head of the plant (the top of the list) and the remaining components must be placed in the proper sequence. To assist with ordering the train, click on the component of interest followed by the "Move Up" button to shift its position higher in the list or the "Move Down" button to lower its position (**Figure 3-7**). Similarly, elements of the train can be deleted individually using the "Delete" button or all at once using the "Clear All" button.

Figure 3-8 shows how the sample treatment plant represented in **Figures 3-3** through **3-5** would look on the main window.
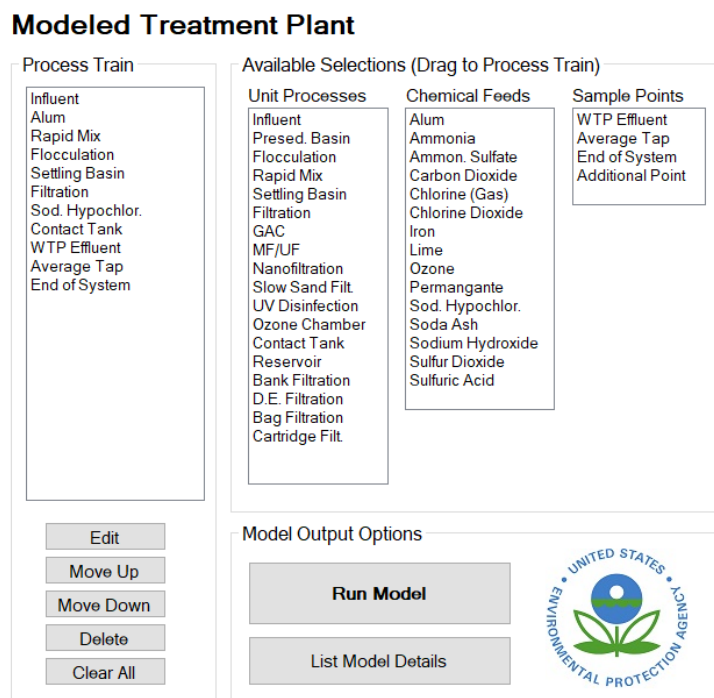
Figure 3-7 Modeled treatment plant options (found on the main window)

3.2.2 Editing Process Train Parameters

Once the process train is complete, the user should specify the parameters for each component. To do so, click on the component and then the "Edit" button in the bottom left corner. If we were to edit the "Rapid Mix" basin, the dialog in **Figure 3-8** would appear. In this dialog, specifically, the user can specify the volume of the basin and its hydraulic properties.
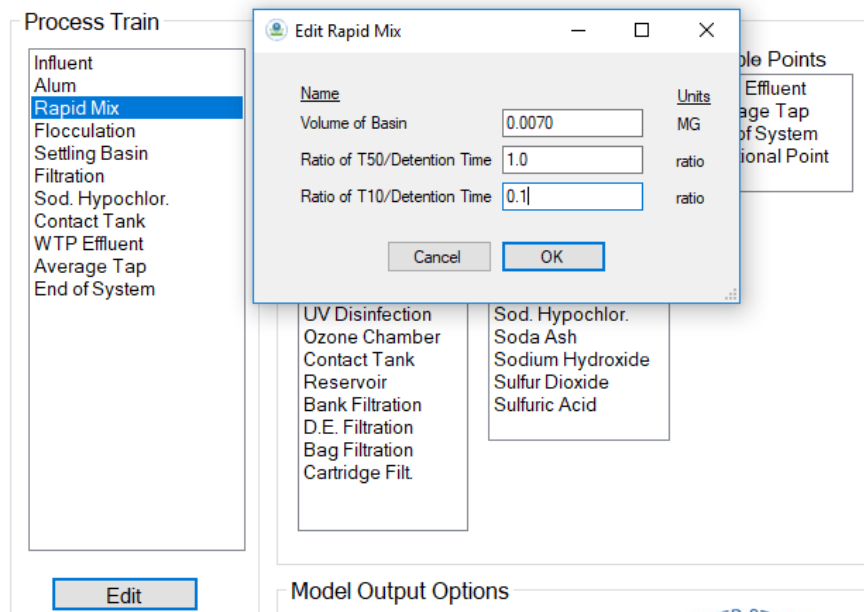
Figure 3-8 Editing the Parameters of the Rapid Mix Basin

After parameters for each part of the process train have been specified, click *File | Save* to save your progress.

3.2.3 Running the Model

To run the WTP Model, select click the "Run Model" button on the main window or *Model | Run.* When the model is run, the user will see summary tables (see **Figures 4-1** through **4-11**) of water quality parameters and DBPs for each unit process.

4. WTP MODEL OUTPUT

This chapter provides a brief overview of the outputs generated by the WTP Model. **Section 4.1** describes the content of the various WTP Model output tables. **Section 4.2** presents some helpful guidance for interpreting results. **Chapter 5** describes the WTP Model's predictive equations that are used to produce the model outputs.

4.1 WTP MODEL OUTPUT TABLES

An example process train was shown in **Figure 3-4**, and input parameters were summarized in **Figure 3-5**. **Section 4.1** presents output from a run of this example process train. The *Model | Run* option generates a display of the full output of the WTP Model, as contained in 11 output tables. Note that the water quality predictions shown in Tables 1 through 9 are associated with the (typical average) "Plant Flow" and "Influent Temperature" inputs. Outputs for "Table 10" are associated with worst-case disinfection input parameters of "Peak Flow" and "Minimum Temperature." Table 11 contains predicted CT Ratios using the (worst-case) "Peak Flow" and "Minimum Temperature" inputs and predicted free chlorine, chloramines, and DBP concentrations using the (typical average) "Plant Flow" and "Influent Temperature" inputs. The intent of this table is to capture the most critical outputs in one concise format.

The WTP Model output tables, containing data from the example process train of **Figure 3-4**, are shown in **Figures 4-1** through **4-11**. The following summarizes the content of each:

- Output "Table 1" (see **Figure 4-1**) is a summary table for raw, finished and distributed water quality. This table also indicates whether or not Stage 1 D/DBP Rule Step 1 Enhanced Coagulation TOC removal requirements were met and what the final CT ratios for virus, *Giardia*, and *Cryptosporidium* were.
- Output "Table 2" (see **Figure 4-2**) lists the input parameters describing the process being simulated. These include items such as temperatures, flow rates, disinfection requirements and credits, chemical doses, and process hydraulic parameters.
- Output "Table 3" (see **Figure 4-3**) and "Table 4" (see **Figure 4-4**) list predicted values of major water quality parameters (inorganics, TOC, UVA, major disinfectant residuals, etc.) in the *effluent* of each process unit. *Note that in all subsequent output tables, predicted water quality parameters are also for the <u>effluent</u> of each unit.*
- Output "Table 5" (see **Figure 4-5**) lists predicted values of:
  - bromate as "BrO3-"

- chlorite as "ClO2-"
- total organic halides "TOX"
- THM species
  - chloroform as "CHCl3"
  - bromodichloromethane as "BDCM"
  - dichlorobromomethane as "DBCM"
  - bromoform as "CHBr3"
- total THMs as "TTHMs"

- Output "Table 6" (see **Figure 4-6**) lists predicted values of:
  - HAA species:
    - monochloroacetic acid as "MCAA"
    - dichloroacetic acid as "DCAA"
    - trichloroacetic acid as "TCAA"
    - monobromoacetic acid as "MBAA"
    - dibromoacetic acid as "DBAA"
  - Sum of the above five haloacetic acid species as "HAA5"

- Output "Table 7" (see **Figure 4-7**) lists predicted values of:
  - the remaining HAA species:
    - bromochloroacetic acid as "BCAA"
    - bromodichloroacetic acid as "BDCAA"
    - dibromochloroacetic acid as "DBCAA"
    - tribromoacetic acid as "TBAA"
  - sum of 6 haloacetic acids (HAA5 + BCAA) as "HAA6"
  - sum of all nine haloacetic acids as "HAA9"

- Output "Table 8" (see **Figure 4-8**) summarizes predicted parameters associated with disinfection, including temperature, pH, disinfectant residuals and CT ratios.

- Output "Table 9" (see **Figure 4-9**) summarizes predicted values of $CT_{achieved}$ for the four disinfectants considered by the model.

- Output "Table 10" (see **Figure 4-10**) is unique in that it contains some predicted parameters for a run of the model using the input values of "Peak Flow" and "Minimum Temperature." The format of the output in "Table 10" is the same as that used for "Table 8," but, as noted, the results are for worst-case disinfection inputs of short in-plant residence times (due to high flow) and cold temperatures.

- Output "Table 11" (see **Figure 4-11**) contains output data from two runs of the WTP Model. It contains predicted CT Ratios using the (worst-case) "Peak Flow" and "Minimum Temperature" inputs and predicted free chlorine, chloramines, and DBP concentrations using the (typ. avg.) "Plant Flow" and "Influent Temperature" inputs.

```
                                Table 1
          Water Quality Summary for Raw, Finished, and Distributed Water
            At Plant Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
-------------------------------------------------------------------------------
Parameter               Units       Raw Water   Effluent   Avg. Tap   End of Sys
-------------------------------------------------------------------------------
pH                       (-)           8.0         8.3        8.4        8.5
Alkalinity       (mg/L as CaCO3)       100         102        102        102
TOC                    (mg/L)          3.0         2.6        2.6        2.6
UV                     (1/cm)         0.060       0.029      0.029      0.029
 (T)SUVA               (1/cm)          2.0         1.1        1.1        1.1
Ca Hardness      (mg/L as CaCO3)       100         100        100        100
Mg Hardness      (mg/L as CaCO3)        20          20         20         20
Ammonia-N              (mg/L)         0.01        0.00       0.00       0.00
Bromide                (ug/L)           50          29         25         20
Free Cl2 Res.     (mg/L as Cl2)        0.0         2.3        1.7        1.2
Chloramine Res.   (mg/L as Cl2)        0.0         0.0        0.0        0.0
TTHMs                  (ug/L)           0           59         77         97
HAA5                   (ug/L)           0           28         31         35
HAA6                   (ug/L)           0           32         36         40
HAA9                   (ug/L)           0           43         49         56
TOX                    (ug/L)           0          183        213        245
Bromate                (ug/L)           0           0          0          0
Chlorite               (mg/L)          0.0         0.0        0.0        0.0
TOC Removal          (percent)                      15
E.C. not required - raw TOC, raw SUVA, and/or finished TOC <= 2
E.C. Step 1 TOC removal requirement NOT ACHIEVED
CT Ratios
  Virus                 (-)           0.0         902.5      902.5      902.5
  Giardia               (-)           0.0          77.7       77.7       77.7
  Cryptosporidium*      (-)           1.0          1.0        1.0        1.0
*Crypto. Disinfection Calcs. Based on Proposed LT2 Rule
-------------------------------------------------------------------------------
Crypto. CT Ratio = 1 because other credits met full disinfection requirements
```

Figure 4-1 Example WTP Model Output "Table 1"

```
                                   Table 2
                          Selected Input Parameters
--------------------------------------------------------------------------------
-
Parameter                                      Value  Units
--------------------------------------------------------------------------------
-
TEMPERATURES
     Average                                    20.0  (deg. C)
     Minimum                                     5.0  (deg. C)
PLANT FLOW RATES
     Average                                    2.000 (mgd)
     Peak Hourly                                5.000 (mgd)


DISINFECTION INPUTS/CALCULATED VALUES
Surface Water Plant?                            TRUE
Giardia: Total Disinfection Credit Required     3.0  (logs)
Giardia: Credit Achieved (other than by CT)     2.5  (logs)
Giardia: Inactivation Credit by CT Required     0.5  (logs)

Virus: Total Disinfection Credit Required       4.0  (logs)
Virus: Credit Achieved (other than by CT)       2.0  (logs)
Virus: Inactivation Credit by CT Required       2.0  (logs)

Crypto.: Total Disinfection Credit Required     3.0  (logs)
Crypto.: Credit Achieved (other than by CT)     3.0  (logs)
Crypto.: Inactivation Credit by CT Required     0.0  (logs)


DISINFECT. CREDITS (not incl. CT): Giardia    Virus      Crypto
(in order of appearance)
Filtration                          2.5       2.0         3.0
CHEMICAL DOSES
(in order of appearance)
Alum                                           25.0  (mg/L as Al2(SO4)3*14H2O)
Chlorine (Gas)                                  4.0  (mg/L as Cl2)
Sodium Hydroxide                               15.0  (mg/L as NaOH)

PROCESS HYDRAULIC PARAMETERS:    T10/Tth   T50/Tth   VOL. (MG)
(in order of appearance)
Rapid Mix                           0.1       1.0       0.0070
Flocculation                        0.1       1.0       0.0400
Settling Basin                      0.3       1.0       0.1670
Filtration                          0.0       0.5       1.0000
Contact Tank                        0.5       1.0       1.0000
```

Figure 4-2 Example WTP Model Output "Table 2"

```
                              Table 3
                   Predicted Water Quality Profile
          At Plant Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
--------------------------------------------------------------------------------
-
                                                     | Residence Time |
             pH   TOC    UVA   (T)SUVA   Cl2   NH2Cl | Process|  Cum. |
Location     (-)  (mg/L) (1/cm) (L/mg-m) (mg/L) (mg/L) |  (hrs) | (hrs)  |
--------------------------------------------------------------------------------
-
Influent      8.0  3.0   0.060   2.0    0.0   0.0    0.00     0.00
Alum          7.2  3.0   0.060   2.0    0.0   0.0    0.00     0.00
Rapid Mix     7.2  2.6   0.041   1.6    0.0   0.0    0.08     0.08
Flocculation  7.2  2.6   0.041   1.6    0.0   0.0    0.48     0.56
Settling Basin 7.2 2.6   0.041   1.6    0.0   0.0    2.00     2.57
Chlorine (Gas) 7.0 2.6   0.029   1.1    3.9   0.0    0.00     2.57
Filtration    7.1  2.6   0.029   1.1    3.0   0.0    6.00     8.57
Contact Tank  7.1  2.6   0.029   1.1    2.3   0.0   12.00    20.57
Sodium Hydroxide 8.3 2.6 0.029   1.1    2.3   0.0    0.00    20.57
WTP Effluent  8.3  2.6   0.029   1.1    2.3   0.0    0.00    20.57
Average Tap   8.4  2.6   0.029   1.1    1.7   0.0   24.00    44.57
End of System 8.5  2.6   0.029   1.1    1.2   0.0   72.00    92.57
--------------------------------------------------------------------------------
-
TOC Removal (percent):     15
E.C. not required - raw TOC, raw SUVA, and/or finished TOC <= 2
E.C. Step 1 TOC removal requirement NOT ACHIEVED
```

Figure 4-3 Example WTP Model Output "Table 3"

```
                              Table 4
                   Predicted Water Quality Profile
          At Plant Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
--------------------------------------------------------------------------------
-
                       Calcium    Magnesium
             pH   Alk   Hardness   Hardness   Solids  NH3-N   Bromide
Location     (-)  (mg/L) (mg/L)    (mg/L)     (mg/L)  (mg/L)  (ug/L)
--------------------------------------------------------------------------------
-
Influent      8.0  100    100        20        0.0    0.0      50
Alum          7.2   87    100        20        0.0    0.0      50
Rapid Mix     7.2   87    100        20        0.0    0.0      50
Flocculation  7.2   87    100        20        0.0    0.0      50
Settling Basin 7.2  87    100        20       18.4    0.0      50
Chlorine (Gas) 7.0  84    100        20       18.4    0.0      50
Filtration    7.1   84    100        20       18.4    0.0      33
Contact Tank  7.1   84    100        20       18.4    0.0      29
Sodium Hydroxide 8.3 102  100        20       18.4    0.0      29
WTP Effluent  8.3  102    100        20       18.4    0.0      29
Average Tap   8.4  102    100        20       18.4    0.0      25
End of System 8.5  102    100        20       18.4    0.0      20
```

Figure 4-4 Example WTP Model Output "Table 4"

```
                             Table 5
                Predicted Trihalomethanes and other DBPs
            At Average Flow ( 2.0 MGD) and Temperature (20.0 C)
-------------------------------------------------------------------------------
-
                   BrO3- ClO2-   TOX  |CHCl3   BDCM     DBCM     CHBr3   TTHMs
Location           (ug/L) (mg/L) (ug/L)|(ug/L)  (ug/L)   (ug/L)   (ug/L)  (ug/L)
-------------------------------------------------------------------------------
-
Influent              0    0.0     0      0      0        0        0        0
Alum                  0    0.0     0      0      0        0        0        0
Rapid Mix             0    0.0     0      0      0        0        0        0
Flocculation          0    0.0     0      0      0        0        0        0
Settling Basin        0    0.0     0      0      0        0        0        0
Chlorine (Gas)        0    0.0     0      0      0        0        0        0
Filtration            0    0.0   150     24     13        6        0       44
Contact Tank          0    0.0   183     35     17        7        0       59
Sodium Hydroxide      0    0.0   183     35     17        7        0       59
WTP Effluent          0    0.0   183     35     17        7        0       59
Average Tap           0    0.0   213     48     20        9        1       77
End of System         0    0.0   245     63     24       10        1       97
```

Figure 4-5 Example WTP Model Output "Table 5"

```
                             Table 6
                Predicted Haloacetic Acids - through HAA5
            At Average Flow ( 2.0 MGD) and Temperature (20.0 C)
-------------------------------------------------------------------------------
-
                   MCAA    DCAA    TCAA    MBAA    DBAA    HAA5
Location           (ug/L)  (ug/L)  (ug/L)  (ug/L)  (ug/L)  (ug/L)
-------------------------------------------------------------------------------
-
Influent              0       0       0       0       0       0
Alum                  0       0       0       0       0       0
Rapid Mix             0       0       0       0       0       0
Flocculation          0       0       0       0       0       0
Settling Basin        0       0       0       0       0       0
Chlorine (Gas)        0       0       0       0       0       0
Filtration            4      10       9       0       0      24
Contact Tank          4      13      11       0       0      28
Sodium Hydroxide      4      13      11       0       0      28
WTP Effluent          4      13      11       0       0      28
Average Tap           3      15      12       0       0      31
End of System         3      17      14       0       0      35
```

Figure 4-6 Example WTP Model Output "Table 6"

```
                               Table 7
                Predicted Haloacetic Acids (HAA6 through HAA9)
              At Average Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
-------------------------------------------------------------------------------
-
                   BCAA   BDCAA  DBCAA   TBAA   HAA6   HAA9
Location           (ug/L) (ug/L) (ug/L) (ug/L) (ug/L) (ug/L)
-------------------------------------------------------------------------------
-
Influent              0      0      0      0      0      0
Alum                  0      0      0      0      0      0
Rapid Mix             0      0      0      0      0      0
Flocculation          0      0      0      0      0      0
Settling Basin        0      0      0      0      0      0
Chlorine (Gas)        0      0      0      0      0      0
Filtration            4      6      1      0     28     35
Contact Tank          5      9      1      0     32     43
Sodium Hydroxide      5      9      1      0     32     43
WTP Effluent          5      9      1      0     32     43
Average Tap           5     10      2      0     36     49
End of System         6     12      3      0     40     56
```

Figure 4-7 Example WTP Model Output "Table 7"

```
                              Table 8
            Predicted Disinfection Parameters - Residuals and CT Ratios
             At Plant Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
-------------------------------------------------------------------------------
-
                                                              CT Ratios
               Temp  pH    Cl2   NH2Cl  Ozone   ClO2  --------------------
Location       (C)   (-)   (mg/L) (mg/L) (mg/L) (mg/L) Giardia Virus Crypto
-------------------------------------------------------------------------------
-
Influent        20.0  8.0   0.0    0.0    0.00   0.00   0.0     0.0    1.0
Alum            20.0  7.2   0.0    0.0    0.00   0.00   0.0     0.0    1.0
Rapid Mix       20.0  7.2   0.0    0.0    0.00   0.00   0.0     0.0    1.0
Flocculation    20.0  7.2   0.0    0.0    0.00   0.00   0.0     0.0    1.0
Settling Basin  20.0  7.2   0.0    0.0    0.00   0.00   0.0     0.0    1.0
Chlorine (Gas)  20.0  7.0   3.9    0.0    0.00   0.00   0.0     0.0    1.0
Filtration      20.0  7.1   3.0    0.0    0.00   0.00   5.2    64.7    1.0
Contact Tank    20.0  7.1   2.3    0.0    0.00   0.00  77.7   902.5    1.0
Sodium Hydroxide 20.0 8.3   2.3    0.0    0.00   0.00  77.7   902.5    1.0
WTP Effluent    20.0  8.3   2.3    0.0    0.00   0.00  77.7   902.5    1.0
Average Tap     20.0  8.4   1.7    0.0    0.00   0.00  77.7   902.5    1.0
End of System   20.0  8.5   1.2    0.0    0.00   0.00  77.7   902.5    1.0
-------------------------------------------------------------------------------
-


Crypto. CT Ratio = 1 because other credits met full disinfection requirements
```

Figure 4-8 Example WTP Model Output "Table 8"

```
                                 Table 9
                 Predicted Disinfection Parameters - CT Values
             At Plant Flow ( 2.0 MGD) and Influent Temperature (20.0 C)
--------------------------------------------------------------------------------
-

                          Cl2     NH2Cl    Ozone    ClO2
Location                  <-----(mg/L * minutes)----->
--------------------------------------------------------------------------------
-
Influent                  0.0      0.0      0.0      0.0
Alum                      0.0      0.0      0.0      0.0
Rapid Mix                 0.0      0.0      0.0      0.0
Flocculation              0.0      0.0      0.0      0.0
Settling Basin            0.0      0.0      0.0      0.0
Chlorine (Gas)            0.0      0.0      0.0      0.0
Filtration               64.7      0.0      0.0      0.0
Contact Tank            902.5      0.0      0.0      0.0
Sodium Hydroxide        902.5      0.0      0.0      0.0
WTP Effluent            902.5      0.0      0.0      0.0
Average Tap             902.5      0.0      0.0      0.0
End of System           902.5      0.0      0.0      0.0
```

Figure 4-9 Example WTP Model Output "Table 9"

```
                                 Table 10
                    Predicted Disinfection Parameters
             At Peak Flow ( 5.0 MGD) and Minimum Temperature (5.0 C)
              for Surface Water Plant with Coagulation and Filtration
--------------------------------------------------------------------------------
-
                                                              CT Ratios
              Temp  pH    Cl2   NH2Cl  Ozone   ClO2   --------------------
Location      (C)   (-)  (mg/L) (mg/L) (mg/L) (mg/L) Giardia Virus Crypto
--------------------------------------------------------------------------------
-
Influent      5.0  8.0   0.0    0.0    0.00   0.00    0.0    0.0    1.0
Alum          5.0  7.3   0.0    0.0    0.00   0.00    0.0    0.0    1.0
Rapid Mix     5.0  7.3   0.0    0.0    0.00   0.00    0.0    0.0    1.0
Flocculation  5.0  7.3   0.0    0.0    0.00   0.00    0.0    0.0    1.0
Settling Basin 5.0 7.3   0.0    0.0    0.00   0.00    0.0    0.0    1.0
Chlorine (Gas) 5.0 7.2   3.9    0.0    0.00   0.00    0.0    0.0    1.0
Filtration    5.0  7.2   3.1    0.0    0.00   0.00    0.7    6.8    1.0
Contact Tank  5.0  7.2   2.7    0.0    0.00   0.00   11.8  102.8    1.0
Sodium Hydroxide 5.0 8.3 2.7    0.0    0.00   0.00   11.8  102.8    1.0
WTP Effluent  5.0  8.3   2.7    0.0    0.00   0.00   11.8  102.8    1.0
Average Tap   5.0  8.3   2.2    0.0    0.00   0.00   11.8  102.8    1.0
End of System 5.0  8.4   1.8    0.0    0.00   0.00   11.8  102.8    1.0
--------------------------------------------------------------------------------
-
Crypto. CT Ratio = 1 because other credits met full disinfection requirements
```

Figure 4-10 Example WTP Model Output "Table 10"

```
                           Table 11
         Predicted Inactivation at Minimum Temperature and Peak Flow
              and DBPs at Plant Flow and Influent Temperature
---------------------------------------------------------------------------
                   ____ CT Ratios ____   Cl2   NH2Cl  ClO2- BrO3- TTHM  HAA5
Location           Giardia Virus Crypto (mg/L as Cl2)(mg/L) <----(ug/L)---->
---------------------------------------------------------------------------
Influent             0.0    0.0    1.0   0.0   0.0    0.0     0    0     0
Alum                 0.0    0.0    1.0   0.0   0.0    0.0     0    0     0
Rapid Mix            0.0    0.0    1.0   0.0   0.0    0.0     0    0     0
Flocculation         0.0    0.0    1.0   0.0   0.0    0.0     0    0     0
Settling Basin       0.0    0.0    1.0   0.0   0.0    0.0     0    0     0
Chlorine (Gas)       0.0    0.0    1.0   3.9   0.0    0.0     0    0     0
Filtration           0.7    6.8    1.0   3.0   0.0    0.0     0    44    24
Contact Tank        11.8  102.8    1.0   2.3   0.0    0.0     0    59    28
Sodium Hydroxide    11.8  102.8    1.0   2.3   0.0    0.0     0    59    28
WTP Effluent        11.8  102.8    1.0   2.3   0.0    0.0     0    59    28
Average Tap         11.8  102.8    1.0   1.7   0.0    0.0     0    77    31
End of System       11.8  102.8    1.0   1.2   0.0    0.0     0    97    35


E.C. not required - raw TOC, raw SUVA, and/or finished TOC <= 2
E.C. Step 1 TOC removal requirement NOT ACHIEVED
Crypto. CT Ratio = 1 because physical removal provided all disinfection
```

Figure 4-11 Example WTP Model Output "Table 11"

Table 4-1 describes the parameters listed in WTP Model output "Table 1" through "Table 11." For each unit process, the predicted value in the table is the value at the effluent of that unit process.

4.2   INTERPRETING MODEL OUTPUTS

4.2.1   Predictive Limitations

As discussed previously in Section 1, the WTP Model is not intended to replace engineering judgment or treatability testing to evaluate the impact of various unit processes on disinfectant decay and DBP formation in specific water supplies; however, it does provide a useful tool for evaluating the *potential* effect of different unit processes on these parameters. Users of the program should be familiar with water treatment plant process theory, design, operations, and techniques used to disinfect water and control DBP formation. It must be stressed that the model is largely empirical in nature. It cannot be used as the sole tool for "full-scale" or "real-time" decisions for individual public water supplies. The WTP Model, like any computer program, cannot replace sound engineering judgment where input and output interpretation is required. Further, the technical adequacy of the output is primarily a function of the extent and quality of plant-specific

Table 4-12 Summary of WTP Model Output Parameters

pH	
TOC	Total organic carbon (mg/L)
UVA	Ultraviolet absorbance at 254 nm (1/cm)
SUVA	Specific UVA (L-mg-m), equal to UVA÷TOC*100
Cl2	Free chlorine concentration (mg/L)
NH2Cl	Combined chlorine concentration (mg/L)
Process Residence Time	Hydraulic res. time (hours), = volume÷flow, for each unit process
Cumulative Residence Time	Cumulative hydraulic residence time (hours) through the process train
Alk	Alkalinity (mg/L as calcium carbonate)
Ca Hard	Calcium hardness (mg/L as calcium carbonate)
Mg Hard	Magnesium hardness (mg/L as calcium carbonate)
Solids	Precipitated (or strained) solids from process stream[1] (mg/L)
NH3-N	Ammonia concentration (mg/L as nitrogen)
Bromide	Bromide concentration (μg/L)
Temp	Average temperature (ºC)
Ozone	Ozone residual (mg/L)
ClO2	Chlorine dioxide residual (mg/L)
CT ratios	
Giardia	CT ratio, equal to $CT_{achieved}÷CT_{required}$, for *Giardia*
Virus	CT ratio, equal to $CT_{achieved}÷CT_{required}$, for viruses
Crypto.	CT ratio, equal to $CT_{achieved}÷CT_{required}$, for *Cryptosporidium*
DBPs	
CHCl3	Chloroform concentration (μg/L)
BDCM	Bromodichloroform concentration (μg/L)
DBCM	Dibromochloroform concentration (μg/L)
CHBr3	Bromoform concentration (μg/L)
TTHM	Sum of 4 trihalomethane species (μg/L)
MCAA	Monochloroacetic acid concentration (μg/L)
DCAA	Dichloroacetic acid concentration (μg/L)
TCAA	Trichloroacetic acid concentration (μg/L)
MBAA	Monobromoacetic acid concentration (μg/L)
DBAA	Dibromoacetic acid concentration (μg/L)
TBAA	Tribromoacetic acid concentration (μg/L)
BCAA	Bromochloroacetic acid concentration (μg/L)
DCBAA	Dichlorobromoacetic acid concentration (μg/L)
CDBAA	Chlorodibromoacetic acid concentration (μg/L)
TBAA	Tribromoacetic acid concentration (μg/L)
HAA5	Sum of 5 haloacetic acid species (μg/L) = MCAA+DCAA+TCAA+MBAA+DBAA
HAA6	Sum of 6 haloacetic acid species (μg/L) = HAA5 +BCAA
HAA9	Sum of 9 haloacetic acid species (μg/L) = HAA6+ DCBAA+CDBAA+TBAA
TOX	Total organic halogen concentration (μg Cl⁻/L)
BrO3⁻	Bromate concentration (μg/L)
ClO2⁻	Chlorite concentration (mg/L)

1. This is the process stream concentration of solids removed by partical removal processes. The calculation includes raw water solids estimated based on raw water turbidity, precipitated alum or iron solids, and precipitated lime-softening solids. Dissolved solids removal by NF is not considered. The units are mass of solids divided by volume of process water (i.e. it is NOT a settled or thickened sludge solids concentration)

data input, and the extent to which an individual application can be accurately simulated by predictive equations that are based upon the central tendency for treatment.

4.2.2   Strategies for Model Use and Output Interpretation

The following tips are intended to help with using the WTP Model and interpreting its outputs:

- General Applicability: Because the WTP Model is a central tendency model, it should not be expected to accurately predict plant-/water-specific observed disinfectant residuals and DBP concentrations. The model is probably more useful in predicting *changes* in these parameters due to *changes* in raw water quality or treatment processes. Therefore, if an application is to estimate DBP concentrations after a process change in an existing treatment plant, the better approach is to model the existing plant and model the modified plant, then record the predicted DBPs from each model run, calculate a change in predicted DBPs due to the plant modifications, and apply that change to the original observed DBP levels to estimate likely post-change values.

- CT Ratio Calculation: WTP Model predictions of "CT Ratio" for *Giardia* and virus are based upon general guidance, calculation methods, and CT tables contained in the *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources* (USEPA 1991). "CT Ratio" calculations for *Cryptosporidium* are based upon guidance contained in the draft version of the *Long-Term 2 Enhanced Surface Water Treatment Rule Toolbox Guidance Manual* (USEPA 2003a). Additional details can be found in **Section 5.8**. Note that individual state primacy agencies often have disinfection regulations with requirements that differ from those that form the basis of the WTP Model's "CT Ratio" calculations. In these cases, the user may need to either (1) enter pathogen removal credit input values to more accurately reflect what a particular state requires disinfection-wise, or (2) record WTP Model pH (output Table 3) and CT predictions (output Table 9) along with temperatures and make appropriate side calculations of CT ratio to assess a plant's likely ability to comply with state-specific regulations.

- Multiple Points of Chlorination: Because most of the WTP Model's disinfectant demand/decay and DBP formation algorithms are based upon regression analysis of observed data from full-scale, pilot-scale, or bench-scale studies in which only a single disinfectant dose was applied, the accuracy of the WTP Model's predictions is more limited in cases where multiple doses of the same disinfectant are applied throughout a process train. Therefore, the user is cautioned to

exercise care when interpreting model results in such situations. The only treatment scenario for which the WTP Model has an algorithm that directly addresses multiple points of chlorination is pre-chlorination (simultaneous chlorine and coagulant addition at a rapid mix) followed by a single point of downstream re-chlorination. This algorithm was developed to specifically address the typical situation of pre- and post-chlorination within a conventional surface water treatment plant. For this case, the user should be aware that this algorithm has not been independently verified. In situations where multiple chlorine doses are not separated by significant contact time or by chlorine-demand removal processes (such as rapid mix coagulation, GAC adsorption, or NF membrane separation), the user might consider combining the doses into a single dose application point. One common situation would be where chlorine is added immediately upstream and downstream of granular media filters.

- Distribution System Re-chlorination: The WTP Model does not directly accommodate distribution system re-chlorination. The situation is probably best modeled by representing the distribution system contact time upstream of the re-chlorination point with a "Reservoir" unit process (of equivalent residence time) within the in-plant portion of the WTP Model process train. A final "Chlorine" chemical feed point would follow this reservoir and would represent the distribution system re-chlorination point. So, the end of the process train would look like: "Reservoir" → "Chlorine" → "WTP Effluent" → "Additional Point," where "Additional Point" represents the sampling point separated from the re-chlorination point by the remaining residence time with the distribution system. The same cautions noted in the previous bullet point about modeling multiple application points of disinfectant apply to efforts to model distribution system re-chlorination.

- pH Predictions: The WTP Model predicts pH change due to acid/base addition based upon "closed-system" assumptions with respect to the atmosphere (i.e. no exchange of carbon dioxide between process water and the atmosphere). However, treatment plants with basins exposed to the atmosphere, especially mixing basins, or basins with large surface area and relatively shallow depth may exhibit CO_2 exchange. This leads to pH prediction inaccuracy; therefore, whenever possible, the user is advised when modeling existing treatment plants, to set doses for pH-adjusting chemicals to achieve observed pH values within the plant (instead of just using the actual observed acid/base dosages). This guidance does NOT apply to coagulants, which happen to affect pH. Coagulant doses need to be accurately represented in input values so that the WTP Model can properly predict TOC and UVA reductions during coagulation. To adjust the effect

of coagulants on pH, the user should add an acid or base chemical dose that does not exist in the actual plant in order to compensate for any shortcoming in the model's coagulation pH predictions.

- Lime-Softening Predictions: Probably the most inaccurate algorithms within the WTP Model are associated with the lime-softening process. Whether it is due to a lack of consideration of reaction kinetics, or other factors, the WTP Model's predictions of pH and alkalinity changes, and calcium and magnesium precipitation do not often track closely with site-specific observations. Furthermore, predictive algorithms for TOC and UVA removal are also significantly less accurate than those developed for removal by alum or iron coagulation. It is recommended that the WTP Model only be used as a rough screening-type tool for lime-softening process analysis.

- DBP Speciation Predictions: The user should be aware that predictions of DBP summation parameters, such as TTHMs, HAA6, and HAA9 are generally more accurate than those of the individual DBP species. This is the natural result of the summation parameters being a single, generally more stable value to predict, which is much more likely for empirical equations to do than to predict individually the four to nine individual values that comprise that single summation parameter. Therefore, the user is cautioned not to assume that the predictions of individual DBP species concentrations will be as accurate as those of summation parameters in cases where the model seems to be predicting summation parameters quite well. Finally, the lowest predictive accuracy, on a percentage basis, will be for those individual species whose concentrations typically are quite low (<5 ppb) with chlorination of raw and treated natural waters. Such species are bromoform, monobromoacetic acid, monochloroacetic acid, dibromoacetic acid.

5. DESCRIPTION OF MODEL EQUATIONS

Chapter 5 presents the equations and calculation methods used by the WTP Model to simulate water treatment processes.

The WTP Model's basic modeling approach is shown in **Figure 3-2**. The WTP Model predicts the effluent quality of each unit process in a process train, unit by unit. Effluent pH and alkalinity (and if lime-softening applies, magnesium and calcium concentrations) are calculated first. After these basic inorganic parameters are determined, the WTP Model calculates DBP precursor removal if applicable. Next, disinfectant residual demand/decay is calculated. The final step involves the calculation of DBP formation based on applied chemical doses, contact times, temperatures, and the predicted or inputted values of other water quality parameters.

The following process, inactivation, DBP formation and disinfectant decay algorithms, that were already part of the WTP Model, version 1.21, were modified and updated with recent data for version 2.2 to reflect improved understanding of these processes:

- Coagulation
- Softening
- Granular activation carbon (GAC) adsorption
- Membranes
- THM formation - TTHM and individual species
- HAA formation - HAA5, HAA6, and individual species
- Chlorine decay
- Chloramine decay

Several new process, inactivation, DBP formation and disinfectant decay algorithms were developed to extend the WTP Model to more complete coverage of existing treatment practice, as well as extend it to include alternative treatment practice that may be more fully utilized in the future. These include:

- Pre-chlorination - DBP formation
- Ozonation - oxidation of NOM, residual decay, bromate formation, and inactivation of *Giardia*, virus, and *Cryptosporidium*

- Chlorine dioxide - demand/residual decay, chlorite formation, and inactivation of *Giardia*, virus, and *Cryptosporidium*
- Biologically-active rapid-rate filtration with anthracite/sand or GAC media or biologically-active slow sand filtration - reduction of NOM
- *Cryptosporidium* physical removal
- HAA9 (and species) formation
- TOX formation
- DBP formation after specific precursor removal processes - coagulation, softening, GAC, membranes, ozonation.

This chapter summarizes the development of equations for simulating:
- Changes in alkalinity and pH
- Removal of inorganic water quality constituents
- Removal of organic water quality constituents by coagulation, softening, GAC, membranes and ozone/biofiltration
- Disinfectant decay (chlorine, chloramines, chlorine dioxide, ozone)
- Total and individual THM formation
- Total and individual HAA formation
- Total organic halogen (TOX) formation
- Bromate formation
- Chlorite formation
- Pathogen inactivation (CT ratio calculation)

5.1 EMPIRICAL MODEL DEVELOPMENT

The WTP Model primarily uses empirical correlations to predict central tendencies of NOM removal, disinfection, and DBP formation in a treatment plant. The algorithms were generally developed using multiple linear regression techniques. The relationship between various water quality parameters, such as THM species, and the variables that influence their formation, such as pH, temperature, chlorine dosage, TOC and bromide can often be described using a nonlinear function. An appropriate empirical relationship for such a function can be of the following form:

$$Y = A(X_1)^a (X_2)^b (X_3)^c \tag{5-1}$$

---

where A, a, b and c are empirical constants; X_1, X_2 and X_3 are independent variables and Y is the dependent variable. This relationship can be linearized by taking logarithms of both sides of the above equation. The resulting equation therefore becomes:

$$\ln(Y) = \ln(A) + a \ln(X_1) + b \ln(X_2) + c \ln(X_3) \qquad \textbf{(5-2)}$$

Multiple linear regression analysis can be performed to correlate ln(Y) with a linear combination of the transformed independent variables ($ln(X_1)$, $ln(X_2)$ and $ln(X_3)$). This analysis determines the intercept, $ln(A)$, and the slopes (a, b and c) for the independent variables. These constants can then be used in **Equation 5-1** to describe the relationship between Y and the independent variables, X_i.

As a first step of the modeling effort, dependent and independent variables are defined. The development of an appropriate regression equation consists of selecting the most significant variable forms and then performing a stepwise multiple linear regression analysis using the selected variable forms. The selection of the appropriate variable forms was generally done by developing a Pearson's Correlation matrix for all variable forms on the entire database. A Pearson's Correlation matrix shows the correlation coefficients among all the variables in the matrix. The importance of a particular variable in the regression equation is shown by the correlation coefficient, considering the variable as a single predictor. A high correlation between two independent variables indicates that if one is selected, the addition of the other will not improve the significance of the regression.

In a stepwise regression analysis, the most significant independent variable describing the dependent variable is taken into consideration first. Variables are added one at a time according to the highest remaining correlation coefficient after the previously selected variable is removed. Addition of independent variables increases the overall correlation coefficient, but as the degrees of freedom decrease (as a result of increasing the number of variables), the significance of the regression equation (portrayed by the F value) decreases. The stepwise regression was typically performed using commercially available statistics packages.

In selecting independent variable forms for describing the dependent variable, only one occurrence of each of the controlling variables is desired. The elimination of independent variables that are highly correlated with each other is important in avoiding multi-colinearity. This problem is minimized by using the correlation matrix. In some cases, however, the elimination of all such variables is not possible. In cases where two correlated variables are of prime importance in the

development of a WTP Model equation, they both have been included in the equation despite of the high correlation between them.

The equations shown in this chapter are accompanied by regression statistics. Whenever possible, the following regression parameters (Crow et al., 1960) are given for the equations:

- Multiple correlation coefficient (R^2), which measures the strength of the correlation by indicating the proportion of the variability in the dependent variable that is explained by all independent variables combined;

- Adjusted correlation coefficient (R^2_{adj}), which is the multiple correlation coefficient adjusted for the number of independent variables;

- Standard error of the estimate (*SEE*), which measures the amount of scatter in the vertical direction of the data (i.e., around the dependent variable) about the regression plane;

- F-statistic (*F*), which can be used to assess the goodness of fit using the F-test of the variance accounted for by regression;

- Number of data points (*n*) used in equation development.

Algorithm equations, together with data ranges for the input parameters, are given in this chapter. These data ranges represent the boundary conditions within which the equations were developed and should be used. However, the WTP Model does not restrict the use of the equations to within these boundary conditions. It is the user's responsibility to apply the model in an appropriate manner.

5.2   MODEL VERIFICATION

Model equations were individually tested and verified using independent data sets, i.e., data not used in the development of the predictive equations. For some equations (e.g. ozone decay, chlorine dioxide decay, DBP formation in re-chlorinated pre-chlorinated water), limited databases were available for model development and no additional data were available for verification.

Version 2.2 of the WTP Model was calibrated and validated using complete plant data from the ICR database (Swanson et al., 2002). For some parameters, a correction factor was developed as a result of the calibration. Correction factors were developed when the slope of a regression line (forced through the origin) on a plot of predicted versus observed values differed from unity by more than ±5 percent. As the model was applied to ICR plant data, the parameters were verified and corrected (if necessary) in the following order: pH, NOM removal, disinfectant residuals and

DBP formation (with free chlorine, then with chloramines). If, for example, the pH prediction was corrected, the NOM removal parameters were verified using the corrected pH parameter.

The correction factors were developed using data that excluded paired data associated with the highest 10 percent of absolute errors to minimize the effect of outlier data points. The correction factors are listed with the equations. If no correction factor is given, the model equations for that parameter did not require adjustment or could not be tested.

5.3   EQUATIONS FOR ALKALINITY AND pH ADJUSTMENT

The WTP Model, version 2.2, equations to predict pH changes due to chemical addition were not revised from the WTP Model, version 1.21, and are calculated based on raw water alkalinity, chemical doses, and carbonate chemistry. The model uses only equilibrium considerations and does not take into account the kinetics of processes such as calcium carbonate precipitation or carbon dioxide dissolution. Furthermore, from a carbon dioxide mass transfer standpoint, the model assumes that the water treatment plant can be represented as a closed system.

5.3.1   Carbonate System

The addition of alum in drinking water treatment consumes alkalinity and, consequently, depresses the pH. Alkalinity is defined by the following expression (Stumm and Morgan, 1981):

$$Alkalinity = [\ HCO_3^- \ ] + 2\ [\ CO_3^{2-} \ ] + [\ OH^- \ ] - [\ H^+ \ ] \qquad (5\text{-}3)$$

Where $[HCO_3^-]$ is the molar concentration of the bicarbonate ion, $[CO_3^{2-}]$ is the molar concentration of the carbonate ion, $[OH^-]$ is the molar concentration of the hydroxide ion and $[H^+]$ is the molar concentration of the hydrogen ion. The concentrations of the carbonate and bicarbonate ions are pH-dependent and may be defined as:

$$[\ HCO_3^- \ ] = \alpha_1 \, C_{T,CO_3} \qquad (5\text{-}4)$$

$$[\ CO_3^{2-} \ ] = \alpha_2 \, C_{T,CO_3} \qquad (5\text{-}5)$$

where,

$$C_{T,CO_3} = [\ H_2CO_3 \ ] + [\ HCO_3^- \ ] + [\ CO_3^{2-} \ ] \qquad (5\text{-}6)$$

$$\alpha_1 = \frac{K_1 [\, H^+ \,]}{[\, H^+ \,]^2 + K_1 [\, H^+ \,] + K_1 K_2} \tag{5-7}$$

$$\alpha_2 = \frac{K_1 K_2}{[\, H^+ \,]^2 + K_1 [\, H^+ \,] + K_1 K_2} \tag{5-8}$$

In the above equations, $[H_2CO_3]$ is the molar concentration of dissolved carbon dioxide (carbonic acid), while K_1 and K_2 are the acidity constants for carbonic acid and bicarbonate ion, respectively. At 25ºC and an ionic strength of zero, K_1 equals $10^{-6.3}$ mole/L while K_2 equals $10^{-10.3}$ mole/L.

The model assumes that K_1 and K_2 are temperature dependent as follows (Stumm and Morgan, 1981):

$$\ln \left(\frac{K_1}{K_1{}^\circ} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T^\circ} \right) \tag{5-9}$$

where ΔH° is the standard enthalpy change of the dissociation of carbonic acid to bicarbonate, T° is the standard temperature of 298ºK (25ºC) and $K_1{}^\circ$ is the value of the equilibrium constant at T°. Solving **Equation 5-9** for K_1 produces the following:

$$K_1 = \exp \left\{ \left[\frac{\Delta H^\circ}{R} \left(\frac{1}{T^\circ} \right) \right] - \ln K_1{}^\circ \right\} \tag{5-10}$$

Equations 5-9 and **5-10** assume that ΔH° is independent of temperature.

Using **Equation 5-10**, the following equations were developed for K_1 and K_2:

$$K_1 = \exp \left\{ \left[\left(\frac{7700 \, \frac{J}{mole}}{8.314 \, \frac{J}{^\circ K \bullet mole}} \right) \left(\frac{1}{298.15^\circ K} \right) \right] - 14.5 \right\} \tag{5-11}$$

$$K_2 = \exp \left\{ \left[\left(\frac{14900 \, \frac{J}{mole}}{8.314 \, \frac{J}{^\circ K \bullet mole}} \right) \left(\frac{1}{298.15^\circ K} \right) \right] - 23.7 \right\} \tag{5-12}$$

Equations 5-11 and **5-12** require the use of degrees Kelvin for the temperature, T. Degrees Kelvin can be calculated by adding 273.15 to the temperature determined as degrees Centigrade.

The concentration of hydroxide ion, $[OH^-]$, is calculated as follows:

$$[OH^-] = \frac{K_w}{[H^+]} \tag{5-13}$$

where K_w is the ion product of water and is 10^{-14} mole^2/L^2 at 25°C. Like K_1 and K_2, K_w is temperature-dependent. The model uses an empirical equation described in Stumm and Morgan (1981) to calculate K_w at temperatures other than 25°C (298.15°K) as follows:

$$\log_{10}(K_w) = \frac{-4470.99}{T} + 6.0875 - 0.01706\,T \tag{5-14}$$

where T is the temperature in degrees Kelvin.

Based on **Equations 5-3** through **5-8** and on **Equation 5-13**, **Equation 5-3** can be rewritten as follows:

$$Alkalinity = (\alpha_1 + 2\alpha_2)C_{T,CO_3} + [OH^-] - [H^+]$$

$$= \left(\frac{K_1[H^+] + K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}\right) C_{T,CO_3} + \frac{K_w}{[H^+]} - [H^+] \tag{5-15}$$

As shown by this equation, alkalinity is dependent on $[H^+]$, $C_{T,CO3}$ and several equilibrium constants. The equilibrium constants are dependent on temperature. Therefore, any change in alkalinity, $C_{T,CO3}$ or temperature will produce a change in $[H^+]$. Because pH is equal to $-\log_{10}[H^+]$, any change in alkalinity, $C_{T,CO3}$ or temperature will produce a change in pH.

Electroneutrality also requires that alkalinity be defined by the following expression:

$$Alkalinity = C_B - C_A \tag{5-16}$$

where C_B is the equivalent concentration of the strong base cations and C_A is the equivalent concentration of the strong acid anions.

Equation 5-16 can also be written as follows:

$$
\begin{aligned}
Alkalinity = C_{B'} &+ 2\,[\,Ca^{2+}\,] + [\,CaOH^+\,] \\
&+ 2\,[\,Mg^{2+}\,] + [\,MgOH^+\,] + [\,NH_4^+\,] \\
&- C_{A'} - [\,OCl^-\,]
\end{aligned}
\qquad \textbf{(5-17)}
$$

where,

$$
[\,CaOH^+\,] = \frac{[\,Ca^{2+}\,]\,K_{Ca^{2+}\_CaOH^+}}{[\,H^+\,]}
\qquad \textbf{(5-18)}
$$

$$
[\,MgOH^+\,] = \frac{[\,Mg^{2+}\,]\,K_{Mg^{2+}\_MgOH^+}}{[\,H^+\,]}
\qquad \textbf{(5-19)}
$$

$$
K_{Ca^{2+}\_CaOH^+} = \exp\left(\frac{-\Delta G^{\,\circ}}{RT}\right)
$$

$$
= \exp\left[\frac{-72320\,\dfrac{J}{mole}}{\left(8.314\,\dfrac{J}{mole\bullet\,^\circ K}\right)(T)}\right]
\qquad \textbf{(5-20)}
$$

and

$$
K_{Mg^{2+}\_MgOH^+} = \exp\left(\frac{-\Delta G^{\,\circ}}{RT}\right)
$$

$$
= \exp\left[\frac{-65180\,\dfrac{J}{mole}}{\left(8.314\,\dfrac{J}{mole\bullet\,^\circ K}\right)(T)}\right]
\qquad \textbf{(5-21)}
$$

Using **Equations 5-18** and **5-19**, **Equation 5-17** can be rewritten as follows:

$$Alkalinity = C_{B'} + [Ca^{2+}] \left(2 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} \right)$$

$$+ [Mg^{2+}] \left(2 + \frac{K_{Mg^{2+} - MgOH^+}}{[H^+]} \right) \tag{5-22}$$

$$+ [NH_4^+] - C_{A'} - [OCl^-]$$

The concentration of dissolved calcium is assumed to be the following:

$$C_{T,Ca} = [Ca^{2+}] + [CaOH^+] + [Ca(OH)_{2\ (aq)}] \tag{5-23}$$

where,

$$[Ca(OH)_{2\ (aq)}] = \frac{[Ca^{2+}]\ K_{Ca^{2+} - Ca(OH)_{2\ (aq)}}}{[H^+]^2} \tag{5-24}$$

and

$$K_{Ca^{2+} - Ca(OH)_{2\ (aq)}} = \exp\left(\frac{-\Delta G^{\circ}}{RT}\right)$$

$$\tag{5-25}$$

$$= \exp\left[\frac{-159800\ \dfrac{J}{mole}}{\left(8.314\ \dfrac{J}{mole \bullet {}^{\circ}K}\right)(T)}\right]$$

Combining **Equations 5-18**, **5-23** and **5-24**, the following relationship is obtained:

$$[Ca^{2+}] = \frac{C_{T,Ca}}{1 + \dfrac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \dfrac{K_{Ca^{2+} - Ca(OH)_{2\ (aq)}}}{[H^+]^2}} \tag{5-26}$$

The concentration of dissolved magnesium is assumed to be the following:

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^+] + [Mg(OH)_{2\ (aq)}] \tag{5-27}$$

where,

$$[Mg(OH)_{2\ (aq)}] = \frac{[Mg^{2+}]\ K_{Mg^{2+}\ \_\ Mg(OH)_{2\ (aq)}}}{[H^+]^2} \tag{5-28}$$

Combining **Equations 5-18**, **5-27** and **5-28**, the following relationship is obtained:

$$K_{Mg^{2+}\ \_\ Mg(OH)_{2\ (aq)}} = \exp\left(\frac{-\Delta G\ °}{RT}\right) \tag{5-29}$$

$$= \exp\left[\frac{-159760\ \dfrac{J}{mole}}{\left(8.314\ \dfrac{J}{mole\ \bullet\ °K}\right)(T)}\right]$$

$$[Mg^{2+}] = \frac{C_{T,Mg}}{1 + \dfrac{K_{Mg^{2+}\ \_\ MgOH^+}}{[H^+]} + \dfrac{K_{Mg^{2+}\ \_\ Mg(OH)_{2\ (aq)}}}{[H^+]^2}} \tag{5-30}$$

The concentration of dissolved free chlorine is assumed to be the following:

$$C_{T,OCl} = [HOCl] + [OCl^-] \tag{5-31}$$

where:

$$[HOCl] = \frac{[OCl^-][H^+]}{K_{HOCl\ \_\ OCl^-}} \tag{5-32}$$

and

$$K_{HOCl\ \_\ OCl^-} = \exp\left\{\left[\left(\frac{13800\ \dfrac{J}{mole}}{8.314\ \dfrac{J}{°K\ \bullet\ mole}}\right)\left(\frac{1}{298.15°K}\right)\right] - 17.5\right\} \tag{5-33}$$

Combining **Equations 5-31** and **5-32**, the following relationship is obtained:

$$[OCl^-] = \frac{C_{T,OCl}}{1 + \dfrac{[H^+]}{K_{HOCl\_OCl^-}}}$$

(5-34)

The concentration of dissolved ammonia is assumed to be the following:

$$C_{T,NH_3} = [NH_4^+] + [NH_3]$$

(5-35)

where,

$$[NH_3] = \frac{[NH_4^+] \, K_{NH_4^+\_NH_3}}{[H^+]}$$

(5-36)

and

$$K_{NH_4^+\_NH_3} = \exp\left\{\left[\left(\frac{52210\,\dfrac{J}{mole}}{8.314\,\dfrac{J}{°K \bullet mole}}\right)\left(\frac{1}{298.15°K}\right)\right] - 21.4\right\}$$

(5-37)

Combining **Equations 5-35** and **5-36**, the following relationship is obtained:

$$[NH_4^+] = \frac{C_{T,NH_3}}{1 + \dfrac{K_{NH_4^+\_NH_3}}{[H^+]}}$$

(5-38)

Combining **Equations 5-22**, **5-26**, **5-30**, **5-34** and **5-38**, the following expression may be written:

$$Alkalinity = C_{B'} - C_{A'}$$

$$+ \frac{C_{T,Ca}\left(2 + \dfrac{K_{Ca^{2+} - CaOH^+}}{[H^+]}\right)}{1 + \dfrac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \dfrac{K_{Ca^{2+} - Ca(OH)_{2(aq)}}}{[H^+]^2}}$$

$$+ \frac{C_{T,Mg}\left(2 + \dfrac{K_{Mg^{2+} - MgOH^+}}{[H^+]}\right)}{1 + \dfrac{K_{Mg^{2+} - MgOH^+}}{[H^+]} + \dfrac{K_{Mg^{2+} - Mg(OH)_{2(aq)}}}{[H^+]^2}}$$

$$+ \frac{C_{T,NH_3}}{1 + \dfrac{K_{NH_4^+ - NH_3}}{[H^+]}} - \frac{C_{T,OCl}}{1 + \dfrac{[H^+]}{K_{HOCl - OCl^-}}} \qquad\qquad \textbf{(5-39)}$$

The model calculates $[H^+]$ based on the equality of **Equations 5-15** and **5-39**. As shown by these equations, the model assumes that a change in $[H^+]$ occurs when a change occurs in C_A', C_B', $C_{T,Ca}$, $C_{T,Mg}$, $C_{T,NH3}$, $C_{T,OCl}$, $C_{T,CO3}$ or temperature. The calculation method is described below.

5.3.2   Calcium and Magnesium Removal by Softening

The WTP Model calculates calcium and magnesium removal by precipitative softening when the user includes a "Lime" chemical feed point in the process train *and* the "Lime" feed point is designated by an input parameter as intended for softening (as opposed to just pH adjustment).

Calcium Carbonate Solubility

The calcium ion and the carbonate ion are assumed to be in equilibrium with calcium carbonate when water quality conditions cause calcium carbonate to precipitate from solution.   Under these circumstances, the molar quantity of calcium ions leaving the aqueous phase is equivalent to the molar quantity of carbonate ions leaving the aqueous phase. Therefore, the model assumes the following:

$$C_{Ca,ppt} = C_{CO_3,ppt} \qquad\qquad \textbf{(5-40)}$$

where $C_{Ca,ppt}$ is the concentration of precipitated calcium in equilibrium with the aqueous phase and $C_{CO3,ppt}$ is the concentration of precipitated carbonate in equilibrium with the aqueous phase. These

concentrations are related to dissolved phase concentrations, and **Equation 5-40** can be rewritten as follows:

$$C_{Ca} - C_{T,Ca} = C_{CO_3} - C_{T,CO_3} \tag{5-41}$$

where C_{Ca} is the sum of the aqueous phase calcium concentration ($C_{T,Ca}$) and the concentration of precipitated calcium in equilibrium with the aqueous phase. C_{CO_3} is the sum of the aqueous phase carbonate concentration (C_{T,CO_3}) and the concentration of precipitated carbonate in equilibrium with the aqueous phase.

The solubility of calcium and carbonate ions in equilibrium with calcium carbonate is given by the following expression:

$$[Ca^{2+}][CO_3^{2-}] = K_{so,CaCO_3} \tag{5-42}$$

where,

$$K_{so,CaCO_3} = \exp\left\{\left[\left(\frac{-12530\frac{J}{mole}}{8.314\frac{J}{{}^\circ K \bullet mole}}\right)\left(\frac{1}{298.15{}^\circ K}\right)\right] - 19.1\right\} \tag{5-43}$$

Based on **Equations 5-5**, **5-7** and **5-22**, **Equation 5-32** can be rewritten as follows:

$$K_{so,CaCO_3} = \left(\frac{C_{T,Ca}}{1 + \frac{K_{Ca^{2+}-CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+}-Ca(OH)_{2(aq)}}}{[H^+]^2}}\right)\left(\frac{K_1 K_2 C_{T,CO_3}}{[H^+]^2 + K_1[H^+] + K_1 K_2}\right) \tag{5-44}$$

Solving **Equation 5-44** for $C_{T,Ca}$ yields the following:

$$C_{T,Ca} = \frac{K_{so,CaCO_3}\left(1 + \frac{K_{Ca^{2+}-CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+}-Ca(OH)_{2(aq)}}}{[H^+]^2}\right)}{C_{T,CO_3}\left(\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}\right)} \tag{5-45}$$

Solving **Equation 5-41** for C_{T,CO_3} and substituting **Equation 5-45** for $C_{T,Ca}$ yields the following:

$$C_{T,CO_3} = C_{CO_3} - C_{Ca}$$

(5-46)

$$+ \frac{K_{so,CaCO_3} \left(1 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2} \right)}{C_{T,CO_3} \left(\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \right)}$$

Multiplying each term in **Equation 5-46** by C_{T,CO_3} yields:

$$0 = C_{T,CO_3}^2 - C_{T,CO_3}(C_{CO_3} - C_{Ca})$$

(5-47)

$$- K_{so,CaCO_3} \left(\frac{1 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2}}{\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}} \right)$$

Using the quadratic formula to solve for C_{T,CO_3} yields:

$$C_{T,CO_3} = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$
(5-48)

where,

$$a = 1 \qquad \textbf{(5-49)}$$

$$b = C_{Ca} - C_{CO_3} \qquad \textbf{(5-50)}$$

and

$$c = - K_{so,CaCO_3} \left(\frac{1 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2}}{\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}} \right) \qquad \textbf{(5-51)}$$

The model calculates C_{T,CO_3} from **Equations 5-48** through **5-52** when

---

$$K_{so,CaCO_3} < \left(\cfrac{C_{T,Ca}}{1 + \cfrac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \cfrac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2}} \right) \left(\cfrac{K_1 K_2 C_{T,CO_3}}{[H^+]^2 + K_1[H^+] + K_1 K_2} \right) \qquad \textbf{(5-52)}$$

After calculating $C_{T,CO3}$, the model calculates $C_{T,Ca}$ from **Equation 5-41**. The calculated values of $C_{T,CO3}$ and $C_{T,Ca}$ are substituted into the alkalinity expressions in **Equations 5-15** and **5-39**.

The model uses **Equation 5-41** and **Equations 5-48** through **5-51** only when the aqueous phase is considered to be in equilibrium with calcium carbonate precipitate. If the precipitate is removed by a treatment process and pH conditions are changed such that the aqueous phase is undersaturated with respect to calcium carbonate precipitate, the model assumes that the aqueous phase is no longer in equilibrium with calcium carbonate precipitate.

Magnesium Hydroxide Solubility

The magnesium ion and the hydroxide ion are assumed to be in equilibrium with magnesium hydroxide when water quality conditions cause magnesium hydroxide to precipitate from solution. The solubility of magnesium and hydroxide ions in equilibrium with magnesium hydroxide is given by the following expression:

$$\frac{[Mg^{2+}]}{[H^+]^2} = K_{so,Mg(OH)_2} \qquad \textbf{(5-53)}$$

where,

$$K_{so,Mg(OH)_2} = \exp \left\{ \left[\left(\frac{-113960 \frac{J}{mole}}{8.314 \frac{J}{°K \bullet mole}} \right) \left(\frac{1}{298.15°K} \right) \right] + 38.8 \right\} \qquad \textbf{(5-54)}$$

Based on **Equation 5-30**, **Equation 5-53** can be rewritten as follows:

$$K_{so,Mg(OH)_2} = \frac{C_{T,Mg}}{[H^+]^2 + [H^+] K_{Mg^{2+} - MgOH^+} + K_{Mg^{2+} - Mg(OH)_{2\,(aq)}}} \qquad \textbf{(5-55)}$$

Solving **Equation 5-55** for $C_{T,Mg}$ yields the following:

$$C_{T,Mg} = K_{so,Mg(OH)_2} \left([H^+]^2 + [H^+] K_{Mg^{2+}\_MgOH^+} + K_{Mg^{2+}\_Mg(OH)_{2\,(aq)}} \right) \quad \textbf{(5-56)}$$

The model calculates $C_{T,Mg}$ from **Equation 5-56** when

$$K_{so,Mg(OH)_2} < \frac{C_{T,Mg}}{[H^+]^2 + [H^+] K_{Mg^{2+}\_MgOH^+} + K_{Mg^{2+}\_Mg(OH)_{2\,(aq)}}} \quad \textbf{(5-57)}$$

The model uses **Equation 5-56** only when the aqueous phase is considered to be in equilibrium with magnesium hydroxide precipitate. If the precipitate is removed by a treatment process and pH conditions are changed such that the aqueous phase is undersaturated with respect to magnesium hydroxide precipitate, the model assumes that the aqueous phase is no longer in equilibrium with magnesium hydroxide precipitate.

5.4   pH CHANGES DUE TO CHEMICAL ADDITION

An iterative procedure is used to calculate the change in pH associated with chemical addition. This iterative procedure uses a bisection method to search for the concentration of hydrogen ions, $[H^+]$, that allows the alkalinity calculated by **Equation 5-15** to be equivalent to the alkalinity calculated by **Equation 5-39**. The flowchart shown in **Figure 5-1** provides a detailed description of this procedure.

5.4.1   Open System Versus Closed System

The calculation of pH changes in the model is based only on equilibrium considerations. This is an important limitation of the model because the kinetics of some processes, such as calcium carbonate precipitation and carbon dioxide dissolution, may prohibit the observed pH from reaching an equilibrium value.

A more realistic model would account for the kinetics of carbon dioxide transfer between the air and water by using an appropriate mass transfer model with the appropriate mass transfer coefficients. Because such a detailed mass transfer model would require many (often unknown or difficult-to-determine) site-specific input parameters, two equilibrium models were considered for the WTP Model instead. One equilibrium model, referred to as the "open system model," assumes that the concentration of carbon dioxide dissolved in the water in treatment plant basins is in equilibrium with the concentration of carbon dioxide in the atmosphere above the water. The other
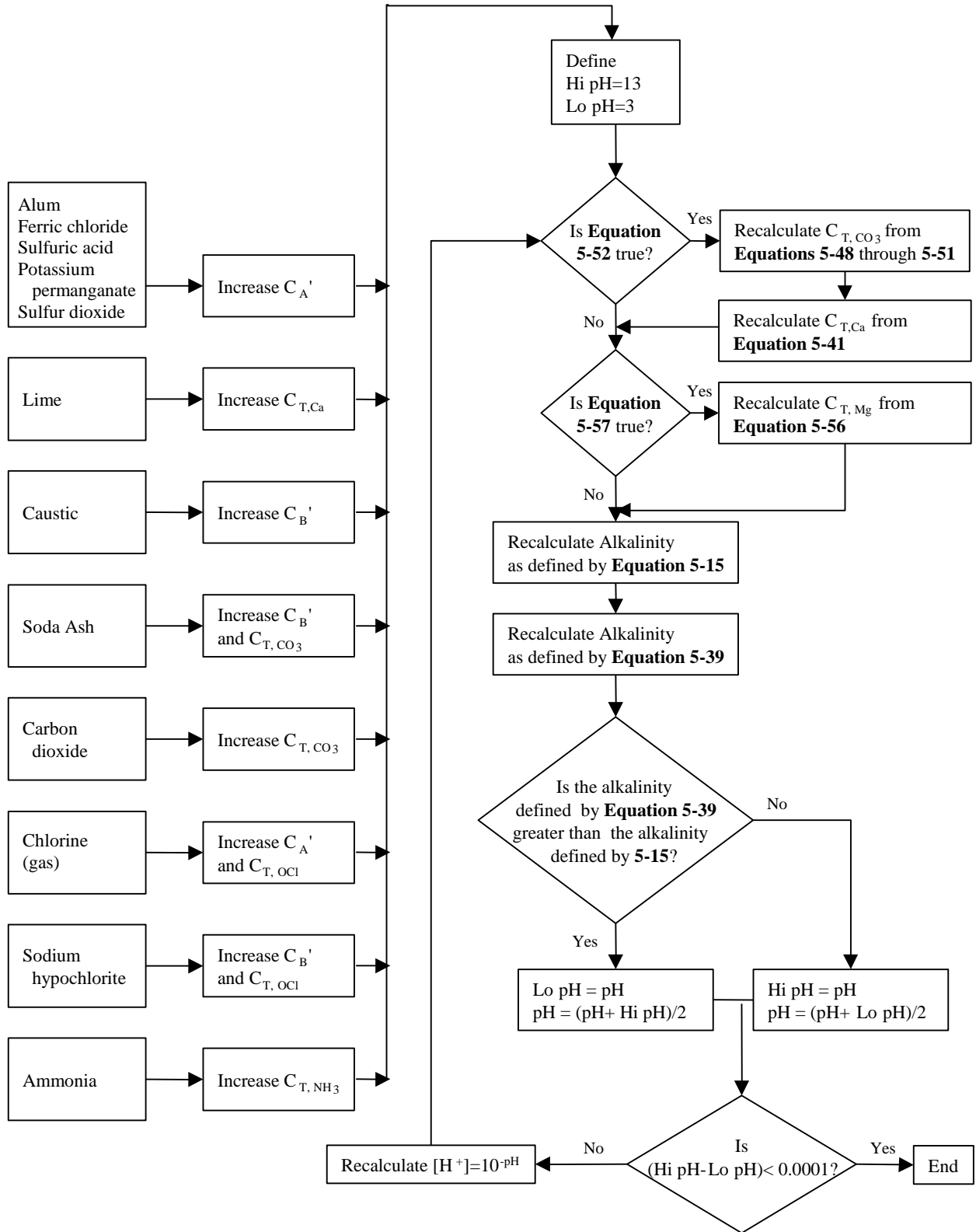
Define
Hi pH=13
Lo pH=3

Alum
Ferric chloride
Sulfuric acid
Potassium
  permanganate
Sulfur dioxide
→ Increase C_A'

Lime → Increase $C_{T,Ca}$

Caustic → Increase C_B'

Soda Ash → Increase C_B' and C_{T,CO_3}

Carbon dioxide → Increase C_{T,CO_3}

Chlorine (gas) → Increase C_A' and $C_{T,OCl}$

Sodium hypochlorite → Increase C_B' and $C_{T,OCl}$

Ammonia → Increase C_{T,NH_3}

Is **Equation 5-52** true? — Yes → Recalculate C_{T,CO_3} from **Equations 5-48** through **5-51**

Recalculate $C_{T,Ca}$ from **Equation 5-41**

No

Is **Equation 5-57** true? — Yes → Recalculate $C_{T,Mg}$ from **Equation 5-56**

No

Recalculate Alkalinity as defined by **Equation 5-15**

Recalculate Alkalinity as defined by **Equation 5-39**

Is the alkalinity defined by **Equation 5-39** greater than the alkalinity defined by **5-15**?

No → Hi pH = pH
pH = (pH+ Lo pH)/2

Yes → Lo pH = pH
pH = (pH+ Hi pH)/2

Is (Hi pH-Lo pH)< 0.0001? — Yes → End

No → Recalculate $[H^+]=10^{-pH}$

Figure 5-1 Algorithm for Calculating pH Changes Due to Chemical Addition

equilibrium model, referred to as the "closed system model," assumes no exchange of carbon dioxide between the water and the atmosphere. The WTP Model was developed assuming that the closed system model more closely approximates actual conditions in a water treatment plant and distribution system than the open system model. This assumption was not verified during model development.

5.4.2   Alum Coagulation

When alum is added to water, it dissociates according to the following equation:

$$Al_2(SO_4)_3 \bullet 14\ H_2O \rightarrow 2\ Al^{3+} + 3\ SO_4^{2-} + 14\ H_2O \qquad \textbf{(5-58)}$$
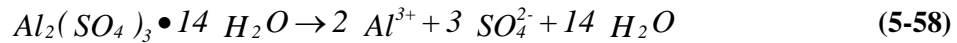
The WTP Model equations for alum addition assume that all of the sulfate ions remain dissociated and all of the aluminum ions form insoluble aluminum hydroxide, $Al(OH)_3(s)$. Therefore, when one mole of alum is added to one liter of water, the quantity $(C_B' - C_A')$ decreases by six equivalents per liter and the alkalinity correspondingly decreases by six equivalents per liter (see **Equation 5-39**). The assumption that all aluminum ions form insoluble aluminum hydroxide becomes less valid at pH levels farther from the pH of minimum solubility (pH = 5.9 at 25ºC). The iterative procedure described in **Figure 5-1** is used for pH calculation upon addition of alum.

5.4.3   Ferric Coagulation

When ferric chloride is added to water, it dissociates according to the following equation:

$$FeCl_3 \bullet 6\ H_2O \rightarrow Fe^{3+} + 3\ Cl^- + 6\ H_2O \qquad \textbf{(5-59)}$$

For the purposes of this model, all of the chloride ions are assumed to remain dissociated and all of the ferric ions are assumed to form insoluble ferric hydroxide, $Fe(OH)_3$. Therefore, when one mole of ferric chloride is added to one liter of water, the quantity $(C_B' - C_A')$ decreases by three equivalents per liter and the alkalinity correspondingly decreases by three equivalents per liter (see **Equation 5-39**). The assumption that all ferric ions form insoluble ferric hydroxide becomes less valid at pH levels farther from the pH of minimum solubility (pH = 9.0 at 25ºC). The iterative procedure described in **Figure 5-1** is used for pH calculation upon addition of ferric chloride. Also, the model does not account for any excess acidity that might accompany commercial ferric chloride.

5.4.4 Precipitative Softening

When added to water, lime dissociates according to the following expression:

$$Ca(OH)_{2\ (s)} \rightarrow Ca^{2+} + 2\ OH^{-} \tag{5-60}$$

Therefore, when one mole of lime is added to one liter of water, $C_{T,Ca}$ increases by one mole per liter (see **Equations 5-52** and **5-39**). If the condition described by **Equation 5-52** is met (this is the objective in precipitative softening), $C_{T,CO3}$ is recalculated with **Equations 5-48** through **5-51** and $C_{T,Ca}$ is recalculated with **Equation 5-41**. If the condition described by **Equation 5-52** is not met, however, $C_{T,CO3}$ does not change and $C_{T,Ca}$ increases by one mole per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH upon lime addition.

Softening pH Correction

WTP Model calibration with ICR softening plant data showed a slight overprediction of lower pH values in softened water and a slight underprediction of higher pH values in softened water. Therefore, the following correction was made to WTP Model predictions of pH in softening plants:

$$pH_{corr} = \frac{pH_{pred} - 1.86}{0.71} \tag{5-61}$$

5.4.5 Chlorine (Gas) Addition

When chlorine gas is added to water, it reacts according to the following equation:

$$Cl_{2\ (g)} + H_2O \rightarrow HOCl + H^{+} + Cl^{-} \tag{5-62}$$

For the purposes of this model, all of the chloride ions are assumed to remain dissociated. Therefore, when one mole of chlorine gas is added to one liter of water, $C_{T,OCl}$ increases by one mole per liter and the quantity $(C_B{}' - C_A{}')$ decreases by one equivalent per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.6 Sodium Hypochlorite Addition

When sodium hypochlorite is added to water, it reacts according to the following equation:

$$NaOCl \rightarrow Na^+ + OCl^-$$ (5-63)

For the purposes of this model, all of the sodium ions are assumed to remain dissociated. Therefore, when one mole of sodium hypochlorite is added to one liter of water, $C_{T,OCl}$ increases by one mole per liter and the quantity $(C_B' - C_A')$ increases by one equivalent per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.7   Potassium Permanganate Addition

When potassium permanganate is added to water, it dissociates according to the following equation:

$$KMnO_4 \rightarrow K^+ + MnO_4^-$$ (5-64)
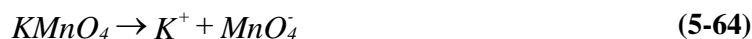
For the purposes of this model, all of the potassium ions are assumed to remain dissociated and all of the permanganate ions are assumed to react and form insoluble manganese dioxide as shown by the following equation:

$$MnO_4^- + 4\ H^+ + 3\ e^- \rightarrow MnO_2 + 2\ H_2O$$ (5-65)
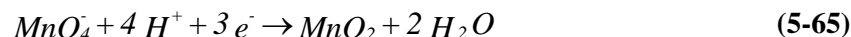
The assumption that all permanganate ions form insoluble manganese dioxide becomes less valid at pH levels farther from the pH of minimum solubility.

When one mole of potassium permanganate is added to one liter of water, the net effect of **Equations 5-64** and **5-65** is to increase the quantity $(C_B' - C_A')$ by four equivalents per liter. This net effect is only true if the oxidized product remains in solution. For instance, if the permanganate ion oxidizes ferrous ions to ferric ions, the ferric ions can precipitate as ferric hydroxide. The net effect of this precipitation in concert with **Equations 5-64** and **5-65** is to increase the quantity $(C_B' - C_A')$ by only one equivalent per liter rather than four equivalents per liter. The model presently assumes that the quantity $(C_B' - C_A')$ increases by one equivalent per liter when one mole of potassium permanganate is added to one liter of water. Under most water treatment conditions, potassium permanganate is added in quantities that do not change alkalinity to the degree that are affected by coagulants. Therefore, this assumption is not expected to be critical in most cases.

5.4.8　Sulfuric Acid Addition

Sulfuric acid is typically used to decrease pH and alkalinity in drinking water treatment. When added to water, sulfuric acid dissociates according to the following equation:

$$H_2SO_4 \rightarrow 2\ H^+ + SO_4^{2-} \tag{5-66}$$

Sulfate ions are assumed to remain completely dissociated (this assumption is valid for pH greater than 2 and when the solubility limit of calcium sulfate is not exceeded). Thus, when one mole of sulfuric acid is added to one liter of water, the quantity $(C_B' - C_A')$ is decreased by two equivalents per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.9　Sodium Hydroxide (Caustic) Addition

Sodium hydroxide is used to increase pH and alkalinity in drinking water treatment. When added to water, sodium hydroxide dissociates according to the following equation:

$$NaOH \rightarrow Na^+ + OH^- \tag{5-67}$$

Sodium ions are assumed to remain completely dissociated. Thus, when one mole of sodium hydroxide is added to one liter of water, the quantity $(C_B' - C_A')$ is increased by one equivalent per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.10　Calcium Hydroxide (Lime) Addition

Lime is also added to increase alkalinity and pH levels in drinking water treatment. When added to water, lime dissociates according to the following expression:

$$Ca(OH)_{2\ (s)} \rightarrow Ca^{2+} + 2\ OH^- \tag{5-68}$$

Therefore, when one mole of lime is added to one liter of water, $C_{T,Ca}$ increases by one mole per liter (see **Equations 5-52** and **5-39**). If the condition described by **Equation 5-62** is met (this is not the objective when using lime for pH adjustment), $C_{T,CO3}$ is recalculated with **Equations 5-48** through **5-51** and $C_{T,Ca}$ is recalculated with **Equation 5-41**. If the condition described by **Equation 5-52** is not

met, however, $C_{T,CO3}$ does not change and $C_{T,Ca}$ increases by one mole per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.11   Sodium Carbonate (Soda Ash) Addition

Soda ash is another chemical added to increase alkalinity and pH levels in drinking water treatment. When added to water, soda ash dissociates according to the following expression:

$$Na_2CO_3 \rightarrow 2\,Na^+ + CO_3^{2-} \tag{5-69}$$

Therefore, when one mole of soda ash is added to one liter of water, the quantity $(C_B' - C_A')$ is increased by two equivalents per liter and $C_{T,CO3}$ is increased by one mole per liter (see **Equations 5-52** and **5-39**). If the condition described by **Equation 5-52** is met, $C_{T,CO3}$ is recalculated with **Equations 5-48** through **5-51** and $C_{T,Ca}$ is recalculated with **Equation 5-41**. The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.12   Carbon Dioxide Addition

Carbon dioxide is added to lower pH levels and increase the carbonate concentration in some precipitative softening systems. When one mole of carbon dioxide is added to one liter of water, $C_{T,CO3}$ is increased by one mole per liter (see **Equation 5-15**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.13   Ammonia Addition

When ammonia is added to water, an equilibrium state must be established between the ammonia molecule and the ammonium ion. The following expression describes the chemical reaction involved:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{5-70}$$

Therefore, when one mole of ammonium hydroxide is added to one liter of water, $C_{T,NH3}$ increases by one mole per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.14   Ammonium Sulfate Addition

When ammonia is added to water, an equilibrium state must be established between the ammonia molecule and the ammonium ion. The following expression describes the chemical reaction involved:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$ **(5-71)**

Therefore, when one mole of ammonium sulfate is added to one liter of water, $C_{T,NH3}$ increases by one mole per liter (see **Equation 5-39**). The iterative procedure described in **Figure 5-1** is used to obtain a new value for pH.

5.4.15 Nanofiltration

Salt-removing membrane processes, such as nanofiltration, can alter the alkalinity of a given water through the rejection of specific ions. The WTP Model uses empirical algorithms developed through the analysis of results from 16 published studies to predict removal of calcium, magnesium, and alkalinity through a nanofiltration process based on the user-entered values of molecular weight cutoff and recovery of the membrane system as well as feed water concentrations of calcium, magnesium, and alkalinity. The WTP Model assumes that pH is unchanged through the nanofilter. The WTP Model then calculates predicted values for total carbonate, $C_{T,CO3}$, and ($C_B' - C_A'$) in the permeate water. The 16-study database consisted of a range of water sources, membrane types, and operating conditions.

The WTP Model equation for removal of hardness by nanofiltration is represented by **Equation 5-72**. The WTP Model assumes that the percent removals of $C_{T,Ca}$ and $C_{T,Mg}$ are equivalent to the percent removal of total hardness as calculated by **Equation 5-73**.

$$\ln\left[\left(\frac{TH_0}{TH_f}\right) - 1\right] = 36.801 - 3.327[\ln(TH_0)] - 6.787[\ln(MWC)] - 0.027(R)[\ln(TH_0)]$$
$$+ 0.229[\ln(R)][\ln(TH_0)][\ln(MWC)]$$ **(5-72)**

$$(R^2 = 0.87,\ R^2_{adj} = 0.86,\ SEE = 0.84,\ F = 58,\ n = 39)$$

where,

TH_0 = feed water total hardness (mg CaCO$_3$/L): $61 \leq TH_0 \leq 340$

TH_f = product water total hardness (mg CaCO$_3$/L): $14 \leq TH_f \leq 340$

R = recovery (%): $10 \leq R \leq 90$

MWC = molecular weight cut-off of the membrane (Da): $100 \leq MWC \leq 40,000$

where *recovery* is the ratio between the product water flow rate and the feed water flow rate in percent.

The rejection of alkalinity by membranes is calculated by the following equation:

$$\ln\left[\left(\frac{ALK_0}{ALK_f}\right) - 1\right] = 14.602 - [\ln(MWC)]\{1.667 - 0.054[\ln(Alk_0)] - 0.203[\ln(R)]\} \qquad \textbf{(5-73)}$$

$$(R^2 = 0.86, R^2_{adj} = 0.84, SEE = 0.83, F = 65, n = 36)$$

where,

Alk_0 = feed water alkalinity (mg $CaCO_3$/L): $23 \leq Alk_0 \leq 310$

Alk_f = product water alkalinity (mg $CaCO_3$/L): $0 \leq Alk_f \leq 100$

R = recovery (%): $10 \leq R \leq 90$

MWC = molecular weight cut-off (Da): $50 \leq MWC \leq 40,000$

After the WTP Model uses **Equations 5-72** and **5-73** to calculate nanofilter permeate concentrations of calcium, magnesium, and alkalinity, it performs a mass balance using the user-entered input values of the fraction of the total process stream treated by nanofiltration and the nanofilter recovery to calculate calcium, magnesium, and alkalinity concentrations in the blended permeate and nanofilter bypass stream. These predicted parameter values are then used in combination with **Equations 5-15** and **5-17** to calculate predicted values in the blended stream for $C_{T,CO3}$ and $(C_B' - C_A')$. pH is assumed to remain constant across the nanofilter.

5.5   EQUATIONS FOR NOM REMOVAL AND/OR OXIDATION

5.5.1   Alum Coagulation

The 1992 WTP Model used equations for NOM removal by alum coagulation based on full-scale process data collected in three studies (Montgomery and Metropolitan, 1989; Singer, 1988; and Edzwald, 1984). The complete field-scale database included only 45 data points obtained from the 17 treatment plants, but covered a wide range of raw water qualities and treatment conditions. The final equation used the variables of raw water TOC, alum dose, and coagulation pH to describe the TOC removal behavior for the 17 treatment plants. A database developed by USEPA's Technical Support Division (Fair, 1990; Harrington, et al., 1991)) was used to develop a relationship for UVA removal based on raw water UVA, alum dose and coagulation pH also. This database contained 30 data points only. The original TOC removal equation performed reasonably well, but the UVA removal equation exhibited a much poorer fit. This was most likely due to oxidation processes

conducted during the coagulation, flocculation, clarification and filtration processes whose effect on UVA was not accounted for. Furthermore, both the TOC and UVA databases contained very few data points.

The WTP Model, version 2.2.1, incorporates the product of significant research that has been performed in the area of TOC and UVA removal by coagulation.

TOC Removal

Version 2.2.1 of the WTP Model uses a semi-empirical sorption model developed by Edwards (1997) to predict TOC removal by coagulation. The model proposed by Edwards (1997) is based on dissolved organic carbon (DOC) which typically approximates TOC within 5-10 percent in source waters. The DOC model does not consider particulate organic matter (POC), which, together with DOC, comprise TOC. However, Edwards showed that using this DOC-based model for TOC had good predictive ability on independent TOC jar-test results and acceptable predictive ability for full-scale and pilot-scale test data. The author notes, however, that because POC removal is nearly 100 percent during coagulation, that the DOC model typically underpredicts TOC removal. In this way, the TOC removal estimates tend to be conservative. To refine TOC removal estimates, Tseng and Edwards (1999) developed methods for calibrating the TOC model for full-scale use; however, due to data limitations this approach could not be implemented in the WTP Model.

The Edwards model was developed using a subset of the AWWA National Enhanced Coagulation and Softening Database (NECSD) (Tseng et al., 1996). The database contained 608 data points from 39 water sources. Data were not included if coagulation pH was below 5 or above 8, if parameters required as model inputs were missing, or if the coagulated DOC was higher than the raw water DOC plus 0.2 mg/L.

The model divides TOC into fractions that are sorbable (TOC_{sorb}) and non-sorbable ($TOC_{nonsorb}$) with respect to the coagulant. The amount of TOC remaining in solution following coagulation is equal to the fraction of sorbable TOC ($TOC_{sorb,eq}$) that is dissolved and in equilibrium with the fraction of sorbable TOC that is actually sorbed to the coagulant, plus the non-sorbable fraction ($TOC_{nonsorb}$), which cannot be removed by coagulation. This relationship is indicated in **Equation 5-74**. **Equations 5-75** and **5-76** further define the estimation of ($TOC_{nonsorb}$).

Equation 5-77 presents the relationship between $TOC_{sorb,eq}$ and input parameters and model constants. The relationship between $TOC_{sorb,eq}$ and input parameters is based on the Langmuir equilibrium adsorption isotherm model. The model uses similar input parameters as were used previously (raw water TOC, coagulant dose, and coagulation pH), but also uses calculated model coefficients and the raw water SUVA. The raw water SUVA is a more refined indicator of NOM characteristics and indicates the humic content in the water. Coagulation typically preferentially removes humic NOM. Thus, a water with a low humic content, indicated by a low SUVA, is expected to have a large nonsorbable fraction, whereas a water with a higher humic content and a higher SUVA will have a lower nonsorbable fraction (White et al., 1997). Additional information and detail about the equations can be found in Edwards (1997).

$$TOC_{coagulatedwater} = TOC_{sorb,eq} + TOC_{nonsorb} \tag{5-74}$$

where,

$$TOC_{nonsorb} = TOC_{raw} * F_{nonsorb} \tag{5-75}$$

and

$$F_{nonsorb} = K_1 * SUVA_{raw} + K_2 \tag{5-76}$$

(K_1 and K_2 have coagulant-specific values; for alum, $K_1 = -0.075$ and $K_2 = 0.56$)

$$(TOC_{removed}) / Dose_{coag} = \frac{a * b * TOC_{sorb,eq}}{1 + b * TOC_{sorb,eq}} \tag{5-77}$$

where,

$$a = x_1 * pH + x_2 * pH^2 + x_3 * pH^3 \tag{5-78}$$

(the x parameters are fitting constants with values of x_1=284, x_2=-74.2, and x_3=4.91)

and

$$b = 0.147$$

($R^2_{adj} = 0.98$, SEE = 0.40 mg/L, n = 608)

where,

$TOC_{coagulatedwater}$ = coagulated water TOC (mg/L): $1.0 \leq TOC_{coagulatedwater} \leq 26$

TOC_{raw} = raw water TOC (mg/L): $1.8 \leq TOC_{raw} \leq 26.5$

$TOC_{removed}$ = [raw water TOC - coagulated water TOC] (mg/L)

$SUVA_{raw}$ = raw water SUVA (L/mg·m): $1.32 \leq SUVA_{raw} \leq 6.11$

$Dose_{coag}$ = coagulant dose (mmol Al/L): $0 \leq Dose_{coag} \leq 1.51$

pH = coagulation pH: $5.5 \leq pH \leq 8.0$

Coagulated Water TOC Verification

WTP Model predictions of coagulated water TOC were compared to observed values from the ICR database. The central tendency of the model's coagulated water predictions did not warrant any adjustment. This finding applies to both alum and ferric TOC removal algorithms.

UVA Removal

In the 1992 version of the WTP model, the predictive capability of UVA removal equations were limited by the small data sets from which they were derived. The new equations predicting UVA removal by coagulation are based on data analysis performed on the American Water Works Association (AWWA) Water Industry Technical Action Fund (WITAF) database (Tseng et al., 1996). This represents an extended data set for equation development.

$$UVA_{removed} = 5.716(UVA_{raw})^{1.0894}(Dose_{coag})^{0.306}(pH_{coag})^{-0.9513} \qquad \textbf{(5-79)}$$

$(R^2 = 0.90, R^2_{adj} = 0.90, SEE = 0.040 \ 1/cm, F = 3372, n = 1127)$

where,

$UVA_{removed}$ = UVA removed by coagulation (1/cm): $0.000 \leq UVA_{removed} \leq 0.691$

UVA_{raw} = raw water UVA(1/cm): $0.015 \leq UVA_{raw} \leq 0.751$

$Dose_{coag}$ = applied coagulant dose, alum or ferric, (meq/L): $0.008 \leq Dose_{coag} \leq 0.151$

pH_{coag} = pH of coagulation: $3.0 \leq pH_{coag} \leq 8.3$

5.5.2 Ferric Coagulation

Unlike the equations for alum coagulation (based solely on full-scale observations) the equations for ferric coagulation in the 1992 version of the WTP Model were based on bench and pilot studies. An empirical equation for NOM removal by ferric salt coagulation was based on data collected from several bench and pilot scale studies conducted by Malcolm Pirnie, Inc. (1989; 1990) and from one study conducted by John Carollo Engineers (1989). The equations to simulate NOM

removal for the general case were not as good as the alum coagulation equations because fewer waters were included in the analysis and because the results may have been skewed by the large number of observations from two sources.

TOC Removal

Version 2.2 of the WTP Model uses the same semi-empirical sorption model developed by Edwards (1997) to predict TOC removal by iron coagulation as for alum coagulation. The model was developed from 250 data points resulting from 21 source waters from the AWWA NECSD database (Tseng et al., 1996). Data were not included if ferric coagulation pH was below 4, if parameters required as model inputs were missing, and if the coagulated DOC was higher than the raw water DOC plus 0.2 mg/L.

The model to describe ferric coagulation uses the same equations as given by **Equations 5-74** through **5-78**. The model ferric coagulation parameters, regression statistics, and data ranges are given below:

$$K_1 = -0.028$$
$$K_2 = 0.23$$
$$x_1 = 280$$
$$x_2 = -73.9$$
$$x_3 = 4.96$$

$$(R^2_{adj} = 0.99, SEE = 0.47 \text{ mg/L}, n = 250)$$

$TOC_{coagulatedwater}$ = coagulated water TOC (mg/L): $0.9 \leq TOC_{removed} \leq 26$

TOC_{raw} = raw water TOC (mg/L): $2.3 \leq TOC_{raw} \leq 26.5$

$SUVA_{raw}$ = raw water SUVA (L/mg·m): $1.26 \leq SUVA_{raw} \leq 6.11$

$Dose_{coag}$ = coagulant dose (mmol Fe/L): $0 \leq Dose_{coag} \leq 1.22$

pH = coagulation pH: $3.0 \leq pH \leq 8.0$

UVA Removal

In the 1992 version of the WTP Model, the equation used for UVA removal by ferric coagulation was based on data from the same data set as was used for TOC removal.

For the WTP Model, Version 2.2, **Equation 5-79** is also used to calculate UVA removal for ferric coagulation. During equation development, it was determined that one equation could accurately describe UVA removal for both coagulants if the coagulant doses were expressed as milliequivalents of metal per liter.

5.5.3 Precipitative Softening

For WTP Model, Version 1.21, process and water quality data were collected for only twelve precipitative softening plants. Nine field-scale observations were available for these plants, which were used to develop empirical correlations. The TOC and UVA removal equation only used raw TOC and UVA and the changes in calcium and magnesium due to the addition of lime. The equations did not consider lime dose or softening pH. Due to the limited data available for the development of the above equations, an extensive survey of field scale precipitative softening plants was recommended at the time.

TOC Removal

Version 2.2 of the WTP Model contains new softening equations. **Equation 5-80** for TOC removal by softening was developed based on raw water TOC, softening pH, and lime and coagulant doses from the AWWA/WITAF database (Tseng et al., 1996). The equation predicts TOC removal for precipitative softening plants with or without coagulant addition. For plants that do not use a coagulant together with lime, the coagulant dose input parameter is zero and the overall coagulant term in the equation goes to unity.

$$TOC_{removed} = 4.657 \times 10^{-4} \left(TOC_{raw}\right)^{1.3843} \left(pH_{sft}\right)^{2.2387} \left(Dose_{lime}\right)^{0.1707} \left(1 + Dose_{coag}\right)^{2.4402} \quad \textbf{(5-80)}$$

$$(R^2 = 0.96,\ R^2_{adj} = 0.96,\ SEE = 0.352\ mg/L,\ F = 486,\ n = 92)$$

where,

$TOC_{removed}$ = TOC removed by softening (mg/L): $0.1 \leq TOC_{removed} \leq 6.8$

TOC_{raw} = raw water TOC (mg/L): $0.9 \leq TOC_{raw} \leq 14.1$

pH_{sft} = pH of softening: $8.9 \leq pH_{sft} \leq 12.5$

$Dose_{lime}$ = applied lime dose (mg/L): $33 \leq Dose_{lime} \leq 410$

$Dose_{coag}$ = applied coagulant dose (meq/L): $0 \leq Dose_{coag} \leq 0.138$

Softened Water TOC Correction

The predictions of softened water TOC were compared to corresponding observations in the ICR database. The softened water TOC predictions were generated using corrected pH values for softened water as described in **Equation 5-61**. The WTP Model algorithms tended to slightly underpredict softened water TOC values. Thus, the following correction factor was developed for softened water TOC:

$$TOC_{corr} = \frac{TOC_{pred}}{0.87}$$
(5-81)

UVA Removal

The same AWWA/WITAF database (Tseng et al., 1996) was used to develop an UVA removal equation for softening, shown in **Equation 5-82**. The equation uses TOC predicted by **Equation 5-81** and raw water SUVA to predict UVA removal. Difficulty was encountered in obtaining enough UVA removal data for a robust predictive equation. The database consists of 36 data points, and the SUVA data range includes two abnormally high values (above 11.2 L/mg-m). Ninety percent of the data used to develop the equation for UVA removal had SUVA values between 1.8 and 5.2 L/mg-m.

$$UVA_{removed} = 0.01685(TOC_{removed})^{0.8367}(SUVA_{raw})^{1.2501}$$
(5-82)

($R^2 = 0.98$, $R^2_{adj} = 0.98$, SEE = 0.032 1/cm, F = 1019, n = 36)

where,

$UVA_{removed}$ = UVA removed by softening (1/cm): $0.014 \leq UVA_{removed} \leq 0.874$

$TOC_{removed}$ = TOC removed by softening (mg/L): $0.1 \leq TOC_{removed} \leq 6.8$

$SUVA_{raw}$ = raw water SUVA (L/mg-m): $1.8 \leq SUVA_{raw} \leq 12.5$

5.5.4 Granular Activated Carbon (GAC) Adsorption

TOC breakthrough curves for a GAC adsorption process with alum coagulated, settled and filtered feed water were described by the general logistic function (Clark, et al., 1986; Clark, 1987) in the WTP Model, version 1.21. The parameters of the logistic function were established based on a single GAC adsorption case study. The logistic function parameters were defined as a function of empty bed contact time (EBCT) and did not take into account the type of GAC used or feed water

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quality parameters such as pH. The model calculated a running average TOC removal based on the empty bed contact time (EBCT) of the reactor and the reactivation interval for the carbon. The model was not intended to simulate the dynamics of TOC removal by this process, but rather, to simulate average water quality conditions within the treatment plant being considered.

For the development of the 1992 WTP Model, a sufficient database was not available to develop a separate equation for UVA removal; thus, for the purposes of the model, it was assumed that UVA removal was equivalent to TOC removal on a percentage basis. Since 1992, significant research has been carried out investigating GAC breakthrough behavior (Summers et al. 1998; Hooper et al.1996; Solarik et al. 1997a) including the ICR GAC treatment studies. This research was used to develop new GAC algorithms for TOC and UVA removal.

TOC Removal

A new TOC removal algorithm for GAC adsorption was developed based on representing the breakthrough curve with the logistic function. The parameters of the logistic function were developed to take into account the impact of influent TOC and pH, empty bed contact time (EBCT) and the impact of the single contactor configuration versus that of multiple, blended-effluent contactors operating in parallel.

In most large-scale GAC applications, GAC adsorbers are not implemented as single contactors. Instead, multiple contactors are operated in a parallel configuration with effluent blending to stabilize effluent quality and maximize bed life. Parallel GAC contactors are operated in a staggered mode wherein each contactor operates at a different point on the TOC breakthrough curve and has been in operation for a different length of time. In this mode of operation, one contactor at a time is taken off-line and its GAC reactivated whenever the blended effluent exceeds the target effluent concentration. The effluent from the contactor in operation the longest will likely be higher than the target breakthrough concentration, as it is blended with water from the contactors that have effluent concentrations much lower than the target concentrations. Consequently, the effluent of many parallel contactors will be blended prior to disinfection. Under ideal conditions, staged blending with multiple parallel columns leads to a near steady-state effluent concentration (Roberts and Summers, 1982).

The overall GAC plant performance for a system of *m* parallel contactors can be described by the equations discussed in Roberts and Summers (1982) by which a single contactor breakthrough curve can be numerically integrated to yield a blended breakthrough curve using **Equation 5-83**.

$$\bar{f} = \frac{\overline{C}_E}{C_0} = \frac{1}{t_R} \int_0^{t_R} f(t)\, dt \qquad \textbf{(5-83)}$$

in which f is the TOC fraction remaining ($TOC_{effluent}$ / $TOC_{influent}$) from a single contactor at a given time, t; $\bar{f}$ is the average TOC fraction in the blended effluent; $\overline{C}_E$ is the average effluent concentration of the blended water; C_0 is the influent concentration; and t_R is the reactivation interval. Roberts and Summers (1982) indicate that this approximation is valid when the number of parallel contactors exceeds ten.

To approximate the blended effluent TOC concentration in a set of parallel contactors for a given set of operating conditions (EBCT and reactivation interval) and feed water quality parameters (TOC and pH), the single contactor breakthrough curve first had to be defined. This was done using the logistic function as described in **Equation 5-84**. This single contactor breakthrough curve is integrated using **Equation 5-83** to produce the blended effluent TOC prediction.

$$TOC_{eff} = A_0 + \frac{A_f}{1 + Be^{-D*bv}} \qquad \textbf{(5-84)}$$

A, B, and D are fitting parameters. Replacing $f(t)$ in **Equation 5-83** with the logistic function, **Equation 5-84**, and integrating yields the following equation which represents the blended effluent breakthrough curve:

$$TOC_{eff} = A_0 + A_f + A_f * \left\{ \frac{\ln\left(\dfrac{1 + Be^{-D*bv}}{1 + B}\right)}{D*bv} \right\} \qquad \textbf{(5-85)}$$

The WTP Model, version 2.2, uses **Equation 5-85** to predict TOC concentrations after GAC treatment with multiple, parallel, blended-effluent contactors.

The model was developed using data sets from all bench-scale ICR GAC treatment studies (using bituminous GAC) that evaluated a 10- or a 20-minute full-scale equivalent EBCT value. The data set consisted of thirty-two studies, which included 302 GAC column TOC breakthrough curves.

Each of the TOC breakthrough curves used in model development was fit with a logistic function model (**Equation 5-84**). These models were used to solve for bed volumes (BV) for TOC percent breakthrough levels of 10 to 72.5 percent in increments of 2.5 percent. At each TOC breakthrough level, a linear correlation was developed between bed volumes and influent TOC concentration (TOC_{inf}). At any influent TOC level, these BV functions could be used to develop a set of effluent TOC concentrations ranging from 10 to 72.5 percent breakthrough. For the BV functions, (correlations between bed volumes and influent TOC concentration), the mean R^2 value was 0.41.

The BV functions and the effluent TOC data were used to construct a breakthrough curve for a wide range of influent TOC concentrations. Each of these breakthrough curves was fit with a logistic function to generate a family of logistic curves for a range of TOC values.

The coefficients from this family of logistic function breakthrough curves were correlated to influent TOC concentration. This established linear relationships between the logistic function coefficients and influent TOC : A_0 = f(TOC_{inf}), A_f = f(TOC_{inf}) and D = f(TOC_{inf}). The linear relationships were described by R^2 values of 0.90 and above. Coefficient B was not strongly impacted by influent TOC and was thus set equal to a constant, 100.

The logistic coefficient correlations (to influent TOC) were first developed separately for 10 and 20 minute EBCTs. Next the coefficients (i.e., the coefficients in the A_0, A_f and D equations) were correlated to EBCT. Since there were only two EBCTs, a linear coefficient was assumed. However, the EBCT adjustment was very minor since the logistic functions were defined in terms of bed volumes. The effect of EBCT on these equations captured the slight improvement in performance that is observed for 20-minute EBCT contactors, compared to 10-minute EBCT contactors, on a normalized basis. This resulted in logistic function coefficients that were a function of influent TOC and EBCT, shown in **Equations 5-86** through **5-90** below.

$$A_0 = TOC_{\inf}\left\{\left(-1.148\times10^{-3} * EBCT_{adj}\right)+1.208\times10^{-1}\right\}-2.710\times10^{-6}\left(EBCT_{adj}\right)+1.097\times10^{-5}$$

(5-86)

$$A_f = TOC_{\text{inf}} \left\{ \left(3.244 \times 10^{-3} * EBCT_{adj} \right) + 5.383 \times 10^{-1} \right\} + 1.033 \times 10^{-5} \left(EBCT_{adj} \right) + 1.759 \times 10^{-5}$$

<div align="right">(5-87)</div>

$$D = TOC_{\text{inf}} \left\{ \left(-1.079 \times 10^{-5} * EBCT_{adj} \right) + 4.457 \times 10^{-4} \right\} + 1.861 \times 10^{-5} \left(EBCT_{adj} \right) - 2.809 \times 10^{-4}$$

<div align="right">(5-88)</div>

$$B = 100$$

<div align="right">(5-89)</div>

$$bv = \frac{1440(RT)}{EBCT_{adj}}$$

<div align="right">(5-90)</div>

To account for the impact of influent pH on performance, data from a studies by Hooper et al. (1996; 1997) that showed the change in capacity (from isotherm tests) resulting from changes in pH was used. The study found a 4.4% change in capacity for every unit change in pH (over a range of 3.8 to 10.1). This change in capacity could be thought of as an effective change in EBCT, e.g., lowering influent pH by 1 unit effectively resulted in a 4.4% increase in EBCT (e.g., 10.55 minutes instead of 10 minutes). The pH effect was incorporated into an adjusted EBCT term given by **Equation 5-91**.

.

$$EBCT_{adj} = EBCT \left\{ 1 + 0.044 \left(pH_{baseline} - pH_{\text{inf}} \right) \right\}$$

<div align="right">(5-91)</div>

where,

for *EBCT* = 10 minutes:

   TOC_{inf} = influent TOC (mg/L): $1.51 \leq TOC_{inf} \leq 11.5$

   $pH_{baseline}$ = average pH for data sets used for model development: 7.93

   pH_{inf} = influent pH: $6.07 \leq pH_{inf} \leq 9.95$

   bv = bed volumes

   RT = blended runtime, days

   $EBCT$ = empty bed contact time, minutes

And for *EBCT* = 20 minutes:

   TOC_{inf} = influent TOC (mg/L): $1.51 \leq TOC_{inf} \leq 11.5$

$pH_{baseline}$ = average pH for data sets used for model development: 7.93

pH_{inf} = influent pH: $6.14 \leq pH_{inf} \leq 9.95$

bv = bed volumes

RT = blended runtime (days)

$EBCT$ = empty bed contact time (minutes)

Note that in the WTP Model's implementation of these algorithms for TOC removal by GAC adsorption, the user-entered EBCT value for a single-contactor-type system is assumed to correspond to the "Plant Flow" input. When the model is used to run a cold water, peak flow condition, the WTP Model adjusts the EBCT downward proportionally based on the ratio of "Peak Flow" to "Plant Flow" user inputs. For the multiple contactor modeling case, the WTP Model does *not* adjust the EBCT under the "Peak Flow" condition because it is assumed that such a GAC system would be run to maintain a constant EBCT by operational adjustment of the number of contactors being used at any given time.

UVA Removal

In the 1992 WTP Model, the percentage removal of UVA by GAC adsorption was assumed to be equivalent to the percentage TOC removal. Because UVA is a surrogate measure of the more adsorbable humic, non-polar fraction of organic material, this assumption is conservative. UVA removal typically exceeds that of TOC, which is comprised of both non-polar and polar (less adsorbable) organic material (Owen et al., 1992; Jackson et al., 1993). Thus, new equations were developed to predict UVA removal by GAC.

Two equations for UVA removal were developed: (1) for waters coagulated prior to GAC, and (2) for waters coagulated, ozonated and biotreated prior to GAC. Significant differences in GAC performance have been reported for ozonated and biotreated waters compared to conventionally treated waters (Solarik et al., 1997a).

GAC effluent UVA was strongly linearly correlated to effluent TOC concentration, as shown in **Equations 5-92** and **5-93**.

Coagulation Prior to GAC:

Data from the ICR treatment studies were used to develop a GAC adsorption UVA removal algorithm for waters pre-treated by coagulation. The database consisted of over 4,000 paired TOC and UVA GAC effluent data.

$$UVA_{eff} = 0.0195(TOC_{eff}) - 0.0077 \qquad\qquad \textbf{(5-92)}$$

(R[2] = 0.93, R[2]$_{adj}$ = 0.86, SEE = 0.010 1/cm, F = 25728, n = 4141)

where,

UVA_{eff} = GAC effluent UVA (1/cm): $0.000 \leq UVA_{eff} \leq 0.393$

TOC_{eff} = GAC effluent TOC (mg/L): $0.1 \leq TOC_{eff} \leq 14.7$

Coagulation, Ozonation and Biofiltration Prior to GAC:

For waters also ozonated and biotreated prior to GAC, the database represents 4 source waters and 4 bench-scale breakthrough curves from a study by Summers et al. (1998a).

$$UVA_{eff} = 0.0014(TOC_{eff}) - 0.00141 \qquad\qquad \textbf{(5-93)}$$

(R[2] = 0.96, R[2]$_{adj}$ = 0.96, SEE = 0.001 1/cm, F = 2222, n = 104)

where,

UVA_{eff} = GAC effluent UVA (1/cm): $0.000 \leq UVA_{eff} \leq 0.0364$

TOC_{eff} = GAC effluent TOC (mg/L): $0.1 \leq TOC_{eff} \leq 6.1$

Note that when the WTP Model implements either of the above correlations, it will set the GAC effluent UVA equal to the influent UVA if the correlations predict an effluent UVA value that exceeds the influent UVA.

5.5.5   Nanofiltration

NOM Rejection

For the WTP Model, version 1.21, removal of NOM by membrane systems was based on bench-scale process evaluations performed by Taylor, et al. (1987 and 1989) and Amy, et al. (1990). Data

from these three studies were combined and analyzed for relationships between nominal molecular weight cutoff (MWC) and NOM removal. The equation was based on 44 observations from 6 different waters. Data for UVA removal were not available in either study and, therefore, the model assumed that UVA and TOC were removed to the same extent in membrane systems.

For version 2.2 of the WTP Model, data from numerous studies were compiled to develop algorithms for membrane treatment. New regulations governing filtration, disinfection and DBPs have fueled an interest in membrane technology for drinking water treatment. Therefore, since 1992 and with the ICR, the availability of membrane performance data has significantly increased. Membranes are becoming increasingly cost-effective alternatives for NOM removal and DBP control compared to other advanced treatment options as they are being developed specifically to target removals of organic and inorganic compounds. Currently, it is possible to find membranes to meet a wide range of treatment objectives. Thus, given the current status of membrane design and availability, it was decided to allow the user to define removals of TOC and UVA by membrane treatment through input parameters in WTP Model, version 2.2, than to develop predictive algorithms.

The user is given two options for membrane treatment: (1) microfiltration (MF)/ultrafiltration (UF), and (2) nanofiltration (NF). For MF/UF, the WTP Model does not calculate any NOM rejection, as these membranes generally only reject particulate NOM, which is typically a small fraction of total NOM. For NF membranes, which can reject 90 percent, or more, of dissolved NOM, the user defines the level of TOC, UVA and bromide removal. UVA removal cannot exceed TOC removal. This behavior was predominantly seen in the data examined.

5.5.6   Ozone

Ozonation has been shown to reduce UVA by 25 to 50 percent, while TOC is typically not affected (Owen et al., 1992). Thus, the model assumes no TOC removal through ozonation alone. It is important to note, however, that ozonation leads to enhanced TOC removal for biofiltration (see 0 Biofiltration).

Ozone: UVA Removal

Data for the ozonation equation was collected from research studies. The database used to develop the equation to predict UVA oxidation by ozone was comprised of bench-scale data collected from a batch reactor and included both raw and settled water ozonation conditions. UVA oxidation was

difficult to model, partially due to the relatively small database, and partially due to the lack of variability in the source data. Few data were available for UVA oxidation observed in pilot- or full-scale systems. The equation was developed from data presented by Ozekin (1994). The database contained UVA oxidation from 7 utilities, 95 raw water data points, and 25 settled water data points.

The equation to predict UVA oxidation by ozone is given by **Equation 5-94**. Multiple linear regression analysis was used to correlate oxidized UVA to transferred ozone dose and influent water TOC and UVA. The database was not extensive enough to include water quality parameters such as pH, ammonia, and temperature or bromide concentration. Additionally, contact time was not included.

$$UVA_{O_3} = 0.622(UVA)^{0.931}\left(\frac{O_3}{TOC}\right)^{-0.252} \tag{5-94}$$

(R^2 =0.89, R$^2_{adj}$ = 0.89, SEE = 0.034 1/cm, F =536, n =120)

where,

UVA_{O3} = UVA after ozonation (1/cm): $0.010 \leq UVA_{O3} \leq 0.577$

UVA = UVA before ozonation (1/cm): $0.019 \leq UVA \leq 0.585$

O_3/TOC = transferred O$_3$ dose/TOC (mg-L/mg-L): $0.35 \leq O_3/TOC \leq 2.30$

Research has shown that ozonation results in the formation of compounds that are highly oxidized and more biodegradable (Langlais et al., 1991; Miltner and Summers, 1992; Schechter and Singer, 1995). If left untreated, these biodegradable compounds could cause biological regrowth in the distribution system. Thus, biological treatment is often employed downstream from ozonation. Biological drinking water treatment most commonly occurs in slow sand or conventional media (anthracite and sand) filters. Biomass can develop on the surface of the media if a disinfectant residual is not maintained throughout the filter.

5.5.7 Biofiltration

In WTP Model version 2.2, algorithms were developed to predict NOM (as measured by UVA and TOC) removal by ozone and biofiltration. In version 2.2.1, the biofiltration prediction model was updated to account for biofiltration for both ozonated and non-ozonated waters and the impact of

empty bed contact time on TOC removal. The Terry and Summers (2018) model is used to model rapid-rate filters and GAC contactors and a simple algorithm based on temperature is used to model slow sand filters.

Biofiltration eligibility

Whether biofiltration is modeled for a rapid-rate filter or GAC contactor is dependent on several factors: disinfectant residual (considering total Cl_2, O_3, or ClO_2), filter backwash practices, filter media type, and whether biofiltration has already been applied upstream. Figure 5-2 depicts several scenarios for determining biofiltration eligibility.

In the top row of Figure 5-2 there are two anthracite/sand filters. On the left, biofiltration is not modeled because there is either disinfectant residual or chlorinated backwash practices. Biofiltration is modeled in the filter to the right there is no residual or chlorinated backwash practices. In the middle row of Figure 5-2, biofiltration is active in both filters regardless of disinfectant residuals because it is assumed that any disinfectant residual is eliminated by filters with GAC media.
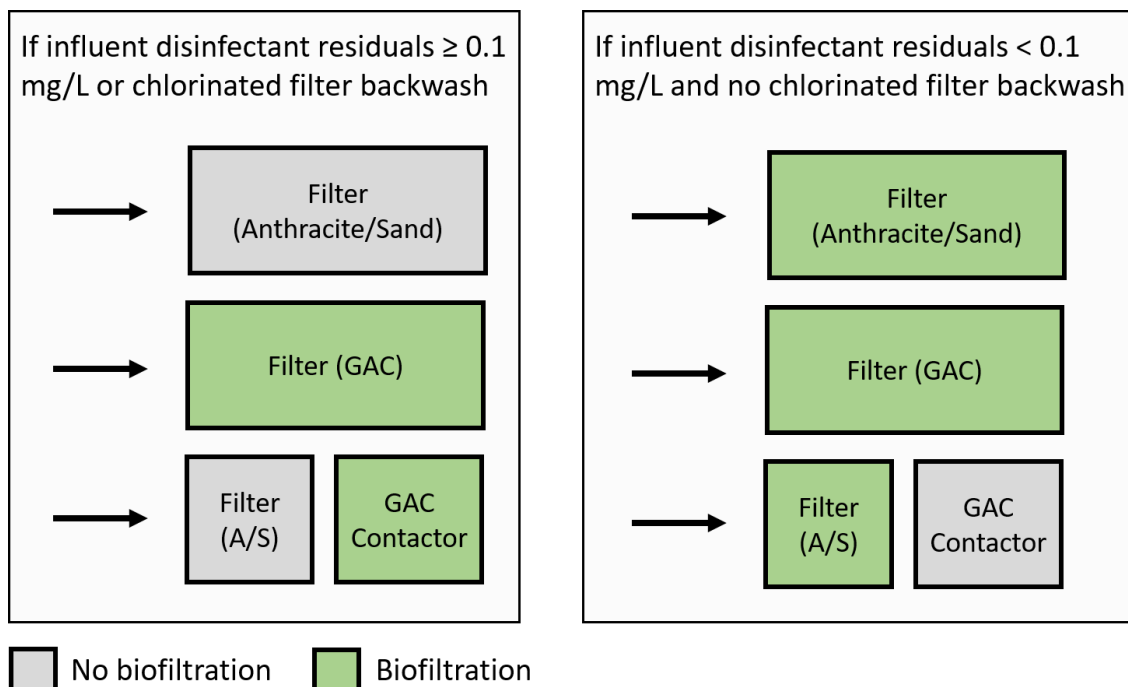
Figure 5-2. Biofiltration eligibility diagram. Unit processes in which biofiltration would be modeled are green and those that would not are gray.

Figure 5-2 also demonstrates how biofiltration is modeled when a treatment train has multiple filters or contactors. If multiple unit processes are eligible for biofiltration, biofiltration is only modeled in the *first* eligible unit process. This approach is intended to conservatively estimate TOC and UVA removal due to biofiltration. For example, if there is an anthracite/sand filter followed by a GAC contactor—shown in the bottom row of Figure 5-2—biofiltration will only be modeled in one of the unit processes. If there is a disinfectant residual, the filter will not be eligible for biofiltration but the GAC contactor will be. If there is no disinfectant residual, the filter will be eligible for biofiltration; however, because biofiltration is modeled upstream, the GAC contactor will not be eligible.

Biofiltration: TOC Removal

The WTP model uses the relationship developed by Terry and Summers (2018) for the prediction of biodegradable organic carbon (BDOC) removal via rapid-rate biofiltration for both ozonated and non-ozonated waters and accounts for the impact of empty bed contact time (EBCT) on biodegradable organic carbon (BDOC) removal (**Equation 5-95**) as a pseudo-first order process.

$$\frac{c}{c_{inf}} = e^{-k' * EBCT} \tag{5-95}$$

where,

c = the BDOC of the effluent (mg/L)

c_{inf} = the BDOC concentration of the influent (mg/L)

k' = the observed rate constant (min-1) and EBCT (min)

By assuming that the ratio between BDOC and TOC (BDOC/TOC) is 20% and 30% BDOC/TOC for non-ozonated and ozonated surface waters, respectively, this equation can be used for TOC estimation. This assumption is based on the median values of BDOC/TOC from the literature review of 203 surface waters by Terry and Summers (**Table 5-1**). Because the WTP Model is designed to capture the central tendency of surface water treatment in the United States, this appears to be a reasonable assumption. To improve the predictive accuracy of the model, Terry and Summers (2018) determine rate constants for BDOC removal based on three temperature categories (temp ≤ 10°C, 10°C < temp < 20°C, and temp ≥ 20°C). These three constants and their resulting TOC removal as a function of EBCT are shown in **Figure 5-3.**

Table 5-1. BDOC/TOC in non-ozonated and ozonated surface waters (adapted from Table 2 in Terry and Summers (2018))

	BDOC/TOC (%): Non-ozonated	BDOC/TOC (%): ozonated
Median	20	30
Mean (Average)	23	29
Maximum	72	62
Minimum	1	8
Standard deviation	12	11
Coefficient of variation	0.5	0.4
N	100	103
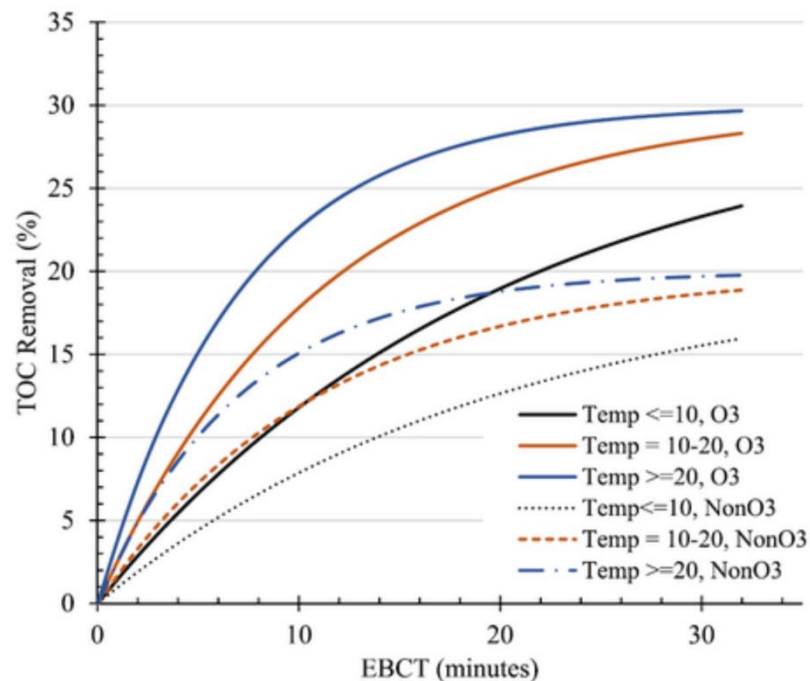
Figure 5-3. Simulated TOC removal as a function of EBCT at three temperature ranges for ozonated and non-ozonated waters with associated k' values (k' = 0.05 min-1 for ≤ 10°C, k' = 0.09 min-1 for 10-20°C, k' = 0.14 min-1 for ≥ 20°C). (Terry and Summers (2018), Figure 6)

The Terry and Summers (2018) model was developed with anthracite, sand and GAC media. However, data from biofilters with GAC were only used if the GAC had been in use for at least 18 months (75,000 bed volumes at an EBCT of 10 min). After this time most of the GAC adsorption capacity had been exhausted and the removal was dominated by bioremoval. This is often termed biological activated carbon (BAC). See **Figure 5-4.** To simulate both adsorption (short-term) and biofiltration (steady-state) with GAC, the WTP Model v2.2.1 can be run first with the biofiltration module to get the steady-state (long term) bioremoval, followed by a GAC module to get the short-

term adsorption removal (see "5.5.4 Granular Activated Carbon (GAC) Adsorption" for details). This series approach should provide a good estimate of the short-term advantage of adsorption in a GAC filter-adsorber.
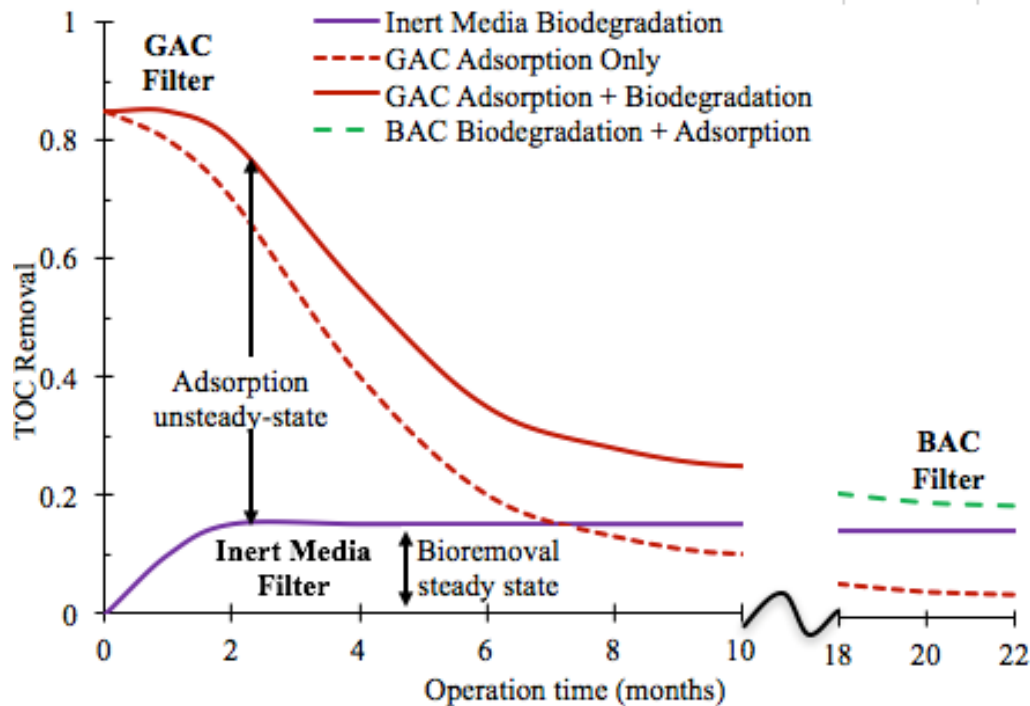

Figure 5-4. TOC removal acclimation for an inert media filter and a granular activated (GAC) filter, which becomes a biological activated carbon (BAC) filter once the adsorption capacity is exhausted (Terry and Summers, 2018)

Biofiltration: UVA Removal

The Terry and Summers (2018) model does not explicitly account for UVA; however, the results of a single pilot study (unpublished data) by these authors suggests that there is no statistically significant impact on SUVA—the ratio between UVA and TOC—due to biofiltration. This suggests that UVA is approximately proportional to TOC removal when considering biofiltration alone. When considering ozone and biofiltration together, the Ozekin (1994) model would be used to account for changes in UVA and the Terry and Summers (2018) model for TOC removal in WTP Model v2.2.1. For the non-ozonated case, the Terry and Summers (2018) model would also be used to model TOC removal but with an additional assumption of constant SUVA before and after biofiltration. This means that UVA removal is assumed to be proportional to TOC removal predicted by the Terry and Summers model.

Slow Sand Filter Biofiltration

Version 2.2.1 of the WTP Model uses a simple algorithm for NOM removal by biological activity within slow sand filtration unit processes. Based on a recommendation from an academic expert in slow sand filtration (Collins, 2005), the WTP Model includes the following default TOC removals through slow sand filters (the percentages listed are user-adjustable inputs to the "Slow Sand Filt." unit process):

- Water temperature ≥ 20ºC: 20% TOC removal
- 10ºC $\leq$ Water temperature < 20ºC: 15% TOC removal
- Water temperature < 10ºC: 10% TOC removal

Version 2.2.1 of the WTP Model does not assume any change in UVA through slow sand filtration.

5.5.8   Chlorination

When chlorine is added along with coagulation, UVA values will be lower than by coagulation only, due to UVA oxidation by the chlorine. The WTP Model accounts for this reduction in UVA observed during chlorination by applying **Equation 5-96**, developed from the 20-water database of Summers et al. (1998b):

$$UVA_{\Pr e-Cl_2} = 0.7437\left(UVA_{no\,Cl_2}\right) + 0.0042 \tag{5-96}$$

$$(R^2 = 0.93,\ R^2_{adj} = 0.93,\ SEE = 0.006\ 1/cm,\ F = 991,\ n = 76)$$

where,

$UVA_{Pre-Cl2}$ = coagulated water UVA with prechlorination (1/cm): $0.015 \leq UVA_{Pre-Cl2} \leq 0.120$

$UVA_{no\,Cl2}$ = coag. water UVA without prechlorination (1/cm): $0.017 \leq UVA_{no\,Cl2} \leq 0.150$

The model development database was created from experiments that considered only the difference in UVA between pre-chlorinated, coagulated water and coagulated (only) water; however, the WTP Model applies this reduction more broadly to account for chlorine oxidation of DBP precursors in coagulated water. For example, the WTP Model applies this reduction at a first point of chlorination *following* coagulation, so that the oxidation effect will be accounted for in DBP formation predictions at subsequent re-chlorination points. Note that the WTP Model will only apply this reduction once for coagulated water UVA due to chlorine oxidation in the process train.

5.6   DISINFECTANT DECAY

5.6.1   Modeling Disinfectant Decay in Treatment Plants

Version 2.2 of the WTP Model predicts free chlorine, chloramine, and chlorine dioxide decay by assuming that the rate of residual decay is a function of the residual concentration at a given point in time. Such a dependency requires that mixing conditions within the treatment plant be simulated. For this reason (and to support the calculation of pathogen inactivation credits), the user is required to specify baffling factors (as $T_{10}/T_{theoretical}$ ratios) to describe the hydraulics of each treatment basin within the plant. Using this ratio, the WTP Model represents each basin as a number of continuous-flow, stirred tank reactors (CFSTRs) connected in series. A complete description of this modeling approach is provided elsewhere (Denbigh and Turner, 1971; Levenspiel, 1972; Teefy and Singer, 1990); however, some key points will be discussed here.

For a single CFSTR, the effluent concentration of a solute is determined with the following expression:

$$C_f = C_i + tr \qquad\qquad \textbf{(5-97)}$$

where C_f is the final concentration of the solute within and leaving the CFSTR, C_i is the initial concentration of the solute entering the CFSTR, t is the mean residence time in the CFSTR and r is the reaction rate. The reaction rate is greater than zero for solute formation and is less than zero for solute decay (such is the case for disinfectant decay). The theoretical residence time in the CFSTR is calculated by dividing the volume of the CFSTR by the volumetric flow rate of the fluid moving through the CFSTR.

For a set of N CFSTRs connected in series, the final concentration of a solute leaving the Nth CFSTR is given by the following set of equations:

$$C_{1,f} = C_{1,i} + t_1 r_1 \qquad\qquad \textbf{(5-98)}$$

$$C_{2,i} = C_{1,f} \qquad\qquad \textbf{(5-99)}$$

$$C_{2,f} = C_{2,i} + t_2 r_2 \qquad\qquad \textbf{(5-100)}$$

$$.$$
$$.$$
$$.$$

$$C_{N,i} = C_{N-1,f} \qquad\qquad \textbf{(5-101)}$$

$$C_{N,f} = C_{N,i} + t_N r_N \qquad \text{(5-102)}$$

where $C_{N,f}$ is the final concentration of the solute within and leaving the Nth CFSTR, $C_{N,i}$ is the initial concentration of the solute entering the Nth CFSTR, t_N is the mean residence time in the Nth CFSTR and r_N is the reaction rate in the Nth CFSTR. **Equation 5-98** can be used to calculate $C_{1,f}$ from known values of $C_{1,i}$, t_1 and r_1. Once $C_{1,f}$ is calculated, **Equation 5-99** is used to obtain $C_{2,i}$. **Equation 5-100** can then be used to calculate $C_{2,f}$ from known values of t_2 and r_2. The process is repeated through **Equation 5-102** until $C_{N,f}$ is calculated.

In **Equations 5-98** through **5-102**, the reaction rate is given by the differential equation appropriate for the reaction of interest. For a first order decay process, like that assumed for chlorine dioxide, r_N is given by **Equation 5-103**:

$$r_N = - k\, C_{N,f} \qquad \text{(5-103)}$$

For a saturation-type model, like that used for simulating free chlorine and chloramine decay, r_N is given by **Equation 5-104**:

$$r_N = - \frac{\alpha_2\, C_{N,f}}{\alpha_1 + C_{N,f}} \qquad \text{(5-104)}$$

where k, α_1, and α_2 are constants.

In order to use a set of equations such as those defined by **Equations 5-98** through **5-102**, one must determine the number of CFSTRs connected in series that best simulates the basin or filter of interest. This number is determined by using a theoretical "F curve," which describes the time-dependent concentration of a tracer solute leaving the set of CFSTRs in a step-dose tracer study (for a more complete discussion, see Denbigh and Turner, 1971; Levenspiel, 1972; or Teefy and Singer, 1990). The theoretical F curve is defined by **Equation 5-105**:

$$F = \frac{C_{N,f}}{C_{1,i}}$$

$$= 1 - \exp\left(\frac{-Nt}{t_m}\right)\left[1 + \frac{Nt}{t_m} + \frac{1}{2!}\left(\frac{Nt}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt}{t_m}\right)^{N-1}\right]$$

(5-105)

where N is the number of CFSTRs connected in series, t_m is the mean residence time for an entire series of equally sized CFSTRs and t is the time of interest.

The Surface Water Treatment Rule (SWTR), finalized by USEPA in 1989, has placed great importance on the time at which F is equal to 0.1 (USEPA, 1989). This time is frequently referred to as t_{10} because it represents the time required for the effluent tracer concentration to reach 10 percent of the influent tracer concentration in a step-dose tracer study. At a time equal to t_{10}, the following holds:

$$0.1 = 1 - \exp\left(\frac{-Nt_{10}}{t_m}\right)\left[1 + \frac{Nt_{10}}{t_m} + \frac{1}{2!}\left(\frac{Nt_{10}}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt_{10}}{t_m}\right)^{N-1}\right]$$

(5-106)

Using **Equation 5-106**, the theoretical value of N can be calculated for any value of $t_{10}:t_m$ by using an iteration procedure. **Table 5-2** summarizes the results.

Table 5-2 Determination of the Number of CFSTRs in Series

t_{10}:t_m	N
0.000 to 0.186	1
0.186 to 0.317	2
0.317 to 0.402	3
0.402 to 0.461	4
0.461 to 0.506	5
0.506 to 0.540	6
0.540 to 0.569	7
0.569 to 0.593	8
0.593 to 0.613	9
0.613 to 0.630	10
0.630 to 0.645	11
0.645 to 0.659	12
0.659 to 0.671	13
0.671 to 0.682	14
0.682 to 0.691	15
0.691 to 0.700	16
0.700 to 0.708	17
0.708 to 0.716	18
0.716 to 0.723	19
0.723 to 0.729	20
0.729 to 0.735	21
0.735 to 0.741	22
0.741 to 0.746	23
0.746 to 0.751	24
0.751 to 1.000	25

A given basin or filter is simulated as N equally sized CFSTRs based on the calculated value of t_{theo}, and user-input values of t_{10}:t_{theo} and t_m:t_{theo} where t_{theo} is the theoretical residence time of the basin or filter as given by:

$$t_{theo} = \frac{V}{Q} \qquad\qquad \textbf{(5-107)}$$

where V is the volume of water in the basin or filter and Q is the volumetric flow rate through the basin or filter. The volume of water in a filter must not include the volume of the filter media. The ratios $t_{10}{:}t_{theo}$ and $t_m{:}t_{theo}$ can be determined by field-scale tracer studies or estimated from results reported elsewhere (USEPA, 1991; Teefy and Singer, 1990).

Actual tracer studies will not likely find the specific $t_{10}{:}t_m$ ratios. Therefore, the selected value of N is based on the $t_{10}{:}t_m$ ranges listed in **Table 5-2**. Once the WTP Model determines the value of N from **Table 5-2**, **Equations 5-98** through **5-102** are used in conjunction with the appropriate rate equations to calculate free chlorine, chloramines, and/or chlorine dioxide decay in the basin or filter being simulated.

5.6.2 Chlorine Decay

Rate equations for calculating the decay of chlorine in the 1992 version of the WTP Model were developed by Dharmarajah, et al. (1991). The experimental design consisted of collecting raw water samples from 16 utilities nationwide and observing the decay of chlorine under laboratory conditions. The model used two equations to predict free chlorine decay: (a) second-order reaction with respect to chlorine concentration was assumed for times less than 5 hours, and (b) a first-order reaction was assumed for times between 5 and 120 hours. The reaction constants were correlated with raw water quality parameters by multiple, stepwise regression analyses. Temperature was not varied in these experiments and bromide spiking was not performed (ambient bromide concentrations were not reported). The equations developed for raw water were also applied to treated waters.

The WTP Model chlorine decay reactions have been updated to use a Monod-type kinetic reaction that has been shown to predict chlorine decay well (Dugan et. al, 1995; Koechling et. al, 1998; Isabel et al., 2000). The database used to develop chlorine decay equations consisted of bench-scale bottle point chlorine decay experiments. Separate chlorine decay equations were developed for raw and treated waters.

The equations have the following form:

$$\frac{dC_t}{dt} = \frac{-\alpha_2 * C_t}{\alpha_1 + C_t} \qquad\qquad \textbf{(5-108)}$$

Equation 5-107 takes the following form when integrated:

$$C_t = \alpha_1 * \ln\frac{C_0}{C_t} - \alpha_2 * t + C_0 \qquad\qquad \textbf{(5-109)}$$

where C_t is the chlorine residual concentration at any reaction time t, C_0 is the initial chlorine dose, and α_1 and α_2 are kinetic rate parameters. The chlorine residual at any time t is calculated iteratively.

Equation 5-109 was fitted to the data to develop a set of α_1 and α_2 parameters that were then correlated to water quality parameters.

Raw Water

The database used to develop the raw water chlorine decay equation was comprised of 48 different source waters, dosed using chlorine to TOC ratios ranging from 0.5 to 2.5. Decay data were typically taken between 15 minutes and 120 hours, and most decay curves consisted of at least 7 data points.

The kinetic parameter α_1 was found to be dependent on the chlorine dose and is estimated in the WTP Model, Version 2 with the linear model shown in **Equation 5-110**:

$$\alpha_1 = -0.8147(C_0) \qquad\qquad \textbf{(5-110)}$$

$(R^2_{adj} = 0.90,\ SEE = 0.010\ mg/L,\ F = 16864,\ n = 176)$

The kinetic parameter α_2 was found to be best correlated to TOC and a kinetic parameter k_2

$$\alpha_2 = k_2 * TOC \qquad\qquad \textbf{(5-111)}$$

k_2 was correlated with chlorine dose and raw water UVA, as shown in **Equation 5-112**.

$$k_2 = -2.2808 \left(\frac{C_0}{UVA} \right)^{-1.2971}$$ **(5-112)**

$$(R^2_{adj} = 0.53,\ SEE = 0.089\ mg/L,\ F = 199,\ n = 176)$$

Thus, combining **Equations 5-110** and **5-112**, **Equation 5-109** can be rewritten as follows:

$$C_t = \{-0.8147(C_0)\} * \ln \left(\frac{C_0}{C_t} \right) + \left\{ -2.2808 \left(\frac{C_0}{UVA} \right)^{-1.2971} \right\} * TOC * time + C_0 \quad \textbf{(5-113)}$$

where,

C_0 = initial chlorine dose (mg/L): $0.995 \le C_0 \le 41.7$

TOC = total organic carbon (mg/L): $1.2 \le TOC \le 16$

UVA = ultraviolet absorbance before chlorination (1/cm): $0.010 \le UVA \le 0.730$

α_1 and α_2 are kinetic parameters

Coagulated Water

The database used to develop the treated water chlorine decay predictive equations was comprised of 24 different source waters, dosed at chlorine to TOC ratios ranging from 0.5 to 2.5. Similar to the raw water database, chlorine residuals were typically measured between 15 minutes and 120 hours, and most decay curves consist of at least 7 data points.

As was found for raw water decay, the kinetic parameter α_1 was found to have a linear correlation with chlorine dose, as shown in **Equation 5-114**.

$$\alpha_1 = -0.8408(C_0)$$ **(5-115)**

$$(R^2_{adj} = 0.99,\ SEE = 0.008\ mg/L,\ F = 10875,\ n = 52)$$

The kinetic parameter α_2 was developed in a similar manner to the raw water parameter and is given in **Equations 5-115** and **5-116**.

$$\alpha_2 = k_2(TOC) \tag{5-115}$$

and

$$k_2 = -0.404\left(\frac{C_0}{UVA}\right)^{-0.9108} \tag{5-116}$$

$(R^2_{adj} = 0.28,\ SEE = 0.081\ mg/L,\ F = 58,\ n = 52)$

Thus, treated water chlorine decay can be determined iteratively by the following equation:

$$C_t = \{-0.8404(C_0)\} * \ln\left(\frac{C_0}{C_t}\right) + \left\{-0.404\left(\frac{C_0}{UVA}\right)^{-0.9108}\right\} * TOC * time + C_0 \tag{5-117}$$

where,

C_0 = initial chlorine dose (mg/L): $1.11 \le C_0 \le 24.7$

TOC = total organic carbon (mg/L): $1.0 \le TOC \le 11.1$

UVA = ultraviolet absorbance before chlorination (1/cm): $0.012 \le UVA \le 0.250$

α_1 and α_2 are kinetic parameters

Implementation of Chlorine (and Chloramine) Decay Equations in the WTP Model

As discussed in **Section 5.6.1**, the WTP Model simulates disinfectant decay within the treatment plant and distribution system by accounting for both the residence time distribution of the water within the disinfection segment and the decay kinetics of the disinfectant. The WTP Model simulates the hydraulic residence time distribution by representing the disinfection segment as a series of CFSTRs. Disinfectant decay is then modeled sequentially through each of these CFSTRs from the beginning to the end of the disinfection segment. For the Nth CFSTR, the concentration leaving, $C_{out,N}$, is equal to the concentration entering, $C_{in,N}$, plus the product of the reaction rate, r, and the mean residence time of that N^{th} CFSTR, t_N. This relationship is presented in **Equation 5-118**, which is shown again below:

$$C_{out,N} = C_{in,N} + rt_N \tag{5-118}$$

As discussed in this section (and **Section 5.6.3**), the WTP Model simulates the reaction rate, r, for chlorine (and chloramines) decay, with a Monod-type expression (**Equation 5-107**). Combining **Equations 5-96** and **5-107**, and recognizing that the concentration within a CFSTR is the same as its outlet concentration, yields **Equation 5-119** for chlorine decay within the Nth CFSTR:

$$C_{out,N} = C_{in,N} - \left(\frac{\alpha_2 * C_{out,N}}{\alpha_1 + C_{out,N}} \right) * t_N \tag{5-119}$$

where $C_{in,N}$ is the concentration entering the Nth CFSTR (which is either the influent concentration of the overall disinfection segment, if the CFSTR in question is the first in the series, or it is equal to $C_{out,N-1}$ the outlet concentration of the previous CFSTR), $C_{out,N}$ is the predicted outlet concentration of the Nth CFSTR, and t_N is the mean residence time of the Nth CFSTR, which is equal to the mean residence time of the disinfection segment divided by the number of CFSTRs representing the segment. **Equation 5-119** can be solved using the quadratic formula for $C_{out,N}$, the concentration in the effluent of an individual CFSTR, which is given below by Equation 5-117:

$$C_{out,N} = -\frac{1}{2}(\alpha_1 - C_{in,N} + \alpha_2 t_N) - \frac{1}{2}\sqrt{(\alpha_1 - C_{in,N} + \alpha_2 t_N)^2 + 4\alpha_1 C_{in,N}} \tag{5-120}$$

If the WTP Model predicts a chlorine residual less than 0.1 mg/L in the effluent in any CFSTR, it will set the residual to zero. This will result in a predicted unit process effluent concentration of zero. Note that in this case, DBP formation will be calculated for the overall unit process using a cumulative reaction time representative of that through the last CFSTR with a predicted residual greater than or equal to 0.1 mg/L.

Chlorine Residual Prediction Verification

Chlorine residual concentrations were verified in the plant and in the distribution system through comparison to ICR plant data. It was determined that the central tendency of model predictions did not require any adjustment.

5.6.3   Chloramine Decay

The 1992 WTP Model predicted chloramine using the same raw water database that was used for free chlorine decay. The chloramine doses in the database were for preformed chloramines at Cl_2/N ratios of 4.0. Similar to chlorine decay, chloramine decay was predicted by an mth order reaction

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for 0 to 10 hours, where the order was modeled as a function of chloramine dose with a poor correlation ($R^2 = 0.05$). Decay after 10 hours was modeled using a first-order reaction.

New chloramine decay equations were developed for version 2.2 of the WTP Model using data from a study from Rajbandhari (2001). The database contained observations of chloramine demand and decay in five different waters treated by coagulation, flocculation and sedimentation, waters treated by ozonation of the settled water followed by biofiltration, and waters treated by nanofiltration of the raw water. The same model form as was used for free chlorine decay is used to predict chloramine decay.

The equations have the following form:

$$\frac{dCA_t}{dt} = \frac{-\alpha_2 * CA_t}{\alpha_1 + CA_t} \tag{5-121}$$

Equation 5-121 takes the following form when integrated:

$$CA_t = \alpha_1 * \ln\frac{CA_0}{CA_t} - \alpha_2 * t + CA_0 \tag{5-122}$$

where CA_t is the chloramine residual concentration at any reaction time t, CA_0 is the initial chloramine dose, and α_1 and α_2 are kinetic rate parameters. The chloramine residual at any time t is calculated iteratively.

The database used three target chloramine residuals at 24 hours (2, 3, and 4 mg/L) and three different free chlorine contact times (the water was either directly chloraminated or chlorine was first added and let react either 0.25, 1, or 3 hours and then ammonia was added at a chlorine to ammonia ratio of 4.5 to 1.

The correlations for the kinetic parameters α_1 and α_2 were developed as described for free chlorine decay. When the data set was divided by treatment, however, there were not significant differences in the parameters. Thus, only one chloramine decay model was developed.

The first kinetic rate parameter, α_1, was correlated to chloramine dose, per **Equation 5-123**.

$$\alpha_1 = -0.99(CA_0)$$
(5-123)

$(R^2_{adj} = 0.99, SEE = 0.095\ mg/L, F = 87582, n = 63)$

The second kinetic rate parameter, α_2, is given by **Equation 5-124**:

$$\alpha_2 = -0.015(UVA)$$
(5-124)

$(R^2_{adj} = 0.85, SEE = 0.0004\ 1/cm, F = 350, n = 62)$

Implementation of Chloramine Decay Equations in the WTP Model

Chloramine decay equations are implemented in the same fashion as chlorine decay equations. See **Section 5.6.2** for details.

Chloramine Residual Prediction Verification

Chloramine residual concentrations were verified in the plant and in the distribution system through comparison to ICR plant data. The results indicated that the central tendency of predicted residuals varied by more than 5% from observed residuals. However, no adjustment was made within the model to correct for the disparity for the following reasons:

- Predicted chlormine residuals are sensitive to reported doses of chlorine and ammonia due to breakpoint chlorination calculations. The combined errors in reported doses during the ICR reduced the value of the verification analysis for chloramines decay.

- Because chloramines are not typically used for CT, and dose, not residual, is used as the input for DBP formation predictive equations, predictions of chloramine residuals are not as critical in the overall context of the WTP Model.

5.6.4   Chlorine Dioxide Decay

The 1992 version of the WTP Model did not handle chlorine dioxide. For version 2.2 of the WTP Model, new chlorine dioxide decay equations were developed based on unpublished data from Colorado State University (Carlson, 2001). The database is comprised of nine different waters and 72 chlorine dioxide decay curves. Separate decay equations were developed for raw and coagulated/flocculated/settled waters.

The WTP Model simulates chlorine dioxide decay by first predicting a time zero chlorine dioxide residual after chlorine dioxide dosing (this accounts for the assumed instantaneous initial demand for the oxidant), then by using a first-order decay model to predict the longer-term, slower residual decay. The first-order model is characterized by decay constant k_1.

The initial residual is simulated using the following two equations for raw and coagulated/flocculated/settled water:

Raw Water:

$$ClO_{2,init} = 0.0157(TOC * UVA)^{-0.284}(ClO_2\ Dose)^{1.802}(pH)^{1.47}(Temp)^{-0.0475} \qquad \textbf{(5-125)}$$

$$(R^2_{adj} = 0.85,\ SEE = 0.23\ mg/L,\ F = 49,\ n = 40)$$

where,

$ClO_{2,init}$ = initial chlorine dioxide residual after a dosage, mg/L

$ClO_2\ Dose$ = chlorine dioxide dose, mg/L: $0.50 \leq ClO_2\ Dose \leq 3.0$

TOC = total organic carbon, mg/L: $1.4 \leq TOC \leq 8.1$

UVA = ultraviolet absorbance, 1/cm: $0.034 \leq UVA \leq 0.263$

pH: $6.5 \leq pH \leq 7.9$

$Temp$ = Temperature, ºC: $4.3 \leq Temp \leq 21.5$

Coagulated/Flocculated/Settled:

$$ClO_{2,init} = 0.0124(TOC * UVA)^{-0.182}(ClO_2\ Dose)^{1.415}(pH)^{1.85}(Temp)^{-0.0395} \qquad \textbf{(5-126)}$$

(R^2_{adj} = 0.93, SEE = 0.10 mg/L, F = 92, n = 32)

where,

$ClO_{2,init}$ = initial chlorine dioxide residual after a dosage, mg/L

$ClO_2\ Dose$ = chlorine dioxide dose, mg/L: $1.0 \leq ClO_2\ Dose \leq 3.0$

TOC = total organic carbon, mg/L: $1.3 \leq TOC \leq 6.1$

UVA = ultraviolet absorbance, 1/cm: $0.037 \leq UVA \leq 0.097$

pH: $6.4 \leq pH \leq 7.4$

$Temp$ = Temperature, ºC: $4.5 \leq Temp \leq 21.5$

After the initial demand is consumed, the WTP model predicts chlorine dioxide decay using a first order decay model. $ClO_{2,init}$ calculated with **Equations 5-125** and **5-126**, is used as the initial chlorine dioxide concentration. The kinetic parameter, k_1, was correlated to water quality parameters and is modeled using the following two equations:

Raw:

$$k_1 = 0.0117(TOC * UVA)^{0.445}(ClO_{2,init})^{-0.584}(Temp)^{0.485} \qquad \textbf{(5-127)}$$

(R^2_{adj} = 0.42, SEE = 0.0095 1/min, F = 11, n = 40)

where,

$ClO_{2,init}$ = chlorine dioxide residual after initial demand, mg/L: $0.21 \leq ClO_{2,init} \leq 2.37$

TOC = total organic carbon, mg/L: $1.4 \leq TOC \leq 8.1$

UVA = ultraviolet absorbance, 1/cm: $0.034 \leq UVA \leq 0.263$

$Temp$ = Temperature, ºC: $4.3 \leq Temp \leq 21.5$

Coagulated/Flocculated/Settled:

$$k_1 = 0.0146(TOC * UVA)^{0.941}(ClO_{2,init})^{-0.140}(Temp)^{0.533} \qquad \textbf{(5-128)}$$

$$(R^2_{adj} = 0.90, \; SEE = 0.0031 \; 1/min, \; F = 95, \; n = 32)$$

where,

$ClO_{2, \, init}$ = chlorine dioxide residual after initial demand, mg/L: $0.62 \leq ClO_{2, \, init} \leq 1.86$

TOC = total organic carbon, mg/L: $1.3 \leq TOC \leq 6.1$

UVA = ultraviolet absorbance, 1/cm: $0.037 \leq UVA \leq 0.097$

$Temp$ = Temperature, ºC: $4.5 \leq Temp \leq 21.5$

Implementation of Chlorine Dioxide Decay Equations in the WTP Model

The WTP Model simulates chlorine dioxide decay using the same general approach as described in **Section 5.6.2** for chlorine. That is, the WTP Model accounts for both the residence time distribution of the water within the disinfection segment and the decay kinetics of the disinfectant. The primary difference in implementing chlorine dioxide decay equations (as compared to chlorine or chloramines) is that of the form of the rate expression. As noted above, a first-order rate expression is used for chlorine dioxide decay. Substituting a first-order rate expression into **Equation 5-96**, the equation for the outlet concentration within a CFSTR, and solving for outlet concentration yields Equation 5-128:

$$C_{out,N} = \frac{C_{in,N}}{1 + k_1 t_N} \tag{5-129}$$

where $C_{in,N}$ is the concentration entering the Nth CFSTR, $C_{out,N}$ is the predicted outlet concentration of the Nth CFSTR, t_N is the mean residence time of the Nth CFSTR, and k_1 is the first-order rate constant for chlorine dioxide decay as given by **Equations 5-125** through **5-128**.

If the WTP Model predicts a chlorine dioxide residual less than 0.1 mg/L in the effluent in any CFSTR, it will set the residual to zero. This will result in a predicted unit process effluent concentration of zero.

Chlorine Dioxide Residual Prediction Verification

Chlorine dioxide residual predictions were unable to be verified using the ICR database due to limitations in the amount of chlorine dioxide data available through the ICR.

5.6.5   Ozone Decay

Ozonation was not handled by the 1992 version of the WTP Model. For version 2.2 of the WTP Model, a new algorithm was created for ozone decay. The equation was developed from a database for utilities with full- and pilot-scale ozonation applied to raw and/or settled water. Full- and pilot-scale ozonation data were not readily available for verification purposes, so 80 percent of the data were randomly selected and used for equation development and the remaining 20 percent were used for verification as an independent data set. Note that raw and settled water data were combined to develop a single model equation for ozone decay.

The ozone residuals represent those measured in "ozone dissipation chambers" (see implementation discussion below) only. The ozone residual can be calculated by subtracting the ozone demand from the transferred ozone dose shown below.

$$O_3 \ Residual = O_3 \ Dose - O_3 \ Demand \qquad \textbf{(5-130)}$$

and

$$O_3 \ Demand = 0.995(O_3 \ Dose)^{1.312}\left(\frac{O_3 Dose}{UVA}\right)^{-0.386}(SUVA)^{-0.184}(Time)^{0.068}(Alk)^{0.023}(pH)^{0.229}(Temp)^{0.087}$$

$$\textbf{(5-131)}$$

$$(R^2_{adj} = 0.89, \ SEE = 0.066 \ \mu g/L, \ F = 4569, \ n = 385)$$

where,

$O_3 \ Dose$ = ozone dose transferred to the water, mg/L: $0.50 \le O_3 \ Dose \le 6.4$

$O_3 \ Dose/UVA$ = transferred ozone dose/UVA, mg-cm/L: $12.5 \le O_3/UVA \le 98.5$

$SUVA$ = specific UVA = 100*UVA/DOC, L/mg-m: $0.8 \le SUVA \le 2.8$

$Time$ = time, minutes: $5.2 \le Time \le 24.3$

Alk = Alkalinity, mg/L as $CaCO_3$: $16 \le Alk \le 197$

pH: $5.8 \le pH \le 8.7$

$Temp$ = Temperature, ºC: $5 \le Temp \le 32$

Implementation of Ozone Decay Equations in the WTP Model

The equation for ozone residual demand/decay is not intended to predict ozone residual in an "ozone application chamber," a chamber in which ozone gas is being introduced and the simultaneous processes of ozone transfer to the water phase and ozone demand/decay in the water phase are occurring. Instead, the WTP Model uses the equation to predict ozone residuals in "ozone dissipation chambers," which are chambers in which no ozone gas is being introduced, but dissolved ozone residual is present in the influent water. A "typical" ozone dosing/contacting process is shown in **Figure 5-5**. This is the type of ozone process for which the model equations are best suited, although, if necessary, the user may simulate an ozone process that has multiple ozone application chambers. In setting up an ozone disinfection process, the user should enter an "Ozone" chemical feed point followed by a series of "Ozone Chamber" unit processes to provide contact time for oxidation and disinfection by the added ozone. The WTP Model assumes that the first "Ozone Chamber" is an ozone application chamber, where the dose is simply being transferred to the water. Ozone application chambers are typically lower in residence time (volume) than ozone dissipation chambers since their primary purpose is to carry-out mass transfer of the ozone.
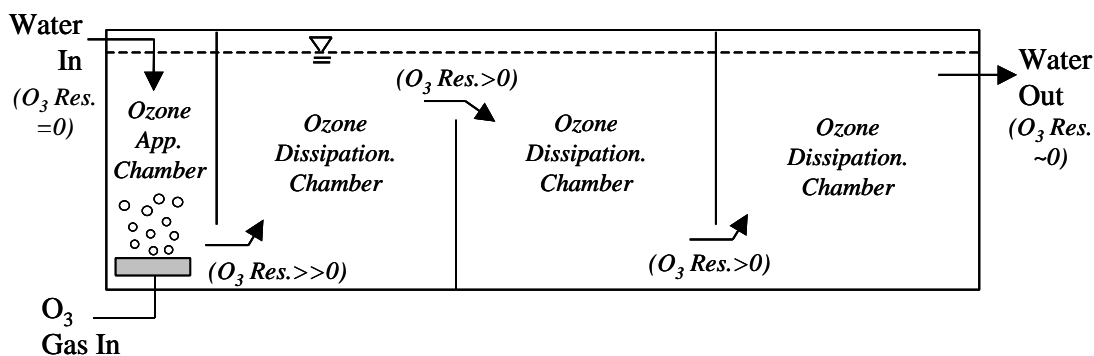
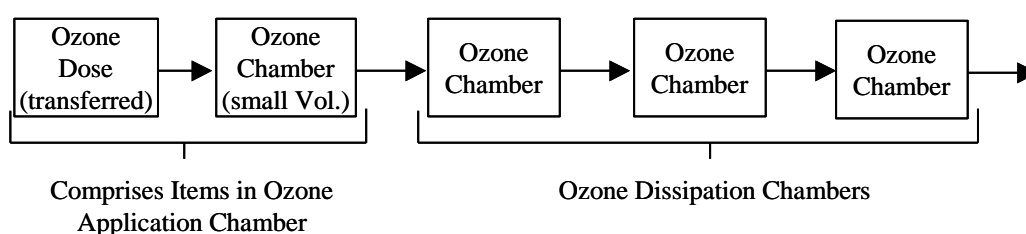**Figure 5-5a: Typical Ozone Dosing and Contacting System**

Figure 5-5b: Representation of an Ozone System as a Unit Process Sequence in WTP Model

Note that since the equation for ozone decay is independent of the ozone residual concentration, the WTP Model calculates decay in a single step through an "Ozone Chamber" (the chamber is not modeled as a series of CFSTRs in series for the purposes of decay calculations). Also, if the equation predicts an ozone residual less than 0.1 mg/L or the cumulative mean residence time since the last ozone dose exceeds two hours by the effluent of a given "Ozone Chamber," the WTP Model will set the predicted effluent ozone residual for that "Ozone Chamber" to zero. Finally, the WTP Model does not permit ozone residuals to persist through processes downstream of the last "Ozone Chamber."

Ozone Residual Prediction Verification

Ozone residual predictions were unable to be verified using the ICR database due to limitations in the amount of ozone data available through the ICR.

5.7   DBP FORMATION

Version 2.2 represents a significant improvement over the 1992 version of the WTP Model with respect to DBP formation algorithms. The THM formation algorithm in the 1992 version of the

WTP Model was much more limited in its direct applicability than the algorithms contained in this version 2.2. Limitations of the 1992 version THM formation algorithm include:

- THM formation equations were developed only from chlorination of raw water,
- The chlorine doses used in the model development studies were relatively high,
- The equations predicted THM concentrations on a molar basis, then were converted to a mass basis using a second empirical correlation,
- The model development database contained primarily low-bromide waters; this, coupled with the high chlorine doses used, created a model development database with large chlorine:bromide ratios, which led to observed THMs with generally low bromide incorporation (i.e. relatively high chloroform formation), and
- The model development database contained data collected from thirteen waters (Amy, et. al., 1987)

At the time of development of the 1992 version of the WTP Model, only limited data were available to develop predictive equations for HAAs. HAAs were predicted either by correlations with predicted THM formation or by empirically-developed equations from laboratory studies using one set of reaction conditions and one chlorine dose.

Version 2.2 of the WTP Model simulates the formation of THMs, HAAs and TOX within a water treatment plant and distribution system under a broad range of treatment scenarios. The primary challenge in developing a program to simulate DBP formation is that the only models currently available that require a manageable number of inputs are empirical in nature. Therefore, in order to develop a program with a sufficiently high level of accuracy to be useful, a large number of empirical DBP formation algorithms covering a range of specific treatment scenarios was required. Version 2.2 of the WTP Model contains DBP formation algorithms generated with observed data from chlorination of the following specific water types:

- Raw water
- Ozonated raw water
- Pre-chlorinated water (simultaneous chlorination and coagulation)
- Coagulated, precipitatively-softened, or bio-treated water
- Re-chlorinated, pre-chlorinated water
- GAC adsorption-treated or nanofiltered water

All of the empirical DBP formation algorithms were developed using data from bench- and/or pilot-scale chlorination experiments. Algorithms were then verified with an independent set of data, whenever possible, again from small-scale experiments. Algorithm predictions were then adjusted with calibration factors based on comparison of WTP Model predictions with observations from the Information Collection Rule (ICR) database. The intent of this calibration was to "scale-up" the algorithms to better represent full-scale DBP formation behavior.

The WTP Model predicts THM, HAA, and TOX formation with both free chlorination and chloramination. The model predicts values for the four THM species as well as the nine HAA species. In general, the WTP Model bases THM, HAA, and TOX predictions on the following water quality and treatment variables (specific parameters used for each algorithm vary - see subsequent sub-sections):

- Natural organic matter, as represented by:
  - Total organic carbon (TOC) concentration
  - Absorbance of ultraviolet light at 254 nm (UVA)
- Chlorine dose (Cl_2) - not residual
- Bromide ion (Br^-) concentration
- pH
- Water temperature ($Temp$)
- Reaction time ($time$)

The following general notes apply to the WTP Model's simulation of DBP formation:

- DBP formation under chloraminated conditions is calculated as a factor (less than unity) applied to the results of the free chlorine DBP formation equations.
- Separate equations for DBP formation in the distribution system do not exist. The distribution system is considered to be merely an extension of the plant, and DBP formation is assumed to follow the same formation kinetics and rates (with the exception of distribution-specific ICR-derived calibration factors for several DBP species as listed in **Table 5-12**)
- Version 2.2 of the WTP Model also predicts bromate formation during ozonation and chlorite formation during chlorine dioxide treatment.
- The WTP Model does not consider removal or decay of DBPs already formed.

5.7.1 DBP Formation Modeling Under Different Treatment Conditions

As noted in the previous section, version 2.2 of the WTP Model contains six different sets of THM, HAA, and TOX (collectively referred to as "DBPs" in this sub-section) formation equations to cover various treatment scenarios. This sub-section describes under what conditions the WTP Model applies the different DBP formation algorithms. Note that in the following descriptions, the terms "chlorination" and "chlorinated" cover both free chlorine and chloramines addition.

1. <u>Raw Water Algorithm</u>: The WTP Model uses this set of equations to predict DBP formation in chlorinated waters upstream of any TOC-removal treatment processes. As soon as a TOC removal process, such as coagulation, precipitative softening, biofiltration, GAC adsorption, or nanofiltration, is reached, this algorithm is no longer used. For treatment trains that do not possess any TOC-removal processes, the WTP Model uses these equations to simulate DBP formation through the entire treatment plant and distribution system. The most typical use of these equations is in two scenarios: (1) simulation of DBP formation within a raw water pipeline/impoundment or pre-sedimentation basin that receives upstream chlorination, and (2) chlorination of groundwater that never is subjected to a TOC-removal process.

2. <u>Ozonated Raw Water Algorithm</u>: The WTP Model uses this algorithm for the very specific case of modeling DBP formation in raw water that has been ozonated and chlorinated, but not yet subjected to a TOC-removal process. Therefore, the most common use of this algorithm is for DBP formation simulation within a raw water ozone contacting system in which a chlorine residual is also present. This algorithm is *not* used in cases where ozonated water was previously subjected to a TOC removal process. In those cases, the corresponding algorithm for DBP formation for water treated by that TOC removal process is used instead.

3. <u>Pre-chlorinated Water Algorithm:</u> This algorithm was incorporated into the WTP Model to address a treatment scenario common to conventional surface water plants that involves simultaneous chlorination and coagulation. The algorithm uses the same equations as the raw water algorithm (with input TOC and UVA values representative of water entering the rapid mix), but with an adjustment factor that is dependent upon the amount of TOC removed during coagulation. The algorithm is used to predict DBP formation within a rapid mix basin and within a limited number of downstream unit processes (most commonly flocculation basins and sedimentation basins) for the case where chlorine is introduced upstream or directly downstream of a rapid mix. The WTP Model uses this algorithm to predict DBPs in unit processes

downstream of the rapid mix until one of the following "triggers" is encountered in the treatment train: another chlorine dose, any type of filtration unit process, or GAC adsorption. Once one of these trigger points occurs in the downstream treatment train, the WTP Model simulates subsequent DBP formation with one of the following algorithms:

   a. *Coagulated Water Algorithm* - when any type of filtration unit process is the first downstream trigger point,

   b. *Re-chlorinated, Pre-chlorinated Water Algorithm* - when a single re-chlorination dose is the first downstream trigger point; this algorithm is also used downstream of the first re-chlorination point to follow a filtration process that is the first downstream trigger point.

   c. *GAC/Nanofiltered Water Algorithm* - when a GAC adsorption or nanofiltration unit process is the first downstream trigger point.

4. <u>Coagulated Water Algorithm</u> (includes also precipitatively softened or biofiltered water) - This algorithm is the most utilized of the WTP Model's DBP formation algorithms. This algorithm's prime use is simulating DBP formation in chlorinated water previously treated by coagulation. It is also used when the previous treatment is precipitative (lime) softening, ozone biofiltration, or slow sand biofiltration. As indicated in #3 above, this algorithm will pick-up when the Pre-chlorinated Water Algorithm leaves off at any type of filtration unit process. This algorithm is superseded by the GAC/Nanofiltered Water Algorithm for simulating formation in processes downstream of a GAC adsorption or nanofiltration process.

5. <u>Re-chlorinated, Pre-chlorinated Water Algorithm:</u> This algorithm was developed for the WTP Model to cover the relatively common, but very specific, treatment scenario defined by a single re-chlorination dose following pre-chlorination, where "pre-chlorination" is defined as in the Pre-chlorinated Water Algorithm discussion above (except that in this case, a chlorine dose upstream of the rapid mix must be applied *directly* upstream - i.e. no significant residence time between the upstream chlorine dose and the rapid mix). This algorithm uses the Coagulated Water Algorithm's base equations, with adjustment factors to account for the effects of previous pre-chlorination. The most common application of this algorithm is for DBP formation simulation within a conventional treatment plant's sedimentation basins, filters, and/or clearwell and within the distribution system for the case where pre-chlorination is used and chlorine residual is boosted with a single dose to gain sufficient primary disinfection CT or to provide an adequate residual for secondary disinfection. As soon as a second re-chlorination point is

encountered within a pre-chlorination plant's treatment train, the WTP Model no longer uses this algorithm is no longer used; the Coagulated Water Algorithm would take-over that such a point. The user should be aware that the equations in this algorithm were not able to be verified with an independent data set prior to incorporation within the WTP Model.

6. <u>GAC/Nanofiltered Water Algorithm</u> - This algorithm was developed for the WTP Model for simulating DBP formation in the low-TOC, low-UVA waters typically produced by GAC adsorption and nanofiltration treatment processes. The database used to develop these equations, a segment of the ICR Treatment Studies (Hooper et al., 2002) database, consisted of waters with TOC less than 2 mg/L. Therefore, the WTP Model uses this algorithm for simulating DBP formation in all processes and distribution system locations downstream of either of these processes if the treated water TOC is less than or equal to 2 mg/L. For GAC-treated or nanofiltered waters with TOC levels greater than 2 mg/L, the WTP Model uses the Coagulated Water Algorithm, which was developed from a database with more representative TOC values. Once GAC or nanofiltration has occurred within a treatment train, this algorithm will remain in effect for DBP formation simulation for all downstream processes to follow.

5.7.2   DBP Formation Modeling Through a Treatment Process Train

This section describes the approach that the WTP Model uses to calculate DBP formation through a simulated water treatment process train in a sequential fashion, unit process by unit process.

5.7.2.1 Unit Process Delta DBP Formation Approach

The WTP Model's empirical DBP formation equations are non-linear regression equations generally of the following form (this exact form is not used in all cases - for details, see subsequent discussions of individual algorithm equations):

$$DBP = A(TOC \times UVA)^a \left(Cl_2\right)^b \left(Br^-\right)^c \left(Temp\right)^d \left(pH\right)^e \left(time\right)^f$$

where, in the regression analysis of experimental data for equation development, all the independent variable values are taken at the point of chlorination, except for *time*. This was done because *TOC*, *Temp*, and *pH* either remained, or were held roughly, constant over time in the experimental work; *UVA*, and *Br*- only needed to be defined at the point of chlorination; and *Cl₂* (dose) was defined at that point by default. However, within a water treatment plant, as represented by the WTP Model, the values of *pH* and *UVA* can change while a given DBP formation algorithm is in effect due to the application of other chemicals, such as acids/bases and oxidants. Therefore,

in order to predict DBP formation through multiple unit processes, each of which may have a different *pH*, the WTP Model predicts the change (delta) in DBPs across that process. The WTP Model does this by using the regression equations to predict the influent and effluent DBP concentrations for a given unit process and subtracting to find the change. The values of the *TOC*, *Cl₂*, *Br⁻*, and *Temp* variables are defined at the last point of chlorination, while the *UVA* and *pH* values defined are those associated with the unit process in which the DBP change is being calculated. Furthermore, the values of the time variable are those as measured from the point of chlorination ("time zero") to the influent and the effluent of the unit process being simulated. The changes in DBPs across the unit process are then added to the DBP values at the effluent of the previous unit process to calculate the DBP values at the effluent of the current process. **Figure 5-6** graphically illustrates this method as applied to the example case of a *pH* change where the Coagulated Water algorithm is in effect.
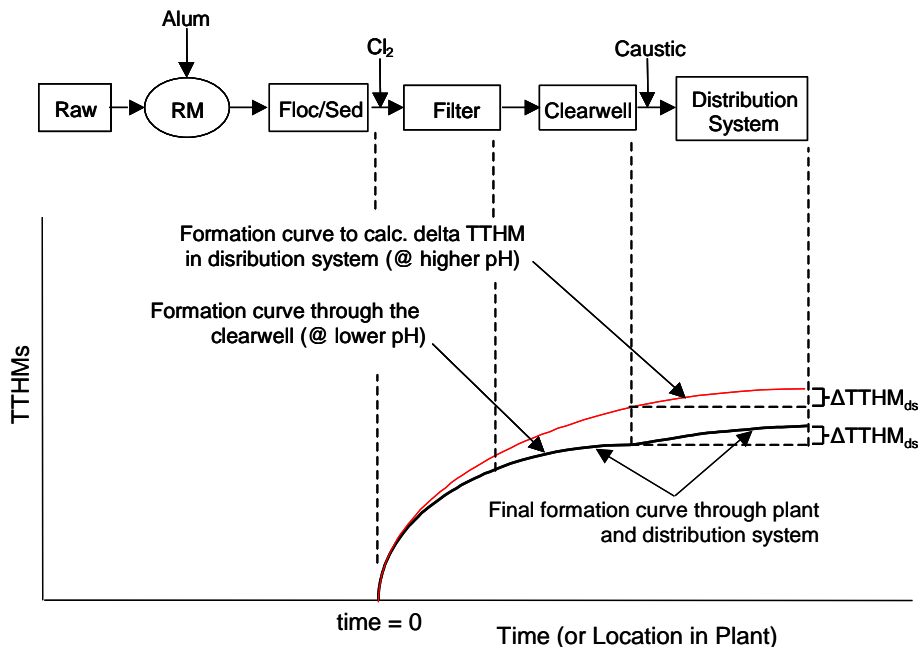
Figure 5-6: Illustration of Unit Process Delta DBP Formation Modeling Approach

5.7.2.2 Re-chlorination

The WTP Model's Re-chlorinated, Pre-chlorinated Water Algorithm predicts DBP formation from a single re-chlorination point following a pre-chlorination process. This is the only specific instance of re-chlorination for which version 2.2 of the WTP Model has an algorithm that is based upon an analysis of experimental data. To simulate the general case of multiple points of

chlorination, referred to herein simply as "re-chlorination," the WTP Model uses the other DBP formation algorithms in the following manner:

1. DBP formation following a point of re-chlorination is simulated using equation input values where water quality parameters (TOC, UVA, bromide, pH, and temperature) are defined at the point of re-chlorination.

2. The chlorine dose input parameter value is taken as the sum of the chlorine residual just upstream of the re-chlorination dose, plus the re-chlorination dose.

3. The "time zero" point from which the DBP formation equation time input parameter values are calculated is set as the point of re-chlorination.

Figure 5-7 illustrates the WTP Model's calculation process for multiple points of chlorination. The WTP Model accounts for the consumption of DBP precursor reactive species due to a prior point of chlorine addition by reducing UVA as described in **Section 5.5.8**. This has the effect of reducing the amount of DBPs that would otherwise be predicted by the Coagulated Water Algorithm at a re-chlorination point; however, because the WTP Model re-sets the "time zero" point on the DBP formation curves (which are steeper at low time values) at each new point of chlorination, the WTP Model is more likely to over-predict DBP formation as the number of re-chlorination points in a simulated process train increases.
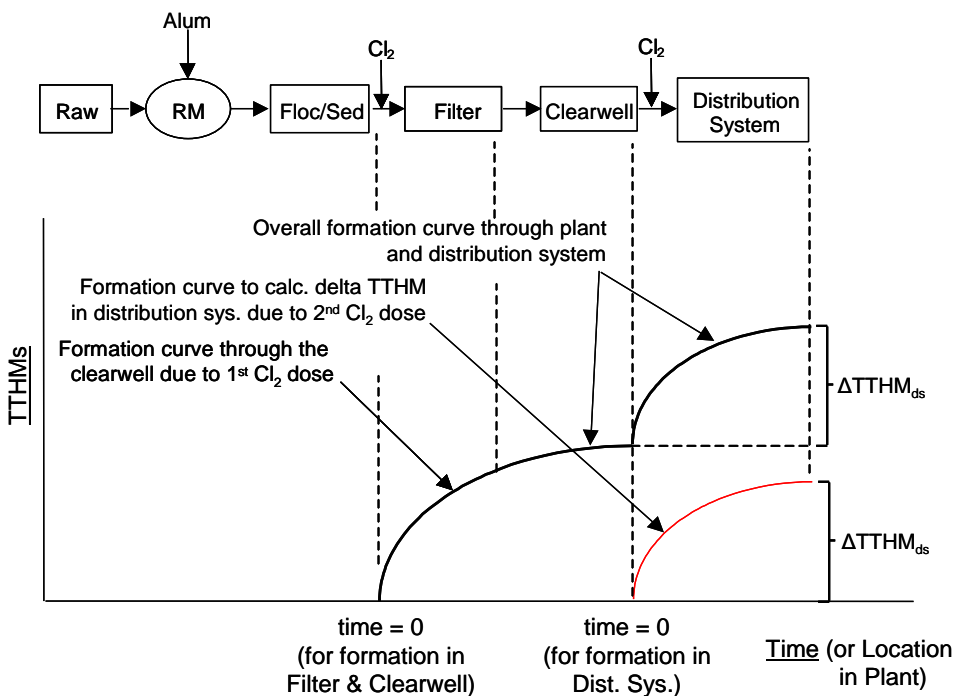

Figure 5-7: Illustration-Multiple Chlorination Points DBP Formation Modeling Approach

5.7.2.3 Bromide Incorporation

Bromide ion's impact on DBP formation and speciation has been evaluated in many studies. At increased bromide concentrations, the speciation shifts towards more brominated DBP species since bromide is incorporated into the organic DBP precursors at a faster rate than is chlorine. The WTP Model's empirical equations inherently account for the decrease in available bromide ion as DBP formation reactions proceed from a single point of chlorination. However, the WTP Model explicitly tracks bromide incorporation into DBPs in order to have a more accurate accounting of the bromide ion concentration for DBP formation with downstream re-chlorination points. To track the reduction in bromide ion concentration, the model converts DBP mass concentrations to molar concentrations to determine the bromide incorporation on a molar basis. The molar bromide incorporation is then converted to a mass basis, and subtracted from the bromide concentration at the influent of the unit process. This new bromide concentration is then used as the influent to the following unit process. When a re-chlorination point is encountered, the WTP Model uses the calculated new (reduced) bromide ion concentration at that point in DBP formation equations and continues tracking bromide incorporation. Version 2.2 of the WTP Model does not account for bromide oxidation by chlorine.

5.7.3   Predicting DBP Species and Bulk Parameters

The WTP Model generally uses separate empirical regression equations to predict concentrations of both DBP bulk parameters, such as TTHM, and individual DBP species, such as chloroform. Because the predictions are generated from separate equations, the sum of the predicted individual species concentrations is not necessarily equal to the predicted value of the corresponding bulk parameter for the same set of input values to all the equations. Furthermore, because bulk parameter equations were generally found during model development verification analyses to be more accurate in predicting observed bulk parameter concentrations than was the sum of the individually-predicted species concentrations, and regulatory focus has been on bulk parameter concentrations, the WTP Model uses the predicted individual species concentrations only for predicting the *relative* values of the individual species. That is, the bulk parameter equation results are used to set the total value to which the individual species are forced to sum.

The predictions for HAA5 and HAA9 are dependent on bulk parameter predictions of TTHM and HAA6 and their individual species. HAA5 is calculated as the predicted HAA6 value from a bulk parameter equation minus the calculated value of bromochloroacetic acid (BCAA), where BCAA is

calculated based on HAA6 as described above. HAA9 is calculated based on the HAA5 prediction plus the four remaining HAA species. The prediction of these four HAA species based on bromide incorporation assumptions and the concentration of individual species from the TTHM and HAA5 groups (see **Section 5.7.10**). HAA9 is the only bulk parameter that is not predicted by a power law regression equation.

The following summarizes the WTP Model's steps in calculating the increase in DBP bulk parameter and species values across a unit process:

1. Individual equations (see **Sections 5.7.4** through **5.7.10**) are used to predict preliminary ΔDBP values for:
   a. TTHM
   b. All four DBP species
   c. HAA6
   d. All six HAA6 species
   e. All four HAA9 species not included in HAA5

2. Correction factors per ICR calibration are applied to all ΔDBP values, except those for HAA9, the four HAA9 species not included in HAA5, and TOX. Under free chlorine conditions, this results in final predictions for ΔTTHM and ΔHAA6.

3. If applicable, ICR-derived factors to convert all ΔDBP values from those corresponding to free chlorine formation conditions to those for chloraminated conditions are applied. Under chloraminated conditions, this results in final predictions for ΔTTHM and ΔHAA6.

4. Final ΔDBP values for the four TTHM species are calculated by forcing their sum to equal the final predicted value of ΔTTHM, while maintaining the same relative proportions among the species. Final ΔDBP values for the six HAA6 species are calculated similarly.

5. The final ΔHAA5 value is calculated as final ΔHAA6 minus final ΔBCAA.

6. The final ΔHAA9 value is calculated as the predicted final ΔHAA5 value (from Step *#2/#3*) plus the individual species values predicted in Steps *#1e*, which are calculated based on individual species predicted in Steps *#1b* and *#1d*.

Example.

Consider the case where application of the individual THM equations generate the following preliminary ΔDBP predictions across a "Reservoir" unit process under free chlorine conditions, as follows:

$$95\mu g/L = \Delta total\ trihalomethanes\ (\Delta TTHM)$$

$$50 \ \mu g/L = \Delta chloroform \ (\Delta CHCl_3)$$

$$25 \ \mu g/L = \Delta bromodichloromethane \ (\Delta BDCM)$$

$$20 \ \mu g/L = \Delta dibromochloromethane \ (\Delta DBCM)$$

$$5 \ \mu g/L = \Delta bromoform \ (\Delta CHBr_3)$$

The preliminary ΔDBP predictions are then modified by the appropriate ICR calibration factors (applicable to in-plant formation), as follows:

$$95 \mu g/L \div 0.77 = 123.5 \ \mu g/L \ = \Delta TTHM$$

$$50 \ \mu g/L \div 1.00 = 50.0 \ \mu g/L \ = \Delta CHCl_3$$

$$25 \ \mu g/L \div 0.50 = 50.0 \ \mu g/L \ = \Delta BDCM$$

$$20 \ \mu g/L \div 0.86 = 23.2 \ \mu g/L \ = \Delta DBCM$$

$$5 \ \mu g/L \ \div 1.00 = 5.0 \ \mu g/L \ = \Delta CHBr_3$$

The sum of the four individual ΔDBP species predictions is then calculated as 50.0 + 50.0 + 23.2 + 5.0 = 128.2 μg/L. The ratio of the predicted value for ΔTTHM to the sum of the ΔDBP values for the four species is then calculated as 123.5 μg/L divided by 128.2 μg/L, which yields 0.963. This ratio is applied to each of the ICR-calibrated preliminary predictions for the individual species to calculate final ΔDBP predictions for the four species as shown below:

$$50.0 \ \mu g/L \times 0.963 = 48.2 \ \mu g/L \ = \Delta CHCl_3$$

$$50.0 \ \mu g/L \times 0.963 = 48.2 \ \mu g/L \ = \Delta BDCM$$

$$23.2 \ \mu g/L \times 0.963 = 22.3 \ \mu g/L \ = \Delta DBCM$$

$$5.0 \ \mu g/L \ \times 0.963 = \underline{4.8 \ \mu g/L} \ = \Delta CHBr_3$$

123.5 μg/L = sum of ΔDBP values for the 4 species = ΔTTHM

5.7.4   Free Chlorine DBPs: Raw Water Algorithm Equations

Empirical equations predicting THMs (total and four species) and HAA6 (and six species) based on low to moderate chlorine doses applied to raw/untreated water were developed by Amy et al. (1998). Water quality parameters such as TOC, UVA, bromide, pH, and temperature, as well as applied chlorine dose and reaction time, are used to model DBP formation.

THMs

$$TTHM = 4.121 \times 10^{-2} (TOC)^{1.098} (Cl_2)^{0.152} (Br^-)^{0.068} (Temp)^{0.609} (pH)^{1.601} (time)^{0.263} \qquad \textbf{(5-132)}$$

$$(R^2_{adj} = 0.90, \ F = 1198, \ n = 786)$$

where,

TOC = total organic carbon (mg/L): $1.2 \leq TOC \leq 10.6$

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \leq UVA \leq 0.318$

Cl_2 = applied chlorine dose (mg/L): $1.51 \leq Cl_2 \leq 33.55$

Br^- = bromide concentration (µg/L): $7 \leq Br^- \leq 600$

$Temp$ = temperature (°C): $15 \leq Temp \leq 25$

pH: $6.5 \leq pH \leq 8.5$

$time$ = reaction time (hours): $2 \leq time \leq 168$

The equations for the 4 THM species have a similar form, shown in **Equation 5-133**. The coefficients and regressions statistics for the equations are given in **Table 5-3**.

$$THM = A(TOC)^a (Cl_2)^b (Br^-)^c (Temp)^d (pH)^e (time)^f \qquad \textbf{(5-133)}$$

Table 5-3   Coefficients and Regression Statistics for Raw Water THM Species Equations

THM Species	*Coefficients for Equation 5-133*						
	A	*a*	*b*	*c*	*d*	*e*	*f*
CHCl$_3$	6.237x10^{-2}	1.617	-0.094	-0.175	0.607	1.403	0.306
BDCM	1.445x10^{-3}	0.901	0.017	0.733	0.498	1.511	0.199
DBCM	2.244x10^{-6}	-0.226	0.108	1.810	0.512	2.212	0.146
CHBr$_3$	1.49x10^{-8}	-0.983	0.804	1.765	0.754	2.139	0.566

THM Species	*Regression Statistics*		
	R^2_{adj}	*F*	*n*
CHCl$_3$	0.87	847	786
BDCM	0.90	1164	786
DBCM	0.89	1087	786
CHBr$_3$	0.61	199	786

HAAs

The same empirical equation format was used for HAA predictive equations in raw waters using the same database as was used for THM formation. **Equation 5-134** shows the equation for HAA6 predictions:

$$HAA6 = 9.98(TOC)^{0.935}(Cl_2)^{0.443}(Br^-)^{-0.031}(Temp)^{0.387}(pH)^{-0.655}(time)^{0.178} \qquad \textbf{(5-134)}$$

$$(R^2_{adj} = 0.87,\ F = 831,\ n = 738)$$

where,

TOC = total organic carbon (mg/L): $1.2 \leq TOC \leq 10.6$

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \leq UVA \leq 0.318$

Cl_2 = applied chlorine dose (mg/L): $1.51 \leq Cl_2 \leq 33.55$

Br^- = bromide concentration (µg/L): $7 \leq Br^- \leq 600$

$Temp$ = temperature (°C): $15 \leq Temp \leq 25$

pH: $6.5 \leq pH \leq 8.5$

$time$ = reaction time (hours): $2 \leq time \leq 168$

Individual HAA species equations were developed in similar format and are generally described by **Equation 5-135**. The equation coefficients and regression statistics are given in **Table 5-4**.

$$HAA = A(TOC)^a(Cl_2)^b(Br^-)^c(Temp)^d(pH)^e(time)^f \qquad \textbf{(5-135)}$$

Boundary conditions for reaction time, temperature, and pH should be noted. Due to a lack of data, the equations were only developed for reaction times longer than two hours, temperatures between 15 and 25°C, and pH values between 6.5 and 8.5. For cases where the WTP Model is used to simulate treatment conditions outside these ranges, the equations will be used outside their boundary conditions, which will result in increased uncertainty in predictions.

The method for HAA9 prediction and the four species not included in HAA5, is calculated based on the method described in **Section 5.7.10**.

Table 5-4 Coefficients and Regression Statistics for Raw Water HAA Species Equations

HAA Species	*Coefficients for Equation 5-135*						
	A	*a*	*b*	*c*	*d*	*e*	*f*
MCAA	0.45	0.173	0.379	0.029	0.573	-0.279	0.009
DCAA	0.30	1.396	0.379	-0.149	0.465	0.200	0.218
TCAA	92.68	1.152	0.331	-0.2299	0.299	-1.627	0.180
MBAA	6.21×10^{-5}	-0.584	0.754	1.10	0.707	0.604	0.090
DBAA	3.69×10^{-5}	-1.087	0.673	2.052	0.380	-0.001	0.095
BCAA	5.51×10^{-3}	0.463	0.522	0.667	0.379	0.581	0.220

HAA Species	*Regression Statistics*		
	R^2_{adj}	*F*	*n*
MCAA	0.14	18	738
DCAA	0.83	589	738
TCAA	0.87	821	738
MBAA	0.43	83	738
DBAA	0.77	360	738
BCAA	0.76	370	738

5.7.5   Free Chlorine DBPs: Ozonated Raw Water Algorithm Equations

Empirical equations predicting TTHM (and four THM species) and HAA6 (and six HAA species) based on chlorination of raw water were developed specifically to address DBP formation in raw, ozonated water. The equations were developed based on data by Amy et al. (1998). The equations were specifically developed with UVA representing NOM, so that the WTP Model's predictions in this treatment scenario would account for ozonation's ability to reduce UVA (and subsequent chlorinated DBP formation). The reason that the WTP Model does not use the Raw Water Algorithm to cover raw, ozonated water is that it does not have a *UVA* term; that algorithm represents NOM with a *TOC* term since that parameter produced an equation with the best fit to the data.

THMs

Equation 5-136 presents the Ozonated Raw Water Algorithm's TTHM equation:

$$TTHM = 4.12 \times 10^{-1} (UVA)^{0.482} (Cl_2)^{0.339} (Br^-)^{0.023} (Temp)^{0.617} (pH)^{1.609} (time)^{0.261} \qquad \textbf{(5-136)}$$

$$(R^2_{adj} = 0.70,\ F = 305,\ n = 786)$$

where,

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \le UVA \le 0.318$

Cl_2 = applied chlorine dose (mg/L): $1.51 \le Cl_2 \le 33.55$

Br^- = bromide concentration (μg/L): $7 \le Br^- \le 600$

$Temp$ = temperature (°C): $15 \le Temp \le 25$

pH: $6.5 \le pH \le 8.5$

$time$ = reaction time (hours): $2 \le time \le 168$

The Ozonated Raw Water Algorithm's equations for the 4 THM species have a similar form, shown in **Equation 5-137**. The coefficients and regressions statistics for the equations are given in **Table 5-5**.

$$THM = A(UVA)^a (Cl_2)^b (Br^-)^c (Temp)^d (pH)^e (time)^f \qquad \textbf{(5-137)}$$

Table 5-5 Coefficients and Regression Statistics for Ozonated Raw Water THM Species Equations

THM Species	Coefficients for Equation 5-137						
	A	*a*	*b*	*c*	*d*	*e*	*f*
CHCl$_3$	1.247	0.604	0.286	-0.242	0.619	1.42	0.304
BDCM	1.96x10^{-2}	0.590	-0.022	0.697	0.505	1.52	0.196
DBCM	2.02x10^{-6}	-0.005	-0.024	1.820	0.510	2.21	0.146
CHBr$_3$	5.41x10^{-10}	-0.722	0.926	1.804	0.741	2.16	0.571

THM Species	Regression Statistics		
	R^2_{adj}	*F*	*n*
CHCl$_3$	0.61	199	786
BDCM	0.88	915	786
DBCM	0.89	1072	786
CHBr$_3$	0.61	199	786

HAAs

The same empirical equation format was used to develop HAA predictive equations for ozonated raw water applications using the same database as was used for THM formation. **Equation 5-138** shows the equation for HAA6 predictions:

$$HAA6 = 171.4(UVA)^{0.584}(Cl_2)^{0.398}(Br^-)^{-0.091}(Temp)^{0.396}(pH)^{-0.645}(time)^{0.178}$$ **(5-138)**

$$(R^2_{adj} = 0.80,\ F = 486,\ n = 738)$$

where,

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \leq UVA \leq 0.318$

Cl_2 = applied chlorine dose (mg/L): $1.51 \leq Cl_2 \leq 33.55$

Br^- = bromide concentration (µg/L): $7 \leq Br^- \leq 600$

$Temp$ = temperature (°C): $15 \leq Temp \leq 25$

pH: $6.5 \leq pH \leq 8.5$

$time$ = reaction time (hours): $2 \leq time \leq 168$

Individual HAA species equations were developed in similar format and are generally described by **Equation 5-139**. The equation coefficients and regression statistics are given in **Table 5-6**.

$$HAA = A(UVA)^a(Cl_2)^b(Br^-)^c(Temp)^d(pH)^e(time)^f$$ **(5-139)**

Like the Raw Water Algorithm, WTP Model users should be wary about using the model to simulate treatment conditions where this algorithm will be applied outside of the boundary conditions used in equation development. Finally, the equations of the Ozonated Raw Water Algorithm were included in the process that used ICR data to calibrate the WTP Model; therefore, the ICR calibration factors discussed in **Section 5.7.11** are applied to the results of these equations within the WTP Model.

The method for HAA9 prediction and the four species not included in HAA5, is calculated based on the method described in **Section 5.7.10**.

Table 5-6 Coefficients and Regression Statistics for Ozonated Raw Water HAA Species Equations

| HAA Species | *Coefficients for Equation 5-139* | | | | | | |
	A	*a*	*b*	*c*	*d*	*e*	*f*
MCAA	1.39	0.256	0.194	0.038	0.571	-0.283	-0.008
DCAA	30.4	0.963	0.211	-0.238	0.474	0.212	0.219
TCAA	1.64×10^3	0.593	0.439	-0.305	0.317	-1.613	0.180
MBAA	1.23×10^{-5}	-0.318	0.728	1.15	0.701	0.598	0.090
DBAA	1.75×10^{-6}	-0.607	0.650	2.14	0.353	-0.012	0.093
BCAA	7.20×10^{-2}	0.578	0.121	0.675	0.375	0.578	0.222

| HAA Species | *Regression Statistics* | | |
	R^2_{adj}	*F*	*n*
MCAA	0.16	21	738
DCAA	0.78	429	738
TCAA	0.73	330	738
MBAA	0.41	78	738
DBAA	0.74	370	738
BCAA	0.83	540	738

5.7.6   Free Chlorine DBPs: Pre-chlorinated Water Algorithm Equations

To predict DBP formation for pre-chlorination plants, an empirical pre-chlorination factor was developed, using data from 20 waters (Summers et al., 1998b), to account for the decrease in DBP formation that occurs when chlorine is added either pre- or post-rapid mixing (RM), as compared to chlorine addition to raw water without simultaneous coagulation. This relationship is used to modify the DBP formation that would be predicted by the Raw Water DBP formation Algorithm equations. The percent decrease in DBP formation (compared to raw water DBP formation) that can be attributed to coagulation was related to the percentage of TOC removal by coagulation, to account for the effects of varying precursor removals during coagulation.

$$Decrease\ in\ TTHM\ Formation\ (\%) = 0.875(\%\ TOC\ Removal) \qquad \textbf{(5-140)}$$

$$(R^2_{adj} = 0.62,\ SEE = 0.09\ \%,\ F = 37,\ n = 60)$$

$$Decrease\ in\ HAA\ Formation\ (\%) = 0.776 (\%\ TOC\ Re\ moval)\qquad\text{(5-141)}$$

$$(R^2_{adj} = 0.58,\ SEE = 0.09\ \%,\ F = 16\ ,\ n = 41)$$

$$Decrease\ in\ TOX\ Formation\ (\%) = 0.865 (\%\ TOC\ Re\ moval)\qquad\text{(5-142)}$$

$$(R^2_{adj} = 0.31,\ SEE = 0.11\ \%,\ F = 19,\ n = 43)$$

For the 20 waters used in the equation development, the average decreases for TTHM and HAA6 were predicted by the above equations to be 24 and 22 percent, respectively. This corresponds well with the average TTHM and HAA6 decreases reported by Solarik et al. (1997b) of 23 and 18 percent, respectively. The Pre-chlorinated Water Algorithm equations were not verified due to a lack of available independent verification data. However, the equations were included in the process that used ICR data to calibrate the WTP Model; therefore, the ICR calibration factors discussed in **Section 5.7.11** are applied to the results of these equations within the WTP Model.

5.7.7   Free Chlorine DBPs: Coagulated Water Algorithm Equations

New DBP formation equations, based on work performed by Amy et al. (1998) using both iron and alum coagulated waters, were incorporated into version 2.2 of the WTP Model. As noted previously, the WTP Model uses these equations to predict DBP formation in coagulated waters, lime-softened waters, and biofiltered waters (both ozone-biofiltered and slow sand filtered water). These equations are also used for GAC-treated and/or nanofiltered waters with effluent TOC greater than 2.0 mg/L. These DBP formation equations include the combined TOC and UVA ($TOC{\times}UVA$) input parameter. The $TOC{\times}UVA$ input parameter accounts for the impact of treatment on NOM removal as well as NOM characteristics, i.e., reactivity. The boundary conditions for these equations are similar to those of the Raw Water Algorithm. Insufficient pH and temperature-dependent data were available to develop DBP formation equations for treated waters. Instead, temperature and pH factors were developed from raw water data and applied to the treated water equations. However, these factors are only valid in the 15 to 25°C temperature range and the 6.5 to 8.5 pH range. The user should be wary that when simulating enhanced coagulation or lime-softening treatment, the chance that the pH boundary conditions will be violated increases.

THMs

Equation 5-143 contains the equation used to predict TTHM formation:

$$TTHM = 23.9(TOC*UVA)^{0.403}(Cl_2)^{0.225}(Br^-)^{0.141}(1.1560)^{(pH-7.5)}(1.0263)^{(Temp-20)}(time)^{0.264}$$

(5-143)

(R^2 = 0.92, R^2_{adj} = 0.92, SEE = 0.218 µg/L, F = 798, n = 288)

The equations for the 4 THM species have a similar form, shown in **Equation 5-144**. The coefficients and regressions statistics for the equations are given in **Table 5-7**.

$$THM = A(TOC*UVA)^a(Cl_2)^b(Br^-)^c(D)^{(pH-7.5)}(E)^{(Temp-20)}(time)^f$$ **(5-144)**

Table 5-7   Coefficients and Regression Statistics for Coag. Water THM Species Equations

THM Species	*Coefficients for Equation 5-144*						
	A	*a*	*b*	*c*	*D*	*E*	*f*
CHCl$_3$	266	0.403	0.424	-0.679	1.1322	1.0179	0.333
BDCM	1.68	0.260	0.114	0.462	1.0977	1.0260	0.196
DBCM	8.0x10^{-3}	-0.056	-0.157	1.425	1.1271	1.0212	0.148
CHBr$_3$	4.4x10^{-5}	-0.300	-0.221	2.134	1.3907	1.0374	0.143

THM Species	*Regression Statistics*		
	R^2_{adj}	*F*	*n*
CHCl$_3$	0.90	682	288
BDCM	0.85	393	288
DBCM	0.94	948	245
CHBr$_3$	0.93	579	171

HAAs

Equation 5-145 presents the HAA6 formation equation for coagulated water based on work performed by Amy et al. (1998).

$$HAA6 = 30.7(TOC*UVA)^{0.302}(Cl_2)^{0.541}(Br^-)^{-0.012}(0.932)^{(pH-7.5)}(1.021)^{(Temp-20)}(time)^{0.161}$$

(5-145)

(R^2_{adj} = 0.94, F = 1040, n = 288)

where,

TOC = total organic carbon (mg/L): $1.00 \le DOC \le 7.77$

UVA = UV absorbance at 254 nm (1/cm): $0.016 \le UVA \le 0.215$

Cl_2 = applied chlorine dose (mg/L): $1.11 \le Cl_2 \le 24.75$

Br^- = bromide concentration (µg/L): $23 \le Br \le 308$

Temp = water temperature (°C): *Temp* = 20 °C

pH: 7.5

time = reaction time (hours): $2 \le time \le 168$

Individual HAA species equations were developed in similar format and are generally described by **Equation 5-146**. The equation coefficients and regression statistics are given in **Table 5-8**.

$$HAA = A(TOC * UVA)^a (Cl_2)^b (Br^-)^c (D)^{(pH-7.5)} (E)^{(Temp-20)} (time)^f \qquad \textbf{(5-146)}$$

The method for HAA9 prediction and the four species not included in HAA5, is calculated based on the method described in **Section 5.7.10**.

Table 5-8 Coefficients and Regression Statistics for Coag. Water HAA Species Equations

| HAA Species | *Coefficients for Equation 5-146* | | | | | | |
	A	*a*	*b*	*c*	*D*	*E*	*f*
MCAA	4.58	-0.090	0.662	-0.224	1.042	1.024	0.043
DCAA	60.4	0.397	0.665	-0.558	1.034	1.017	0.222
TCAA	52.6	0.403	0.749	-0.416	0.8739	1.014	0.163
MBAA	2.06×10^{-2}	0.358	-0.101	0.812	0.6526	1.162	0.043
DBAA	9.42×10^{-5}	0.0590	0.182	2.109	1.210	1.007	0.070
BCAA	3.23×10^{-1}	0.153	0.257	0.586	1.181	1.042	0.201

| HAA Species | *Regression Statistics* | | |
	R^2_{adj}	*F*	*n*
MCAA	0.27	28	288
DCAA	0.84	371	288
TCAA	0.90	642	288
MBAA	0.40	49	288
DBAA	0.82	323	288
BCAA	0.87	501	288

TOX

A new empirical correlation was developed for treated water TOX formation, shown by **Equation 5-148**. This equation was also developed from analysis of ICR Treatment Studies database, using GAC influent samples that were coagulated and softened only. The data used in development of the TOX equation included only the median values for each study. The WTP Model also uses this equation in the GAC-treated/Nanofiltered Water Algorithm (only for waters with treated TOC > 2.0 mg/L), the Raw Water Algorithm, the Ozonated Raw Water Algorithm, and the Pre-chlorinated Water Algorithm.

$$TOX = 109(TOC * UVA)^{0.362}(Cl_2)^{0.129}(Temp)^{0.211}(time)^{0.182} \tag{5-148}$$

$$(R^2_{adj} = 0.73,\ SEE = 269\ \mu g\ Cl^-/L,\ F = 267,\ n = 386)$$

where,

TOX = total organic halogen ($\mu g\ Cl^-/L$): $25 \le TOX \le 893$

TOC = total organic carbon (mg/L): $1.5 \le DOC \le 8.5$

UVA = UV absorbance at 254 nm (1/cm): $0.010 \le UVA \le 0.300$

Cl_2 = applied chlorine dose (mg/L): $1.3 \le Cl_2 \le 14$

$Br-$ = bromide concentration (μg/L): $10 \le Br- \le 665$

$Temp$ = temperature (°C): $3 \le Temp \le 20$

pH: $6.9 \le pH \le 9.5$

$time$ = reaction time (hours): $2.0 \le time \le 120$

It should be noted that the WTP Model does not apply full-scale plant ICR calibration factors to TOX predictions due to the limited full-scale plant ICR data available for TOX.

5.7.8   Free Chlorine DBPs: Re-chlorinated, Pre-chlorinated Water Algorithm Equations

Version 2.2 of the WTP Model incorporates adjustment factors applied to the predictions of the Coagulated Water Algorithm to account for the effects of pre-chlorination on DBP formation in coagulated water that is subsequently re-chlorinated. The adjustment factors were developed from an analysis of unpublished data from bench-scale work performed at the University of Colordo (Summers et al., 2005). The data set used was generated from three chlorination experiments for each of six waters. Of the three experiments for each water, two involved pre-chlorination followed by re-chlorination, and one involved post-chlorination only. To generate adjustment factors for DBP formation upon re-chlorination, the first step was to compare the predictions of the Coagulated

Water Algorithm equations for TTHMs, HAA6, HAA6 (for HAA9 species calculation), and HAA9 with the observed values of these DBPs in the experiments using post-chlorination only. From this comparison, a scalar correction factor was generated for each water. The Coagulated Water Algorithm equations, adjusted by these water-specific correction factors, were then used to predicted DBP formation following re-chlorination for the pre-chlorination/re-chlorination experiments. The ratio of these predictions to the observed formation values was then calculated and regressed against various parameters. The best predictor of this ratio (the inverse of which is the "adjustment factor" ultimately developed) for TTHM and HAA6 equations was the variable, "time since re-chlorination." That is, the Coagulated Water Algorithm equations for TTHM and HAA6 did not adequately represent the kinetics of DBP formation in water that had also been pre-chlorinated. However, the results for TTHM and HAA6 differed. While observed TTHM formation in re-chlorinated water was generally lower than would be predicted by the Coagulated Water Algorithm equation over all contact times out to 72 hours, or more, HAA6 formation was slower than predicted initially (out to about 12 hours) and then exceeded predicted values over the long contact times typically observed in distribution systems. This result was a direct product of the observations in Arias' work which showed that in many of the test waters, *more* HAA6 formation occurred after the point of re-chlorination (in pre-chlorinated water) than occurred after a single point of post-chlorination (in post-chlorination only) experiments with the chlorine dosing conditions targeting uniform formation conditions (UFC). This suggests that pre-chlorination may have inhibited the removal of HAA-specific precursors during coagulation. The amount of DBPs (TTHM or HAA6, as appropriate) formed during pre-chlorination was also included as a variable in the adjustment factor expression. This was included as an indicator of the amount of precursor exertion that occurred during pre-chlorination. This variable was found to be a much weaker predictor of the ratio of the Coagulated Water Algorithm equation predictions to the observed re-chlorination DBPs formed; however, it should be noted that dependency of the adjustment factor on this variable was opposite for TTHMs and HAA6, possibly for the same reason as noted above.

TTHM and HAA6

Equations 5-149 and **5-150** present the adjustment factors applied (by multiplication) to the Coagulated Water Algorithm equations for TTHM and HAA6 to generate TTHM and HAA6 equations for the Re-chlorinated, Pre-chlorinated Water Algorithm.

$$\textit{TTHM Rechlorination Factor} = 0.543 \times (\textit{PreCl}_2 \ \textit{TTHM})^{-0.0210} \times (\textit{time})^{0.143} \qquad \textbf{(5-149)}$$
$$(R^2_{adj} = 0.55, \ \textit{SEE} = 0.084, \ F = 19, \ n = 30)$$

$$HAA6\ Rechlorination\ Factor = 0.431 \times (PreCl_2\ HAA6)^{0.044} \times (time)^{0.240} \qquad \textbf{(5-150)}$$

$$(R^2_{adj} = 0.70,\ SEE = 0.10,\ F = 35,\ n = 30)$$

where,

TTHM Rechlor. Factor = factor applied to Coag. Water Alg. TTHM: $0.33 \leq Factor \leq 1.20$

PreCl$_2$ TTHM = TTHMs formed during pre-chlorination (μg/L): $15 \leq PreCl_2\ TTHM \leq 162$

time = contact time since point of re-chlorination (hours): $3 \leq time \leq 123$

HAA6 Rechlor. Factor = factor applied to Coag. Water Alg. HAA6: $0.44 \leq Factor \leq 1.94$

PreCl$_2$ HAA6 = HAA6 formed during pre-chlorination (μg/L): $15 \leq PreCl_2\ HAA6 \leq 168$

HAA9

The same process as described for TTHM and HAA6 above was executed for HAA9. However, the ratio of the predicted Coagulated Water Algorithm HAA9 formation to observed HAA9 formation after re-chlorination was not found to be a strong function of either of the variables used in the TTHM and HAA6 adjustment factors. The reason for this is that, in general, the HAA9 equation (with water-specific corrections based on data from the post-chlorination water only experiments) represented the central tendency of observed HAA9 formation after re-chlorination quite well ($R^2 = 0.95$ for a predicted versus observed data scatter plot). However, since the uncorrected Coagulated Water Algorithm HAA9 equation tended to slightly over-predict low HAA9 formation values and under-predict higher re-chlorination HAA9 formation values, an adjustment factor was developed as a function of the predicted formation value from the Coagulated Water Algorithm HAA9 equation. The same process was carried out for the Coagulated Water Algorithm HAA6 equation that is used only to develop final predictions for HAA9 and the three HAA9 species not included in HAA6. **Equations 5-151** and **5-152** below present the adjustment factors.

$$HAA9\ Rechlorination\ Factor = [1.16 - 0.0012 \times (Predicted\ HAA9\ Formation)]^{-1} \quad \textbf{(5-151)}$$

$$(R^2_{adj} = 0.06,\ SEE = 0.28,\ F = 2.2,\ n = 36)$$

$$HAA6\ Rechlorination\ Factor = [1.076 - 0.0016 \times (Predicted\ HAA6\ Formation)]^{-1} \quad \textbf{(5-152)}$$

$$(R^2_{adj} = 0.08,\ SEE = 0.27,\ F = 2.9,\ n = 36)$$

where,

HAA9 Rechlor. Factor = factor applied to Coag. Water Alg. HAA9: $0.53 \leq Factor \leq 1.55$

Predicted HAA9 Formation = HAA9 predicted to form during re-chlorination (μg/L):

$$8 \leq Pred.\ HAA9 \leq 242$$

HAA6 Rechlor. Factor = factor applied to Coag. Water Alg. HAA6: $0.58 \leq Factor \leq 1.71$

Predicted HAA9 Formation = HAA9 predicted to form during re-chlorination (μg/L):

$$7 \leq Pred.\ HAA9 \leq 204$$

Factors for the individual TTHM, HAA6, and HAA9 species were not developed. Instead, the WTP Model uses the unadjusted Coagulated Water Algorithm equations to predict relative species concentrations that are uniformly scaled to sum to the appropriate bulk parameter. Note also that predictions of TTHM, HAA6, and associated species are adjusted using the ICR-derived calibration factors for full-scale plants.

TOX

Predictions from the Coagulated Water Algorithm TOX equation were adjusted to predict formation in re-chlorinated, pre-chlorinated water. The WTP Model performs this adjustment by applying a weighted average of the TTHM and HAA6 correction factors.

5.7.9   Free Chlorine DBPs: GAC-Treated/Nanofiltered Water Algorithm Equations

One of the difficulties in modeling DBP formation of treated waters following specific treatment processes is a lack of sufficient data. In previous versions, the WTP Model did not uses separate equations for DBP predictions following advanced treatment processes, such as GAC adsorption. However, the ICR Treatment Studies (Hooper et al., 2002) database represented a significant resource available for development of new equations for GAC-treated and nanofiltered waters.

Version 2.2 of the WTP Model includes a separate algorithm with DBP formation equations for GAC-treated. These equations were developed using the ICR Treatment Studies database of individual samples, which contained approximately 4,000 records. The equations were developed for GAC effluent waters with TOC concentrations of less than or equal to 2.0 mg/L. Outliers and data with incomplete records were not used for equation development. A significant percentage of the data was reported as below the detection limit. This would be expected for GAC effluent with very low TOC concentrations. Instead of discarding all below detection limit data, the data were replaced with a value of one half of the detection limit. These equations were also found to predict

DBP formation in nanofiltered waters of the ICR Treatment Studies database; therefore, the equations were incorporated into a WTP Model algorithm for both GAC-treated and nanofiltered waters. Predictive equations were developed for individual THM species and TTHM, individual HAA species and HAA6, as well as for TOX.

THMs

Equation 5-153 shows the GAC-Treated/Nanofiltered Water Algorithm equation for TTHM. The format of the species equations is given by **Equation 5-154**, and the coefficients and regression statistics are shown in **Table 5-9**.

$$TTHM = 17.7(TOC*UVA)^{0.475}(Cl_2)^{0.173}(Br^-)^{0.246}(1.316)^{(pH-8.0)}(1.036)^{(Temp-20)}(time)^{0.366}$$

(5-154)

$$(R^2_{adj} = 0.83,\ SEE = 9.3\ \mu g/L,\ F = 2336,\ n = 2946)$$

$$THM = A(TOC*UVA)^a(Cl_2)^b(Br^-)^c(D)^{(pH-7.5)}(E)^{(Temp-20)}(time)^f \qquad \textbf{(5-155)}$$

Table 5-1   Coefficients and Regression Stats. for GAC-Treated/Nanofiltered Water THM Species Equations

THM Species	Coefficients for Equation 5-155						
	A	a	b	c	D	E	f
$CHCl_3$	101.0	0.615	0.699	-0.468	1.099	1.035	0.336
BDCM	7.57	0.443	0.563	0.0739	1.355	1.030	0.281
DBCM	3.99	0.535	0.125	0.365	1.436	1.037	0.322
$CHBr_3$	1.47×10^{-1}	0.408	-0.115	0.961	1.438	1.048	0.324

THM Species	Regression Statistics			
	R^2_{adj}	$SEE\ (\mu g/L)$	F	n
$CHCl_3$	0.73	4.3	1320	2960
BDCM	0.58	4.1	678	2959
DBCM	0.73	3.9	1338	2948
$CHBr_3$	0.77	4.8	1642	2948

HAAs

Equations 5-156 and 5-157 and show the predictive equation for HAA6 and the individual HAA6 species, respectively. The coefficients and regression statistics related to **Equation 5-158** are shown in **Table 5-10**.

The method for HAA9 prediction and the four species not included in HAA5, is calculated based on the method described in **Section 5.7.10**.

$$HAA6 = 37.8(TOC * UVA)^{0.511}(Cl_2)^{0.374}(Br^-)^{-0.079}(0.913)^{(pH-8.0)}(1.022)^{(Temp-20)}(time)^{0.280}$$

(5-156)

$$(R^2_{adj} = 0.63, \; SEE = 5.0 \; \mu g/L, \; F = 793, \; n = 2880)$$

where,

TOC = total organic carbon (mg/L): $0.14 \leq DOC \leq 2.0$

UVA = UV absorbance at 254 nm (1/cm): $0.001 \leq UVA \leq 0.048$

Cl_2 = applied chlorine dose (mg/L): $0.5 \leq Cl_2 \leq 3.0$

Br^- = bromide concentration (μg/L): $10 \leq Br \leq 570$

pH: $6.7 \leq pH \leq 10$

$Temp$ = temperature (°C): $3 \leq Temp \leq 33$

$time$ = reaction time (hours): $2 \leq time \leq 168$

$$HAA = A(TOC * UVA)^a (Cl_2)^b (Br^-)^c (D)^{(pH-8.0)}(E)^{(Temp-20)}(time)^f \qquad \textbf{(5-157)}$$

TOX

Equation 5-159 presents the WTP Model's GAC-Treated/Nanofiltered Water Algorithm equation for TOX formation. Data from the ICR Treatment Studies database were used. Like the data used for THM and HAA equations, data with GAC effluent TOC concentration of less than or equal to 2 mg/L only were used.

Table 5-2 Coefficients and Regression Statistics for GAC-Treated/Nanofiltered Water HAA Species Equations

HAAs	Coefficients for Equation 5-157						
	A	*a*	*b*	*c*	*D*	*E*	*f*
MCAA	1.31×10^{-1}	0.202	0.275	-0.958	0.124	1.036	0.923
DCAA	38.4	0.503	0.421	-0.393	0.867	1.019	0.293
TCAA	47.8	0.627	0.729	-0.425	0.602	1.011	0.174
MBAA	3.0×10^{-1}	0.093	0.964	-0.408	0.134	1.054	0.554
DBAA	3.96×10^{-1}	0.509	-0.251	0.689	1.302	1.019	0.310
BCAA	3.89	0.560	0.260	0.117	1.077	1.018	0.334

HAAs	Regression Statistics			
	R^2_{adj}	SEE ($\mu g/L$)	*F*	*n*
MCAA	0.29	1	190	2841
DCAA	0.54	3	559	2881
TCAA	0.61	2	743	2891
MBAA	0.19	1	111	2892
DBAA	0.75	1	1415	2886
BCAA	0.64	1	862	2892

$$TOX = 168(TOC * UVA)^{0.529}(Cl_2)^{0.349}(1.009)^{(Temp-20)}(time)^{0.239} \qquad \textbf{(5-158)}$$

$$(R^2_{adj} = 0.74,\ SEE = 18\ \mu g\ Cl^-/L,\ F = 1000,\ n = 1373)$$

where,

TOX = total organic halogen ($\mu g\ Cl^-/L$): $0.4 \leq TOX \leq 200$

TOC = total organic carbon (mg/L): $0.14 \leq DOC \leq 2.0$

UVA = UV absorbance at 254 nm (1/cm): $0.001 \leq UVA \leq 0.045$

Cl_2 = applied chlorine dose (mg/L): $0.6 \leq Cl_2 \leq 7.5$

Br^- = bromide concentration ($\mu g/L$): $10 \leq Br^- \leq 645$

$Temp$ = temperature (°C): $2.4 \leq Temp \leq 31$

pH: $6.9 \leq pH \leq 9.5$

$time$ = reaction time (hours): $3.0 \leq time \leq 100$

Because the ICR database for full-scale treatment plants contained a very limited amount of data for GAC or nanofiltration installations, equations in the GAC-Treated/Nanofiltered Water Algorithm (for TOC values less than 2 mg/L) were *not* calibrated using full-scale ICR data. Note

also that this algorithm uses the ICR-calibrated Coagulated Water Algorithm equations for GAC-treated or nanofiltered water with effluent TOC values greater than 2.0 mg/L.

5.7.10   HAA9 Prediction

The WTP Model v2.2.1 incorporates important advances in HAA9 prediction since WTP Model v2.2 was updated (Obolensky and Singer, 2005; Roberts et al., 2002; Shoaf and Singer, 2007; Samson et al., 2017). Samson et al. (2017) states that the improved HAA9 modeling depends on the assumption "that the bromide/chlorine competition for sites on organic precursors is constant and the brominated HAA species and chlorinated HAA species either have minimal decay or nearly the same rates of decay." This is shown in **Equations 5-159** through **5-162** below.

$$[BDCAA] = [TCAA] * [BDCM]/[CHCl_3] \qquad \textbf{(5-159)}$$

$$[DBCAA] = [TCAA] * [CDBM]/[CHCl_3] \qquad \textbf{(5-160)}$$

$$[TBAA] = [TCAA] * [CHBr_3]/[CHCl_3] \qquad \textbf{(5-161)}$$

$$[BCAA] = 0.5([BDCM] + [CDBM]) * [DCAA]/[CHCl_3] \qquad \textbf{(5-162)}$$

$$[HAA9] = [HAA5] + [BDCAA] + [DBCAA] + [TCAA] + [BCAA] \qquad \textbf{(5-163)}$$

BDCAA = Bromodichloroacetic acid (molar concentration)

TCAA = Trichloroacetic acid (molar concentration)

BDCM = Bromodichloromethane (molar concentration)

CHCl$_3$ = Chloroform (molar concentration)

DBCAA = Dibromochloroacetic acid (molar concentration)

CDBM = Chlorodibromomethane (molar concentration)

TBAA = Tribromoacetic acid (molar concentration)

BCAA = Bromochloroacetic acid (molar concentration)

DCAA = Dichloroacetic acid (molar concentration)

HAA9 = Sum of nine species of haloacetic acids (molar concentration)

HAA5 = Sum of five species of haloacetic acids (molar concentration)

These equations were developed to predict HAA9 based on known species data from the regulated DBP groups, HAA5 and TTHM. In the context of the WTP Model, however, these equations can be applied by using the individual species predictions within the model for the regulated DBPs (i.e.,

HAA5 and TTHM) to predict each unregulated HAA9 species. Using this method, there is no bulk prediction of HAA9—this differs from HAA5, HAA6, and TTHM prediction methods used in the WTP Model. Instead, HAA9 is predicted by summing the bulk prediction of HAA5 and species predictions of BDCAA, DBCAA, TCAA, and BCAA (**Equation 5-163**). Based on the accuracy of this model described in Samson et al. (2017), we expect that little to no additional calibration of HAA9 will be necessary. Currently, the HAA9 prediction not been calibrated using the ICR database. This HAA9 method is used in the following DBP formation models and any other models which are dependent on those models: Free Chlorine DBPs – Raw Water, Ozonated Water, Coagulated Water, and GAC-Treated/Nanofiltered Water.

5.7.11   ICR-based DBP Calibration Factors

Observations from full-scale treatment plants regulated under the ICR were used to verify DBP formation under free chlorine conditions in the plant and the distribution system for conventional, direct filter, and lime-softening treatment plants (Swanson, et al., 2002). Analysis of the data showed that some of the DBP predictions were outside the acceptable verification criteria; in these cases, the WTP Model equations were calibrated with a scalar factor to match the central tendency of the ICR observations. Some DBP equations did not require calibration. The correction factors shown in **Table 5-11** are applied to the DBP formation equations, as shown in **Equation 5-164**. Since few ICR full-scale plant data were available for CDBAA, BDCAA, TBAA, HAA9, and TOX , no ICR calibration factors were developed for these species and bulk parameters. Furthermore, the predictions of species such as MCAA, MBAA, and DBAA were not calibrated because their values were typically extremely low.

$$DBP_{corr} = \frac{DBP_{pred}}{Correction\ Factor} \tag{5-164}$$

where,

DBP_{corr} = ICR-calibrated DBP prediction

DBP_{pred} = uncalibrated DBP prediction (from formation equations described in this section)

$CorrectionFactor$ = correction factor developed based on calibration analysis with ICR data

The ICR-based correction factors are applied to TTHM, HAA6 and associated species equations with the following DBP formation algorithms: Raw Water, Raw Ozonated Water, Pre-chlorinated Water, Coagulated Water, and Re-chlorinated Pre-chlorinated Water.

Table 5-3 ICR-based Calibration Factors for Coag. Water Algorithm Equations*

DBPs	Calibration Factors	
	In-Plant	Distribution System
THMs		
CHCl$_3$	1.0	1.1
BDCM	0.50	1.0
DBCM	0.86	0.80
CHBr$_3$	1.0	1.0
TTHM	0.77	1.0
HAAs		
MCAA	1.0	1.0
DCAA	0.71	1.3
TCAA	1.3	1.0
MBAA	1.0	1.0
DBAA	1.0	1.0
BCAA	0.82	2.0
HAA6	1.0	1.0

* Based on analysis of conventional plants using free chlorine in plant and distribution sys.

5.7.12 Chloramine DBPs

The formation of THMs is possible in the presence of a chloramine residual and has been observed (Hubbs and Holdren, 1986). This formation is possible for two reasons:

1. The reaction between free chlorine and ammonia to produce monochloramine is a reversible reaction (Morris and Isaac, 1985). Therefore, free chlorine and monochloramine can coexist in an equilibrium state. The ability of free chlorine present in such a system to form THMs and HAAs depends on the rate of the forward reaction relative to the rate of the reverse reaction.

2. Mixing conditions in the treatment plant are not sufficient to bring free chlorine and ammonia into contact with each other instantaneously. The presence of free chlorine for this limited period of time may result in THM and HAA formation.

Studies have not been conducted to evaluate the conditions under which THM and HAA formation is observed during chloramination. Based on the nature of the reversible reaction between free

chlorine and ammonia, however, it can be speculated that free chlorine is present in higher concentrations when the chlorine to ammonia ratio is increased. Also, because the rate of the reaction between free chlorine and ammonia is optimal at pH 8.2, it can be speculated that free chlorine is present at higher concentrations when pH conditions deviate from pH 8.2.

At the time of WTP Model development there were insufficient data available from controlled experimental conditions to develop equations of THM and HAA formation during chloramination. Nevertheless, because THM and HAA formation is observed during chloramination, and chloraminated systems are prevalent, the WTP Model needs to account for it. The 1992 version assumed that the rate of THM formation with chloramines is 20 percent of the rate with free chlorine. The assumption was based on the work of Bull and Kopfler (1991), who used an estimate developed by Amy, et al. (1990) that THM formation in chloraminated waters "would approximate 20 percent of that observed if the same waters were chlorinated."

The WTP Model, version 2.2 uses the same approach as described above, i.e., applying a constant factor to the predicted free chlorine DBP formation to chloramines DBP formation. However, version 2.2 utilized an analysis of full-scale ICR data from chloraminated systems to develop factors individually for the different DBP species and bulk parameters.

ICR full-scale plant data from facilities using chloramine disinfection were used. The predictions given by the equations developed for free chlorine disinfection were compared with actual observed DBP values. Based on this comparison, factors were developed that, in general, fell around the 20 percent formation assumption. **Table 5-12** summarizes the factors used by the WTP Model to calculate the percent of DBPs formed with chloramines as compared to those formed with free chlorine. Note that full-scale ICR data did not contain sufficient observations to perform this analysis for HAA9, HAA9's three additional species, or TOX. For this reason, the factor for HAA9 and its three additional species was left at 20%, while the TOX factor value was set at 32.5%, which represents the average of the factor values for TTHM and HAA6.

Table 5-4 Percent of DBPs Formed with Chloramination Compared to Free Chlorine Disinfection

DBP	Percent of DBP Formed Compared to Free Chlorine	DBP	Percent of DBP Formed Compared to Free Chlorine
THMs		*HAAs*	
$CHCl_3$	30	MCAA	20
BDCM	30	DCAA	35
DBCM	30	TCAA	5
$CHBr_3$	30	MBAA	20
TTHM	30	DBAA	20
		BCAA	30
TOX	32.5	HAA6	35
		TBAA	20
		CDBAA	20
		BDCAA	20
		HAA9	20

5.7.13   Ozone DBPs

Ozone will react with NOM to form ozonation DBPs. Identified ozonation DBPs include aldehydes, ketones, carboxylic acids and bromate. The only ozone DBP that is currently regulated is bromate. The MCL is set at 10 µg/L. Version 2.2 of the WTP model predicts bromate formation for ozonated waters, either with or without ammonia.

Bromate formation equations were developed by Amy et al. (1998) for waters with and without ammonia, shown by **Equations 5-165** and **5-166**, respectively. The database consisted of 10 raw waters, ozonated under varying conditions in semi-batch bench-scale experiments.

With Ammonia:

$$BrO_3^- = 8.71 \times 10^{-8} (UVA)^{-0.593} (pH)^{5.81} (O_3)^{1.28} (Br^-)^{0.94} (Alk)^{-0.167} (NH_3 - N)^{-0.051} (1.035)^{(T-20)} (time)^{0.337}$$

(5-165)

$(R^2 = 0.71 , R^2_{adj} = 0.70, SEE = 0.561, F = 73, n = 323)$

Without Ammonia:

$$BrO_3^- = 1.19 \times 10^{-7} (UVA)^{-0.623} (pH)^{5.68} (O_3)^{1.31} (Br^-)^{0.96} (Alk)^{-0.201} (1.035)^{(T-20)} (time)^{0.336} \quad \textbf{(5-166)}$$

$$(R^2 = 0.71, R^2_{adj} = 0.70, SEE = 0.562, F = 84, n = 303)$$

where,

BrO_3^- = bromate concentration (µg/L): $1.3 \leq BrO_3^- \leq 314$

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \leq UVA \leq 0.28$

pH = pH of ozonated water: $6.5 \leq pH \leq 8.5$

Br^- = bromide concentration (µg/L): $69 \leq Br^- \leq 440$

O_3 = transferred/utilized ozone (mg/L): $1.05 \leq O_3 \leq 10$

$NH_3\text{-}N$ = nitrogen ammonia, (mg/L): $0.02 \leq NH_3\text{-}N \leq 3$

Alk = alkalinity (mg/L as $CaCO_3$): $13 \leq Alk \leq 316$

time = hydraulic retention time t_{10} (min): $1 \leq time \leq 120$

T = temperature (°C): 20

Bromate Formation Correction Factor

The bromate equation presented above developed from bench-scale ozonation experiments was calibrated using observed bromate formation in pilot-scale and full-scale ozonation dosing/contacting systems. This data set, compiled by Malcolm Pirnie, Inc. during the Stage 2 D/DBP Rule reg-neg process, was generated from pilot- and full-scale ozonation systems treating 8 different waters from California, Texas, and Virginia. The correction factor shown in **Equation 5-167** is applied to the bromate formation equation presented above within version 2.2 of the WTP Model. With this correction, a plot of predicted versus observed bromate values for the pilot-/full-scale data set yielded an R^2 value around a 1:1 line of 0.80.

$$Bromate_{corr} = Bromate_{pred} \div 2.52 \quad \textbf{(5-167)}$$

Bromide Consumption

Amy et al. (1998) also developed and equation for bromide consumption during ozonation. As ozone oxidizes bromide to bromate, the concentration of bromide available for subsequent DBP formation is decreased. **Equation 5-168** predicts this decrease of bromide as a function of bromate formed.

$$Br^- = Br_0 - \left(0.625\left[BrO_3^-\right]_0\right)$$ (5-168)

where,

Br^- = bromide concentration (µg/L): $69 \leq Br^- \leq 440$

BrO_3^- = bromate concentration (µg/L): $1.3 \leq BrO_3^- \leq 314$

5.7.14   Chlorine Dioxide DBPs

The use of chlorine dioxide instead of chlorine to provide microbially safe drinking water is of growing interest as MCLs for chlorine DBPs are lowered. While chlorine dioxide typically does not form THMs or HAAs, it does form its own set of DBPs, namely chlorite, and to a lesser extent chlorate. Typically, chlorine dioxide reacts either with dissolved organic matter, or with dissolved metals to form chlorite. As a rule of thumb, the concentration of chlorite formed is in the range of 50 to 70 % of the applied chlorine dioxide dose.

Little data are available to develop equations to predict chlorite formation. Instead, the WTP Model version 2.2 uses a constant conversion factor applied to the chlorine dioxide dose. This conversion factor is based on research findings. Thus, the formation of chlorite is given by **Equation 5-169**:

$$ClO_2^- = 0.7 * ClO_2$$ (5-169)

where,

ClO_2^- = chlorite formed (mg/L)

ClO_2 = applied chlorine dioxide dose (mg/L)

5.8   DISINFECTION CREDIT AND INACTIVATION

It is anticipated that one of the primary uses of the WTP Model will be to assist in evaluating potential tradeoffs in disinfection achievement and DBP formation within surface water systems. To produce meaningful primary disinfection predictions, the WTP Model performs "CT Ratio" predictions that are based on federal regulatory requirements and guidance and user-entered input data. This is the only portion of the WTP Model, which uses regulatory values in its calculations.

5.8.1 Disinfection Requirements

The WTP Model bases primary disinfection requirement determinations on federal regulations, both final and proposed, at the time of model development. Therefore, the model focuses on the physical removal and inactivation of three specific classes of pathogens: *Giardia*, viruses, and *Cryptosporidium*. Furthermore, primary disinfection requirements within the WTP Model are set, in the broadest sense, based upon whether the source water is classified as:

- groundwater, or
- surface water (or groundwater under the direct influence of surface water - GWUDI)

Groundwater System Disinfection Requirements

For ground water systems, there were no federal regulatory requirements at the time of model development that set specific minimum levels for removal or inactivation of select pathogens. However, the proposed Groundwater Rule would require 4-log removal and/or inactivation of viruses in groundwater sources with significant deficiencies or groundwater systems with positive fecal coliform results from the distribution system. Based upon these considerations, the WTP Model has inputs in the "Influent" unit process that allow the user to specify:

- whether or not the water source is classified as a surface water or groundwater (the default input is "surface water") ,
- whether or not virus inactivation requirements apply if the user has indicated that the water is classified as a groundwater (the default input is "no"), and
- if the water is a groundwater and virus inactivation requirements apply, what is the required total virus disinfection level (removal plus inactivation, in logs with default input of 4.0 logs)

Note that if the user defines the water source as a groundwater, the WTP Model will set disinfection requirements for *Giardia* or *Cryptosporidium* to zero. **Table 5-13** summarizes the disinfection requirement options for groundwaters in the WTP Model.

Table 5-5 Pathogen Total Disinfection Requirements for Groundwater Sources

Source Water	Required Removal and/or Inactivation (logs)		
	Giardia	Viruses	*Cryptosporidium*
Groundwater <u>not</u> requiring virus disinfection	0.0 (set)	0.0 (set)	0.0 (set)
Groundwater requiring virus disinfection	0.0 (set)	4.0 (user-adjustable)	0.0 (set)

Surface Water System Disinfection Requirements

The WTP Model primary disinfection requirements for surface water systems are based upon the requirements established under the Surface Water Treatment Rule (SWTR), the Interim Enhanced SWTR (IESWTR) (or Long-term 1 Enhanced Surfaced Water Treatment Rule for systems serving <10,000 customers), and, as of the time of model development, the proposed Long-Term 2 Enhanced Surface Water Treatment Rule (LT2 Rule). Disinfection requirements under these rules differ significantly based upon whether the system is:

- filtered (achieves disinfection, in part, through an approved filtration process) or
- unfiltered (meets various criteria to avoid filtration requirements; achieves all required disinfection through inactivation alone)

The SWTR requirements set minimum disinfection levels for the removal and/or inactivation of *Giardia* and viruses at 3.0 and 4.0-logs, respectively, for both filtered and unfiltered systems. The IESWTR established a minimum level of removal and/or inactivation of *Cryptosporidium* of 2.0 logs; this level was set primarily because research indicated that well-operated granular media filtration process could achieve a minimum of 2.0-log *Cryptosporidium* removal. In the proposed LT2 Rule, EPA effectively established a minimum 3.0-log *Cryptosporidium* disinfection requirement, except for unfiltered systems with very low concentrations of *Cryptosporidium* in their source water; these systems would only require 2.0-log *Cryptosporidium* disinfection credit. Note that while the total requirement was increased, so was the removal credit assigned to filtration processes. So, the LT2 Rule sets requirements for removal and/or inactivation of *Cryptosporidium* that are based upon the level of *Cryptosporidium* found in the system's source water. For filtered systems, this source water *Cryptosporidium* classification level is referred to as the system's "Bin" number. For unfiltered systems, this classification level is defined simply as exceeding or not exceeding a specified oocyst concentration cut-off. **Table 5-14** summarizes the *Cryptosporidium* oocyst concentration ranges that define these classifications.

Based on the federal regulations noted above and the definitions in **Table 5-14**, **Table 5-15** presents the disinfection requirements used within Version 2.2 of the WTP Model for surface water (or GWUDI) systems.

Table 5-6 Source Water *Cryptosporidium* Classification Definitions

System Status	Source Water *Cryptosporidium* Level Classification	Average Source Water *Cryptosporidium* Concentration Range (oocysts/L)
Filtered Surface Water System	Bin #1	< 0.075
	Bin #2	≥ 0.075 and < 1.0
	Bin #3	≥ 1.0 and < 3.0
	Bin #4	≥ 3.0
Unfiltered Surface Water System	Meeting Cutoff	≤ 0.01
	Exceeding Cutoff	> 0.01

5.8.2 Disinfection Credits

Based upon the federal regulatory framework referenced in the previous section, the WTP Model allows for compliance with primary disinfection requirements through a compilation of pathogen disinfection credits associated with:

- Watershed control programs
- Physical removal through bank filtration and/or treatment plant particle removal processes,
- Inactivation through UV disinfection or chemical disinfection processes.

Watershed Control Program Credit

Under the proposed LT2 Rule's Toolbox approach, filtered surface water systems may be eligible for 0.5-log of *Cryptosporidium* credit. The WTP Model has an input that allows the user to define whether or not a filtered surface water system being modeled will receive this credit.

Physical Removal Credits

Unfiltered surface water systems, by definition, do not meet primary disinfection requirements with credits for physical removal. Groundwater systems, even if required to achieve 4.0-log virus disinfection (per the proposed Groundwater Rule), typically do not meet primary disinfection requirements with removal credits, though they may do so. Filtered surface water systems use a variety of filtration schemes to accumulate physical removal credits to apply to primary disinfection requirements. The WTP Model allows the user to edit most of the physical removal

Table 5-15: Pathogen Total Disinfection Requirements for Surface Water Systems

Source Water *Crypto.* Level Classification	Required Removal and/or Inactivation of *Giardia*, Viruses, and *Cryptosporidium* (logs) System Status	
	Filtered[1]	Unfiltered
Bin #1	G: 3.0 V: 4.0 C: 3.0	N/A
Bin #2	G: 3.0 V: 4.0 C: 4.0/4.5[2,3]	N/A
Bin #3	G: 3.0 V: 4.0 C: 5.0/5.5[2,4]	N/A
Bin #4	G: 3.0 V: 4.0 C: 5.5/6.0[2,4]	N/A
Meeting Cutoff	N/A	G: 3.0 V: 4.0 C: 2.0[5]
Exceeding Cutoff	N/A	G: 3.0 V: 4.0 C: 3.0[5]

1. Filtered systems include those using conventional filtration (which is defined as a combination of coagulation, flocculation, sedimentation, and granular media filtration), precipitative softening systems (which employ sedimentation and granular media filtration), direct filtration (which is conventional filtration without sedimentation), slow sand filtration, diatomaceous earth filtration, microfiltration/ultrafiltration (MF/UF) or alternative filtration technologies (typically as approved by the State)
2. The higher values apply only to direct filtration systems. All others must achieve the lower of the two values for Bins #2 through #4.
3. Any combination of the technologies in the proposed LT2 Rule's "Microbial Toolbox" may be used to meet this *Cryptosporidium* disinfection requirement.
4. Any of the technologies in the proposed LT2 Rule's "Microbial Toolbox" may be used to meet this *Cryptosporidium* disinfection requirement; however, at least 1.0 log of this amount must by achieved using ozone, chlorine dioxide, UV, membranes, bag/cartridge filters, or bank filtration.
5. The proposed LT2 Rule specifies that a minimum of two different disinfectants (from among the choices of chlorine, chloramines, chlorine dioxide, ozone, and UV light) must be used to achieve the overall disinfection required and that each of at least two different disinfectants must be able to meet, by itself, the full disinfection requirements for at least one of the three pathogen classes. However, these requirements are not imposed in WTP Model calculations.

credits associated with particle removal processes and assigns default values based on USEPA guidance. **Table 5-16** lists the built-in and user-adjustable credits and their default values.

Table 5-16: Physical Removal Credits Available within the WTP Model[1]

Technology	User Adjustable Input Values?	Default Value Log Removal Credits[2]
Bank filtration		
25-49.9 feet separation	Yes	C (only): 0.5
50+ feet separation	Yes	C (only): 1.0
Pre-sedimentation (with coagulation)	Yes	C (only): 0.5
2-Stage Precipitative Softening	No	C (only): 0.5
Conventional filtration[3,4]		
as primary stage	Yes	G: 2.5, V: 2.0, C: 3.0
as 2nd stage	Yes	C (only): 0.5
Direct filtration[3]		
as primary stage	Yes	G: 2.0, V: 1.0, C: 3.0
as 2nd stage	Yes	C (only): 0.5
Rapid sand filter optimization		
Low combined filter turbidity	No	C (only): 0.5
Low individual filter turbidity	No	C (only): 1.0
Slow sand filtration		
as primary stage	Yes	G: 2.0, V: 2.0, C: 3.0
as 2nd stage	Yes	C (only): 2.5
Diatomaceous earth filtration		
as primary stage	Yes	G: 2.0, V: 1.0, C: 3.0
as 2nd stage	Yes	C (only): 0.5
GAC filtration		
as 2nd stage (only)	Yes	C (only): 0.5
Bag filtration		
as primary stage	Yes	G: 2.0, V: 0.0, C: 3.0
as 2nd stage	Yes	C (only): 1.0
Cartridge filtration		
as primary stage	Yes	G: 2.0, V: 0.0, C: 3.0
as 2nd stage	Yes	C (only): 2.0
Microfiltration/Ultrafiltration[5]		
as primary stage	Yes	G: 2.5, V: 1.0, C: 3.0
as 2nd stage	Yes	C (only): 2.5
Nanofiltration[5]		
as primary stage	Yes	G: 2.0, V: 2.0, C: 2.0
as 2nd stage	Yes	G: 2.0, V: 2.0, C: 2.0

1. Removal credit default values for all processes with the exception of membranes are based upon guidance contained in either the *Surface Water Treatment Rule Guidance Manual* (USEPA, 1991) or the draft *LT2ESWTR Toolbox Guidance Manual* (USEPA, 2003a). G = *Giardia*, V = viruses, C = *Cryptosporidium*
2. The WTP Model assumes that the filters meet the turbidity requirements of the IESWTR, which is the condition by which the regulations allow the full removal credit.
3. Includes precipitative softening systems (using sedimentation basins and filters).
4. MF/UF and NF defaults were arbitrarily set. Site-specific values will be dictated by State regulations and membrane challenge and integrity testing results.

UV Disinfection Inactivation Credits

UV light disinfection process inactivation credits are user-adjustable input values with the following default values (based on values in the draft *UV Disinfection Guidance Manual* (USEPA, 2003b):

- *Giardia*:   3.0 logs
- Viruses: 0.0 logs
- *Cryptosporidium*:   3.0 logs

Actual credits allowed for UV in a site-specific context will likely be dependent upon individual state primacy agency requirements and UV reactor validation testing results.

Chemical Disinfection Inactivation Credits

Table 5-17 lists the chemical disinfection processes handled by the WTP Model and the corresponding reference serving as the basis for WTP Model CT calculations. Note that due to their relative ineffectiveness, free chlorine and chloramines are assumed by the WTP Model to not contribute any credit to *Cryptosporidium* disinfection.

Table 5-17 Summary of CT Table Sources

Disinfectant	Giardia	Viruses	Crypto
Free Chlorine	USEPA, 1991	USEPA, 1991	n/a
Chloramines	USEPA, 1991	USEPA, 1991	n/a
Chlorine Dioxide	USEPA, 1991	USEPA, 1991	USEPA, 2003a
Ozone	USEPA, 1991	USEPA, 1991	USEPA, 2003a

The WTP Model calculates the amount of chemical inactivation credit required for each pathogen as the difference between the total disinfection credit required (see **Tables 5-13** and **5-15**) and the sum of the applicable watershed control program credit, physical removal process credits (**Table 5-16**), and UV disinfection credits. The only exception is filtered surface water systems falling into Bins #3 or Bin #4 with respect to *Cryptosporidium*. In these cases, the chemical inactivation credit required for *Cryptosporidium* will be calculated as at least that amount needed to bring the sum of the disinfection credits for chemical inactivation, bank filtration, bag or cartridge or membrane filtration, and/or UV disinfection to at least 1.0 logs.

The WTP Model uses the total chemical inactivation credit needed to calculate the amount of CT (disinfectant concentration multiplied by contact time) that is required. The amount of CT achieved and CT ratio are then calculated as described in subsequent sections.

5.8.3 CT Calculations

CT Ratio

The WTP Model calculates CT ratio to provide an indication of the performance of a water treatment plant's primary disinfection process. If CT ratios for all pathogens are either greater than 1.0 or unable to be calculated (because no inactivation credit is required), then the system is likely to be in compliance with primary disinfection regulations. However, the user should be knowledgeable about State-specific primary disinfection requirements in order to enter appropriate input values so that the CT ratio calculations reflect the requirements in that State.

The overall CT ratio achieved within a treatment plant for a given pathogen type *"p"* using *"M"* different chemical disinfectants, *"c"* through *"N"* different disinfection segments, *"s"* can be defined as follows:

$$CTRatio_p = \sum_{c=1}^{M} \sum_{s=1}^{N} CTRatio_{p,c,s} \qquad \textbf{(5-170)}$$

where,

$$CTRatio_{p,c,s} = \frac{CT \text{ achieved for chemical "c" in segment "s"}}{CT \text{ req'd for "p" with "c" in "s" to achieve overall target inact. of "p"}}$$

$$\textbf{(5-171)}$$

Within the WTP Model, a disinfection segment is a unit process with a defined water detention time and measurable disinfectant residual; the pathogens are *Giardia*, viruses, and *Cryptosporidium*; and the chemicals are free chlorine, chloramines, chlorine dioxide, and ozone. Furthermore, the "overall target inactivation of *p*" is the total log-inactivation required for pathogen *p*, calculated as described in the previous section.

CT Achieved

The WTP Model calculates the CT achieved with chemical disinfectant c in disinfection segment s (which is a unit process in the treatment plant's process train that has a defined water detention time) as follows:

$$CTAchieved_{c,s} = \left(\text{Re}\,sidual_{c,s}\right)\left(t_{theo,s}\right)\left(\frac{t_{10,s}}{t_{theo,s}}\right)$$
(5-172)

where,

$Residual_{c,s}$ = the disinfectant residual (in mg/L) at the effluent of the unit process (in the cases of free chlorine, chloramines, and chlorine dioxide) or as an average through the unit process based on the residual profile (in the case of ozone)

$t_{theo,s}$ = the theoretical contact time for the unit process (in minutes), which is calculated as the unit process volume divided by the flow rate (both user inputs),

$t_{10,s}/t_{theo,s}$ = the user-inputted value defining the ratio of t_{10}, the detention time by which 10% of the water entering the unit process at a given time has passed through the basin, to the theoretical detention time

An important note regarding the calculation of CT achieved values for ozone is that the WTP Model does not assign any credit to the first "Ozone Chamber" unit process following the first "Ozone" dose in a simulated ozone contacting system. Furthermore, the WTP Model only allows for persistence of ozone residual, and hence achievement of ozone CT, within "Ozone Chamber" unit processes. These assumptions are based upon one of the standard approaches outlined within the various USEPA guidance manuals that address this topic. The user should be aware that other approaches are available to possibly increase the CT credit achieved in an ozone contacting system, but these are currently not handled by the WTP Model.

CT Required

The WTP Model uses values of the CT required to achieve a given level of inactivation of pathogen p with chemical disinfectant c under the specific treatment conditions (temperature, pH, and disinfectant residual) existing in disinfection segment s as identified in the sources listed in **Table 5-17**. **Appendix A** contains the CT tables (taken from these references) used by the WTP Model to calculate values of CT required for:

- *Giardia* by chloramines, chlorine dioxide, and ozone

- Viruses by chloramines, chlorine dioxide, and ozone

The WTP Model linearly interpolates between tabulated values to calculate CT required values for process-specific conditions that fall between the tabulated values.

For *Giardia* inactivation with free chlorine, the WTP Model employs following regression equations (Smith et al., 1995) to calculate the CT required for a given unit process:

For *Temp* < 12 degrees C,

$$CT_{Required} = LI_{req'd} \times 0.353 \times [12.0 + \exp(2.46 - 0.073 * Temp + 0.125 * Cl_2 res + 0.389 * pH)]$$

(5-173a)

For *Temp* >= 12 degrees C,

$$CT_{Required} = LI_{req'd} \times 0.361 \times [-2.261 + \exp(2.69 - 0.065 * Temp + 0.111 * Cl_2 res + 0.361 * pH)]$$

(5-173b)

where,

$LI_{req'd}$ = total inactivation (logs) of *Giardia* required through the plant

Temp = water temperature (ºC)

$Cl_2 res$ = free chlorine residual (mg/L) in the effluent of the unit process

pH = pH in the effluent of the unit process

Equations 5-173 a & b are based on a regression analysis of the tabulated CT values contained within the *SWTR Guidance Manual* (USEPA, 1991). The equations generally represent the tabulated values with an accuracy of better than 10 percent.

The WTP Model uses **Equation 5-174** to represent the CT table as contained in the draft *LT2 Rule Toolbox Guidance Manual* (USEPA, 2003a) for *Cryptosporidium* inactivation with chlorine dioxide. This equation represents tabulated values to within 1% accuracy.

For *Cryptosporidium* inactivation with chlorine dioxide:

$$CT_{Required} = LI_{req'd} \times 664.3 \times \exp(-0.0873 * Temp)$$

(5-174)

where,

$LI_{req'd}$ = total inactivation (logs) of *Cryptosporidium* required through the plant

Temp = water temperature (ºC)

The WTP Model uses **Equation 5-175** to represent the CT table as contained in the draft *LT2 Rule Toolbox Guidance Manual* (USEPA, 2003a) for *Cryptosporidium* inactivation with ozone. This equation represents tabulated values to within 1% accuracy.

For *Cryptosporidium* inactivation with ozone:

$$CT_{\mathrm{Re}quired} = LI_{req'd} \times 25.16 \times \exp(-0.0929 * Temp) \qquad \textbf{(5-175)}$$

where the variables $LI_{req'd}$ and *Temp* have the same definitions as in Equation 5-114.

For temperatures outside the range of 0.5ºC to 25ºC, the WTP Model uses 0.5ºC or 25ºC in the equations.

5.9   SOLIDS FORMATION

The WTP Model tracks solids produced by the removal of raw water solids, precipitation of inorganic aluminum or iron solids from either alum or ferric coagulation, and by the precipitation of calcium carbonate or magnesium hydroxide during lime softening. The WTP Model uses the following equations by Cornwell et al. (1987):

Raw water solids (mg/L) = 1.4 × Raw water turbidity (NTU)   **(5-176)**

Aluminum solids (mg/L) = 0.44 × Alum dose (mg/L as alum)   **(5-177)**

Iron solids (mg/L) = 2.9 × Iron dose (mg/L as iron)   **(5-178)**

5.10 TEMPERATURE

Version 2.2 of the WTP Model does not calculate changes in temperature through a treatment plant or distribution system. Treated and distributed water temperatures used in calculations and shown as WTP Model outputs are all assumed to be equal to the user-inputted value of raw water temperature.

6   REFERENCES

Amy, G.L, P.A. Chadik and Z.K. Chowdhury (1987).   "Developing Models for Predicting Trihalomethane Formation Potential and Kinetics." J. AWWA, 79(7), p. 89.

Amy, G.L., B.C. Alleman and C.B. Cluff (1990).   "Removal of Dissolved Organic Matter by Nanofiltration." J. Env. Eng., 116(1), p. 200.

Amy, G.L., J.H. Greenfield, and W.J. Cooper (1990). "Organic Halide Formation during Water Treatment under Free Chlorine versus Chloramination Conditions." in Water Chlorination: Chemistry, Environmental Impact and Health Effects, Vol. 6.; R.L. Jolley, eds; Lewis Publishers, Chelsea, MI.

Amy, G.L., M. Siddiqui, K. Ozekin, H.W. Zhu, and C. Wang, (1998). Empirically Based Models for Predicting Chlorination and Ozonation By-Products: Haloacetic Acids, Chloral Hydrate, and Bromate. EPA Report CX 819579. USEPA Office of Groundwater and Drinking Water: Cincinnati, OH, 1998.

Bull, R.J, and F.C. Kopfler (1991). Health Effects of Disinfectants and Disinfection By-Products. AWWA Research Foundation, Denver, CO.

Carlson, K. (2001). Personal correspondence.

Clark, R.M. (1987).   "Modeling TOC Removal by GAC: The General Logistic Function." J. AWWA, 79(1), p. 33.

Clark, R.M, J.M. Symons and J.C. Ireland (1986).   "Evaluating Field Scale GAC Systems for Drinking Water." J. Env. Eng., 112(4), p. 744.

Clark, R.M., and S. Regli (1991). "The Basis for Giardia CT Values in the Surface Water Treatment Rule; Inactivation by Chlorine." In: Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Supplies; USEPA, Washington, D.C.

Collins, R. (2005) Personal correspondence.

Cornwell, D.A., M.M. Bishop, R.G. Gould, and C. Vandermeyden (1987). Handbook of Practice: Water Treatment Plant Waste Management. AWWA Research Foundation, Denver, CO.

Crow, E.L., F.A. Davis, and M.W. Maxfield, (1960). *Statistics Manual*; Dover Publications Inc.: Mineola, NY, pp 147-190.

Denbigh, K.G. and J.C.R. Turner (1971). Chemical Reactor Theory: An Introduction. 2nd Edition, Cambridge University Press, Cambridge, UK.

Dharmarajah, H., N.L. Patania, J.G. Jacangelo, and E.M. Aieta (1991) "Empirical Modeling of Chlorine and Chloramine Residual Decay." in Water Quality for the new Decade, 1991 Annual Conference Proceedings, AWWA.

Dugan, N.R., R.S. Summers, R.J. Miltner, H.M. Shukairy, (1995) "An Alternative Approach to Predicting Chlorine Residual Decay", Proceedings, AWWA-WQT Conference, Nov. 12-16, New Orleans, LA, pp. 1317.

Edwards, M. (1997). "Predicting DOC Removal During Enhanced Coagulation." J.AWWA 89 (5), p.78.

Edzwald, J.K. (1984). Removal of Trihalomethane Precursors by Direct Filtration and Conventional Treatment. USEPA Municipal Environmental Research Laboratory, Rept. No. EPA-600/2-84/068, NTIS Publ. No. PB84-163278.

Fair, P. (1990). Letter to S. Regli, USEPA.

Glaze, W.H., H.S. Weinberg, and J.E. Cavanaugh (1993). "Evaluating the Formation of Brominated DBPs During Ozonation," Journal AWWA, 85(1), p.96.

Harrington, G.W., Z.K. Chowdhury, and D.M. Owen (1991). "Integral Water Treatment Plant Model: A Computer Model to Simulate Organics Removal and Trihalomethane Formation." in Water Quality for the New Decade, Proceedings, AWWA Annual Conference.

Harrington, G.W., Z.K. Chowdhury, and D.M. Owen (1992). J. AWWA, 84(11), p.78

Hooper, S.M., and S.C. Allgeier (2002). "GAC and Membrane Treatment Studies," in Information Collection Rule Data Analysis. AWWA Research Foundation and AWWA: Denver, CO, 2002.

Hooper, S.M., R.S. Summers, G. Solarik, and D.M. Owen (1996). "Improving GAC Performance by Optimized Coagulation," Journal AWWA, 88:8:107.

Hooper, S.M., R.S. Summers, G. Solarik, and S. Hong (1996). Proceedings, American Water Works Association Annual Conference, Toronto, Canada, June 1996.

Hubbs, S.A., and G.C. Holdren (1986). Chloro-Organic Water Quality Changes Resulting from Modification of Water Treatment Practices. AWWA Research Foundation, Denver, CO.

Isabel, R.S., G. Solarik, M.T, Koechling, M. H. Anzek, and R.S. Summers, 2000. Modeling Chlorine Decay in Treated Waters, Proceedings, AWWA Annual Conference, June 11-15, Denver, CO.

J. Corollo Engineers (1989). "Pilot Study Final Report; Union Hills Water Treatment Plant Water Quality Enhancement Study." Prepared for the City of Phoenix, AZ.

Jackson, J.L., S. Hong, and R.S. Summers (1993). "The Use of Ultrafiltration to Characterize GAC Breakthrough of Organic Matter in Molecular Size Fractions," Proceedings, Water Quality Technology Conference, Miami, FL.

James M. Montgomery Consulting Engineers and Metropolitan Water District of Southern California (1989). Disinfection By-Products in U.S. Drinking Waters. United States Environmental Protection Agency and Association of Metropolitan Water Agencies; Cincinnati, OH and Washington, DC.

Joselyn, B.L. and R.S. Summers (1992). "Control of Disinfection By-Product Precursors by Ozonation, Biofiltration and Carbon Adsorption," Proceedings, AWWA Conference, Vancouver, BC.

Koechling M.T., A.N. Rajbhandari, and R.S. Summers (1998). *Proceedings,* American Water Works Association Annual Conference, Dallas, TX, June 1998, p. 363.

Langlais, B., D.A. Reckhow, and D.R. Brink, (editors) (1991). Ozone in Water Treatment: Application and Engineering, Cooperative Research Report, AWWA Research Foundation and Compagnie Generale des Eaux, Lewis Publ., Chelsea, MI.

Levenspiel, O. (1972). Chemical Reaction Engineering. 2nd Edition, John Wiley & Sons, New York, NY.

Malcolm Pirnie, Inc. and City of Phoenix (1989). Water Quality Master Plan.

Malcolm Pirnie, Inc. and City of San Diego (1990). Water Quality Report.

Miltner, R.J. and R.S. Summers (1992). "A Pilot-Scale Study of Biological Treatment," Proceedings, Water Quality Technology Conference, Vancouver, BC.

Morris, J.C., and R.A. Isaac (1985). "A Critical Review of Kinetic and Thermodynamic Constants for the Aqueous Chlorine-Ammonia System." in Water Chlorination: Chemistry, Environmental Impact and Health Effects, Vol 4; Lewis Publishers, Chelsa MI.

Obolensky, Alexa, and Philip C. Singer. "Halogen Substitution Patterns among Disinfection Byproducts in the Information Collection Rule Database." *Environmental Science & Technology* 39, no. 8 (April 1, 2005): 2719–30. https://doi.org/10.1021/es0489339.

Owen, D.M., G.L. Amy, and Z.K. Chowdhury (1992). "Characterization of Natural Organic Matter and its Relationship to Treatability," AWWA Research Foundation.

Rajbhandari, A.N. (2000) Masters Thesis, University of Cincinnati, Cincinnati, OH

Roberson, J.A., J.E. Cromwell III, S.W, Krasner, M.J. McGuire, D.M. Owen, S. Regli, and R.S. Summers (1995). J. AWWA, 87(10), p.46.

Roberts, P.V., and R.S. Summers, 1982. "Granular Activated Carbon Performance for Organic Carbon Removal," Journal AWWA, 74:113

Roberts, Megan G., Philip C. Singer, and Alexa Obolensky. "Comparing Total HAA and Total THM Concentrations Using ICR Data." *Journal - American Water Works Association* 94, no. 1 (January 1, 2002): 103–14. https://doi.org/10.1002/j.1551-8833.2002.tb09386.x.

Samson, Carleigh C., Chad J. Seidel, R. Scott Summers, and Timothy Bartrand. "Assessment of HAA9 Occurrence and THM, HAA Speciation in the United States." *Journal - American Water Works Association* 109, no. 7 (July 1, 2017): E288–301. https://doi.org/10.5942/jawwa.2017.109.0083.

Schechter, D.S., and P.C. Singer (1995). "Formation of Aldehydes During Ozonation," <u>Ozone Sci. and Eng.</u>, 17(1), p.53.

Shoaf, David R., and Philip C. Singer. "An Analysis of Monitoring Data for the Stage 1 Disinfectants/Disinfection Byproducts Rule." *Journal (American Water Works Association)* 99, no. 10 (2007): 69–80.

Singer, P.C. (1988). <u>Alternative Oxidant and Disinfectant Treatment Strategies for Controlling Trihalomethane Formation</u>. USEPA Risk Reduction Engineering Laboratory, Rept. No. EPA/600/2-88/044, NTIS Publ. No. PB88-238928.

Smith, et al. (1995). <u>J. Water Supply: Research and Technology-Aqua</u>, 44(5), p.203-211.

Solarik, G, R.S. Summers, S.M. Hooper, and D.M. Owen, 1997a. Enhancement of GAC Performance by Ozonation and Biofiltration. <u>Proceedings</u>, IOA Conference on Water, April 21-23, Berlin, Germany.

Solarik, G., V.A. Hatcher, R.S. Isabel, J.F. Stile, and R.S. Summers, 1997b. Prechlorination and DBP Formation: The Impact of Chlorination Point and Enhanced Coagulation. <u>Proceedings</u>, AWWA Water Quality Technology Conference, November 9-12, Denver, CO.

Stumm, W., and J.J Morgan (1981). *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*; John Wiley and Sons: New York, NY, 1981.

Summers, R.S. and P.V. Roberts (1988). "Activated Carbon Adsorption of Humic Substances. II. Heterodispers Mixtures and Desorption," <u>J. Colloid Interface Sci</u>. 122(2), p.382.

Summers, R.S., M.A. Benz, H.M. Shukairy and L. Cummings (1993). "Effect of Separation Processes on the Formation of Brominated THMs," <u>Journal AWWA</u>, 85(1), p. 88.

Summers, R.S., D.M. Owen, Z.K. Chowdhury, S.M. Hooper, G. Solarik, and K. Gray, (1998a). Removal of DBP Precursors by GAC Adsorption. American Water Works Association (AWWA) Research Foundation and AWWA: Denver, CO, 1998.

Summers, R.S., G. Solarik, V.A. Hatcher, R.S. Isabel, and J.F. Stile (1998b). Impact of Point of Chlorine Addition and Coagulation. Final Project Report. USEPA Office of Groundwater and Drinking Water: Cincinnati, OH, 1998.

Summers, R.S. and M. Arias (2005). Unpublished data and personal communication regarding Arias bench-scale re-chlorination experiments.

Swanson, W.J., Z. Chowdhury, L. Aburto, and R. Summers (2002). "Predicting ICR Surface Water Treatment Plant Behavior with the Water Treatment Plant Model," in <u>Information Collection Rule Data Analysis</u>. AWWA Research Foundation and AWWA: Denver, CO, 2002.

Taylor, J.S., D. M. Thompson and J. K. Carswell, (1987). "Applying Membrane Processes to Groundwater Sources for Trihalomethane Precursor Control." <u>J. AWWA</u>, 79(8), p. 72.

Taylor, J.S., L. A. Mulford, W. M. Barrett, S. J. Duranceau and D. K. Smith (1989). <u>Cost and Performance of Membranes for Organic Control in Small Systems: Flagler Beach and Punta Gorda, Florida</u>. USEPA Risk Reduction Engineering Laboratory.

Teefy, S.M. and P. C. Singer, (1990). "Performance and Analysis of Tracer Tests to Determine Compliance with the SWTR." J. AWWA, 82(12), p. 88.

Terry, Leigh G., and R. Scott Summers. "Biodegradable Organic Matter and Rapid-Rate Biofilter Performance: A Review." Water Research 128 (January 1, 2018): 234–45. https://doi.org/10.1016/j.watres.2017.09.048.

Tseng, T., M. Edwards, and Z.K Chowdhury, (1996). American Water Works Association National Enhanced Coagulation and Softening Database, 1996.

Tseng, T. and M. Edwards, (1999). "Predicting Full-Scale TOC Removal." J. AWWA, 91(4), p. 159.

USEPA (1991). Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources. Washington, D.C.

USEPA (2003a). Long-term 2 Enhanced Surface Water Treatment Rule Toolbox Guidance Manual, June 2003 Draft. Washington, D.C.

USEPA (2003b). Ultraviolet Disinfection Guidance Manual, June 2003 Draft. Washington, D.C.

White, M.C., J.D. Thompson, G.W. Harrington, and P.S. Singer, (1997). J. AWWA, 89(5), p. 64.

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APPENDIX A – CT TABLES VALUES FOR INACTIVATION

Appendix A lists the tables from the SWTR used by the WTP Model to calculate CT requirements for inactivation of viruses by free chlorine, and for inactivation of *Giardia* and viruses by chloramines, chlorine dioxide and ozone. Regression equations (Section 5.8.3) are used to represent CT tables for inactivation of *Giardia* by free chlorine and *Cryptosporidium* by chlorine dioxide and ozone.

A.1   *GIARDIA* INACTIVATION TABLES

Table A-1 CT Values for Inactivation of *Giardia* Cysts by Chloramine pH 6 to 9

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
0.5-log	635	365	310	250	185	125
1.0-log	1,270	735	615	500	370	250
1.5-log	1,900	1,100	930	750	550	375
2.0 log	2,525	1,470	1,230	1,000	735	500
2.5-log	3,170	1,830	1,540	1,250	915	625
3.0-log	3,800	2,200	1,850	1,500	1,100	750

Table A-2 CT Values for Inactivation of *Giardia* Cysts by Chlorine Dioxide

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
0.5-log	10	4.3	4	3.2	2.5	2
1.0-log	21	8.7	7.7	6.3	5	3.7
1.5-log	32	13	12	10	7.5	5.5
2.0 log	42	17	15	13	10	7.3
2.5-log	52	22	19	16	13	9
3.0-log	63	26	23	19	15	11

Table A-3 CT Values for Inactivation of *Giardia* Cysts by Ozone

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
0.5-log	0.48	0.32	0.23	0.16	0.12	0.08
1.0-log	0.97	0.63	0.48	0.32	0.24	0.16
1.5-log	1.5	0.95	0.72	0.48	0.36	0.24
2.0 log	1.9	1.3	0.95	0.63	0.48	0.32
2.5-log	2.4	1.6	1.2	0.79	0.60	0.40
3.0-log	2.9	1.9	1.43	0.95	0.72	0.48

A.2   VIRUS INACTIVATION TABLES

Table A-4 CT Values for Inactivation of Viruses by Free Chlorine

Temperature (ºC)	Inactivation					
	2.0-log		3.0-log		4.0-log	
	pH		pH		pH	
	6 – 9	10	6 – 9	10	6 – 9	10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

Table A-4 CT Values for Inactivation of Viruses by Chloramine

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
2.0-log	1,243	857	643	428	321	214
3.0-log	2,063	1,423	1,067	712	534	356
4.0-log	2,883	1,988	1,491	994	746	497

Note: CT values apply for systems using combine chlorine where chlorine is added prior to ammonia in the treatment sequence

Table A-5 CT Values for Inactivation of Viruses by Chlorine Dioxide pH 6 to 9

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
2.0-log	8.4	5.6	4.2	2.8	2.1	1.4
3.0-log	25.6	17.1	12.8	8.6	6.4	4.3
4.0-log	50.1	33.4	25.1	16.7	12.5	8.4

Table A-6 CT Values for Inactivation of Viruses by Ozone

Inactivation	Temperature (ºC)					
	≤ 1	5	10	15	20	25
2.0-log	0.9	0.6	0.5	0.3	0.25	0.15
3.0-log	2.4	0.9	0.8	0.5	0.4	0.25
4.0-log	1.8	1.2	1.0	0.6	0.5	0.3