WATER TREATMENT PLANT MODEL

Version 2.0

User's Manual

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The WTP Model was developed for the United States Environmental Protection Agency (USEPA) by the Center for Drinking Water Optimization, University of Colorado – Boulder and Malcolm Pirnie, Inc.

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 the Center for Drinking Water Optimization shall not be liable for any direct, indirect, consequential, or incidental damages resulting from the use of the WTP model.

FORWARD

This User's Manual for Version 2.0 of the WTP Model has been prepared to provide a basic understanding of 1) how to operate the program, and 2) the underlying assumptions and equations that are used to calculate the removal of natural organic matter (NOM), disinfectant decay and the formation of disinfection by-products (DBPs).

It is not to be construed that the results from the model will necessarily be applicable to individual raw water quality and treatment effects at unique municipalities and agencies. This model does *not* replace sound engineering judgment for an individual application.

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1. INTRODUCTION

1.1 BACKGROUND

The U.S. 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) Reg/Neg process in 1993-94 (Roberson et al., 1995). The original model and its verification were discussed by Harrington et al. (1992).

The model predicted (1) the behavior of water quality parameters that impact the formation of disinfection by-products (DBPs) and (2) the formation of DBPs. By 1999, the 1992 model was limited in several ways:

a.) many existing process, inactivation, DBP formation, and disinfectant decay algorithms within the WTP model were limited and/or outdated;
b.) new process, inactivation, DBP formation, and disinfectant decay algorithms needed to be added; and
c.) multiple points of chlorination

The 1992 WTP model was updated for the USEPA by the Center for Drinking Water Optimization (CDWO) at the University of Colorado and University of Cincinnati and Malcolm Pirnie, Inc., to create WTP Model version 2.0. The objectives were to modify existing model algorithms to reflect increased data availability and knowledge of treatment processes since 1992. Furthermore, the objectives were to extend the model with new algorithms for advanced treatment processes and alternative disinfectants. The new model algorithms are described in Chapter 5 of this manual.

The WTP model was developed to assist utilities in achieving total system optimization (TSO), i.e., a method by which treatment processes can be implemented such that a utility meets the required levels of disinfection while maintaining compliance with requirements of Stage 1 and potential Stage 2 the D/DBP Rule.

The purpose of the WTP model is to:

- determine DBP levels that can be achieved by existing treatment technologies, given the requirements for microbiological safety.

- identify those technologies that may be considered for DBP control.
- provide a tool that will assess the impacts of new regulations on DBP formation in existing treatment plants.

The model is not intended as a replacement for treatability testing to evaluate the effectiveness of various processes on disinfectant decay and DBP formation in specific water supplies, but does provide a useful tool for evaluating the potential effect of different unit processes on the interrelationships between many of the new and forthcoming regulations. Users of the program should be familiar with water treatment plant operation, as well as procedures and methodologies used to disinfect water and control DBP formation. The WTP model, like any computer program, can not 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 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.

1.2 WTP MODELING APPROACH

The basic modeling approach includes estimation of:

- NOM removal by individual unit processes;
- Disinfectant decay based upon demands exerted by NOM and other sources; and
- DBP formation based upon water quality throughout the treatment plant and in the distribution system.

The model simulates DBP formation under given treatment conditions and permits the user to evaluate the effects of changes in these conditions 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 can not be used as the sole tool for "full-scale" or "real-time" decisions for individual public water supplies.

Figure 1-1 illustrates the WTP process schematic including model inputs and outputs. The WTP model version 2.0 includes the treatment processes and disinfection options shown in Table 1-1. The model simulates the following DBP formation:

- Trihalomethanes (THM) – four individual species and their sum (TTHM)
- Haloacetic acids (HAA) – 9 species and the total of five (HAA5), six (HAA6) and nine (HAA9)
- Total organic halogen (TOX)
- Bromate
- Chlorite

Table 1-1 WTP Model Treatment Processes and Disinfectant Options

Treatment Processes
Coagulation/Flocculation/Sedimentation
Precipitative Softening/Clarification/Filtration
Granular Activated Carbon (GAC) Adsorption
Membranes
Ozonation
Biotreatment
Disinfectants
Chlorine
Chloramines
Ozone
Chlorine Dioxide

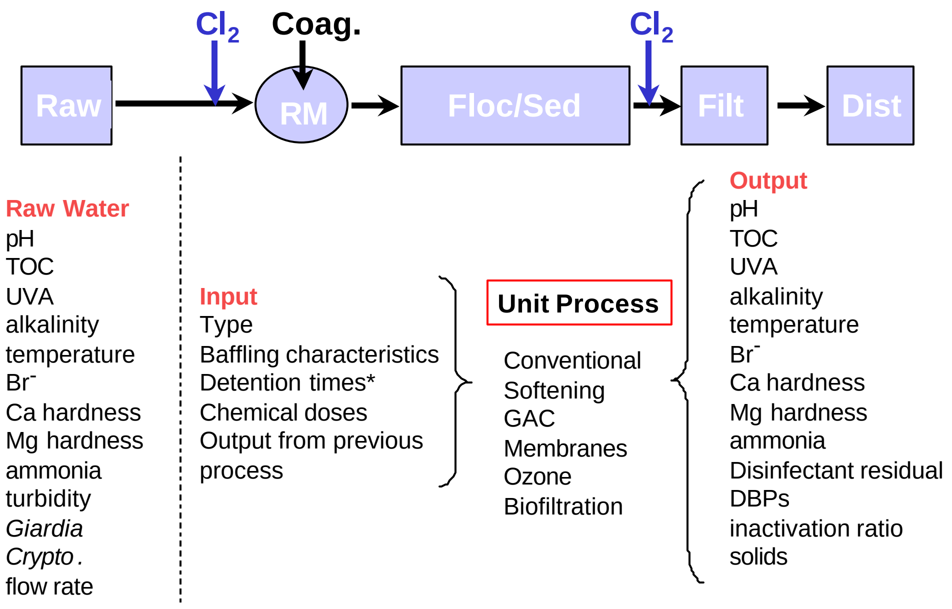


Figure 1-1 Water Treatment Plant Model Schematic

1.3 PURPOSE OF THIS MANUAL

This manual is intended to guide the user in operating the WTP model and to assist in the preparation of information necessary to execute the program. The manual provides a step-by-step guide for operation, and describes how to utilize and interpret the program output. The manual includes the following components:

- Instructions for using the computer program
- A description of the equations used in the program
- Results of model verification efforts

The manual is heavily based on the manual developed for the 1992 WTP Model version 1.21. Descriptions of model algorithms that were not changed for version 2.0 are taken directly from the 1992 manual.

1.4 MANUAL ORGANIZATION

This manual assumes that WTP model users have a working knowledge of water treatment plants. This basic understanding is necessary to provide meaningful input data to the program and correctly interpret the output.

It is not necessary for the user to have any programming knowledge or extensive computer experience. The WTP model operates through a user-friendly prompting program. It is assumed, however, that the user is familiar with fundamental computer operating systems. This manual will not address functions such as loading disks or connecting a printer. Operating system information of this type is usually contained in the users manual for a given computer system along with other fundamental computer operations.

In addition to this introductory chapter, this user's manual contains 4 other chapters:

- Chapter 2 describes how to set up and run the model and explains menu components.
- Chapter 3 describes the information needed to run WTP and how the data should be input. A diagram 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 program.
- Chapter 5 offers a description of the equations used in the program.

2. GETTING STARTED

This chapter contains information on installing and using WTP model 2.0

2.1 INSTALLING AND STARTING WTP MODEL

The distribution disk contains a simple "Install" program that will create a directory c:\WTPWIN and copy the distribution files into the directory. The installation will also create a group icon for WTP and create and item icon for WTP.EXE model.

Insert the distribution disk into drive A or B and, from the Windows Start Menu choose "Run" and type in the following: "a:\setup.exe"

Starting WTP Model:

1. Double click on the WTP group icon
2. Double click on the WTP item icon
3. First time use of the WTP model: At this point the main screen of WTP will fill the monitor. Across the bottom of the window is a series of six buttons that can be clicked using the mouse. The user interface is designed such that the buttons across the bottom control most of the action. A menu is at the top that contains additional selections for "File", "Display", and "Edit".

2.2 MAIN MENU COMPONENTS

2.2.1 Main Window

The title at the top of the main window is generally: "U.S. Environmental Protection Agency – Water Treatment Plant Model". This title at the top of the main window is replaced with the working file name when WTP model is working with process train data that is stored on disk.

Menu

<u>*File*</u>

New – This selection allows the user to enter a new process train with new unit process data, and replaces any previous train and data with the new train and data.

Open – This selection will read process train data from a disk file and track the working file name. Internally the "Open" function performs a "New" operation before reading the data. The function retrieves a process train and unit process data previously entered and saved to disk by the user.

Save – This selection will write process train data to the working file without prompting the use. If a working file name does not exist then a "Save As" selection is automatically performed.

Save As – This selection will prompt the user for a working file name then save the process train data to the data file. This selection provides an opportunity to change the working file name.

Print – This selection will print the main window display on the system printer

Print to File – This selection will save the main window display to a disk file in ASCII format. Any previous contents of the disk file are lost. The user is prompted to supply a file name with a .lst extension. The disk file can then be loaded into a word processor for further use.

Append to File – This selection will append the main window display to the end of a disk file this not loosing the previous contents of the disk file. The user is prompted to supply a file name with a .lst extension. The disk file can then be loaded into a word processor for further use.

Exit – Quit WTP and return to MS Windows.

Display

Process Train – This selection will display the names of the unit process, chemical feeds, and sample points in the process train. The display is in the main window display area.

Unit Process Data – This selection is similar to "Display | Process Train" but includes the Unit Process Data.

Water Quality – This selection will run the model and display 10 tables of water quality parameters.

Disinfection and DBPs – This selection will run the model and display one summary table containing disinfection and average DBP formation at minimum temperature and peak flow conditions.

Edit

Process Train – This selection will open the "Edit Process Train" screen. See "Edit Process Train" for details.

Control Buttons

There are six control buttons along the bottom of the main window. These buttons control most of the actions and are similar to actions performed by the menu selections at the top of the main window:

Table 2-1 Model Control Buttons

Open:	Same as menu selection	File | Open
Edit:	---"---	Edit | Process Train
Run:	---"---	Display | Water Quality
Reg:	---"---	Display | Disinfection and DBPs
Save:	---"---	File | Save
Exit:	---"---	File | Exit

2.2.2 Edit Process Train

The "Edit Process Train" screen is used to configure the process train. Unit processes, chemical feed and sample points can be inserted, repositioned or deleted in this screen. Using the mouse, click (left button) on the "Edit" button. The "Edit Process Train" screen will appear. On the left half of the screen is the list box which displays the process train – at the moment there is only an "Influent".

List Box – This section of the Process Train display illustrates the current process train, which can consist of any number of unit processes, chemical feeds, and sample points (collectively referred to as items). Any of the items in the process train can be highlighted by clicking with the mouse. The highlighted item is the point where new items are inserted into the process train. The highlighted item is also used with the "Move" button. Double clicking an item will open the parameter data entry screen starting with the selected item. A scroll bar is on the right side of the list box and will become active if the process train contains more items than will fit in the display.

At the bottom of the left half of the screen are four buttons to manipulate the process train. The four buttons are labeled "Move", "Edit", "Delete", and "Clear".

Move Button – This selection will reposition an item in the process train. The procedure is to first highlight an item, click the "Move" button and click on the point in the process train where the highlighted item should be repositioned. The "Move" operation will reposition the highlighted item such that the highlighted item will follow the clocked item in the process train.

Edit Button – This selection will open the parameter data entry screen starting with the highlighted unit process. Note: double clicking any item in the process train list box will open the parameter data entry starting at the selected item.

Delete Button – This selection will delete the highlighted item from the process train. Any data associated with the item are lost.

Clear Button – This selection will delete all items from the process train. Be careful, "Clear" may appear to be similar to the main window "File | New" selection but there are differences. The difference is that the "Clear" button will retain the working file name while the main window menu "File | New" selection will also clear the working file name. With "Clear", WTP considers the now empty process train to be associated with the working file name. Clicking the "Save" button on the main window will overwrite the working file without a second warning. Please use "File | New" if a new disk data file is desired.

Cancel Button – this button will cancel all changes made to the process train and also cancel all changes made in the parameters data entry screens. Control is returned to the main window.

OK Button – this is the normal method to return to the main window. All changes are passed back to the main window and the display area of the main window is updated

Available Selections

On the right half of the screen are three lists of "Available Selections" that can be added to the process train. The three lists are "Unit Processes", "Chemical Feeds", and "Sample Points". The options for each of the three lists are shown in Table 2.2. Clicking on any selection will insert the selection into the process train following the highlighted item in the process train, or, if no highlight, append the selection to the end of the process train.

Table 2-2 Available Unit Process, Chemical Feed, and Sample Point Selections

Unit Processes	Chemical Feeds	Sample Points
Rapid Mix	Alum	WTP Effluent
Flocculation	Ammonia Sulfate	Average Tap
Settling Basin	Ammonia	End of System
Filtration	Carbon Dioxide	Additional Point
Ozone Chamber	Chlorine (Gas)	
Contact Tank	Chlorine Dioxide	
Reservoir	Iron	
	Lime	
	Ozone	
	Permanganate	
	Sodium Hydroxide	
	Sodium Hypochlorite	
	Soda Ash	
	Sulfur Dioxide	
	Sulfuric Acid	

2.2.3 Data Entry Screens

There are many data entry screen for unit process data, chemical feed doses, and location of sample points, collectively referred to as data entry screens. All the data entry screens have the following features and control buttons.

Screen Title – The title at the top of the data entry screen indicates the name of the unit process, chemical feed, or sample point that the data entry screen is associated with.

Control Buttons

Next and Prev Buttons – The "Next" and "Prev" buttons will index through the data entry screens associated with the process train. "Next" indexes to the next data entry screen while "Prev" indexes to the previous data entry screen. The "OK" button will return to the "Edit Process Train" screen. When clicked, "Next", "Prev", and "OK" check for valid data in each data element and pass new data back to Edit Process Train. Both "Next" and "Prev" will return to the "Edit Process Train" screen if the data entry screen is the first or last data entry screen in the process train.

Cancel Button – The "Cancel" button will cancel changes made in the current data entry screen and return to the "Edit Process Train" screen. Note: changes made on other data entry screens are passed back to "Edit Process Train" when "Next" and/or "Prev" are clicked. If changes are made on other data entry screens and the current data entry screen is arrived via "Next" and/or "Prev" then pressing "Cancel" will cancel only the current data, not changes made to the other data entry screens.

3. MODEL OUTLINE AND USE

This chapter describes how to develop and enter data into the WTP model. It describes how to develop a simulated model of the specific plant being analyzed, and how to enter the proper information to activate the program.

3.1 SIMULATING THE TREATMENT PLANT

Before the model can be executed, a simulated version of the treatment plant process train must be developed. Data specific to this plant must also be collected for input when creating the simulated plant.

WTP is an interactive computer program that consists of a main program that acts as a manager for the number of plant simulation subroutines created for the input, output, and manipulation of data. A conceptual schematic of program inputs/outputs is shown in Figure 3-1. The program algorithm (steps the program follows) for a simulated process train is shown in Figure 3-2.

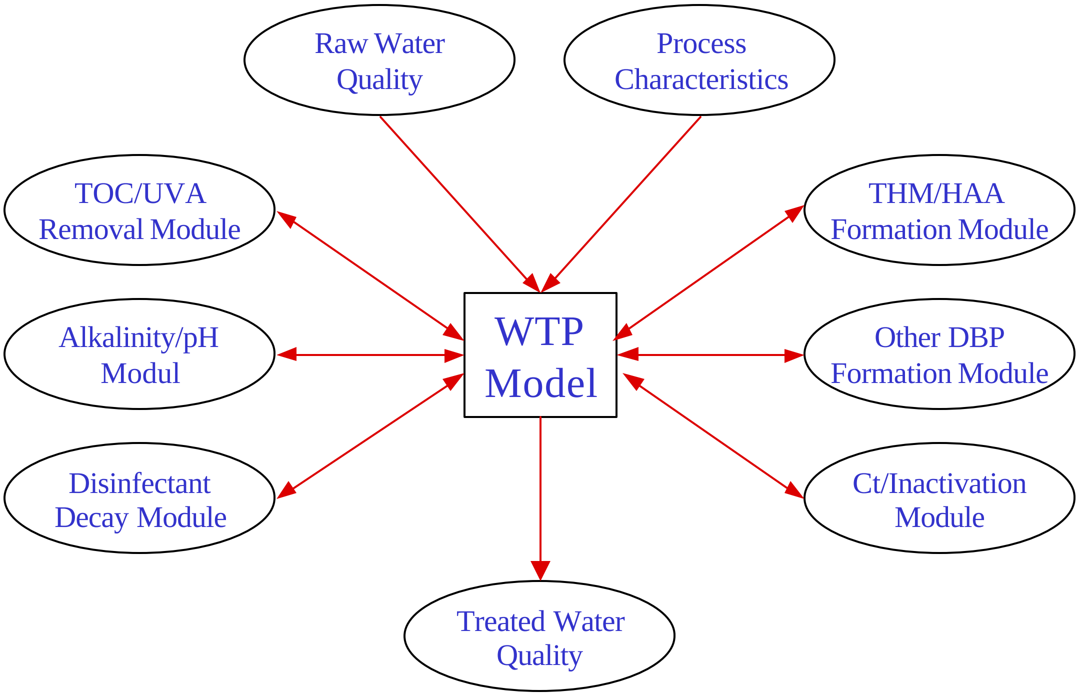


Figure 3-1 Interaction for Various Process Units for Water Treatment Plant Model

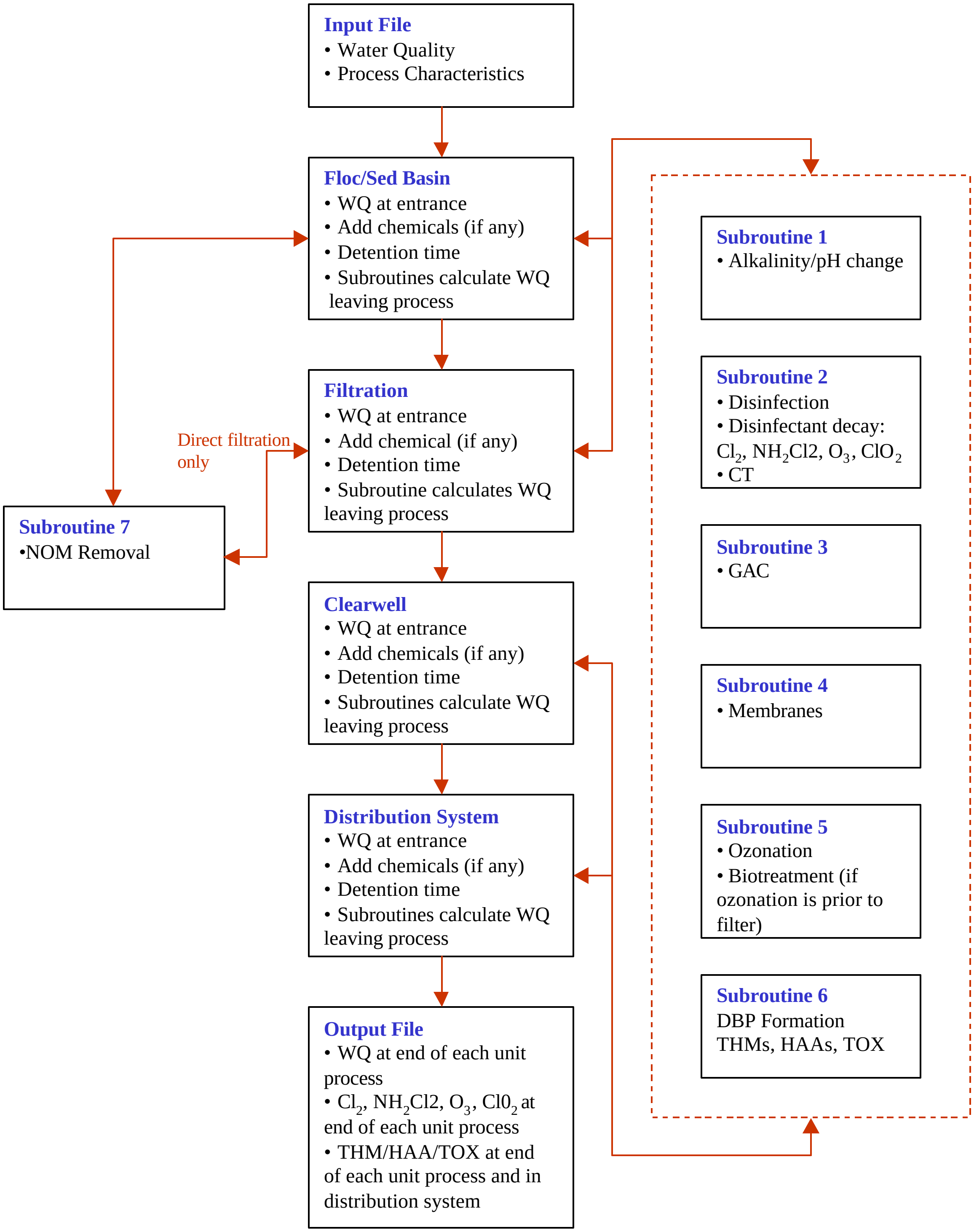


Figure 3-2 Algorithm for WTP Simulation

The executable version of the 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 runs; and
- Print input/output files.

An input file for the simulation program consists of the following:

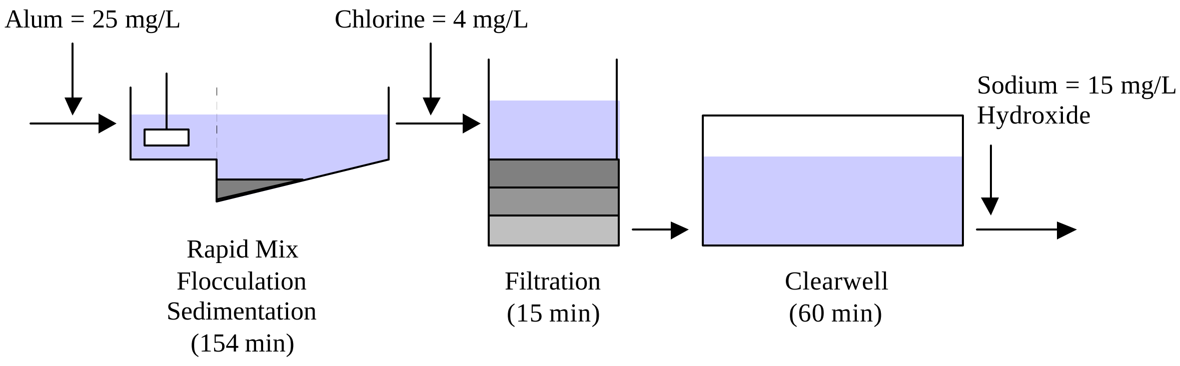
- Source type (surface water or groundwater)
- Organic raw water quality parameters
  - TOC
  - UVA
- Inorganic raw water quality parameters
  - Bromide concentration
  - Alkalinity concentration
  - Total and calcium hardness concentration
  - Ammonia Nitrogen concentration
- Water Treatment Process Characteristics
  - Type of unit process
  - Plant flow at average and peak hour conditions
  - Baffling characteristics and detention times
- Chemical doses
- Other raw water quality parameters
  - *Giardia* cyst concentration
  - *Cryptosporidium* removal and inactivation required
  - pH
  - Turbidity
  - Average and minimum temperature

The output file from a water treatment plant simulation run contains information for all the input parameters such as the raw water quality and the treatment plant process characteristics. In addition, the output contains information for calculated concentrations of the following parameters at the end of each of the unit processes for the simulated water treatment plant:

- Organic and inorganic water quality;
- Disinfectant residuals;
- DBPs (THMs, HAAs, and TOX) formed; and
- Inactivation ratio and CT achieved

3.2 CREATING AN EXAMPLE 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 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. Detention times and a summary of input parameters and raw water quality data as shown by the WTP model are given in the Process Train Data table in the WTP model, shown in Figure 3-5. 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.



Influent Water Quality:
TOC = 4.0 mg/L
UVA = 0.120 1/cm
SUVA = 3 L/mg-m
Bromide = 50 µg/L
pH = 8.0
Alkalinity = 100 mg/L as $CaCO_3$

Figure 3-3 Flow Schematic for Example Process Train

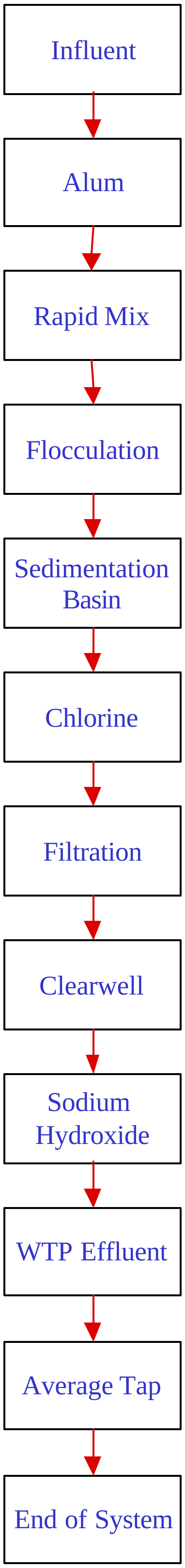


Figure 3-4 Block Diagram of Example Process Train

```
Process train data for c:\example2.wtp
Influent
        pH .......................................   8.0
        Influent Temperature .....................  20.0  (Celsius)
        Minimum Temperature ......................   5.0  (Celsius)
        Total Organic Carbon .....................   4.0  (mg/L)
        UV Absorbance at 254nm ...................   0.120(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)
        Cryptosporidium Removal+Inact. Required ..   3.0  (logs)
        Multiplier for Crypto. CT by ClO2 ........   7.5
        Peak Flow ................................   5.0  (MGD)
        Plant Flow ...............................   2.0  (MGD)
        Surface Water by SWTR .................... TRUE   (TRUE/FALSE)
Alum
        Alum Dose ................................  25.0  (mg/L as
Al2(SO4)3*14H2O)
Rapid Mix
        Volume of Basin ..........................   0.007(MG)
        Ratio of T50/Detention Time ..............   1.00 (ratio)
        Ratio of T10/Detention Time ..............   0.10 (ratio)
Flocculation
        Volume of Basin ..........................   0.040(MG)
        Ratio of T50/Detention Time ..............   1.00 (ratio)
        Ratio of T10/Detention Time ..............   0.50 (ratio)
Settling Basin
        Volume of Basin ..........................   0.167(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
        Liquid Volume ............................    0.02(MG)
        Ratio of T50/Detention Time ..............   1.00 (ratio)
        Ratio of T10/Detention Time ..............   0.50 (ratio)
        Chlorinated Backwash Water? .............. TRUE   (TRUE/FALSE)
        Filter Media (Anthracite/Sand or GAC) .... A/S    (S or G)
        Crypto Log Removal by Filters ............   2.00 (logs)
Contact Tank
        Volume of Basin ..........................   0.083(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                                   2.0  (mgd)
     Peak Hourly                               5.0  (mgd)

DISINFECTION INPUTS/CALCULATED VALUES
Surface Water Plant?                           TRUE
Giardia Removal + Inactivation Required        3.0  (logs)
Giardia Removal Credit by Filtration           2.5  (logs)
Giardia Removal Credit by Membranes            0.0  (logs)
Giardia Inactivation Credit Required           0.5  (logs)

Virus Removal + Inactivation Required          4.0  (logs)
Virus Removal Credit by Filtration             2.0  (logs)
Virus Removal Credit by Membranes              0.0  (logs)
Virus Inactivation Credit Required             2.0  (logs)

Crypto Removal + Inactivation Required         3.0  (logs)
Crypto Removal Credit by Filtration            2.0  (logs)
Crypto Removal Credit by Membranes             0.0  (logs)
Crypto Inactivation Credit Required            1.0  (logs)

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                        0.5        1.0        0.0400
Settling Basin                      0.3        1.0        0.1670
Filtration                          0.5        1.0        0.0200
Contact Tank                        0.5        1.0        0.0830
-------------------------------------------------------------------------------
```

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

3.2.1 Creating a Process Train

Once the information has been collected and organized, the following procedures can be followed to create the process train and operate the program:

Step 1 – Start WTP Model. The main menu will be displayed on the screen.

Step 2 – At the main menu, select "New" process train.

Step 3 – Type the name of the plant to be simulated and press "Enter". This displays the "Edit Process Train" screen. The screen offers unit process options the user can select to create your process train.

Step 4 – Highlight each unit process desired and press "Enter" to construct the process train. The options selected move to a list at the left side of the screen as in Figure 3-5. When the user has completed choosing options, the unit processes selected should match those in the block diagram in Figure 3-4.

Step 5 – Select "OK" to finalize the process train. The simulated plant is now created.

3.2.2 Unit Process Parameters

After the simulated plant has been created, the influent (raw) water data entry screen will appear. This, and a series of similar screens for each unit process selected when constructing the simulated plant, will prompt the user for specific information unique to this plant design, flow, and source water. The following sequence of steps can be used to enter the specified information for each unit process:

Step 1 – Enter the requested information at the data entry point marked by the blinking cursor. To move between data entry points use either the "Tab" function or position the cursor in the data entry field

Step 2 – After all the process information has been entered for a specific process, click the "Next" Button to move to the following data entry screen. The "OK" button will take the user back to the "Edit Process Train" window.

After all unit process data have been entered, the simulated plant model can be run or modified from the main menu.

3.2.3 Modifying a Process Train

The following sequence can be used to modify the input parameters in the created process train:

Step 1 – Return to main menu and select "Edit | Process Train", or click on the "Edit" button.

Step 2 – Highlight item in process train to be modified and click "Edit", or double click on item. Unit processes can be deleted by highlighting them and clicking the "Delete" button.

Step 3 – Modify the input parameters for the selected unit process in the same way the process unit parameters were entered.

3.2.4 Running the Model

To run the WTP model, click on the "Run" button at the bottom of the main window. The model will output summary tables of water quality parameters and DBPs for each unit process. Alternately, click on the "Reg" button at the bottom of the main window to see only a summary table of DBPs and inactivation for each unit process.

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.

4. INTERPRETING MODEL OUTPUT

This chapter provides a description of the output of the WTP program. An example process train was shown in Figure 3-3, and input parameters were summarized in Figures 3.5 and 3.6. The output generated after the "Run" command contains the full output from the simulation exercise. The output tables list the predicted parameters for each unit process in the simulated treatment plant. Each table also indicates the plant flow and temperature conditions for which the predictions were generated. The model is operated at average flow and temperature conditions. The output generated after the "Reg" command contains only one output of selected disinfection results at minimum temperature and peak flow conditions (Table 10).

4.1 EXAMPLE WTP MODEL OUTPUT

Tables 4-1 to 4-10 show the output tables resulting from running the model using the example process train shown in Figure 3-3.

- Table 1 is a summary table for raw, finished and distributed water quality (this table also indicates whether enhanced coagulation requirements were met or not).
- Table 2 lists selected input parameters such as temperatures flow rates, disinfection inputs, chemical doses and process hydraulic parameters.

Tables 3 to 10 summarize WTP model predictions at the end of each unit process.

- Table 3 lists predicted water quality profile (NOM characteristics, disinfectant residual and residence times).
- Table 4 summarizes inorganic water quality predictions.
- Table 5 summarizes predicted THMs and other DBPs (bromate, chlorite, TOX, THM species and TTHM).
- Table 6 summarizes five predicted HAA species and HAA5.
- Table 7 summarizes the remaining HAA species, HAA6, and HAA9.
- Table 8 summarizes predicted disinfection parameters (disinfectant residuals and CT ratios).
- Table 9 summarizes predicted CT values.

- Table 10 contains a summary of selected inactivation and DBP parameters (at peak hour and minimum temperature) related to regulatory constraints. This table is also generated after the "Reg" command.

```
                                    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        103
TOC                   (mg/L)         4.0        3.4        3.4        3.4
UV                    (1/cm)       0.120      0.055      0.055      0.055
(T)SUVA               (1/cm)         3.0        1.6        1.6        1.6
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         50         50         50
Free Cl2 Res.     (mg/L as Cl2)      0.0        2.8        1.7        1.1
Chloramine Res.   (mg/L as Cl2)      0.0        0.0        0.0        0.0
TTHMs                 (ug/L)           0         28         74        104
HAA5                  (ug/L)           0         35         54         65
HAA6                  (ug/L)           0         38         62         74
HAA9                  (ug/L)           0         48         71         83
TOX                   (ug/L)           0        177        360        472
Bromate               (ug/L)           0          0          0          0
Chlorite              (mg/L)         0.0        0.0        0.0        0.0
TOC Removal         (percent)                    15
E.C. raw TOC, raw SUVA, and finished TOC <= 2 exemptions do not apply
E.C. Step 1 TOC removal requirement NOT ACHIEVED
CT Ratios
  Virus                (-)           0.0      103.6      103.6      103.6
  Giardia              (-)           0.0        8.5        8.5        8.5
  Cryptosporidium      (-)           0.0        0.0        0.0        0.0
-----------------------------------------------------------------------------
```

Table 4-1 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                                   2.0  (mgd)
     Peak Hourly                               5.0  (mgd)

DISINFECTION INPUTS/CALCULATED VALUES
Surface Water Plant?                           TRUE
Giardia Removal + Inactivation Required        3.0  (logs)
Giardia Removal Credit by Filtration           2.5  (logs)
Giardia Removal Credit by Membranes            0.0  (logs)
Giardia Inactivation Credit Required           0.5  (logs)

Virus Removal + Inactivation Required          4.0  (logs)
Virus Removal Credit by Filtration             2.0  (logs)
Virus Removal Credit by Membranes              0.0  (logs)
Virus Inactivation Credit Required             2.0  (logs)

Crypto Removal + Inactivation Required         3.0  (logs)
Crypto Removal Credit by Filtration            2.0  (logs)
Crypto Removal Credit by Membranes             0.0  (logs)
Crypto Inactivation Credit Required            1.0  (logs)

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                        0.5        1.0        0.0400
Settling Basin                      0.3        1.0        0.1670
Filtration                          0.5        1.0        0.0200
Contact Tank                        0.5        1.0        0.0830
----------------------------------------------------------------------------
```

Table 4-2 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   4.0    0.120    3.0     0.0    0.0     0.00     0.00
Alum             7.2   4.0    0.120    3.0     0.0    0.0     0.00     0.00
Rapid Mix        7.2   3.4    0.079    2.3     0.0    0.0     0.08     0.08
Flocculation     7.2   3.4    0.079    2.3     0.0    0.0     0.48     0.56
Settling Basin   7.2   3.4    0.079    2.3     0.0    0.0     2.00     2.57
Chlorine (Gas)   7.0   3.4    0.055    1.6     3.9    0.0     0.00     2.57
Filtration       7.1   3.4    0.055    1.6     2.9    0.0     0.24     2.81
Contact Tank     7.1   3.4    0.055    1.6     2.8    0.0     1.00     3.80
Sodium Hydroxide 8.3   3.4    0.055    1.6     2.8    0.0     0.00     3.80
WTP Effluent     8.3   3.4    0.055    1.6     2.8    0.0     0.00     3.80
Average Tap      8.4   3.4    0.055    1.6     1.7    0.0    24.00    27.80
End of System    8.5   3.4    0.055    1.6     1.1    0.0    72.00    75.80
-----------------------------------------------------------------------------
TOC Removal (percent):     15
E.C. raw TOC, raw SUVA, and finished TOC <= 2 exemptions do not apply
E.C. Step 1 TOC removal requirement NOT ACHIEVED
-------------------------------------------------------------------------------
```

Table 4-3 WTP Model Output Table 3

```
                                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       18.6     0.0      50
Chlorine (Gas)    7.0    84       100         20       18.6     0.0      50
Filtration        7.1    84       100         20       18.6     0.0      50
Contact Tank      7.1    84       100         20       18.6     0.0      50
Sodium Hydroxide  8.3   102       100         20       18.6     0.0      50
WTP Effluent      8.3   102       100         20       18.6     0.0      50
Average Tap       8.4   102       100         20       18.6     0.0      50
End of System     8.5   103       100         20       18.6     0.0      50
-------------------------------------------------------------------------------
```

Table 4-4 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  CHBrCl2  CHBr2Cl  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    128     10      6        1       0      18
Contact Tank         0    0.0    177     18      8        2       0      28
Sodium Hydroxide     0    0.0    177     18      8        2       0      28
WTP Effluent         0    0.0    177     18      8        2       0      28
Average Tap          0    0.0    360     55     16        3       0      74
End of System        0    0.0    472     80     20        4       0     104
--------------------------------------------------------------------------
```

Table 4-5 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           6      7     14      0      0     28
Contact Tank         5     10     19      0      0     35
Sodium Hydroxide     5     10     19      0      0     35
WTP Effluent         5     10     19      0      0     35
Average Tap          4     21     28      0      1     54
End of System        4     26     33      0      1     65
--------------------------------------------------------------------------
```

Table 4-6WTP 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           3      8      2      0     30     40
Contact Tank         4      8      2      0     38     48
Sodium Hydroxide     4      8      2      0     38     48
WTP Effluent         4      8      2      0     38     48
Average Tap          7      8      1      0     62     71
End of System        9      8      1      0     74     83
-------------------------------------------------------------------------
```

Table 4-7 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    0.0
Alum             20.0  7.2   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Rapid Mix        20.0  7.2   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Flocculation     20.0  7.2   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Settling Basin   20.0  7.2   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Chlorine (Gas)   20.0  7.0   3.9    0.0   0.00   0.00    0.0     0.0    0.0
Filtration       20.0  7.1   2.9    0.0   0.00   0.00    1.7    20.7    0.0
Contact Tank     20.0  7.1   2.8    0.0   0.00   0.00    8.5   103.6    0.0
Sodium Hydroxide 20.0  8.3   2.8    0.0   0.00   0.00    8.5   103.6    0.0
WTP Effluent     20.0  8.3   2.8    0.0   0.00   0.00    8.5   103.6    0.0
Average Tap      20.0  8.4   1.7    0.0   0.00   0.00    8.5   103.6    0.0
End of System    20.0  8.5   1.1    0.0   0.00   0.00    8.5   103.6    0.0
-------------------------------------------------------------------------
```

Table 4-8 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          20.7      0.0     0.0     0.0
Contact Tank       103.6      0.0     0.0     0.0
Sodium Hydroxide   103.6      0.0     0.0     0.0
WTP Effluent       103.6      0.0     0.0     0.0
Average Tap        103.6      0.0     0.0     0.0
End of System      103.6      0.0     0.0     0.0
-----------------------------------------------------------------------------
```

Table 4-9 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    0.0
Alum              5.0  7.3   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Rapid Mix         5.0  7.3   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Flocculation      5.0  7.3   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Settling Basin    5.0  7.3   0.0    0.0   0.00   0.00    0.0     0.0    0.0
Chlorine (Gas)    5.0  7.2   3.9    0.0   0.00   0.00    0.0     0.0    0.0
Filtration        5.0  7.2   2.9    0.0   0.00   0.00    0.2     2.1    0.0
Contact Tank      5.0  7.2   2.8    0.0   0.00   0.00    1.2    10.6    0.0
Sodium Hydroxide  5.0  8.3   2.8    0.0   0.00   0.00    1.2    10.6    0.0
WTP Effluent      5.0  8.3   2.8    0.0   0.00   0.00    1.2    10.6    0.0
Average Tap       5.0  8.3   2.2    0.0   0.00   0.00    1.2    10.6    0.0
End of System     5.0  8.4   1.6    0.0   0.00   0.00    1.2    10.6    0.0
----------------------------------------------------------------------------
```

Table 4-10 WTP Model Output Table 10

Table 4-11 describes the parameters in the output from a simulation run. For each unit process, the predicted value in the table is the value at the effluent of the unit process.

Table 4-11 Summary of Predicted Parameters at the End of Each Unit Process

Predicted Parameter at End of Given Unit Process	
pH	
TOC	Total organic carbon (mg/L)
UVA	Ultraviolet absorbance at 254 nm (1/cm)
SUVA	Specific UV-254 (L-mg-m)
Cl2	Free chlorine concentration (mg/L)
NH2Cl	Combined chlorine concentration (mg/L)
Process Residence Time	Residence time (hours) in unit process
Cumulative Residence Time	Cumulative residence time (hours) through 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	Concentration of solids (mg/L)[1]
NH3-N	Ammonia concentration (mg/L)
Bromide	Bromide concentration (µg/L)
Temp	Average temperature (ºC)[2]
Ozone	Ozone residual (mg/L)
ClO2	Chlorine dioxide residual (mg/L)
CT ratios	
Giardia	CT ratio for *Giardia lamblia*
Virus	CT ratio Viruses
Crypto.	CT ratio for *Cryptosporidium*
DBPs	
CHCl3	Chloroform concentration (µg/L)
CHBrCl2	Dichlorobromoform concentration (µg/L)
CHBr2Cl	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 (in mg/L)

4.2 INTERPRETING MODEL OUTPUTS

The model is not intended as a replacement for treatability testing to evaluate the impact of various unit processes on disinfectant decay and DBP formation in specific water supplies, but does provide a useful tool for evaluating the potential effect of different unit processes on the interrelationships between many of the new and forthcoming regulations. Users of the program should be familiar with water treatment plant operation, as well as procedures and methodologies used to disinfect water and control DBP formation. It must be stressed that the model is largely empirical in nature. It can not 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, can not 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 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.

4.2.1 DBP Formation

The program predicts THM, HAA, and TOX formation after chlorination and chloramination. The program does not predict THM, HAA or TOX formation directly from the use of ozone or chlorine dioxide (in the absence of chlorination and chloramination). The program predicts bromate formation after ozone and chlorite formation after chlorine dioxide.

DBP Species and Sum of Species Calculations

The WTP model program predicts TTHM, HAA5, HAA6, and HAA9 formation using a single equation for total concentration. The prediction for the bulk DBP parameters are used to determine species concentrations as follows. The individual DBP species are predicted using equations for the concentration of each species. These *relative proportions* of the species are then applied to the bulk parameter concentrations to determine the individual concentrations. The equations are described in detail in Chapter 5.

For example, TTHM presented in the output file represent the concentration predicted by one TTHM equation. These concentrations also appear on the computer screen after the "DBPs" command is selected. The *proportion* of each individual THM concentration to the sum of the four THMs is determined from four individual THM predictive equations.

An example considers a treatment process that predicts the following concentrations of individual THMs:

50 µg/L chloroform ($CHCl_3$)
25 µg/L bromodichloromethane ($CHBrCl_2$)
20 µg/L dibromochloromethane ($CHBr_2Cl$)
5 µg/L bromoform ($CHBr_3$)
100 µg/L TTHM by summing individual species

In this example, the proportion of chloroform to the TTHM concentration is 50/100, or 0.50. The proportions for the other THMs are determined in a similar manner.

If the single equation predicts a TTHM concentration of 95 ìg/L, then the program will predict the following concentrations for the individual THMs:

47.5 µg/L chloroform ($CHCl_3$)
23.8 µg/L bromodichloromethane ($CHBrCl_2$)
19.0 µg/L dibromochloromethane ($CHBr_2Cl$)
4.7 µg/L bromoform ($CHBr_3$)
95 µg/L TTHM from single TTHM equation

Therefore, the individual THM concentrations associated with the TTHM value of 95 µg/L would be presented in the output file.

For HAA formation, the program first predicts HAA5 formation and uses the proportions predicted for the five species from the individual equations applied to the HAA5 bulk parameter prediction (as explained for THMs above). Next, the model predicts HAA6 formation, and follows the same proportional procedure to determine the concentration of BCAA. Thus, HAA6 is the sum of HAA5 and BCAA. This approach is possible as the HAA5 and HAA6 equations were developed using the same database.

HAA9 and the remaining three species equations were developed from a different database. To follow the same proportioning procedure as was used for TTHM, HAA5 and HAA6, a new HAA6 equation was developed from the same database as was used for HAA9. The model then calculates the difference between HAA9 and HAA6, and the proportioning procedure is applied to this difference.

The reason for performing the analyses in this manner is that the equations for TTHM, HAA5, HAA6, and HAA9 have been determined to be more accurate than the sum of the individual species, based upon verification analyses. Because the initial efforts using the model focused upon the impact of different DBP regulatory scenarios, the accuracy of the sum of species prediction was more important than that for the individual predictions.

4.2.2 Determination of Inactivation Ratio

The WTP model determines inactivation ratios for chlorine, chloramines, chlorine dioxide and ozone.

The inactivation ratio is used to evaluate whether a system meets disinfection requirements for surface waters or ground waters. For surface water systems (or ground water systems under the influence of surface water), the Interim Enhanced Surface Water Treatment Rule (IESWTR) **(REF)** maintain removal/inactivation requirements set forth in the 1989 SWTR and requires a 3-log (99.9 percent) removal/inactivation of *Giardia lamblia* cysts and a 4-log (99.99 percent) removal/inactivation of viruses. The IESWTR also requires a 2-log (99 percent) removal inactivation of *Cryptosporidium* for systems serving more than 10,000 persons. For ground water systems (not under the influence of surface waters), the Ground Water Disinfection Rule (GWDR) requires a 4-log removal/inactivation of viruses. In the WTP model, the type of source water (i.e., surface or ground water) is specified in the input file.

Although the IESWTR currently requires surface waters (or ground waters under the influence of surface water) to achieve a minimum 3-log removal/inactivation of *Giardia* and a 4.0-log removal/inactivation of viruses, the USEPA recommends that utilities achieve greater inactivation depending on the *Giardia* concentration in the raw water. According to the SWTR, the recommended levels of removal/inactivation are based on the raw water *Giardia* concentrations as shown in Table 4-12.

Table 4-12 Recommend *Giardia* and Virus Removal/Inactivation

Daily Average *Giardia* Cyst Concetration/100L	Recommended *Giardia* Removal/Inactivation	Recommended Virus Removal/Inactivation
1	3-log	4-log
1 – 10	4-log	5-log
10 – 100	5-log	6-log
100 – 10,000[1]	6-log	7-log
1,000 – 10,000[1]	7-log	8-log

For surface waters, the program establishes the recommended level of *Giardia* and virus removal/inactivation based on the raw water concentration of *Giardia* in the input file. For example, if a *Giardia* concentration in the range of 1 to 10 cysts is input, the removal/inactivation requirement will be 4-log for *Giardia* and 5-log for viruses. The log removal credit through filtration for *Giardia* and viruses is similar to that discussed above. Therefore, a system with a required 4-log and 5-log removal/inactivation for *Giardia* and viruses, respectively, would be required to provide a 1.5-log inactivation of *Giardia* and a 3-log inactivation of viruses.

The model output lists both the CT achieved (in Table 9) and the CT, or inactivation, ratio (Table 8). The inactivation ratio is defined as the level of inactivation (calculated as CT) achieved through a given process divided by the required amount of inactivation for *Giardia*, viruses or *Cryptosporidium* from the IESWTR or GWDR. If the value of the inactivation ratio at the treatment plant effluent (representing the first customer) is equal to or greater than 1.0, the system meets the disinfection requirements. For example, if the required CT value to meet a required level of inactivation is 100, and the calculated CT value through a given treatment process is 80, the resulting inactivation ratio for that process is 80/100, or 0.80. A complete description of the inactivation ratio algorithm (for *Giardia*, viruses and *Cryptosporidium*) is presented in Chapter 5.

The output file for a given modeled treatment system presents the inactivation ratio under two different scenarios. The first scenario describes average temperature and average flow conditions while the second describes minimum temperature and peak hourly flow conditions. The second scenario represents the most stringent disinfection conditions and, therefore, represents the conditions under which plants would most likely design their treatment systems to meet the disinfection requirements. The inactivation ratios visually displayed on the summary screen after the "Reg" command is selected, are the inactivation ratios predicted under the minimum temperature/peak flow conditions.

It is important to note that when free chlorine is used as the primary disinfectant in a surface water system using coagulation and filtration, a 0.5-log inactivation of *Giardia* will provide greater than 2.0-log inactivation of viruses. Similarly, for a non-filtering surface water, a 3.0-log inactivation of *Giardia* will provide a greater than 4.0-log inactivation of viruses. As a result, when free chlorine is used as the primary disinfectant, the level of inactivation required for *Giardia* is always greater than the corresponding level of inactivation required for viruses.

If chloramines are used as the primary disinfectant in a surface water treated with coagulation and filtration, however, a 0.5-log inactivation of *Giardia* will *not* provide greater than 2.0-log inactivation of viruses. In this case, the model will still set the required level of inactivation based on *Giardia* inactivation, not upon viruses. Thus, the inactivation ratio would provide an inaccurate description of the system's disinfection requirements..

4.2.3 Removal/Inactivation Credits

The WTP model allows for *Giardia*, Virus and *Cryptosporidium* removal credits for filtration based on recommendations in the SWTR, shown in Table 4-13. For surface water systems using coagulation and filtration, the model provides a 2.5-log removal credit for *Giardia* and a 2.0-log removal for *Cryptosporidium* and viruses. Therefore, the additional required inactivations (by disinfection or membrane treatment) for such systems are 0.5-log for *Giardia* and 2.0-log for viruses. For ground water systems using coagulation and filtration, the model provides a 2.0 log removal of viruses and therefore the required virus inactivation for such systems is assumed as 2.0-log.

It should also be noted that different types of filtration (i.e., direct, slow sand and diatomaceous earth) can provide different removal of *Giardia* cysts and viruses than coagulation and filtration systems. The current version of the model, however, does not account for different removals that may be associated with other types of filtration systems. It is intended that subsequent versions of the model will address this issue.

Table 4-13 Removal/Inactivation Credits for Treatment Processes

	Removal Credit		
Treatment Process	*Giardia*	Viruses	*Cryptosporidium*
Coagulation/Filtration	2.5-log	2-log	2.0-log
Membranes	0.5-log	--	--

5. DESCRIPTION OF MODEL EQUATIONS

This chapter presents the equations of the of the WTP model algorithms that simulate NOM removal, DBP formation and disinfectant decay in water treatment plants.

The basic modeling approach begins with the estimation of DBP precursor removal by individual process units in the process train of interest. The fate of applied disinfectant through the treatment process train is analyzed and the concentration of the disinfectant at the beginning and end of a process unit is determined. The final step involves the calculation of DBP formation based on water quality through the process train.

The following process, inactivation, DBP formation and disinfectant decay algorithms, that were already part of the 1992 WTP model (version 1.21), were modified and updated with recent data to reflect improved understanding of treatment processes:

- Coagulation
- Softening
- Granular activation carbon (GAC) adsorption
- Membranes
- THM formation - total and individual
- HAA formation - total (HAA5, HAA6) and individual species
- Chlorine decay
- Chloramine decay
- *Giardia* inactivation - high pH and alternative disinfectants

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:

- Prechlorination
- Ozone inactivation, oxidation and decay
- Chlorine dioxide inactivation and decay

- Biofiltration
- *Cryptosporidium* inactivation & physical removal
- HAA9 (and species) formation
- TOX formation
- Bromate formation
- Chlorite formation
- Formation of DBPs 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 parameters
- Removal of organic water quality parameters by coagulation, softening, GAC, membranes and ozone/biotreatment
- Disinfectant decay (chlorine, chloramines, chlorine dioxide, ozone)
- Total and individual THM concentrations
- Total and individual HAA concentrations
- Total organic halogen (TOX) concentrations
- Inactivation and CT

5.1 EMPIRICAL MODEL DEVELOPMENT

The WTP model primarily uses empirical correlation's to predict central tendencies of NOM removal, disinfection, and DBP formation in a treatment plant. The algorithms were generally developed using multiple linear regression. The relationship between various water quality parameters, such as THM species exhibit nonlinear behavior with respect to their controlling variables such as pH, temperature, chlorine dosage, TOC and bromide. An appropriate empirical relationship for such a function can be of the following form:

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

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 regression analysis can be performed to correlate ln(Y) with a linear combination of the independent variables. This analysis determines the intercept, ln(A), and the slopes for the independent variables (a, b and c). These constants can then be used to describe the equation shown in Equation 5-1.

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 a commercially available statistics package.

In selecting independent variable forms for describing the dependent variable, only one occurrence of each of the controlling variables was 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 was not possible. In cases where two correlated variables were of prime importance, they were considered in the equation in spite of the high correlation between them.

The equations shown in this chapter are accompanied by regression statistics. A selection of the following regression parameters are given for the equations: the 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 predictor variables combined; the adjusted correlation coefficient (R^2_{adj}), which is the multiple correlation coefficient adjusted by the number of predictor variables; the standard estimate of error (SEE), which measures the amount of scatter in the vertical direction of the data (i.e., around the dependent variable) about the regression plane; the F-statistic, which can be used to assess the goodness of fit using the F-test of the variance accounted for by regression; and the number of data points (n) used in equation development (Crow et al., 1960).

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 outside 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 that were not used in the development of the predictive equations. For some equations (e.g. ozone decay, chlorine dioxide decay), limited databases were available for model development and no additional data was available for verification.

The WTP model was verified using complete plant data from the ICR database. For some parameters a correction factor was developed as a result of verification. Correction factors were developed when the average ratio of predicted versus measured values differed 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. 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 the verification data that resulted in the 90th percentile errors, i.e., the data with the highest 10 percent absolute errors were not used for correction factor development. The correction factors are listed with the equations. If no correction factor is given, the model behaved within the desired parameters.

5.3 EQUATIONS FOR ALKALINITY AND PH ADJUSTMENT

The WTP model 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. The model assumes that the water treatment plant is, in effect, a closed system.

5.3.1 Carbonate Cycle

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):

$$Alkalinity = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{5-3}$$

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:

$$[HCO_3^-] = \alpha_1 C_{T,CO_3} \tag{5-4}$$

$$[CO_3^{2-}] = \alpha_2 C_{T,CO_3} \tag{5-5}$$

Where:

$$C_{T,CO_3} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{5-6}$$

$$\alpha_1 = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{5-7}$$

$$\mathbf{a}_2 = \frac{K_1 K_2}{[\,H^+\,]^2 + K_1 [\,H^+\,] + K_1 K_2} \tag{5-8}$$

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, the value for K_1 is $10^{-6.3}$ while the value for K_2 is $10^{-10.3}$.

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 ÄHº is the standard enthalpy change of the dissociation of carbonic acid to bicarbonate, Tº is the standard temperature of 298ºK (25ºC) and $K_1{}^o$ is the value of the equilibrium constant at Tº. 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 ÄHº 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} at 25ºC. 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 $25^\circ C$ ($298.15^\circ K$) 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:

$$\begin{aligned} Alkalinity &= (\alpha_1 + 2\alpha_2)C_{T,CO_3} + [OH^-] - [H^+] \\ &= \left(\frac{K_1[H^+] + K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)C_{T,CO_3} + \frac{K_w}{[H^+]} - [H^+] \end{aligned} \tag{5-15}$$

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 all positively charged ions except hydrogen and C_A is the equivalent concentration of all negatively charged ions except hydroxide, bicarbonate and carbonate.

Equation 5-16 can also be written as follows:

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

where:

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

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

$$\begin{aligned} K_{Ca^{2+}\_CaOH^{+}} &= \exp\left(\frac{-\Delta G^{\circ}}{RT}\right) \\ &= \exp\left[\frac{-72320\,\frac{J}{mole}}{\left(8.314\,\frac{J}{mole\bullet{}^{\circ}K}\right)(T)}\right] \end{aligned} \tag{5-20}$$

and

$$\begin{aligned} K_{Mg^{2+}\_MgOH^{+}} &= \exp\left(\frac{-\Delta G^{\circ}}{RT}\right) \\ &= \exp\left[\frac{-65180\,\frac{J}{mole}}{\left(8.314\,\frac{J}{mole\bullet{}^{\circ}K}\right)(T)}\right] \end{aligned} \tag{5-21}$$

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

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

$$= \exp\left[\frac{-159800\dfrac{J}{mole}}{\left(8.314\dfrac{J}{mole\bullet{}^{\circ}K}\right)(T)}\right] \tag{5-25}$$

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:

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

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

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

$$= \exp\left[\frac{-159760\,\dfrac{J}{mole}}{\left(8.314\,\dfrac{J}{mole\bullet{}^{\circ}K}\right)(T)}\right] \qquad \textbf{(5-29)}$$

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

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

$$C_{T,OCl} = [HOCl] + [\,OCl^{-}\,] \qquad \textbf{(5-31)}$$

where:

$$[HOCl] = \frac{[\,OCl^{-}\,][\,H^{+}\,]}{K_{HOCl\,\_\,OCl^{-}}} \qquad \textbf{(5-32)}$$

and

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

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

$$[\,OCl^-\,] = \frac{C_{T,OCl}}{1 + \dfrac{[\,H^+\,]}{K_{HOCl\,\_\,OCl^-}}} \qquad \textbf{(5-34)}$$

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

$$C_{T,NH_3} = [\,NH_4^+\,] + [\,NH_3\,] \qquad \textbf{(5-35)}$$

where:

$$[\,NH_3\,] = \frac{[\,NH_4^+\,]\,K_{NH_4^+\,\_\,NH_3}}{[\,H^+\,]} \qquad \textbf{(5-36)}$$

and

$$K_{NH_4^+\,\_\,NH_3} = \exp\left[\left(\frac{52210\,\dfrac{J}{mole}}{8.314\,\dfrac{J}{{}^\circ K \bullet mole}}\right)\left(\frac{1}{298.15^\circ K}\right)\right] - 21.4 \qquad \textbf{(5-37)}$$

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

$$[\,NH_4^+\,] = \frac{C_{T,NH_3}}{1 + \dfrac{K_{NH_4^+\,\_\,NH_3}}{[\,H^+\,]}} \qquad \textbf{(5-38)}$$

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

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

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

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

$$+ \frac{C_{T,NH_3}}{1 + \frac{K_{NH_4^{+}\_NH_3}}{[H^{+}]}} - \frac{C_{T,OCl}}{1 + \frac{[H^{+}]}{K_{HOCl\_OCl^{-}}}} \qquad \textbf{(5-39)}$$

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

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:

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

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:

$$C_{Ca} - C_{T,Ca} = C_{CO_3} - C_{T,CO_3} \qquad \textbf{(5-41)}$$

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_{CO3} is the sum of the aqueous phase carbonate concentration ($C_{T,CO3}$) 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

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

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 $C_{T,CO3}$ and substituting Equation 5-45 for $C_{T,Ca}$ yields the following:

$$C_{T,CO_3} = C_{CO_3} - C_{Ca} + \frac{K_{so,CaCO_3}\left(1 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2}\right)}{C_{T,CO_3}\left(\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}\right)} \tag{5-46}$$

Multiplying each term in Equation 5-46 by $C_{T,CO3}$ yields:

$$0 = C^2_{T,CO_3} - C_{T,CO_3}(C_{CO_3} - C_{Ca}) - K_{so,CaCO_3}\left(\frac{1 + \frac{K_{Ca^{2+} - CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} - Ca(OH)_{2\,(aq)}}}{[H^+]^2}}{\frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}}\right) \tag{5-47}$$

Using the quadratic formula to solve for $C_{T,CO3}$ yields:

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

where

$$a = 1 \tag{5-49}$$

$$b = C_{Ca} - C_{CO_3} \tag{5-50}$$

and

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

The model calculates $C_{T,CO3}$ from Equations 5-48 through 5-52 when

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

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

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

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:

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

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

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

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 be important.

A more realistic model would account for the kinetics of carbon dioxide transfer from the air into water by using an appropriate mass transfer model with the appropriate mass transfer coefficients. As an alternative to using such a kinetic model, two equilibrium models were considered for the water treatment plant model described in this paper. 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 equilibrium model, referred to as the closed system model, assumes no exchange of carbon dioxide between the water and the atmosphere. The water treatment plant model described in this chapter assumes 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 needs to be verified and the possibility of including the kinetics of carbon dioxide dissolution into the water treatment plant model needs further consideration, particularly for the unit processes in a water treatment plant.

5.4.2 Alum Coagulation, Flocculation, Clarification and Filtration

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

$$Al_2(SO_4)_3\_14\ H_2O \rightarrow 2\ Al^{3+} + 3\ SO_4^{2-} + 14\ H_2O \quad \textbf{(5-58)}$$

For the purposes of this model, all of the sulfate ions are assumed to remain dissociated and all of the aluminum ions are assumed to 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 25^{o}C). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

5.4.3 Ferric Coagulation, Flocculation, Clarification and Filtration

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

$$Fe_2(SO_4)_3\_\ H_2O \rightarrow 2\ Fe^{3+} + 3\ SO_4^{2-} + H_2O \quad \textbf{(5-59)}$$

For the purposes of this model, all of the sulfate 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 sulfate 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 ferric ions form insoluble ferric hydroxide becomes less valid at pH levels farther from the pH of minimum solubility (pH = 9 at 25^{o}C). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH. Also, the model does not account for any excess acidity that might accompany commercial ferric sulfate.

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

$$FeCl_3\_6\ H_2O \rightarrow Fe^{3+} + 3\ Cl^{-} + 6\ H_2O \qquad \textbf{(5-60)}$$

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 25°C). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH. Also, the model does not account for any excess acidity that might accompany commercial ferric chloride.

5.4.4 Precipitative Softening, Clarification and Filtration

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

$$Ca(OH)_{2\ (s)} \rightarrow Ca^{2+} + 2\ OH^{-} \qquad \textbf{(5-61)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, pH.

Softening pH Correction

WTP model verification with ICR softening plant data showed a slight underprediction of softened water pH. The corrected pH is given below:

$$pH_{corr} = \frac{pH_{pred} - 1.86}{0.71} \qquad \textbf{(5-62)}$$

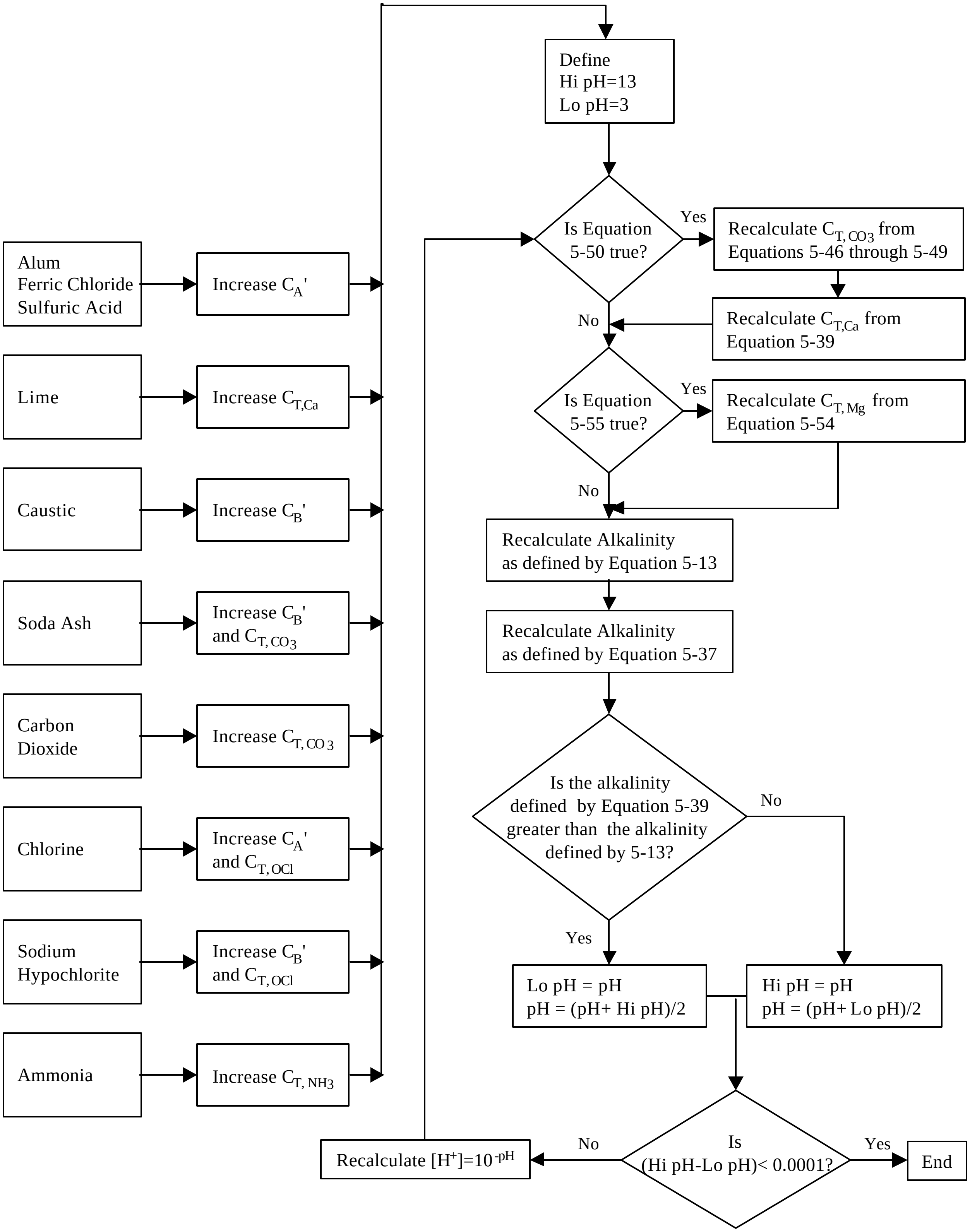


Figure 5-1 Algorithm for Calculating pH Changes Due to Chemical Addition

5.4.5 Chlorine Addition

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

$$Cl_{2\,(g)} + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad \textbf{(5-63)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, pH.

5.4.6 Sodium Hypochlorite Addition

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

$$NaOCl \rightarrow Na^+ + OCl^- \qquad \textbf{(5-64)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, pH.

5.4.7 Potassium Permanganate Addition

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

$$KMnO_4 \rightarrow K^+ + MnO_4^- \qquad \textbf{(5-65)}$$

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:

$$MnO_4^- + 4\,H^+ + 3\,e^- \rightarrow MnO_2 + 2\,H_2O \qquad \textbf{(5-66)}$$

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 5-65 and 5-66 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 5-65 and 5-66 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 effected 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:

$$H_2SO_4 \rightarrow 2\,H^+ + SO_4^{2-} \qquad \textbf{(5-67)}$$

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 above is used to obtain a new value for [H^+] and, hence, 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:

$$NaOH \rightarrow Na^+ + OH^- \qquad \textbf{(5-68)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, 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:

$$Ca(OH)_{2\ (s)} \rightarrow Ca^{2+} + 2\ OH^- \qquad \textbf{(5-69)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, 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:

$$Na_2CO_3 \rightarrow 2\ Na^+ + CO_3^{2-} \qquad \textbf{(5-70)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, 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 above is used to obtain a new value for $[H^+]$ and, hence, 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:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \textbf{(5-71)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, 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:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad \textbf{(5-72)}$$

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 above is used to obtain a new value for $[H^+]$ and, hence, pH.

5.4.15 Impact of Membrane Processes on pH and Alkalinity

Membrane processes can alter the alkalinity of a given water through the rejection of specific ions. Changes in $C_{T,Ca}$, $C_{T,Mg}$, $C_{T,CO3}$ and ($C_B' - C_A'$) through a membrane process determine the alkalinity and pH of the permeate water. The 1992 model used data reported by Taylor, et al. (1987, 1989) to determine their relationships with molecular weight cutoff (MWC), recovery and operating pressure. In an effort to better predict pH changes through membrane processes, removals of hardness, alkalinity and C_T reported in literature studies were compiled and analyzed. The database contained data from 16 published studies, using a range of water sources, membrane types and operating conditions. Microfiltration, nanofiltration and reverse osmosis membranes were represented.

The removal of hardness by membrane processes is represented by Equation 5-73. The 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.

$$\ln\left[\left(\frac{TH_0}{TH_f}\right)-1\right] = 36.801 - 3.327[\ln(TH_0)] - 6.787[\ln(MWC)] - 0.027(R)[\ln(TH_0)] + 0.229[\ln(R)][\ln(TH_0)][\ln(MWC)] \quad \textbf{(5-73)}$$

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

Where,

TH_0 = feed water total hardness (mg $CaCO_3$/L): $61 \le TH_0 \le 340$

TH_f = product water total hardness (mg $CaCO_3$/L): $14 \le TH_f \le 340$

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

MWC = molecular weight cut-off (Da): $100 \le MWC \le 40{,}000$

where TH_0 is the feed water total hardness in mg/L as calcium carbonate, TH_f is the product water total hardness in mg/L as calcium carbonate, MWC is the molecular weight cutoff, and 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:

$$\ln\left[\left(\frac{ALK_0}{ALK_f}\right)-1\right] = 14.602 - [\ln(MWC)]\{1.667 - 0.054[\ln(Alk_0)] - 0.203[\ln(R)]\} \quad \textbf{(5-74)}$$

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

Where,

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

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

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

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

where ALK_0 is the feed water alkalinity in mg/L as calcium carbonate, ALK_f is the product water alkalinity in mg/L as calcium carbonate, MWC is the molecular weight cutoff, Pressure is the operating pressure in lb/in^2 and Recovery is the ratio between the product water flow rate and the feed water flow rate in percent.

The rejection of total carbonates is given by the following equation:

$$\ln\left[\left(\frac{C_{T,CO_3,0}}{C_{T,CO_3,f}}\right) - 1\right] = \left[\ln\left(CO_{3,0}\right)\right]\left\{2.741 - 0.487\left[\ln\left(MWC\right)\right]\right\} - 0.101\left[\ln\left(R\right)\right] \qquad \textbf{(5-75)}$$

$$(R^2 = 0.94,\ R^2_{adj} = 0.93,\ SEE = 0.545,\ F = 155,\ n = 34)$$

Where,

$CO_{3,0}$ = feed water total carbonate (mg $CaCO_3$/L): $86 \le CO_{3,0} \le 328$

$CO_{3,f}$ = product water total carbonate (mg $CaCO_3$/L): $1.4 \le CO_{3,f} \le 94$

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

MWC = molecular weight cut-off (Da): $100 \le MWC \le 40{,}000$

where $C_{T,CO3,0}$ is the feed water total carbonate concentration in mg/L as calcium carbonate, $C_{T,CO3,f}$ is the product water total carbonate concentration in mg/L as calcium carbonate, MWC is the molecular weight cutoff, Pressure is the operating pressure in lb/in^2 and Recovery is the ratio between the product water flow rate and the feed water flow rate in percent.

The changes in alkalinity and $C_{T,CO3}$ calculated by Equations 5-74 and 5-75 are used in combination with Equation 5-15 to calculate changes in pH. 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 5-74. Once the new value of [H$^+$] is obtained, Equation 5-39 is used in combination with the new values of $C_{T,Ca}$ and $C_{T,Mg}$ (calculated by Equation 5-73) to calculate a new value for the quantity ($C_B' - C_A'$).

5.5 EQUATIONS FOR NOM REMOVAL

5.5.1 Alum Coagulation, Flocculation and Filtration

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 interactive variables made up 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 oxidation processes conducted during the coagulation, flocculation, clarification and filtration processes that were not accounted for. Furthermore, both the TOC and UVA databases contained very few data points.

Since 1992 significant research has been done on trying to predict TOC and UVA removal by coagulation.

TOC Removal

Version 2.0 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) was based on dissolved organic carbon (DOC); however, the author showed it to predict TOC removal nearly as well. Tseng and Edwards (1999) developed a similar model for TOC removal; however, the improvements in predictions of the TOC based model were not significant compared to the DOC based model. The DOC model does not consider particulate organic matter (POC), which, together with DOC comprises TOC.

The 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 were below 5 or above 8, 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 divides TOC into fractions that are sorbable ($TOC_{sorb,eq}$) and nonsorbable ($TOC_{nonsorb}$) by the coagulant, shown in Equation 5-74. The nonsorbable fraction cannot be removed by coagulation, and TOC removal is attributed solely to the sorbable fraction, as shown in Equation 5-75. Additional information and detail about the equations can be found in Edwards (1997).

The relationship between TOC_{sorb} and input parameters is based on the Langmuir adsorption 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).

$$TOC_{settled} = TOC_{sorb,eq} + TOC_{nonsorb} \qquad \textbf{(5-76)}$$

and

$$TOC_{sob,eq} = \mathrm{f}\left(pH_{coag}, coag.type, Dose_{coag}, SUVA_{raw}, TOC_{raw}\right) \qquad \textbf{(5-77)}$$

(based on Langmuir adsorption model)

$$TOC_{nonsorb} = TOC_{raw} * F_{nonsorb} \qquad \textbf{(5-78)}$$

where

$$F_{nonsorb} = K_1 * SUVA_{raw} + K_2 \qquad \textbf{(5-79)}$$

(K_1 and K_2 are coagulant dependent; K_1 has a negative value)

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

Where,

$TOC_{settled}$ = settled TOC (mg/L): $1.0 \le TOC_{settled} \le 26$

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

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

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

pH_{coag} = coagulation pH: $5.5 \le pH_{coag} \le 8.0$

UVA Removal

In the 1992 version of the WTP model, UVA removal equations were limited by small data sets. 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), thereby significantly extending the data sets used for equation development..

$$UVA_{removed} = 5.716\left(UVA_{raw}\right)^{1.0894}\left(Dose_{coag}\right)^{0.306}\left(pH_{coag}\right)^{-0.9513} \qquad \textbf{(5-80)}$$

(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 (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, Flocculation and Filtration.

Unlike the equations for alum coagulation (based solely on full-scale observations) the equations for ferric coagulation 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 be skewed by the large number of observations from two sources.

TOC Removal

The semi-empirical sorption model developed by Edwards (1997) was model was designed to handle both alum and iron coagulation and is used in the WTP model. 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 were 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 5-76 through 5-79. The regression statistics and data ranges are given below.

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

Where,

$TOC_{settled}$ = settled 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_{coag} = coagulation pH: $3.0 \leq pH_{coag} \leq 8.0$

UVA Removal

In the 1992 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 2.0, Equation 5-80 is also used to calculate UVA removal for ferric coagulation. During equation development it was determined that one equation could be used to describe removal due to both coagulants assuming coagulant doses are represented in equivalent measures.

5.5.3 Precipitative Softening, Clarification, and Filtration

For WTP model version 1.21, softening data was collected for only twelve precipitative softening plants. Nine field-scale observations were available for these seven 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 even softening pH. Due to the lack of 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

New equations were developed for the modified WTP model. An empirical equation, 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 softening plants with or without coagulant addition. For plants that do not use a coagulant together with lime, the coagulant dose term in the equation goes to a value of one.

$$TOC_{removed} = 4.657 \times 10^{-4} \left(TOC_{raw}\right)^{1.3843} \left(pH_{sft}\right)^{2.2387} \left(Dose_{\lim e}\right)^{0.1707} \left(1 + Dose_{coag}\right)^{2.4402} \qquad \textbf{(5-81)}$$

($R^2 = 0.96$, $R^2_{adj} = 0.96$, 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): $0 \leq Dose_{coag} \leq 0.138$

Softening TOC Removal Correction

The predictions of TOC removal in softening plants were verified using ICR plant data and the corrected predictions of softening pH. TOC was slightly underpredicted. Thus, the following correction factor was developed:

$$TOC_{corr} = \frac{TOC_{pred}}{0.87} \qquad \textbf{(5-82)}$$

UVA Removal

The same AWWA/WITAF database (Tseng et al., 1996) was used to develop an UVA removal equation for softening, shown in Equation 5-83. The equation uses TOC predicted by Equation 5-81 and raw water SUVA to predict UVA removal. It is still difficult to obtain 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). 90 percent of the data used to develop the equation for UVA removal had a SUVA between 1.8 and 5.2 L/mg-m

$$UVA_{removed} = 0.01685 \left(TOC_{removed}\right)^{0.8367} \left(SUVA_{raw}\right)^{1.2501} \qquad \textbf{(5-83)}$$

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

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 GAC Adsorption

TOC breakthrough curves for alum coagulated, settled and filtered 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 logistics function were predicted based on one single GAC adsorption case only which was assumed to be representative. The logistic function parameters were a function of empty bed contact time (EBCT) only and did not take into account the type of GAC used and water quality factors such as pH and ionic strength. The model calculated a running average TOC removal based on the EBCT and the regeneration frequency. The model was not intended to simulate the dynamics of TOC removal by this process but, rather, simulate average water quality conditions within the treatment plant being considered.

In 1992, a sufficient database was not available to develop a separate equation for UVA removal, the model 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 a new GAC algorithm.

TOC Removal

New TOC removal predictions by granular activated carbon (GAC) were developed using the logistics function also to predict a breakthrough curve. The parameters of the logistics functions were developed to take into account the impact of influent TOC and pH, empty bed contact time (EBCT) and the impact of single versus multiple blended contactors.

In most GAC applications of any significant size, GAC adsorbers will not be implemented as single contactors. Instead, multiple contactors will be operated in a parallel configuration. Parallel GAC contactors are operated in a staggered mode wherein each contactor is at a different level of breakthrough 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 the GAC reactivated when the blended effluent exceeds the target effluent concentration. The effluent from the contactor in operation the longest can 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 5-84.

$$\bar{f} = \frac{\overline{C}_E}{C_0} = \frac{1}{t_R}\int_0^{t_R} f(t)\ dt \qquad \textbf{(5-84)}$$

in which f is the fraction remaining after a given contactor at a given time, t; $\bar{f}$ is the average effluent fraction of the blended water remaining; $\overline{C}_E$ is the average effluent concentration of the blended water; C_0 is the influent concentration; and t_R is the reactivation time. Roberts and Summers (1982) indicate that this approximation is valid when the number of parallel contactors exceeds 10.

Another approach is to use the logistics function equation to fit the data from the single contactor and then integrate the logistics equation to produce an equation that will predict the performance of multiple contactors operated in parallel. The fraction remaining in the effluent as a function of time has the form

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

in which A, B, and D are parameters derived from the fit of the model to the data. Replacing f(t) in Equation 5-84 with the logistics function, Equation 5-85, and integrating yields the following equation which represents the blended effluent breakthrough curve:

$$TOC_{eff} = A_0 + A_f + A_f * \frac{\ln\left(\frac{1+Be^{-D*bv}}{1+B}\right)}{D*bv} \tag{5-86}$$

The WTP model uses Equation 5-86 to predict TOC concentrations after GAC treatment.

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 empty bed contact time. The data set consisted of thirty-two studies, which included 302 GAC-TOC breakthrough curves.

The TOC breakthrough curves were fit with a logistic function model which 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, (correlation 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 5-87 through 5-91 below.

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

(5-87)

$$A_f = TOC_{\inf}\left\{\left(3.244\times10^{-3} * EBCT_{adj}\right)+5.383\times10^{-1}\right\}+1.033\times10^{-5}\left(EBCT_{adj}\right)+1.759\times10^{-5}$$

(5-88)

$$D = TOC_{\inf}\left\{\left(-1.079\times10^{-5} * EBCT_{adj}\right)+4.457\times10^{-4}\right\}+1.861\times10^{-5}\left(EBCT_{adj}\right)-2.809\times10^{-4}$$

(5-89)

$$B = 100$$ **(5-90)**

$$bv = \frac{1440\left(RT\right)}{EBCT_{adj}}$$ **(5-91)**

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 5-92

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$$EBCT_{adj} = EBCT\left\{1+0.044\left(pH_{baseline}-pH_{\inf}\right)\right\}$$ **(5-92)**

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 = bedvolumes

RT = blended runtime, days

EBCT = empty bed contact time, minutes

Where,

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 = bedvolumes

RT = blended runtime (days)

EBCT = empty bed contact time (minutes)

UVA Removal

The removal of UVA by GAC was not addressed in the 1992 WTP model; it was assumed to be equivalent to 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 correlated to effluent TOC concentrations by linear correlations, shown in Equations 5-93 and 5-94.

Coagulation Prior to GAC:

For waters coagulated (both conventional and enhanced coagulation) prior to GAC, the database used for model development contained the data the ICR Treatment Studies. The database consisted of over 4000 paired TOC and UVA GAC effluent data.

$$UVA_{eff} = 0.0195(TOC_{eff}) - 0.0077 \quad \textbf{(5-93)}$$

(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 Biotreatment 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).

$$UVA_{eff} = 0.0014(TOC_{eff}) - 0.00141 \quad \textbf{(5-94)}$$

(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): $0.1 \leq TOC_{eff} \leq 6.1$

5.5.5 Membranes

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) for the 1992 WTP model. Data from these three studies were combined and analyzed for relationships between nominal molecular weight cutoff (MWC) and removal of natural organic parameters. 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 2.0 of the model, data from numerous studies was compiled to investigate membrane performance for the model. Recently, regulatory pressures including new regulations governing filtration, disinfection and DBPs have fueled the 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 target removals of organic and inorganic compound. Currently, it is possible to find membranes to meet any given treatment objective. Thus, under the current status of membrane design and availability, it was decided to allow the User to define membrane performance, instead of trying to predict it.

The User is given two options for membranes: (1) microfiltration (MF) or ultrafiltration (UF), and (2) nanofiltration (NF) or reverse osmosis (RO) membranes. For MF/UF, no NOM rejection is allowed, as these membranes generally only reject particulate NOM. The User is requested to input percent recovery, and log removal credits for *Giardia*, viruses, and *Cryptosporidium.* For NF/RO membrane, which can reject 90 percent and more 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. The user is also requested to input molecular weight cut-off, percent recovery, and log removal credits for *Giardia*, viruses, and *Cryptosporidium.*

5.5.6 Ozone and Biotreatment

Ozonation and biotreatment were not previously considered by the WTP model. For version 2.0, a new algorithm was developed to predict NOM removal by ozone and biotreatment.

The amount of NOM removal due to ozonation and biotreatment is a function of the ozone dose and the water being treated and reports have ranged from 5 to 40 percent (Miltner and Summers, 1992; Joselyn and Summers, 1992). 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.

Data for the ozonation and biotreatment algorithm was collected from research studies. The database used to develop the equation to predict UVA oxidation by ozone was comprised of bench-scale batch experimental data and included both raw and settled water oxidation. 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. Little data was available of UVA oxidation at pilot- or full-scale. The equation was developed from data in 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 5-95. Multiple linear regression analysis was used to correlated oxidized UVA to transferred ozone dose, TOC and UVA prior to ozonation. The database was not extensive enough to include water quality parameters such as pH, ammonia, and temperature or bromide concentration. Additionally, time was not included.

$$UVA_{O_3} = 0.622(UVA)^{0.931}\left(\frac{O_3}{TOC}\right)^{-0.252} \quad \textbf{(5-95)}$$

(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): $0.35 \leq O3/TOC \leq 2.30$

Research has shown that ozonation results in the formation 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.

TOC removal by biological filtration in the WTP model occurs only after ozonation for filters with no disinfection in the backwash water. The presence of disinfectant in the backwash water is an User input in the model (either "Yes" or "No"). Attempts were made to develop empirical correlations; however, only relationships with poor predictive abilities could be developed. Instead, the WTP model assumes 15 percent TOC removal for anthracite/sand filters and 20 percent TOC removal for GAC filters. These values represent average removals from 51 and 37 data points reported in literature studies for anthracite/sand filters and GAC filters, respectively. The model assumes no UVA removal through the biofilter.

5.6 DISINFECTANT DECAY

5.6.1 Modeling Disinfectant Decay in Treatment Plants

Basins and filters are modeled as a number of continuous flow, stirred tank reactors (CFSTRs) connected in series. A complete description of this model 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:

$$C_f = C_i + tr \tag{5-96}$$

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. 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 N^{th} CFSTR is given by the following set of equations:

$$C_{1,f} = C_{1,i} + t_1 r_1 \tag{5-97}$$

$$C_{2,i} = C_{1,f} \qquad \textbf{(5-98)}$$

$$C_{2,f} = C_{2,i} + t_2\, r_2 \qquad \textbf{(5-99)}$$

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$$C_{N,i} = C_{N-1,f} \qquad \textbf{(5-100)}$$

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

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 5-97 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 5-98 is used to obtain $C_{2,i}$. Equation 5-99 can then be used to calculate $C_{2,f}$ from known values of t_2 and r_2. The process is repeated through Equation 5-101 until $C_{N,f}$ is calculated.

In Equations 5-97 through 5-101, the reaction rate is given by the differential equation appropriate to the reaction of interest. For a first order decay process, r_N is given by the following expression:

$$r_N = -k\, C_{N,f} \qquad \textbf{(5-102)}$$

For a second order decay process, r_N is given by the following expression:

$$r_N = -k\, C_{N,f}^2 \qquad \textbf{(5-103)}$$

For an mth order decay process, r_N is given by the following expression:

$$r_N = -k\, C_{N,f}^m \qquad \textbf{(5-104)}$$

In order to use a set of equations such as those defined by Equations 5-97 through 5-101, 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 the following expression:

$$F = \frac{C_{N,f}}{C_{1,i}} = 1 - \exp\left(\frac{-Nt}{t_m}\right)\left[1 + \frac{Nt}{t_m} + \frac{1}{2!}\left(\frac{Nt}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt}{t_m}\right)^{N-1}\right] \qquad \textbf{(5-105)}$$

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 be 10 percent of the influent tracer concentration in a step tracer study. At a time equal to t_{10}, the following holds:

$$0.1 = 1 - \exp\left(\frac{-Nt_{10}}{t_m}\right)\left[1 + \frac{Nt_{10}}{t_m} + \frac{1}{2!}\left(\frac{Nt_{10}}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt_{10}}{t_m}\right)^{N-1}\right] \qquad \textbf{(5-106)}$$

Using this equation, the theoretical value of t_{10}:t_m can be calculated for any value of N by using an iteration procedure.

Table 5-1 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 user input values for t_{theo}, 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:

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

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 medium or 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).

Because N can only take on integer values, a continuous distribution of t_{10}:t_m does not theoretically exist. However, 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 5-1. Once the value of N is selected from Table 5-1, Equations 5-97 through 5-101 are used in conjunction with the appropriate rate equations to calculate chlorine and chloramine decay in the basin or filter of interest.

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 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:

$$\frac{dC_t}{dt} = \frac{-a_2 * C_t}{a_1 + C_t} \qquad \textbf{(5-108)}$$

Equation 5-108 takes the following form when integrated:

$$C_t = a_1 * \ln\frac{C_0}{C_t} - a_2 * t + C_0 \qquad \textbf{(5-109)}$$

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 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, chlorinated at Cl_2:TOC ratios ranging from 0.5 to 2.5. Decay data was typically taken between 15 minutes and 120 hours, and most decay curves consist of at least 7 data points.

The kinetic parameter α_1 was found to be very highly dependent on the chlorine dose, and is given by a strong linear relationship in Equation 5-110:

$$a_1 = -0.8147(C_0) \qquad \textbf{(5-110)}$$

(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

$$a_2 = k_2 * TOC \qquad \textbf{(5-111)}$$

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

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

(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:

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

Where,

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

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

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

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, chlorinated at Cl2: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 strong linear correlation with the chlorine dose, shown in Equation 5-114.

$$a_1 = -0.8408(C_0) \qquad \textbf{(5-114)}$$

(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. The relationship for k_2 is poorer than for raw water.

$$a_2 = k_2(TOC) \tag{5-115}$$

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:

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

Where,

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

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

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

α_1 and α_2 are kinetic parameters

Chlorine Residual Correction

Chlorine residual concentrations were verified in the plant and in the distribution system using ICR plant data. Upon verification, a slight underprediction of chlorine residual was observed. Thus the chlorine residual was corrected.

The WTP model predicts the change of chlorine residual through a unit process by taking the difference between the residual at the influent and the effluent of the unit process and subtracting this value from the influent. The correction factor was applied to the difference, as shown in equation 5-118:

$$Cl_2 \text{ residual}_{\text{eff, corr}} = Cl_2 \text{ residual}_{\text{influent}} + \frac{\left(Cl_2 \text{ residual}_{\text{effluent}} - Cl_2 \text{ residual}_{\text{influent}}\right)}{0.85} \qquad \textbf{(5-118)}$$

This resulted in a better fit of the model and residuals analysis of errors with a median value of 0.

5.6.3 Chloramine Decay

The 1992 model predicted chloramine using the same raw water database that was used for 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 m-th order reaction for 0 to 10 hours, where the order was related to chloramine dose using an extremely poor correlation ($R^2 = 0.05$). Decay after 10 hours was modeled using a first order reaction.

New chloramine decay equations were developed for the WTP model version 2.0 using data from a study from Rajbandhari (2001). The database contained data for 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 chlorine decay was used to predict chloramine decay.

The equations have the following form:

$$\frac{dCA_t}{dt} = \frac{-a_2 * CA_0}{a_1 + CA_t} \qquad \textbf{(5-119)}$$

Equation 5-119 takes the following form when integrated:

$$CA_t = a_1 * \ln\frac{CA_0}{CA_t} - a_2 * t + CA_0 \qquad \textbf{(5-120)}$$

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 consisted of 5 waters, three treatment conditions (raw, settled, ozonated and biotreated), 3 target chloramine residuals at 24 hours (2, 3, and 4 mg/L) and 3 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 Cl2:NH4 of 4.5:1.

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

The first kinetic rate parameter, α_1, was strongly correlated to chloramine dose, as show by Equation 5-121.

$$a_1 = -0.99(CA_0) \tag{5-121}$$

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

The second kinetic rate parameter, α_2, is given by the following equation:

$$a_2 = -0.015(UVA) \tag{5-122}$$

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

5.6.4 Chlorine Dioxide Decay

New chlorine dioxide decay equations were developed, based on an unpublished database from Colorado State University (Carlson, 2001). The database is comprised of 9-different waters and 72 chlorine dioxide decay curves. Separate decay equations were developed for raw and settled waters.

For the WTP model, chlorine dioxide decay is modeled by an initial demand followed by first order decay. The initial demand is assumed to be instantaneous. The first order decay is characterized by constant k_1 and uses a starting point chlorine dioxide dose equal to the concentration after the initial demand.

The initial demand, is characterized by the following two equations for raw and settled water:

Raw:

$$ClO_{2,init} = 0.0157(TOC * UVA)^{-0.284}(ClO_2\ Dose)^{1.802}(pH)^{1.47}(Temp)^{-0.0475} \quad \textbf{(5-123)}$$

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

Where,

ClO_2 Dose = chlorine dioxide dose, mg/L: 0.50 ≤ ClO_2 Dose ≤ 3.0

TOC = total organic carbon, mg/L: 1.4 ≤ TOC ≤ 8.1

UVA = ultraviolet absorbance, 1/cm: 0.034 ≤ UVA ≤ 0.263

pH: 6.5 ≤ pH ≤ 7.9

Temp = Temperature, ºC: 4.3 ≤ Temp ≤ 21.5

Settled:

$$ClO_{2,init} = 0.0124(TOC * UVA)^{-0.182}(ClO_2\ Dose)^{1.415}(pH)^{1.85}(Temp)^{-0.0395} \quad \textbf{(5-124)}$$

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

Where,

ClO_2 Dose = chlorine dioxide dose, mg/L: 1.0 ≤ ClO_2 Dose ≤ 3.0

TOC = total organic carbon, mg/L: 1.3 ≤ TOC ≤ 6.1

UVA = ultraviolet absorbance, 1/cm: 0.037 ≤ UVA ≤ 0.097

pH: 6.4 ≤ pH ≤ 7.4

Temp = Temperature, ºC: 4.5 ≤ Temp ≤ 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 by equations 5-123 and 5-124 is used as the initial chlorine dioxide concentration. The kinetic parameter, k_1, was correlated to water quality parameters and is shown in the following two equations:

Raw:

$$k_1 = -0.0117(TOC * UVA)^{0.445}(ClO_{2,init})^{-0.584}(Temp)^{0.485} \quad \textbf{(5-125)}$$

(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: $0.21 \le ClO_{2,\,init} \le 2.37$

TOC = total organic carbon, mg/L: 1.4 ≤ TOC ≤ 8.1

UVA = ultraviolet absorbance, 1/cm: 0.034 ≤ UVA ≤ 0.263

Temp = Temperature, ºC: 4.3 ≤ Temp ≤ 21.5

Settled:

$$k_1 = -0.0146(TOC * UVA)^{0.941}(ClO_{2,init})^{-0.140}(Temp)^{0.533} \qquad \textbf{(5-126)}$$

(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: $0.62 \le ClO_{2,\,init} \le 1.86$

TOC = total organic carbon, mg/L: 1.3 ≤ TOC ≤ 6.1

UVA = ultraviolet absorbance, 1/cm: 0.037 ≤ UVA ≤ 0.097

Temp = Temperature, ºC: 4.5 ≤ Temp ≤ 21.5

5.6.5 Ozone Decay

Ozonation was not previously included in the WTP model and 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 used for equation development and 20 percent were used for verification with an independent data set. A random number generator was used to separate the data. Finally, raw and settled water data were combined to develop a single equation for ozone demand in a dissipation chamber.

The ozone residuals represent those measured in dissipation chambers only. The ozone residual can be calculated by subtracting the ozone demand from the ozone dose shown below.

$$O_3\ demand = O_3\ dose - O_3\ residual \qquad \textbf{(5-127)}$$

and

$$O_3\ demand = 0.995\left(O_3\ dose\right)^{1.312}\left(\frac{O_3}{UVA}\right)^{-0.386}\left(SUVA\right)^{-0.184}\left(T_{50}\right)^{0.068}\left(Alk\right)^{0.023}\left(pH\right)^{0.229}\left(Temp\right)^{0.087} \qquad \textbf{(5-128)}$$

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

Where,

O_3 Dose = transferred ozone dose, mg/L: $0.50 \leq O_3$ Dose ≤ 6.4

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

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

T_{50} = time, minutes: $5.2 \leq T_{50} \leq 24.3$

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

pH: $5.8 \leq pH \leq 8.7$

Temp = Temperature, ºC: 5 Temp 32

5.7 DBP FORMATION

The WTP Model version 2.0 simulates the formation of THMs, HAAs and TOX under conditions of full-scale treatment plants. One of the biggest challenges to DBP modeling is an assessment of the impact of different treatment processes on the formation of DBPs. For many advanced treatment processes, like GAC, membranes, and biofiltration, there is little DBP formation data at the plant level. Multiple points of chlorination also present a challenge, as the DBP formation algorithms are based on single doses of chlorine and not chlorine residuals.

The 1992 version of the WTP model used THM equations that were developed from raw water chlorination studies using very high chlorine doses in some cases. These equations were used to predict TTHM formation in both raw and treated waters. The equations predicted concentrations on a molar basis and had to be converted to a mass basis using a second empirical correlation. The equations were limited in that:

- the database used for developing the equations had waters primarily low in bromide, so the use of these equations for high bromide waters was limited;
- the equations were based on data collected from thirteen waters (Amy, et. al., 1987) and, therefore, represented the best generalized method of simulating THM formation; and
- bromine incorporation during THM formation is a function of chlorine dosage. Excess chlorination does not result in bromine incorporation as high as would be realized under more moderate chlorination schemes. The database used for developing the equations contained experiments with higher chlorine dosages than would normally be expected in water treatment. Therefore, the equations underpredicted bromine incorporation.

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.

The program predicts THM, HAA, and TOX formation after chlorination and chloramination. Three separate sets of DBP equations were developed for raw waters, finished waters, and GAC treated waters. The program does not predict THM, HAA or TOX formation directly from the use of ozone or chlorine dioxide, (in the absence of chlorination and chloramination). The program predicts bromate formation after ozone and chlorite formation after chlorine dioxide.

5.7.1 DBP Modeling Under Different Chlorination Scenarios

The calculation of DBP formation in water treatment plants would be relatively simple if water quality conditions were constant from the point of chlorination to the end of the distribution system. However, water quality conditions are not normally constant from the point of chlorine application to the end of the distribution system.

In the new WTP model, DBP formation under three chlorination scenarios is modeled.

1. Prechlorination only (Figure 5-2): A single point of chlorination prior to rapid mixing. For this approach, DBP formation is modeled in two separate, additive stages. First, the raw water DBP formation model is proportionally adjusted with the prechlorination factor for DBP formation through sedimentation. Formation after sedimentation is modeled using the

treated water model with settled water quality (TOC, UVA, pH) and chlorine residual. Since the water has already been in contact with chlorine, and the fraction of the NOM that reacts very rapidly with the chlorine has most likely been consumed, only the relative formation during the reaction time between the plant effluent and sedimentation is added to the formation predicted in the first step by the raw water model.

When chlorine is added before or during coagulation, UVA values will be lower than by coagulation only, due to UVA oxidation by the chlorine. This is taken into account by the following equation developed from the database of Summers et al. (1998 b) for 20 waters:

Settled water UVA, after prechlorination is given by:

$$UVA_{Pre-Cl_2} = 0.7437\left(UVA_{no\ Cl_2}\right) + 0.0042 \qquad \textbf{(5-129)}$$

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

where,

$UVA_{Pre\text{-}Cl2}$ = settled UVA after prechlorination (1/cm): $0.015 \le UVA_{Pre\text{-}Cl2} \le 0.120$

$UVA_{no\ Cl2}$ = settled UVA without prechlorination (1/cm): $0.017 \le UVA_{no\ Cl2} \le 0.150$

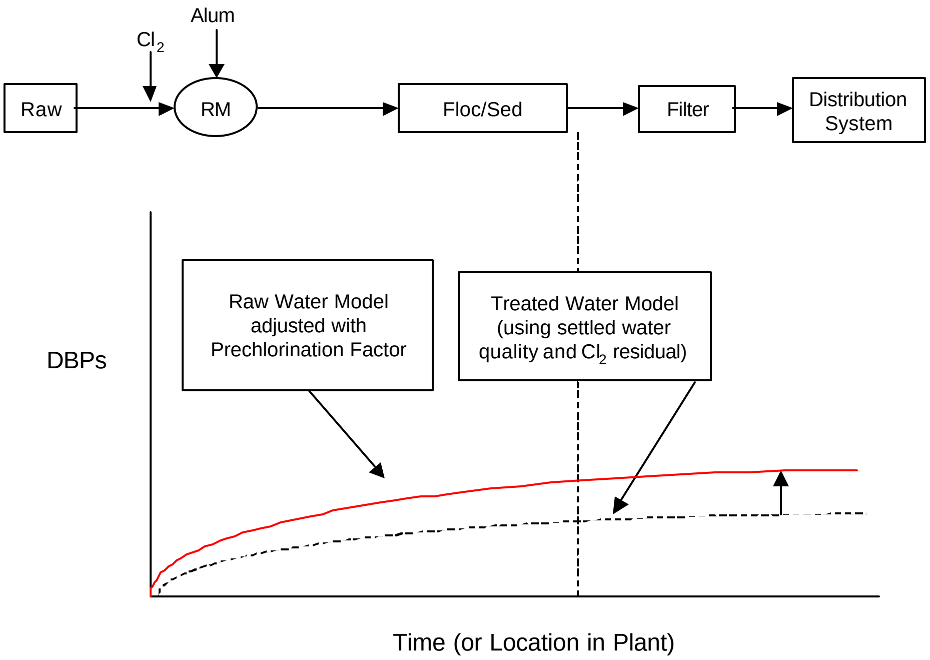

Figure 5-2 DBP Modeling: Pre-Chlorination Only

2. Post-chlorination only (Figure 5-3A): A single point of chlorination after sedimentation. The treated water model is applied using settled water quality and chlorine dose.

3. Pre- and post-chlorination (Figure 5-3B): Two points of chlorination--prior to rapid mixing and after sedimentation. For this approach, the raw water model proportionally adjusted with the prechlorination factor is applied for DBP formation before the filter. After rechlorination, the treated water model is applied using settled water quality, with time = 0 and the UVA decreased by prechlorination. The rechlorination dose is added to the chlorine residual at that point to yield the effective dose for input to the DBP formation model. DBP formation at the second chlorination point is added to that resulting from the first chlorination point to model the cumulative formation.

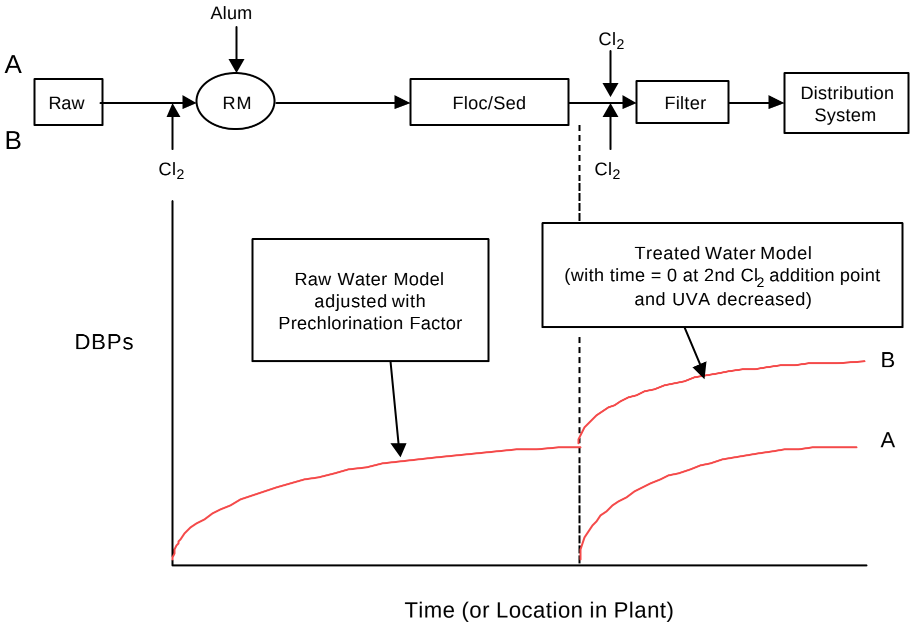

Figure 5-3 DBP Modeling: (A) Post-Chlorination and (B) Pre- and Post-Chlorination

DBP formation is modeled as cumulative formation through processes and with multiple points of chlorination. Currently, 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.

5.7.2 Impact of Bromide Incorporation on DBP Formation

The impact of bromide 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. As DBPs are formed across multiple unit processes, bromide, which has been incorporated into DBPs in previous unit processes, is no longer available for subsequent formation. Thus, the changes in bromide concentration must be taken into account during DBP modeling through a treatment plant.

The WTP model tracks bromide incorporation across each unit process. 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 beginning of the unit process. This new bromide concentration is then used as the influent to the following unit process.

This version of the model does not account for bromide oxidation by chlorine.

5.7.3 Predicting Species and Bulk DBP Parameters

The WTP model program predicts TTHM, HAA5, HAA6, and HAA9 formation using a single equation for total concentration. The prediction for the bulk DBP parameters are used to determine species concentrations as follows. The individual DBP species are predicted using equations for the concentration of each species. These *relative proportions* of the species are then applied to the bulk parameter concentrations to determine the individual concentrations. The DBP equations are described in detail later in this chapter.

For example, TTHM presented in the output file represent the concentration predicted by one TTHM equation. These concentrations also appear on the computer screen after the "DBPs" command is selected. The *proportion* of each individual THM concentration to the sum of the four THMs is determined from four individual THM predictive equations.

An example considers a treatment process that predicts the following concentrations of individual THMs:

50 µg/L chloroform ($CHCl_3$)
25 µg/L bromodichloromethane ($CHBrCl_2$)
20 µg/L dibromochloromethane ($CHBr_2Cl$)
5 µg/L bromoform ($CHBr_3$)
100 µg/L TTHM by summing individual species

In this example, the proportion of chloroform to the TTHM concentration is 50/100, or 0.50. The proportions for the other THMs are determined in a similar manner.

If the single equation predicts a TTHM concentration of 95 ìg/L, then the program will predict the following concentrations for the individual THMs:

47.5 µg/L chloroform ($CHCl_3$)
23.8 µg/L bromodichloromethane ($CHBrCl_2$)
19.0 µg/L dibromochloromethane ($CHBr_2Cl$)
4.7 µg/L bromoform ($CHBr_3$)
95 µg/L TTHM from single TTHM equation

Therefore, the individual THM concentrations associated with the TTHM value of 95 ìg/L would be presented in the output file.

For HAA formation, the program first predicts HAA5 formation and uses the proportions predicted for the five species from the individual equations applied to the HAA5 predictions (as explained for THMs above). Next, the model predicts HAA6 formation, and follows the proportional procedure to determine the concentration of BCAA. Thus, HAA6 is the sum of HAA5 and BCAA. This approach is possible as the HAA5 and HAA6 equations were developed using the same database. For HAA9 and the remaining three species, the same procedure is applied. The model calculates the difference between HAA9 and HAA6, and the proportioning procedure for the three species is applied to this difference. Thus, HAA9 is the sum of HAA6, BDCAA, CDBAA, and TBAA.

The reason for performing the analyses in this manner is that the equations for TTHM, HAA5, HAA6, and HAA9 have been determined to be more accurate than the sum of the individual species, based upon verification analyses. Because the initial efforts using the model focused upon the impact of different DBP regulatory scenarios, the accuracy of the sum of species prediction was more important than that for the individual predictions.

5.7.4 Free Chlorine DBPs: Raw Waters

New empirical equations predicting THMs (total and four species), HAA5, 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, Br, pH, and temperature, as well as applied chlorine dose and reaction time, are used to model DBP formation.

THMs

$$TTHM = 4.121\times10^{-2}(TOC)^{1.098}(Cl_2)^{0.152}(Br^-)^{0.068}(Temp)^{0.609}(pH)^{1.601}(time)^{0.263} \qquad \textbf{(5-130)}$$

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

Where,

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

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: $6.5 \le pH \le 8.5$

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

The equations for the 4 THM species have a similar form, shown in Equation 5-131. The coefficients and regressions statistics for the equations are given in Table 5-2.

$$THM = A(TOC)^a(Cl_2)^b(Br^-)^c(Temp)^d(pH)^e(time)^f \qquad \textbf{(5-131)}$$

Table 5-2 Summary of Coeffiecients and Regression Statisticsfor Raw Water THM Species Predictions

	Coefficients for Equation 5-131						
THM Species	A	a	b	c	d	e	f
$CHCl_3$	$6.237\text{x}10^{-2}$	1.617	-0.094	-0.175	0.607	1.403	0.306
$CHCl_2Br$	$1.445\text{x}10^{-3}$	0.901	0.017	0.733	0.498	1.511	0.199
$CHBr_2Cl$	$2.244\text{x}10^{-6}$	-0.226	0.108	1.810	0.512	2.212	0.146
$CHBr_3$	$1.49\text{x}10^{-8}$	-0.983	0.804	1.765	0.754	2.139	0.566

	Regression Statistics		
THM Species	R^2_{adj}	*F*	n
$CHCl_3$	0.87	847	786
$CHCl_2Br$	0.90	1164	786
$CHBr_2Cl$	0.89	1087	786
$CHBr_3$	0.61	199	786

HAAs

The same empirical equation format was used to develop new HAA predictive equations in raw waters using the same database as was used for THM formation. Equations 5-132 and 5-133 show the equations for HAA5 and HAA6 predictions:

$$HAA5 = 30.0(TOC)^{0.997}(Cl_2)^{0.278}(Br^-)^{-0.138}(Temp)^{0.341}(pH)^{-0.799}(time)^{0.169} \qquad \textbf{(5-132)}$$

$$(R^2_{adj} = 0.87, F = 813, n = 738)$$

$$HAA6 = 9.98(TOC)^{0.935}(Cl_2)^{0.443}(Br^-)^{-0.031}(Temp)^{0.387}(pH)^{-0.655}(time)^{0.178} \qquad \textbf{(5-133)}$$

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

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: $6.5 \leq pH \leq 8.5$

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

Individual HAA species equations were developed in similar format and are generally described by Equation 5-134. The equation coefficients and regression statistics are given in Table 5-3.

$$HAA = A(TOC)^a (Cl_2)^b (Br^-)^c (Temp)^d (pH)^e (time)^f \qquad \textbf{(5-134)}$$

Table 5-3 Summary of Coeffiecients and Regression Statistics for Raw Water HAA Species Predictions

	Coefficients for Equation 5-134						
HAA Species	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

	Regression Statistics		
HAA Species	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

No raw water HAA9 and TOX data was available for model development. Thus, this version of the model uses equations developed for coagulated waters, show in Equation 5-143 to 5-144 and Table 5-6.

Boundary conditions for reaction time, temperature, and pH need to 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 colder or warmer treatment conditions, the equations will be used outside the boundary conditions. For treatment scenarios with very short reaction times, less than two hours, use of the model will also be used outside the boundary conditions

5.7.5 Free Chlorine DBPs: Pre-chlorination

The 1992 version of the model simplified prechlorination, i.e., chlorine added prior to coagulation. It assumed that DBPs formed during the coagulation process from chlorine addition could be modeled using raw water DBP formation models. In a recent prechlorination study performed by Summers et al. (1998b), the authors concluded that coagulation was effective in decreasing the DBPs formed with prechlorination relative to the chlorination of raw water, i.e., DBP precursors were removed by coagulation in the presence of chlorine.

To better predict DBP formation for prechlorination plants, an empirical prechlorination factor was developed to account for the decrease in DBP formation that occurs when chlorine is added either pre- or post-rapid mixing (RM), as compared to raw water DBP formation using data from 20 waters (Summers et al., 1998b). This relationship is used to modify the DBP formation that would be predicted by the raw water DBP formation model. The percent decrease in DBP formation (compared to raw water DBP formation) that can be attributed to coagulation was related to TOC removal by coagulation, to account for the higher precursor removals at higher coagulant doses.

$$Decrease in\ TTHM\ Formation(\%) = 0.875(\%\ TOC\ Removal) \tag{5-135}$$

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

$$Decrease in\ HAA\ Formation(\%) = 0.776(\%\ TOC\ Removal) \tag{5-136}$$

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

$$Decrease in\ TOX\ Formation(\%) = 0.865(\%\ TOC\ Removal) \tag{5-137}$$

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

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 prechlorination equations were not verified due to a lack of availability of prechlorination data.

5.7.6 Free Chlorine DBPs: Coagulated and Softened Waters

New DBP formation equations for treated water were based on work performed by Amy et al. (1998) using both iron and alum coagulated waters.

The DBP prediction equations for treated waters use the combined TOC and UVA (TOC*UVA) input parameter to model DBP formation. The TOC*UVA input parameter accounts for the impact of treatment on NOM removal as well as NOM characteristics, i.e., NOM reactivity. The boundary conditions for these equations are similar to those for raw water. 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 6.5-8.5 pH range. For enhanced coagulation and softening, the pH boundary conditions may be exceeded.

THMs

Equation 5-138 shows the equation used to predict TTHM formation:

$$TTHM = 23.9(DOC * UVA)^{0.403}(Cl_2)^{0.225}(Br^-)^{0.141}(1.1560)^{(pH-7.5)}(1.0263)^{(Temp-20)}(time)^{0.264} \tag{5-138}$$

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

The equations for the 4 THM species have a similar form, shown in Equation 5-139. The coefficients and regressions statistics for the equations are given in Table 5-4.

$$THM = A(DOC * UVA)^{a}(Cl_2)^{b}(Br^-)^{c}(D)^{(pH-7.5)}(E)^{(Temp-20)}(time)^{f} \quad \textbf{(5-139)}$$

Table 5-4 Summary of Coeffiecients and Regression Statisticsfor Treated Water THM Species Predictions

	Coefficients for Equation 5-139						
THM Species	A	a	b	c	d	e	f
$CHCl_3$	266	0.403	0.424	-0.679	1.1322	1.0179	0.333
$CHCl_2Br$	1.68	0.260	0.114	0.462	1.0977	1.0260	0.196
$CHBr_2Cl$	$8.0x10^{-3}$	-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

	Regression Statistics		
THM Species	R^2_{adj}	*F*	n
$CHCl_3$	0.90	682	288
$CHCl_2Br$	0.85	393	288
$CHBr_2Cl$	0.94	948	245
$CHBr_3$	0.93	579	171

HAAs

The equations developed for HAA5 and HAA6 formation in treated waters are shown Equation 5-140 and 5-141, respectively.

$$HAA5 = 30.7(DOC * UVA)^{0.302}(Cl_2)^{0.541}(Br^-)^{-0.012}(0.932)^{(pH-7.5)}(1.021)^{(Temp-20)}(time)^{0.161} \quad \textbf{(5-140)}$$

$(R^2_{adj} = 0.94, F = 1040, n = 288)$

$$HAA6 = 41.6(DOC * UVA)^{0.328}(Cl_2)^{0.585}(Br^-)^{-0.121}(0.9216)^{(pH-7.5)}(1.022)^{(Temp-20)}(time)^{0.150} \quad \textbf{(5-141)}$$

$(R^2_{adj} = 0.94, F = 1040, n = 288)$

Where,

DOC = dissolved 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): $23 \le Br \le 308$

Temperature = 20 °C

pH = 7.5

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

Individual HAA species equations were developed in similar format and are generally described by Equation 5-142. The equation coefficients and regression statistics are given in Table 5-5.

$$HAA = A(DOC * UVA)^{a} (Cl_2)^{b} \left(Br^{-}\right)^{c} (D)^{(pH-7.5)} (E)^{(Temp-20)} (time)^{f} \quad \textbf{(5-142)}$$

Table 5-5 Summary of Coeffiecients and Regression Statistics for Treated Water HAA Species Predictions

	Coefficients for Equation 5-142						
HAA Species	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

	Regression Statistics		
HAA Species	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

Power function equations were also developed for the remaining three HAA species and HAA9 using the ICR Treatment Studies database. The median value in the GAC influent from each study with coagulated waters only was used. Data reported as being below the detection limit was set equal to one half of the detection limit.

HAA9 and the remaining three species equations were developed from a different database than were HAA5 and HAA6. To follow the same proportioning procedure as was used for TTHM, HAA5 and HAA6, a new HAA6 equation was developed from the same database as was used for HAA9. The WTP model calculates HAA9 as a bulk parameter and uses the proportioning procedure for the difference between HAA6 and HAA9 (as described in Section 5.7.3) to calculate the concentrations of the three species.

The equations have a similar format to that shown in Equation 5-142. Similar to the other treated water DBP equations, correction factors were developed for pH and temperature. However, for these three equations, the baseline pH value was 8.0. Equation 5-143 shows the equation format and Table 5-6 shows the equation coefficients and regression statistics are shown in Table 5-6 for the remaining three HAA species. These equations are also applied to raw waters and ozonated and biotreated waters.

$$HAA = A(DOC * UVA)^a (Cl_2)^b (Br^-)^c (D)^{(pH-8.0)} (E)^{(Temp-20)} (time)^f \qquad \textbf{(5-143)}$$

where,

DOC = dissolved organic carbon (mg/L): $1.5 \leq DOC \leq 13.0$

UVA = UV absorbance at 254 nm (1/cm): $0.018 \leq UVA \leq 0.480$

Cl_2 = applied chlorine dose (mg/L): $1.5 \leq Cl_2 \leq 13.1$

Br = bromide concentration (μg/L): $10 \leq Br \leq 630$

Temp = temperature (°C): $3 \leq Temp \leq 32$

pH: $6.2 \leq pH \leq 9.9$

t= reaction time (hours): $3.1 \leq t \leq 72$

Table 5-6 Summary of Coeffiecients and Regression Statistics for Treated Water HAA9 Species Predictions

	Coefficients for Equation 5-143						
HAAs	A	a	b	c	d	e	f
HAA6							
CDBAA	$3.70\text{x}10^{-3}$	-0.0162	-0.170	0.972	0.839	1.054	0.685
DCBAA	$5.89\text{x}10^{-1}$	0.230	0.140	0.301	0.700	1.022	0.422
TBAA	$5.59\text{x}10^{-6}$	0.0657	-2.51	2.32	0.555	1.059	1.26
HAA9	10.78	0.25	0.50	0.054	0.894	1.015	0.348

	Regression Statistics			
HAAs	R^2_{adj}	*SEE (mg/L)*	*F*	n
HAA6				
CDBAA	0.76	2.2	130	244
DCBAA	0.61	4.9	63	241
TBAA	0.82	1.4	188	228
HAA9	0.86	23	233	228

TOX

A new empirical correlation was developed for treated water TOX formation, shown by equation 5-144. This equation was also developed from analysis of ICR Treatment Studies database, using GAC influent samples that were coagulated and softened only. Similar to the equations for HAA9 species, the data used in development of the TOX equation used only the median data value for each study. This equation is also used for raw and ozonated and biotreated waters.

$$TOX = 109(TOC * UVA)^{0.362}(Cl_2)^{0.129}(Temp)^{0.211}(time)^{0.182} \qquad \textbf{(5-144)}$$

$$(R^2_{adj} = 0.73, SEE = 269\, mg\ Cl^-/L, F = 267, n = 386)$$

Where,

TOX = total organic halogen (μg Cl^-/L): 25 ≤ TOX ≤ 893

DOC = dissolved organic carbon (mg/L): 1.5 ≤ DOC ≤ 8.5

UVA = UV absorbance at 254 nm (1/cm): 0.010 ≤ UVA ≤ 0.300

Cl_2 = applied chlorine dose (mg/L): 1.3 ≤ Cl_2 ≤ 14

Br = bromide concentration (μg/L): 10 ≤ Br ≤ 665

Temp = temperature (°C): 3 ≤ Temp ≤ 20

PH: 6.9 ≤ Temp ≤ 9.5

t= reaction time (hours): 2.0 ≤ t ≤ 120

DBP Correction

ICR plant data was used to verify DBP formation in the plant and the distribution system for convention treatment plants. Analysis of the data showed that some of the DBP predictions were outside the acceptable verification criteria. Thus, the equations were recalibrated. Some DBPs equations did not require calibration. The correction factors shown in Table 5-7 are applied to the DBP formation equations, as shown in Equation 5-145. Since ICR plant data was used to develop CDBAA, BDCAA, TBAA, HAA9, and TOX equations, no correction factors were developed for these species and the bulk parameters. Furthermore, the predictions of species such as MCAA, MBAA, and DBAA were not calibrated because their values were typically extremely low.

$$DBP_{corr} = \frac{DBP_{pred}}{CorrectionFactor} \qquad \textbf{(5-145)}$$

Table 5-7 Correction Factors for In-Plant and Distribution System DBP Formation

	Correction Factors	
DBPs	In-Plant	Distribution System
THMs		
$CHCl_3$	1	1.1
$CHCl_2Br$	0.92	1
$CHBr_2Cl$	0.65	0.46
$CHBr_3$	1	1
TTHM	1	1
HAAs		
MCAA	1	1
DCAA	0.72	1.1
TCAA	1.3	1.3
MBAA	1	1
DBAA	1	1
BCAA	0.86	2.0
HAA5	1.1	1.1
HAA6	1.1	1.1

5.7.7 Free Chlorine DBPs: GAC Treated Waters

One of the difficulties in modeling DBP formation of treated waters following specific treatment processes is the lack of availability of data. Previously, the WTP model did not uses separate equations for DBP predictions following advanced treatment processes, such as GAC adsorption. However, the ICR provided a significant database that could be used to develop equations for GAC and membrane treated waters.

Separate DBP equations for GAC treated waters 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 was being below the detection limit. This would be expected for GAC effluents with very low TOC concentrations. Instead of discarding all below detection limit data, the data was replace with a value of one half of the detection limit.

Equations were developed for individual THM species and TTHM, individual HAA species and HAA5, HAA6 and HAA9, as well as for TOX.

THMs

Equation 5-146 shows the predictive equation for TTHM. The format of the species equations is given by Equation 5-147, and the coefficients and regression statistics are shown in Table 5-8.

$$TTHM = 17.7(DOC * UVA)^{0.475}(Cl_2)^{0.173}(Br^-)^{0.246}(1.316)^{(pH-8.0)}(1.036)^{(Temp-20)}(time)^{0.366} \quad \textbf{(5-146)}$$

(R^2_{adj} = 0.83, SEE = 9.3 mg/L, F = 2336, n =2946)

$$THM = A(DOC * UVA)^{a}(Cl_2)^{b}(Br^-)^{c}(D)^{(pH-7.5)}(E)^{(Temp-20)}(time)^{f} \quad \textbf{(5-147)}$$

Table 5-8 Summary of Coeffiecients and Regression Statistics for GAC Treated Water THM Species Predictions

	Coefficients for Equation 5-147						
THM Species	A	a	b	c	d	e	f
$CHCl_3$	101.0	0.615	0.699	-0.468	1.099	1.035	0.336
$CHCl_2Br$	7.57	0.443	0.563	0.0739	1.355	1.030	0.281
$CHBr_2Cl$	3.99	0.535	0.125	0.365	1.436	1.037	0.322
$CHBr_3$	$1.47\text{x}10^{-1}$	0.408	-0.115	0.961	1.438	1.048	0.324

	Regression Statistics			
THM Species	*R^2_{adj}*	*SEE (mg/L)*	*F*	n
$CHCl_3$	0.73	4.3	1320	2960
$CHCl_2Br$	0.58	4.1	678	2959
$CHBr_2Cl$	0.73	3.9	1338	2948
$CHBr_3$	0.77	4.8	1642	2948

HAAs

Equations 5-148, 5-149 and 5-150 show the predictive equation for HAA5, HAA6, and HAA9, respectively. The format of the species equations is given by Equation 5-151, and the coefficients and regression statistics are shown in Table 5-9.

$$HAA5 = 41.2(DOC * UVA)^{0.498}(Cl_2)^{0.388}(Br^-)^{-0.156}(0.867)^{(pH-8.0)}(1.021)^{(Temp-20)}(time)^{0.263} \quad \textbf{(5-148)}$$

(R^2_{adj} = 0.59, SEE = 5.0 mg/L, F = 666, n = 2807)

$$HAA6 = 37.8(DOC * UVA)^{0.511}(Cl_2)^{0.374}(Br^-)^{-0.079}(0.913)^{(pH-8.0)}(1.022)^{(Temp-20)}(time)^{0.280} \quad \textbf{(5-149)}$$

(R^2_{adj} = 0.63, SEE = 5.0 mg/L, F = 793, n = 2880)

$$HAA9 = 20.6(DOC * UVA)^{0.509}(Cl_2)^{0.253}(Br^-)^{0.053}(0.823)^{(pH-8.0)}(1.019)^{(Temp-20)}(time)^{0.425} \quad \textbf{(5-150)}$$

(R^2_{adj} = 0.62, SEE = 7.0 mg/L, F = 386, n = 1417)

Where,

DOC = dissolved 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): $3 \leq Temp \leq 33$

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

$$HAA = A(DOC * UVA)^{a}(Cl_2)^{b}(Br^{-})^{c}(D)^{(pH-8.0)}(E)^{(Temp-20)}(time)^{f} \qquad \textbf{(5-151)}$$

Table 5-9 Summary of Coeffiecients and Regression Statistics for GAC Treated Water HAA Species Predictions

	Coefficients for Equation 5-151						
HAAs	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
CDBAA	5.56×10^{-2}	0.831	-0.296	0.782	0.477	1.016	0.886
DCBAA	2.19	0.665	0.270	0.221	0.587	0.985	0.379
TBAA	1.65×10^{-4}	1.59	-2.19	2.06	0.575	0.983	1.78

	Regression Statistics			
HAAs	R^2_{adj}	*SEE (μg/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
CDBAA	0.45	1	216	1571
DCBAA	0.52	1	285	1589
TBAA	0.21	1	66	1435

TOX

An equation was also developed for TOX formation for GAC treated waters, shown in Equation 5-152. Data from the ICR USEPA TSD database was used. Similar to 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.

$$TOX = 168(TOC * UVA)^{0.529}(Cl_2)^{0.349}(1.009)^{(Temp-20)}(time)^{0.239} \tag{5-152}$$

$(R^2_{adj} = 0.74, SEE = 18\ mg\ Cl^-/L, F = 1000, n = 1373)$

Where,

TOX = total organic halogen (μg Cl^-/L): $0.4 \le TOX \le 200$

DOC = dissolved organic carbon (mg/L): $0.14 \le DOC \le 2.0$

UVA = UV absorbance at 254 nm (1/cm): $0.001 \le UVA \le 0.045$

Cl_2 = applied chlorine dose (mg/L): $0.6 \le Cl_2 \le 7.5$

Br = bromide concentration (μg/L): $10 \le Br \le 645$

Temp = temperature (°C): $2.4 \le Temp \le 31$

PH: $6.9 \le pH \le 9.5$

Time = reaction time (hours): $3.0 \le t \le 100$

5.7.8 Free Chlorine DBPs: Membrane Treated Waters

The ICR Treatment Studies also contained DBP formation data following membrane treatment. This data was not used to develop separate DBP predictive equations for the WTP model. The membrane treated DBP database was significantly smaller than the GAC treated DBP database and the database was strongly biased towards Florida waters. Furthermore, the impacts of pH and chlorine dose were not well defined in the database.

Instead, WTP model applies the DBP equations developed for GAC treated waters to membrane treated waters with good success.

5.7.9 Free Chlorine DBPs: Ozonated and Biotreated Waters

Little data is available for developing free chlorine DBP equations for ozonated and biotreated waters. Instead, the WTP model uses the raw, coagulated and GAC treated water equations where applicable.

5.7.10 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.

Even with this speculation, there are insufficient data available to develop a model of THM and HAA formation during chloramination. Nevertheless, because THM and HAA formation is observed during chloramination, the model must account for it. The 1992 model assumed that the rate of THM formation during chloramination is 20 percent of the rate of trihalomethane formation during chlorination. The assumption was based on 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 2.0 uses the same approach as described above, i.e., applying a constant factor to the predicted free chlorine DBP formation to determine DBPs formed by chloramines. However, the current model used ICR data to develop the constant factors for each species and the bulk parameters.

ICR plant data that contained chloramine disinfection was used. The predictions given by the equations developed for chlorine disinfection were compared with actual recorded DBP values. Based on this comparison, a factor was developed. For the bulk DBP parameters as well as some of the species the 20 percent formation assumption held very well. However for some HAA species, significant differences were observed. Table 5-10 summarizes the factors used to calculate the percent of DBPs formed after chloramines compared to free chlorine.

Table 5-10 Percent of DBPs Formed After 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***	
$CHCl_3$	20	MCAA	20
$CHCl_2Br$	20	DCAA	50
$CHBr_2Cl$	20	TCAA	5
$CHBr_3$	20	MBAA	20
TTHM	20	DBAA	20
		BCAA	30
		HAA5	20
TOX	20	HAA6	20
		TBAA	20
		CDBAA	20
		BDCAA	20
		HAA9	20

5.7.11 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. 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 5-153 and 5-154, respectively. The database consisted of 10 raw waters, ozonated under varying conditions in semi-batch bench-scale experiments.

With Ammonia:

$$BrO_3^- = 8.71\times10^{-8}(UVA)^{-0.593}(pH)^{5.81}(O_3)^{1.28}(Br^-)^{0.94}(Alk)^{-0.167}(NH_3-N)^{-0.051}(1.035)^{(T-20)}(time)^{0.337} \tag{5-153}$$

($R^2 = 0.71$, $R^2_{adj} = 0.70$, SEE = 0.561, F = 73, n = 323)

Without Ammonia:

$$BrO_3^- = 1.19\times10^{-7}(UVA)^{-0.623}(pH)^{5.68}(O_3)^{1.31}(Br^-)^{0.96}(Alk)^{-0.201}(1.035)^{(T-20)}(time)^{0.336} \tag{5-154}$$

($R^2 = 0.71$, $R^2_{adj} = 0.70$, SEE = 0.562, F = 84, n = 303)

Where,

BrO_3^- = bromate concentration (μg/L): $1.3 \le BrO_3^- \le 314$

UVA = ultraviolet absorbance at 254 nm (1/cm): $0.01 \le UVA \le 0.28$

pH = pH of ozonated water: $6.5 \le pH \le 8.5$

Br = bromide concentration (μg/L): $69 \le Br^- \le 440$

O_3 = transferred/utilized ozone (mg/L): $1.05 \le O_3 \le 10$

NH_3-N = nitrogen ammonia, (mg/L): $0.02 \le NH_3\text{-}N \le 3$

Alk = alkalinity (mg/L as $CaCO_3$): $13 \le Alk \le 316$

time = hydraulic retention time t_{10} (min): $1 \le t \le 120$

T = temperature (°C):20

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 5-155 predicts this decrease of bromide as a function of bromate formed.

$$Br^{-} = Br_0 - \left(0.625\left[BrO_3^{-}\right]_0\right) \qquad \textbf{(5-155)}$$

Where,

Br = bromide concentration (μg/L): $69 \leq Br^{-} \leq 440$

BrO_3^{-} = bromate concentration (μg/L): $1.3 \leq BrO_3^{-} \leq 314$

5.7.12 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 doesn't 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 is available to develop equations to predict chlorite formation. Instead the WTP model version 2.0 uses a constant conversion factor applied to the chlorine dose. This conversion factor is based on research findings. Thus, the formation of chlorite is given by Equation 5-156:

$$ClO^{-} = 0.7 * ClO_2 \qquad \textbf{(5-156)}$$

5.8 DISINFECTION CREDIT AND INACTIVATION

The Surface Water Treatment Rule (SWTR) requires systems using surface water or ground water under the direct influence of surface water to (1) disinfect their water, and (2) filter their water or meet criteria for avoiding filtration to control pathogens. The minimum disinfection requirement is based on the removal and/or inactivation of *Giardia* and Viruses. For ground water sources, the disinfection requirement is based on the removal and/or inactivation of viruses. The Interim Enhanced SWTR (IESWTR) maintains *Giardia* and Virus disinfection requirements set in the SWTR as applied to disinfection using free chlorine, chloramines, and chlorine dioxide.

In addition to *Giardia* and Virus inactivation requirements, the IESWTR stipulates that all surface water systems that are required to filter and treat more than 100,000 people, achieve set Cryptosporidium removals and/or inactivation.

The following removal requirements are currently in place:

Table 5-11 Giardia, Virus and Cryptosporidium ESWTR Removal Requirements

	Percent Removed/Inactivated (%)	Inactivation
Giardia	99.9	3-log
Viruses	99.99	4-log
Cryptosporidium	99	2-log

Table 5-12 summarizes the source of CT requirements used in the WTP model.

Table 5-12 Summary of CT Table Sources

Disinfectant	Giardia	Viruses	Crypto
Free Chlorine	SWTR	SWTR	--
Chloramines	SWTR	SWTR	--
Chlorine Dioxide	SWTR	SWTR	--
Ozone	SWTR	SWTR	Finch, 1999

5.8.1 Determination of Inactivation Ratios

The inactivation ratio (IR) is defined as follows:

$$IR = IR_1 + IR_2 + IR_3 + \ldots.. \qquad \textbf{(5-157)}$$

where:

$$IR_i = \frac{CT\ \text{value achieved through process } i}{CT\ \text{value needed for inactivation requirement}} \qquad \textbf{(5-158)}$$

Removal levels by filtration can be combined with disinfection inactivation levels to create an overall inactivation level. The value of the inactivation ratio determines whether a system meet the inactivation requirements of the ESWTR.

The achieved CT value is calculated as follows:

$$CT_{Achieved} = (\mathrm{Re}\,sidual)(t_{theo})\left(\frac{t_{10}}{t_{theo}}\right) \qquad \textbf{(5-160)}$$

where Residual is the disinfectant residual (in mg/L) at the end of the contact time, t_{theo} is the theoretical contact time, and t_{10} is the detention time corresponding to the time for which 90 percent of the water has been in contact with the residual concentration.

The required CT values for different levels of inactivation and specific treatment conditions (i.e. temperature, pH and disinfectant residual) are obtained from the tables in the SWTR Guidance Manual (USEPA, 1991). Appendix A lists the tables for chloramines, chlorine dioxide and ozone for *Giardia* and viruses as shown in the SWTR Guidance Manual and used by the WTP Model. The tables are established for specific temperatures and pH values. The WTP model interpolates required CT values to get CTs in the intermediate temperature and pH ranges.

For surface water systems using chlorine as the primary disinfectant, the required CT value for *Giardia* can be estimated from the following equation (Clark and Regli, 1991):

$$CT_{\mathrm{Re}\,quired} = 0.36(Cl_2)^{0.15}(pH)^{2.69}(T)^{-0.15}\left[-\log_{10}\left(\frac{N}{N_0}\right)\right] \qquad \textbf{(5-161)}$$

where Cl_2 is the chlorine residual at the end of the contact time (measured as free chlorine in mg/L), T is the temperature throughout the contact time, pH is the pH throughout the contact time, N is the number of *Giardia* cysts remaining after the contact time and N_0 is the number of *Giardia* cysts prior to the contact time. Equation 5-161 is based on the data in the CT tables in the SWTR and calculates values of $CT_{req'd}$ that are within 10 percent of the values listed in the SWTR Guidance Manual.

Equation 5-162 is only valid for temperatures between 0.5 and 5°C. To calculate the $CT_{req'd}$ at higher temperatures, the value for $CT_{req'd}$ is halved for every 10°C increment increase in temperature. For example, the $CT_{req'd}$ at 10°C is one-half the $CT_{req'd}$ value at 0.5°C and the $CT_{req'd}$ at 15°C is one-half the $CT_{req'd}$ value at 5°C (all other conditions equal).

For CT values *Cryptosporidium* for water treatment plants applying ozone, the values in Table 5-13 are applied. The inactivation values of *Cryptosporidium* by ozone were estimated from a graph based on experimental data from Finch (1999) in the pH ranges of 6-9. The experiments were performed at three temperatures. To interpolate between these temperatures, multiplier terms were developed to link *Giardia* and *Cryptosporidium* CT values for a given temperature. The multiplier terms can then be interpolated and applied to the *Giardia* CT values obtained from the SWTR Guidance Manual

Table 5-13 Estimates of Inactivation of *Cryptosporidium* by Ozone

	Crypto. CT at Temp. C[1]			*Giardia* CT at Temp. C[2]			Multiplier at Temp. C[3]		
Inactivation	1	13	22	1	13	22	1	13	22
0.5-log	6.00	2.00	0.60	0.48	0.19	0.10	12.5	10.6	5.8
1.0-log	12.0	4.00	1.50	0.90	0.38	0.21	12.4	10.4	7.2
1.5-log	24.0	8.00	3.00	1.50	0.58	0.31	16.0	13.9	9.6
2.0 log	40.0	11.0	4.40	1.90	0.76	0.42	21.1	14.5	10.6
2.5-log	45.0	15.0	6.00	2.40	0.95	0.52	18.8	15.7	11.5
3.0-log	62.0	22.0	8.00	2.90	1.14	0.62	21.4	19.3	12.8

[1] *Cryptosporidium* CT requirements are estimated from a graph presented by Dr. Gordon Finch at the September 10, 1999 D/DBP Technical Workgroup meeting. The values are based on experiments performed at the University of Alberta, funded by AWWARF and USEPA. These values are reported to be acceptable for a pH range 6 – 9.

[2] *Giardia* CT requirements are based on the CT tables included in the SWTR Guidance Manual

[3] Multiplier = *Crypto* CT at a given temperature/*Giardia* CT at the same temperature

The required log inactivation is given as follows:

$$\log inactivation = -\log_{10}\left(\frac{N}{N_0}\right) \qquad \textbf{(5-162)}$$

Although the SWTR currently requires surface waters to achieve a minimum 3-log removal/inactivation of *Giardia*, the USEPA recommended that utilities achieve greater inactivations depending on the *Giardia* concentration in the raw water. According to the SWTR, the recommended levels of removal/inactivation are based on the raw water *Giardia* concentrations, shown in Table 5-14:

Table 5-14 Recommended Giardia and Virus Removal/Inactivation Levels

Daily Average *Giardia* Cyst Concetration/100L	Recommended *Giardia* Removal/Inactivation	Recommended Virus Removal/Inactivation
1	3-log	4-log
1 – 10	4-log	5-log
10 – 100	5-log	6-log
100 – 10,000	6-log	7-log
1,000 – 10,000	7-log	8-log

For surface waters, the program sets the required level of Giardia removal/inactivation based on the raw water concentration of Giardia. Therefore, if a Giardia concentration in the range of 1 to 10 cysts/100 L or 10 to 100 cysts/100 L is input, the removal/inactivation requirement will be 4 logs (99.99 percent) or 5 logs (99.999 percent), respectively.

5.8.2 Removal/Inactivation Credits

The WTP model allows for *Giardia*, Virus and *Cryptosporidium* removal credits for filtration based on recommendations in the SWTR, shown in Table 5-15. Surface water systems (or ground waters under the influence of surface waters) with coagulation and filtration receive a 2.5-log removal credit for Giardia, and a 2.0-log removal credit for *Cryptosporidium* and viruses. Therefore, a surface water plant with a 3.0-log (99.9%) removal/inactivation requirement for *Giardia* for example would only be required to achieve a 0.5-log inactivation for Giardia (by disinfection or membrane treatment).

All ground water systems must achieve a 4.0-log removal/inactivation of viruses. According to the SWTR, a 2.0-log removal credit is given for systems with coagulation and filtration. Therefore, a ground water plant with coagulation/filtration would be required to achieve a 2.0-log inactivation of viruses, while an unfiltered ground water would be required to achieve a 4.0-log inactivation of viruses

It should also be noted that different types of filtration (i.e., direct, slow sand and diatomaceous earth) could provide different removal of *Giardia* cysts and viruses than coagulation and filtration systems. The current version of the model, however, does not account for different removals that may be associated with other types of filtration systems. It is intended that subsequent versions of the model will address this issue.

Table 5-15 Removal/Inactivation Credits for Treatment Processes

		Removal Credit	
Treatment Process	*Giardia*	Viruses	*Cryptosporidium*
Coagulation/Filtration	2.5-log	2-log	2.0-log
Membranes	0.5-log	--	--

5.9 SOLIDS FORMATION

The WTP model tracks solids produced by the addition of either alum or ferric chloride or by the precipitation of calcium carbonate or magnesium hydroxide. The rate of solids production (lbs/day) can be obtained by multiplying this result by the plant flow rate.

5.10 TEMPERATURE

Changes in temperature through a process train are not calculated in this version of the program.

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APPENDIX A – CT TABLES VALUES FOR INACTIVATION

Appendix A lists the tables from the SWTR used to calculate CT requirements for Viruses by free chlorine, and for inactivation of *Giardia* and viruses by chloramines, chlorine dioxide and ozone, as a function of pH and temperature as used by the WTP Model. Inactivation of Giardia by free chlorine is calculated by Equation 5-161.

A.1 *GIARDIA* INACTIVATION TABLES

Table A-1 CT Values for Inactivation of *Giardia* Cysts by Chloramine pH 6 – 9

	Temperature (ºC)					
Inactivation	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

	Temperature (ºC)					
Inactivation	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

	Temperature (ºC)					
Inactivation	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

	Inactivation					
	2.0-log		3.0-log		4.0-log	
Temperature	pH		pH		pH	
(ºC)	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

	Temperature (ºC)					
Inactivation	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 – 9

	Temperature (ºC)					
Inactivation	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

	Temperature (ºC)					
Inactivation	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