WATER TREATMENT PLANT SIMULATION PROGRAM
VERSION 1.21
USER'S MANUAL

DRINKING WATER TECHNOLOGY BRANCH
DRINKING WATER STANDARDS DIVISION
OFFICE OF GROUND WATER AND DRINKING WATER
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C.

JUNE 1992

Prepared by:

MALCOLM PIRNIE, INC.

One International Boulevard
Mahwah, New Jersey 07495-0018

2 Corporate Park Drive
P.O. Box 751
White Plains, New York 10602

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USEPA - Office of Ground Water
and Drinking Water
Technology Transfer

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A	Description of Model Equations
B	Results of Model Verification Efforts
C	Water Treatment Plant Data Questionnaire

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FORWARD

This User's Manual for Version 1.21 of the WTP Simulation Program 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) and the formation of disinfection by-products (DBPs). This manual represents the first public release of the program.

The WTP Simulation Model was developed for the United States Environmental Protection Agency (USEPA) by Malcolm Pirnie, Inc. in support of the Disinfectant/Disinfection By-Products (D/DBP) Rule. It was prepared with the understanding that the predictions may reflect the *central tendency* for treatment. 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 judgement using site-specific treatability data to evaluate the best manner in which to address the potential requirements of the D/DBP Rule for an individual application.

It is understood that one limitation of the model is the extent of the data base available to verify model predictions. In a desire to systematically improve the overall predictive capability, the intent of this release is to solicit public comment on the usefulness and relative accuracy of the predictions on a case-by-case basis. To this end, a questionnaire is provided in Appendix C of this document that requests information on treatment process characteristics and DBP formation from individual utilities.

The USEPA encourages constructive comments on methods to improve the model, results from verification efforts, and utility data that can be used to enhance the overall applicability of the model. Please forward comments to:

Barbara M. Wysock
Water Supply Technology Branch
Technical Support Division
Office of Ground Water and Drinking Water
United States Environmental Protection Agency
Cincinnati, Ohio 45268

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 Malcolm Pirnie, Inc. shall not be liable for any direct, indirect, consequential, or incidental damages resulting from the use of the WTP model.

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1.0 INTRODUCTION

1.1 BACKGROUND

The water treatment plant simulation computer program (WTP) was developed for the U.S. Environmental Protection Agency (USEPA) by Malcolm Pirnie, Inc., in support of the Disinfectant/Disinfection By-Products (D/DBP) Rule. The primary purpose of the program is to simulate the removal of natural organics matter (NOM), the formation of disinfection by-products (DBPs), and disinfection levels in water treatment plants and distribution systems, based upon specified inputs including raw water quality, treatment process characteristics and chemical dosages. At this time, only trihalomethane (THM) and haloacetic acid (HAA) formation can be simulated. The model equations and format were developed primarily with funding from USEPA, with some support from the Metropolitan Water District of Southern California and the D/DBP Technical Advisory Workgroup (TAW) for developing specific predictive equations.

WTP was developed to assist in determining the method by which treatment processes can be implemented to achieve the required levels of disinfection while maintaining compliance with potential requirements of the D/DBP Rule. 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 predictive equations for water quality are described in Appendix A.

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.

The WTP model was used by the USEPA to assist in evaluating treatment strategies for providing adequate disinfection, while controlling the formation of DBPs, using simulated water qualities representative of surface waters throughout the country. A copy

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of a paper describing this effort, as a part of the Regulatory Impact Analysis (RIA) for the D/DBP Rule, is provided at the end of this manual.

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. WTP, like any computer program, can not replace sound engineering judgement 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 PURPOSE OF THIS MANUAL

This manual is intended to guide the user in operating WTP 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 (Appendix A);
- Results of model verification efforts (Appendix B);
- Water treatment plant data questionnaire (Appendix C);
- Copy of a technical paper entitled "Simulation of Compliance Choices for the Disinfection By-Products Regulatory Impact Analysis"; and
- A 5.25-inch floppy disk of the executable version of WTP.

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.

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1.3 MANUAL ORGANIZATION

This manual assumes that WTP 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. WTP 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 two other chapters:

- Chapter 2 describes the information needed to run WTP and how the data should be input. The components of the main menu are described and explained, 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 3 provides guidance for interpretation of the output from the WTP program.

Appendix A offers a description of the equations used in the program. Appendix B provides a summary of model verification efforts, and Appendix C contains a questionnaire for generating additional input data based upon actual water treatment plant operations.

1.4 PC SYSTEM REQUIREMENTS

The source code for this simulation program is written in the computer language C. The executable version of this program can be run on an IBM PC or compatible hardware. The computer must be equipped with:

- DOS 3.1 or later versions of DOS;
- 8086/286/386/486 processor (a math coprocessor is not required);
- A minimum of 640 kilobyte random access memory (RAM); and

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- Graphics capability (CGA, MCGA, EGA, EGA64, EGA-MONO, Herc, ATT400, VGA, PC3270, or IBM 8514).

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2.0 DATA DEVELOPMENT AND INPUT

This chapter describes how to develop and enter data to WTP. It includes sections explaining the features of the main menu, how to develop a simulated model of the specific plant being analyzed, and how to enter the proper information to activate the program.

2.1 MAIN MENU COMPONENTS

The functions of the main menu are illustrated in Figure 2-1, and are described below. To select a particular function, the user must move the arrow keys until the desired function is selected. Alternately, pressing the capitalized letter shown for a function will select that function. At the completion of each function, the user is returned to the main menu.

- Open process train: Retrieves a process train and unit process data previously entered and saved to disk by the user.

  Submenu 1 - File Name: The user is presented with a list of existing file names with .WTP extensions and the user is prompted to enter the name of an existing file (without the ".WTP" extension). If the file name entered by the user exists, the unit process data are loaded into memory and the file name becomes the new working file. The user can optionally return to the main menu without entering a file name by pressing ENTER.

  Submenu 2 - List Process Train: A listing of the process train is presented to the user, and the user is given the option to list more detailed unit process data. Following this listing the user is returned to the main menu.

- New process train: 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. An example of creating a new process train is illustrated in Section 2.3.

  Submenu 1 - File Name: Before any existing data are replaced in the memory, the user is presented with a list of existing file names and prompted to enter a new file name. At this point the user can optionally return to the main menu and not replace data in the memory by pressing ENTER without entering a new file name. After a new file name is entered and verified by the user, existing data are replaced in the memory and the new file name becomes the working file.

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FIGURE 2-1

U.S. Environmental Protection Agency
Water Treatment Plant Model

Main Menu

Open process train	Run model
New process train	Thm & disinfection
Save process train	Delete data file
Modify process train	Quit
List process train	

Highlight Desired Function and Press ENTER

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Submenu 2 - Process Train: Following the new file name menu, the user is presented with a second menu to enter the new process train. Unit processes can be added and deleted from the process train in this menu. When the user is satisfied with the sequence of unit processes in the process train menu, the user selects "Done - Process Train Complete."

Submenu 3 - Unit Process Data: After the process train is complete, the user is presented with a series of menus to enter specific data for each unit process. Each menu has default values for each unit process parameter which may need to be changed to meet the needs of the user application.

The process train and unit process data are saved to a disk file with the name entered in Submenu 1 with a .WTP extension. The user is then returned to the main menu.

- Save process train: Saves process train data and unit process data to a disk file. This function can also be used to make a duplicate copy of the data.

  Submenu - File Name: The user is presented with a list of existing data file names and prompted to enter an existing file name or new file name. Entering a new file name will change the working file name and save the data in the new file, thus making a duplicate of the process train data. Pressing ENTER without entering a file name will save data in the current working file. Existing data files are over-written.

- Modify process train: Allows the user to view and optionally change the process train and unit process data. An example of modifying a process train is illustrated in Section 2.3.

  Submenu 1 - Process Train: The first menu presents the process train and prompts the user to enter a specific unit process. Entering a number which corresponds to a unit process will bring up Submenu 2. Entering a negative number in Submenu 1 will delete the unit process from the process train. Entering a zero or pressing ENTER without entering a number will return to the main menu. **Unit processes can not be inserted into an existing process train.**

  Submenu 2 - Unit Process Data: This menu displays the unit process data and allows the user to change any parameter.

  Submenu 3 - Keep Changes: At this point the user has the option to keep the changes or restore the original data. Answering "Yes" saves the changes to the current working disk file. Answering "No" restores the original data.

  Note: If the user wishes to have an original file and modified file then "Save process train" should be used before "Modify process train" to make a duplicate copy of the working file.

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- List process train: Lists the process train and unit process data currently in memory.

  The user is given the option to view the data on the CRT or down load the data to a printer. An example input data screen is shown in Table 2-1 in Section 2.2.

- Run model: Executes the water treatment plant model.

  Submenu - Output Device: The user is prompted to select between viewing the model output on the CRT, printing the output to the system printer, or saving the output to a disk file. An example output screen or file is shown in Table 2-2 in Section 2.2

  If the output is viewed on the CRT, a series of output screens is displayed. After each screen, the user is prompted to press ENTER to continue or press ESC to return to the main menu.

  If the output is saved in a disk file the user is prompted to enter a file name. The output file name will be given an .OUT extension.

- THM and Disinfection: Executes the water treatment plant model with a summary screen illustrating selected parameters from the output file. This menu does not have any submenu.

- Delete data file: Allows the user to remove data files created by program.

  Submenu 1 - Data File Type: Two types of data files are created by WTP. The process train/unit process data files all contain a .WTP extension while the model output files contain an .OUT extension. The user is prompted to enter which type of file is to be deleted.

  Submenu 2 - File Name: A list of all existing files of the type selected in Submenu 1 is displayed and the user is prompted to enter a file name to be deleted.

- Quit: Exits the program and returns to DOS.

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2.2 SIMULATING THE TREATMENT PLANT

Before WTP 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 are shown in Figure 2-2. The program algorithm (steps the program follows), for a typical simulated process train illustrated in Figure 2-3 is shown on Figure 2-4.

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; and
  - UV-absorbance at 254 nm.
- Inorganic Raw Water Quality Parameters
  - Bromide concentration;
  - Alkalinity concentration;
  - Total and calcium hardness concentration; and
  - Ammonia nitrogen concentration.

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FIGURE 2-2

INTERACTION FOR VARIOUS PROCESS UNITS FOR WATER TREATMENT PLANT SIMULATION MODEL

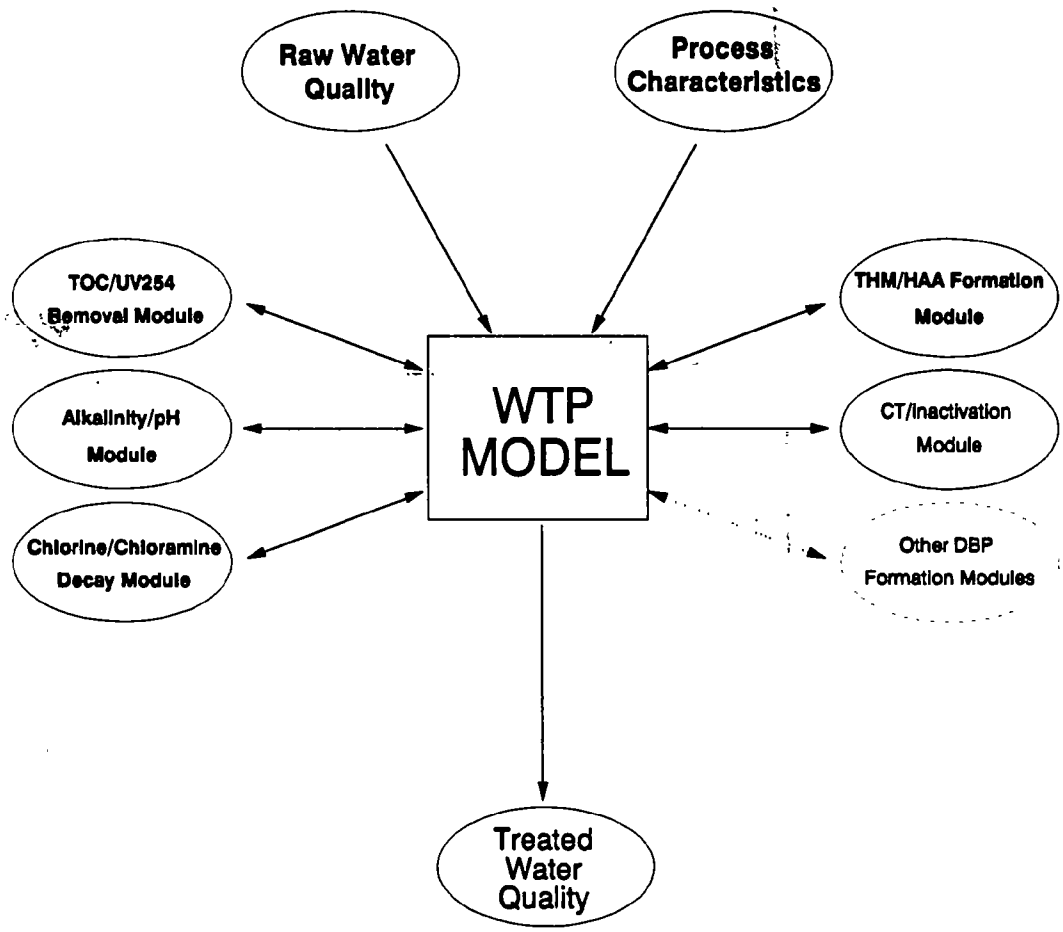

FIGURE 2-3

PROCESS FLOW SCHEMATIC FOR WTP

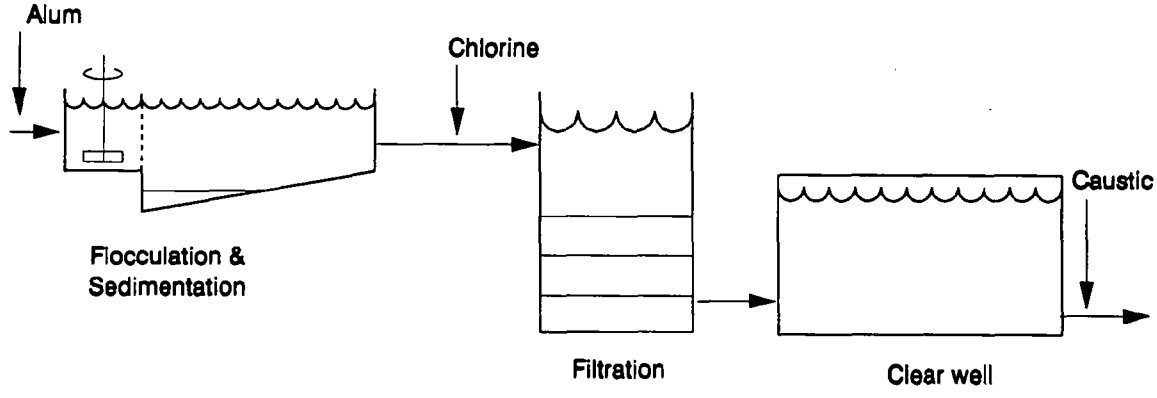

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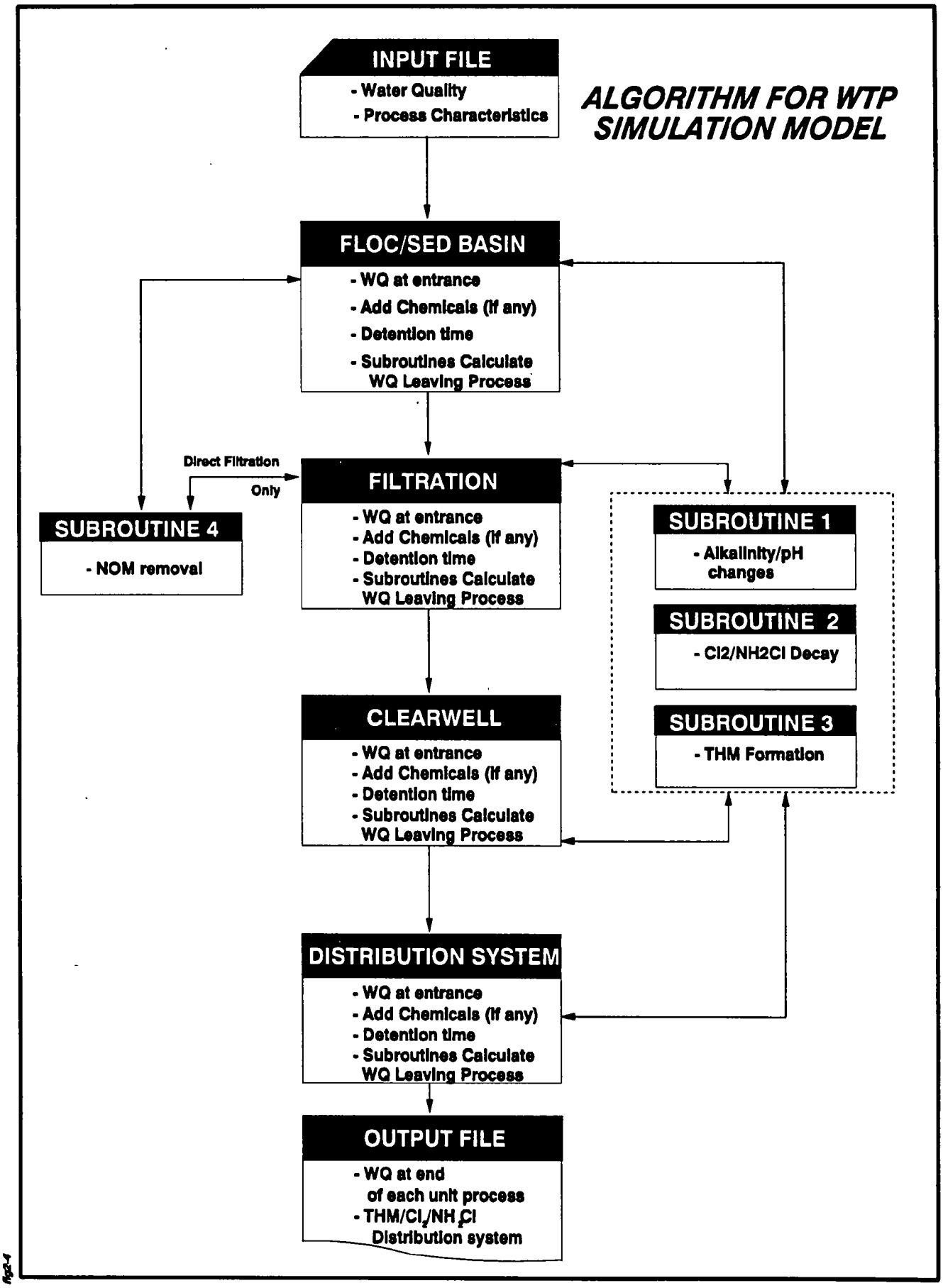
FIGURE 2-4


ALGORITHM FOR WTP SIMULATION MODEL
INPUT FILE
- Water Quality
- Process Characteristics
FLOC/SED BASIN
- WQ at entrance
- Add Chemicals (if any)
- Detention time
- Subroutines Calculate WQ Leaving Process
Direct Filtration Only
SUBROUTINE 4
- NOM removal
FILTRATION
- WQ at entrance
- Add Chemicals (if any)
- Detention time
- Subroutines Calculate WQ Leaving Process
SUBROUTINE 1
- Alkalinity/pH changes
SUBROUTINE 2
- Cl2/NH2Cl Decay
SUBROUTINE 3
- THM Formation
CLEARWELL
- WQ at entrance
- Add Chemicals (if any)
- Detention time
- Subroutines Calculate WQ Leaving Process
DISTRIBUTION SYSTEM
- WQ at entrance
- Add Chemicals (if any)
- Detention time
- Subroutines Calculate WQ Leaving Process
OUTPUT FILE
- WQ at end of each unit process
- THM/Cl2/NH2Cl Distribution system

- Water Treatment Process Characteristics
  - Type of unit process;
  - Plant flow at average and peak hour conditions;
  - Baffling characteristics and detention times; and
  - Chemical dosages.
- Other raw water quality parameters
  - Giardia cyst concentration;
  - pH;
  - Turbidity; and
  - 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 and HAAs) formed; and
- Percentage of CT achieved (based upon the CT numbers provided in the *USEPA Guidance Manual for Compliance With the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources*.

An example of input and output files for the program are presented in Tables 2-1 and 2-2, respectively.

2.3 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 is developed as an example.

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TABLE 2-1

INPUT DATA FOR EXAMPLE 2

```
Raw_Water
        pH..............................  7.5
        Temperature.......................15.0 Degrees Celsius
        Annual Min Temperature............ 0.5 Degrees Celsius
        Total Organic Carbon............... 3.0 mg/L
        UV Absorbance at 254 nm........... 0.10 /cm
        Bromide........................... 0.10 mg/L
        Alkalinity........................80 mg/L as Calcium Carbonate
        Calcium Hardness..................80 mg/L as Calcium Carbonate
        Total Hardness....................100 mg/L as Calcium Carbonate
        Ammonia........................... 0.05 mg/L as N
        Turbidity......................... 1.5 NTU
        Giardia........................... 2.0 cysts/100 L
        Peak Hourly Flow..................20.0 MGD
        Flow Rate.........................10.0 MGD
        Surface Water as defined by SWTR..Yes
Alum_Coagulation
        Alum Dose.........................10.0 mg/L as Al2(SO4)3*14H2O
        Flow Rate.........................10.0 MGD
        Surface Water as defined by SWTR..Yes
        Theoretical Detention Time........270.0 minutes
        Ratio of Mean Detention Time to
           Theoretical Detention Time..... 1.0
        Ratio of t(10) to
           Theoretical Detention Time..... 0.5
Chlorine
        Chlorine Dose..................... 4.0 mg/L as Cl2
Filtration
        Theoretical Detention Time........15.0 minutes
        Ratio of Mean Detention Time to
           Theoretical Detention Time..... 1.0
        Ratio of t(10) to
           Theoretical Detention Time..... 0.5
Basin
        Theoretical Detention Time........60.0 minutes
        Ratio of Mean Detention Time to
           Theoretical Detention Time..... 1.0
        Ratio of t(10) to
           Theoretical Detention Time..... 0.5
Caustic
        Caustic Dose......................11.0 mg/L as NaOH
Distribution
        Average Residence Time............ 3.0 days
        Maximum Residence Time............ 7.0 days
        HAA Equations (H-Haas, T-TAW).....H *
```

* Two sets of equations are available for HAA prediction as discussed in Section 3.2.

TABLE 2-2

OUTPUT FILE FOR EXAMPLE 2

Location	CHCl3 (ug/L)	CHBrCl2 (ug/L)	CHBr2Cl (ug/L)	CHBr3 (ug/L)	TTHMs (ug/L)
Raw Water	0.0	0.0	0.0	0.0	0.0
Alum Addition					
Basin Effluent	0.0	0.0	0.0	0.0	0.0
Chlorine					
Filtered Water	5.7	3.6	1.1	0.3	10.7
Basin Effluent	8.8	5.7	1.6	0.4	16.5
Caustic					
Average Tap	28.4	19.0	5.3	0.6	53.3
End of System	35.8	24.0	6.7	0.7	67.2

Press ENTER to continue or Esc to return to Main Menu.

HAAs Under Average Conditions Using Haas HAA Equations

Location	MCAA (ug/L)	DCAA (ug/L)	TCAA (ug/L)	MBAA (ug/L)	DBAA (ug/L)	THAAs (ug/L)
WTP Effluent...	1.0	7.7	4.3	0.3	0.9	14.2
Average Tap....	1.0	10.6	8.9	0.4	1.2	22.1
End of System..	1.0	11.5	11.1	0.5	1.4	25.5

Predicted Water Quality Profile at Minimum Temperature and Peak Hour Flow

Location	Temp (C)	pH (-)	Cl2 (mg/L)	NH2Cl (mg/L)	Inactivation Ratio
Raw Water.....	0.5	7.5	0.0	0.0	0.0
Alum Addition..					
Basin Effluent.	0.5	7.2	0.0	0.0	0.0
Chlorine					
Filtered Water.	0.5	7.1	3.0	0.0	0.1
Basin Effluent.	0.5	7.1	2.9	0.0	0.4
Caustic					
Average Tap....	0.5	8.0	1.0	0.0	0.4
End of System..	0.5	8.1	0.3	0.0	0.4

OUTPUT FILE FOR EXAMPLE 2 (CON'T)

Predicted Water Quality Profile for EXAMPLE2.WTP Under Average Conditions

Location	pH (-)	TOC (mg/L)	UV-254 (1/cm)	Alk (mg/L)	Temp (C)	Cl2 (mg/L)	NH2Cl (mg/L)	NH3-N (mg/L)
Raw Water.....	7.5	3.0	0.100	80	15.0	0.0	0.0	0.1
Alum Addition..								
Basin Effluent.	7.2	2.3	0.048	75	15.0	0.0	0.0	0.1
Chlorine								
Filtered Water.	7.1	2.3	0.048	72	15.0	3.0	0.0	0.0
Basin Effluent.	7.0	2.3	0.048	71	15.0	2.9	0.0	0.0
Caustic								
Average Tap....	8.0	2.3	0.048	84	15.0	1.0	0.0	0.0
End of System..	8.1	2.3	0.048	83	15.0	0.3	0.0	0.0

Press ENTER to continue or Esc to return to Main Menu.

Location	Bromide (mg/L)	Ca Hard (mg/L)	Mg Hard (mg/L)	Inactivation Ratio	Solids (mg/L)
Raw Water.....	0.10	80	20	0.0	0.0
Alum Addition..					
Basin Effluent.	0.10	80	20	0.0	5.7
Chlorine					
Filtered Water.	0.10	80	20	0.5	5.7
Basin Effluent.	0.10	80	20	2.3	5.7
Caustic					
Average Tap....	0.10	80	20	2.3	5.7
End of System..	0.10	78	20	2.3	5.7

Press ENTER to continue or Esc to return to Main Menu.

A unit process flow diagram, detention times, and raw water quality data are shown in Figure 2-5. 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 2-6.

2.3.1 Create 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 - Insert the program diskette, type WTP, and press "Enter". The main menu will be displayed on the screen.
- Step 2 - At the main menu, select New process train and press "Enter".
- Step 3 - Type the name of the plant to be simulated and press "Enter". This displays the screen shown in Figure 2-7. 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 2-8. When the user has completed choosing options, the unit processes selected should match those in the block diagram in Figure 2-6.
- Step 5 - Select "Done - Process Train Complete" to finalize the process train. The simulated plant is now created.

2.3.2 Unit Process Parameters

After the simulated plant has been created, the screen illustrated in the top of Figure 2-9 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. Press "Enter". If the default value shown left of the arrow is correct, press "Enter" to proceed to the next parameter.
- Step 2 - Enter the requested information for each subsequent prompt. Press "Enter".

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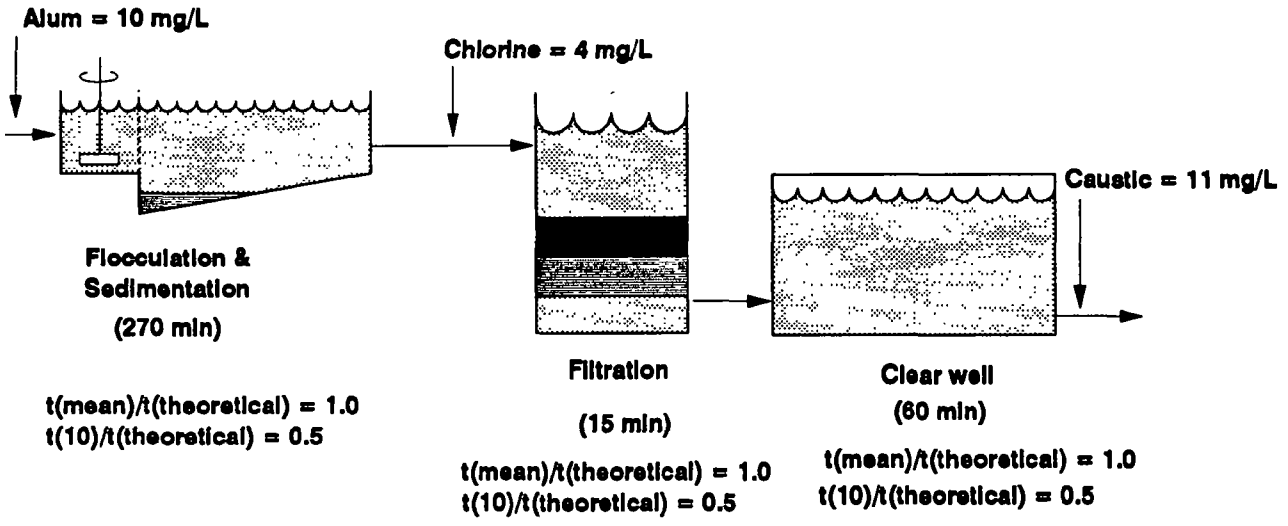
FIGURE 2-5

PROCESS FLOW SCHEMATIC FOR WTP



FLOWSCHM.

FIGURE 2-6

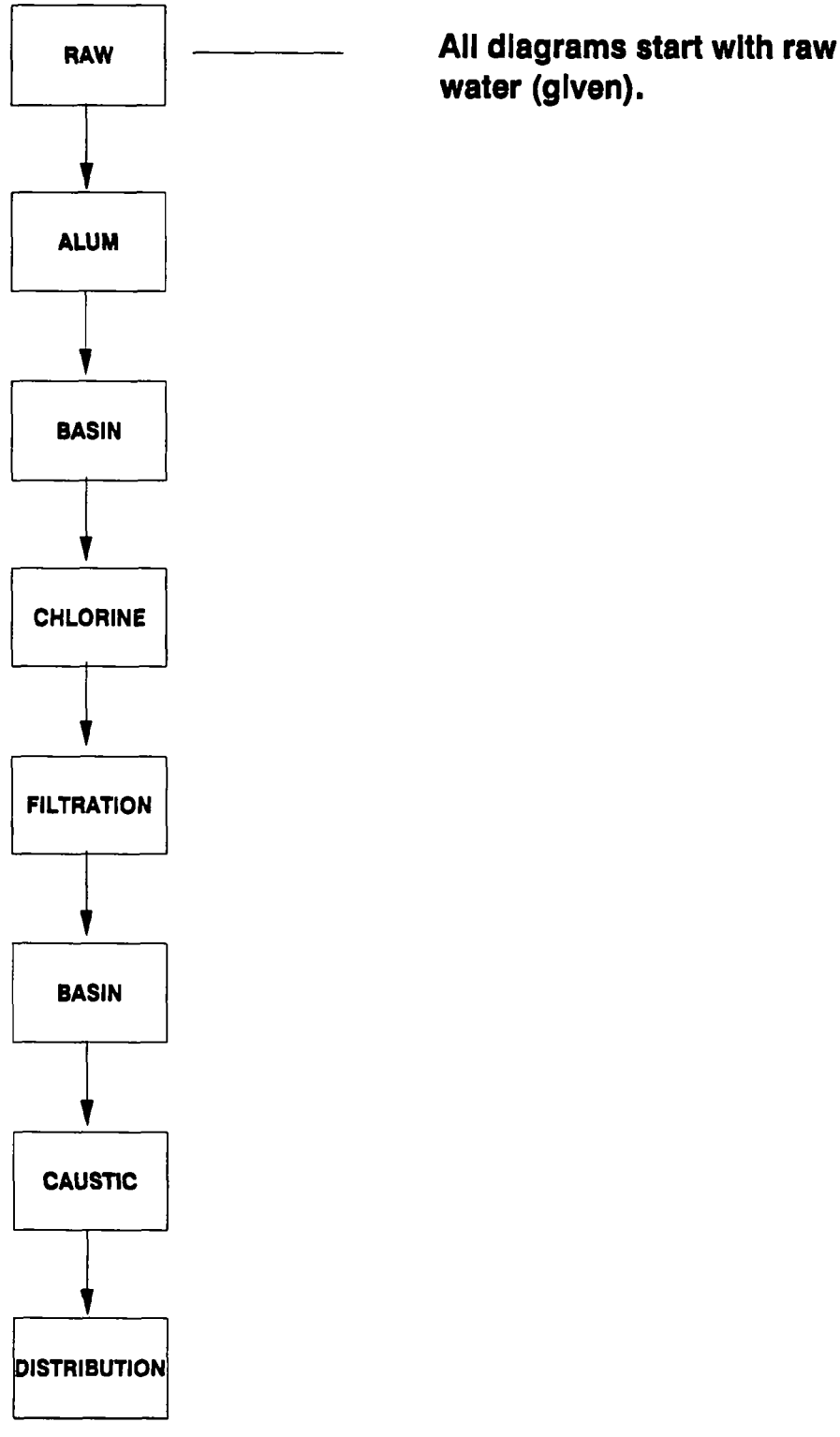


fig2-6

FIGURE 2-7

New Process Train

Unit Process Train:
Raw Water

Available Unit Processes

Alum coagulation	Chlorine
Iron coagulation	ammonia (N)
sulfuric acid	Filtration
caustic	Basin
Lime	Permanganate
soda ash	carbon dioxide
GAC	Distribution
Membranes	

Done -- Process Train Complete

Oops -- Delete Last Entry (X)

Cancel -- Return to Main Menu(Esc)

Select Unit Process & Press ENTER

FIGURE 2-8

New Process Train

Unit Process Train:
- Raw Water
- Alum_Coagulation
- Sulfuric_Acid
- Basin
- Chlorine
- Filtration
- Basin
- Caustic
- Distribution

Available Unit Processes

Alum coagulation	Chlorine
Iron coagulation	ammonia (N)
sulfuric acid	Filtration
caustic	Basin
Lime	Permanganate
soda ash	carbon dioxide
GAC	Distribution
Membranes	

Done -- Process Train Complete

Oops -- Delete Last Entry (X)

Cancel -- Return to Main Menu(Esc)

Select Unit Process & Press ENTER

FIGURE 2-9

a) Initial Screen

```
RAW WATER PARAMETERS

                    pH value:    7.7 -->

Type new value or press ENTER for no change
```

b) Completed Screen

```
RAW WATER PARAMETERS

                    pH value:    7.7 --> 7.5
     Temperature (Celsius):   18.0 --> 15.0
 Annual Min. Temp. (Celsius):    0.5 --> 0.5
                 TOC (mg/L):   3.00 -->
              UV-254 (1/cm):   0.10 -->
             Bromide (mg/L):   0.10 -->
  Alkalinity (mg/L as CaCO3):  50.00 --> 80
Calcium Hardness (mg/L as CaCO3): 100.00 --> 80
  Total Hardness (mg/L as CaCO3): 120.00 --> 100
        Ammonia (mg/L as N):   0.01 --> .05
            Turbidity (NTU):   2.00 --> 1.5
     Giardia (cysts/100 L):    1.0 --> 2.0
   Peak hour flow rate (MGD):   5.00 --> 20
 Daily average flow rate (MGD):   2.00 --> 10
Surface Water as defined SWTR (Y/N):       Y -->

are the data correct (Y or N)
Type new value or press ENTER for no change
```

- Step 3 - After all the process information has been entered for a specific process, the program will prompt: "are the data correct?" The initial screen with filled data is shown in the bottom of Figure 2-9. Enter "y[es]" if the information is correct. Enter "n[o]" if you need to change data, then enter "y[es]" after the corrections have been made.

The program automatically proceeds to the next unit process in the simulated plant. The above steps are duplicated. After all unit process data have been entered, the simulated plant model can be run or modified from the main menu.

2.3.3 Modify Process Train

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

- Step 1 - Return to main menu and highlight Open process train. Press "Enter".
- Step 2 - Type in the name assigned to the simulated process train. Press "Enter". Type "y[es]" to review the unit process data. Type "n[o]" to return to the main menu.
- Step 3 - Highlight Modify process train and press "Enter".
- Step 4 - Enter the number for the unit process to be modified from the ordered processes in the simulated train on the screen (Figure 2-10). Press "Enter". (Unit processes can be deleted by entering a negative number at this step.)
- Step 5 - Modify the input parameters for the selected unit process in the same way the process unit parameters were entered.
- Step 6 - Enter "y[es]" or "n[o]" for modification status.
- Step 7 - Enter "y[es]" or "n[o]" to select the option to edit another process data module. A "y[es]" entry invokes the process train modification menu.
- Step 8 - Enter "y[es]" to save the changes.

2.3.4 Run Model

- Step 1 - Return to main menu and highlight Open process train. Press "Enter".
- Step 2 - Type in the name assigned to the simulated process train. Press "Enter". Type "y[es]" to see the unit process data. Type "n[o]" to return to main menu.

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FIGURE 2-10

```
                    Modify Process Train
              Current Working File: EXAMPLE2.WTP
 0:Exit this Menu
 1:Raw_Water
 2:Alum_Coagulation
 3:Basin
 4:Chlorine
 5:Filtration
 6:Basin
 7:Caustic
 8:Distribution

Enter number to modify unit process data or
enter negative number to delete unit process or
enter 0 to exit this menu with option to save changes
>

Note: A Unit Process can be deleted, or the unit process data can be
      modified, but a unit process cannot be inserted into an existing
      process train.
```

- Step 3 - At main menu, highlight Run model and press "Enter". Type "c[rt]" to send output to CRT; type "p[rinter]" to send output to printer; type "f[ile]" to send output to a file. An example of the output is shown in Table 2-2.

  Alternately, to see a summary of selected parameters, at Step 3 select THMs and disinfection and press "Enter." This will send the selected output only to the CRT. An example of the summary screen is shown in Figure 2-11.

These procedures and illustrative figures provide some direction on the operation of WTP. Main menu options not specifically explained are described in Section 2.1, and are selected by highlighting and entering their function title.

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FIGURE 2-11

Predicted Water Quality Profile

Location	pH (-)	TOC (mg/L)	Cl2 (mg/L)	NH2Cl (mg/L)	IR at Min. T & Peak Hr. Q	THMs (ug/L)
Raw Water.....	7.5	3.0	0.0	0.0	0.00	0.0
Basin Effluent.....	7.2	2.3	0.0	0.0	0.00	0.0
Filtered Water.....	7.1	2.3	3.0	0.0	0.08	10.7
Basin Effluent.....	7.0	2.3	2.9	0.0	0.40	16.5
Average Tap Water..	8.0	2.3	1.0	0.0	0.40	53.3
End of System.....	8.1	2.3	0.3	0.0	0.40	67.2

Press ENTER to return to Main Menu.

3.0 INTERPRETING MODEL OUTPUT

This chapter provides a description of the output of the WTP program. An example output file was presented in Table 2-2, and each of the parameters in the output file is discussed in this chapter. The output generated after the "Run Model" command contains the full output from the simulation exercise. This can be directed to the printer, disk or screen. The output generated after the "THM and Disinfection" command contains a summary of selected parameters displayed on the computer screen.

3.1 THM PREDICTION

The program predicts THM formation after chlorination and chloramination. The program does not predict THM formation strictly from ozonation (in the absence of chlorination and chloramination).

The program predicts TTHM formation using a single equation for total THM (TTHM) concentration. The individual THM components are predicted using four equations for the concentration of each individual THM. These *proportions* are then applied to the TTHM concentration to produce the individual concentrations. The equations are described in detail in Appendix A.

TTHMs presented in the output file represent the concentration predicted by one TTHM equation. These concentrations also appear on the computer screen after the "THM and Disinfection" 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

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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 80 μg/L, then the program will predict the following concentrations for the individual THMs:

40 μg/L	chloroform ($CHCl_3$)
20 μg/L	bromodichloromethane ($CHBrCl_2$)
12 μg/L	dibromochloromethane ($CHBr_2Cl$)
4 μg/L	bromoform ($CHBr_3$)
80 μg/L	TTHM from single TTHM equation

Therefore, the individual THM concentrations associated with the TTHM value of 80 μg/L would be presented in the output file.

The reason for performing the analyses in this manner is that the equation for TTHM has 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 TTHM regulatory scenarios, the accuracy of the TTHM prediction was more important than that for the individual predictions.

3.2 HAA PREDICTION

The program has the capability of predicting the concentrations of five individual haloacetic acids (HAAs) using two different sets of equations. One set of equations is referred to as the "Haas" HAA equations and the other is referred to as the "TAW" HAA equations. A complete background and description of these equations is presented in Section A.3 in Appendix A. The user is given the opportunity to select which set of equations to use in the program, and the output file will present the results using the appropriate equations.

The major difference between the Haas and TAW HAA equations is the method used to calculate the concentrations at various stages of treatment. The TAW equations predict HAA concentrations on a cumulative basis which accounts for HAA formation through sequential treatment processes. In other words, the concentrations at a given point in the treatment process is calculated by summing the concentrations predicted through each treatment process.

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The Haas equations predict HAA concentrations on a "static" basis. The statistical correlations predict individual HAA levels based on concentrations of individual THM concentrations and, therefore, do not account for the cumulative effect of changing water quality parameters on the final levels of HAAs formed.

Because of the method used by the Haas equations to calculate HAA concentrations, the predicted levels of HAAs may *decrease* from the plant effluent to the average distribution system, under some treatment scenarios. For example, if the pH in the distribution system is > 7.5, the Haas equations will predict low levels of HAAs. If low pH values exist during treatment (e.g.< 6.0 during coagulation), however, the Haas HAA equations may predict HAA levels at the plant effluent higher than those predicted at the average distribution system.

The TAW equations do not demonstrate this trend. Using the above scenario, the TAW equations would predict a level of HAA formation through the treatment plant based on the predicted water quality parameters. If the pH is increased entering the distribution system, the formation *rate* will decrease, but the concentrations of HAAs at the average distribution system will always be greater than or equal to the plant effluent concentration.

3.3 DETERMINATION OF INACTIVATION RATIO

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 Surface Water Treatment Rule (SWTR) requires a 3-log (99.9 percent) removal/inactivation of Giardia cysts and a 4-log (99.99 percent) removal/inactivation of viruses. For ground water systems (not under the influence of surface waters) it is anticipated that the Ground Water Disinfection Rule (GWDR) may require 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.

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 viruses. Therefore, the required inactivations 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.

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Although the SWTR 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 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 as follows:

Daily Average Giardia Cyst Concentration/100 L	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
100-1,000[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 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 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 or viruses from the SWTR 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

[1] - Recent surveys (i.e., Le Chevallier, et al., 1991) of the occurrence of Giardia in surface water supplies indicate that Giardia concentrations in some supplies exceed the maximum range (10-100) specified by USEPA in the SWTR. Therefore, linear extrapolation of CT the criteria were made to include 6- and 7- log removal/inactivations for higher raw water Giardia concentrations.

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description of the inactivation ratio algorithm (for Giardia and viruses) is presented in Appendix A.

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. In subsequent versions, the model will use the higher of the two levels of inactivation for either Giardia or viruses as the required inactivation.

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.

Because the WTP model does not yet contain equations for the decay of ozone or chlorine dioxide, inactivation ratios are not calculated for these two disinfectants. When these equations are added to the model, it will be possible to calculate inactivation ratios from the use of these disinfectants.

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 "THM and Disinfection" command is selected, are the inactivation ratios predicted under the minimum temperature/peak flow conditions.

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3.4 PREDICTION OF OTHER PARAMETERS

The following describes the remaining parameters in the output from a simulation run:

- pH - The predicted pH value at the effluent of a given unit process.
- TOC - The predicted TOC concentration (in mg/L) at the effluent of a given unit process.
- UV-254 - The predicted UV-254 value (in 1/cm) at the effluent of a given unit process.
- Alk - The predicted alkalinity (in mg/L as calcium carbonate) at the effluent of a given unit process.
- Temp - The average temperature (in °C) through a given unit process. Changes in temperature through a process train are not calculated in this version of the program.
- Cl2 - The predicted free chlorine concentration (in mg/L) at the effluent of a given unit process.
- NH2Cl - The predicted combined chlorine concentration (in mg/L) at the effluent of a given unit process.
- NH3-N - The predicted concentration of ammonia (in mg/L as N) at the effluent of a given unit process.
- Bromide - The predicted bromide concentration (in mg/L) through a given unit process. (Note: bromide removal is not calculated in any unit process because of the lack of information on the fate of bromide in water treatment).
- Ca Hard - The predicted calcium hardness (in mg/L as calcium carbonate) in the effluent of a given unit process. Calcium hardness is removed when the solubility of calcium carbonate is exceeded.
- Mg Hard - The predicted magnesium hardness (in mg/L as calcium carbonate) in the effluent of a given unit process. Magnesium hardness is removed when the solubility of magnesium hydroxide is exceeded.
- Solids - The predicted concentration of solids (in mg/L) 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.

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APPENDIX A

DESCRIPTION OF MODEL EQUATIONS

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A.1 INTRODUCTION

This appendix presents the basis of a model that simulates disinfection by-product (DBP) formation and removal of natural organic matter (NOM) in water treatment plants. The purpose of the 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 best available technology (BAT) for DBP control; and
- provide a tool that will assess the impacts of new regulations on DBP formation in existing 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.

At this time, the model is only capable of simulating THM and HAA formation because of the lack of information on the kinetics of formation and decay of other DBPs. At this time, the formation of only trihalomethanes (THMs) and haloacetic acids (HAAs) can be predicted. The formation of THMs have been studied much more extensively than HAAs, and therefore the database for THM formation is considerably more robust. Insufficient data are available to develop equations to predict other DBPs at this time.

This appendix summarizes the development of equations for simulating:

- total and individual THM concentrations;
- total and individual HAA concentrations;
- removal of total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV-254);
- changes in alkalinity and pH; and
- decay of chlorine and chloramines.

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A.2 EQUATIONS FOR THM FORMATION

A.2.1 Published Models for THM Formation

Numerous studies have used linear regression techniques to correlate trihalomethane formation potential (THMFP) with TOC and UV-254. While these results showed good correlations, general use of these regression equations is limited because they do not include parameters such as chlorine dose, pH, temperature and time (Edzwald, et al., 1985; Singer and Chang, 1989; Lykins, et al., 1988; Batchelor, et al., 1987).

Additional studies have taken a more thorough approach for modeling kinetics of THM formation. Engerholm and Amy (1983) developed a model that simulates the rate of chloroform formation from pH, temperature, TOC and the ratio between chlorine dose and TOC. The following equation was developed from chlorination of a peat soil humic acid extract:

$$CHCl_3 = k_1 k_2 (TOC)^{0.95} \left(\frac{Cl_2}{TOC} \right)^{0.28} (t)^z \qquad \text{(A-1)}$$

where $CHCl_3$ is the chloroform concentration in μg/L, TOC is the total organic carbon concentration in mg/L, Cl_2 is the chlorine dose in mg/L and t is the reaction time in hours. The value of k_1 is pH dependent while the values of z and k_2 are temperature dependent.

Amy, Chadik and Chowdhury (1987) studied chlorination of 13 natural waters from various locations throughout the United States. These chlorination studies produced the following equation:

$$THM = 0.00309[(TOC)(UV\text{-}254)]^{0.440}(Cl_2)^{0.409}(t)^{0.265}(T)^{1.06}(pH - 2.6)^{0.715}(Br + 1)^{0.036} \qquad \text{(A-2)}$$

where THM is the TTHM concentration in μmole/L, TOC is the total organic carbon concentration in mg/L, UV-254 is the absorbance of ultraviolet light at a 254 nm wavelength (in cm^{-1}), Cl_2 is the chlorine dose in mg/L, t is the reaction time in hours, T is the temperature in degrees Centigrade and Br is the bromide concentration in mg/L. Raw

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water samples were filtered through a 0.45 μm filter. Therefore, the TOC used in the model actually could be considered DOC by operational definition.

A third model, developed by Christ and Dietz (1988), was based on chlorination studies involving two natural waters from Florida. The following equation was generated:

$$THM = 0.068(TOC)^{0.910}(pH)^{1.45}(T)^{0.652}(Cl_2)^{0.439}(Br)^{0.169}(t)^{0.240} \quad \text{(A-3)}$$

where THM is the TTHM concentration in μg/L, TOC is the total organic carbon concentration in mg/L, T is the temperature in degrees Centigrade, Cl_2 is the chlorine dose in mg/L, Br is the bromide concentration in mg/L and t is the reaction time in hours.

Table A-1 shows a comparison of test conditions for each of the three equations shown above. This comparison demonstrates that Equation A-2 was based upon the most thorough database incorporating the largest number of observations and widest range of parameter values.

A fourth model has been developed for the USEPA that is based on a mechanistic framework rather than an empirical framework (Batchelor, 1989). This model simulates the formation and, where applicable, decay of four THMs, five non-THM DBPs and total organic halogen (TOX). Simulations are based on TOC, pH, time, bromide and chlorine dose. Temperature was not considered due to lack of data. Parameter values in the model were based on results observed for water from the Ohio River at Cincinnati, Ohio. Additional tests conducted on water from the Edisto River in South Carolina showed that the parameter values developed for Ohio River water were not applicable to Edisto River water. Tests should be conducted to develop parameter values from a group of waters so that the model can be used to describe the general case. Temperature should be a variable in these tests.

Equation A-2 was selected as the basis for THM formation in the WTP program.

A.2.2 Refinement of Equation A-2

One limitation associated with Equation A-2 is its simulation of TTHM formation in μmoles/L. The molecular weights of the four THM species vary significantly (119 for $CHCl_3$ to 252 for $CHBr_3$) and, therefore, conversion from μmoles/L to μg/L is difficult. In order to convert the TTHM concentrations calculated by Equation A-2 from μmole/L to

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TABLE A-1
COMPARISON OF TRIHALOMETHANE FORMATION MODELS

Authors	Published in	Number of Natural Waters Tested	Number of Data Points	r^2	Range of Values Tested						
					TOC (mg/L)	UV-254 (1/cm)	Chlorine Dose (mg/L)	Bromide (mg/L)	pH	Temperature (°C)	Time (hr)
Engerholm and Amy	1983	0 [1]	648	0.99	2.5 - 10.0	N.U. [3]	5 - 60	N.U.	5.5 - 8.5	10 - 35	1 - 96
Amy, Chadik and Chowdhury	1987	13	1090	0.90	3.0 - 13.8	0.063 - 0.489	1.5 - 69	0.01 - 1.245	4.6 - 9.8	10 - 30	0.1 - 168
Christ and Dietz	1988	2	180	N.R. [2]	3.8 - 7.2	N.U. [3]	8 - 25	0.087 - 0.500	7 - 9	15 - 30	2 - 144

Notes:

[1] Humic acid extracted from a peat soil was used during this effort.

[2] N.R. - Not Reported

[3] N.U. = Not Used in this study.

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μg/L, the database used to develop Equation A-2 was used to develop a model which describes the average molecular weight of the THM species formed. Using a stepwise variable selection procedure, the following equation was developed with multiple linear regression:

$$AMW = 105.3(Br+1)^{0.48}(UV-254)^{-0.089} \qquad \text{(A-4)}$$

where AMW is the average molecular weight of the trihalomethane species formed. The results calculated by Equations A-2 and A-4 can be multiplied together to calculate TTHM formation in μg/L.

A.2.3 Development of Models for Formation of THM Species

The database used to develop Equation A-2 was used to formulate new empirical equations for individual THM species. The relationship between the various THM species and the controlling variables such as pH, temperature, chlorine dosage, TOC and bromide exhibit nonlinear behavior. An appropriate empirical relationship for such a function can be of the following form:

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

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:

$$\ln(Y) = \ln(A) + a\ln(X_1) + b\ln(X_2) + c\ln(X_3) \qquad \text{(A-6)}$$

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 A-5.

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As a first step of the modeling effort, dependent and independent variables were defined as shown in Table A-2. The experiments showed that THM formation from the chlorination of NOM virtually stops at pH 2.6 (Amy, et al., 1987). Therefore, 2.6 was subtracted from pH so that THM formation is not calculated at a pH value of 2.6. Similarly, the variable *Br + 1* was used to ensure no formation of brominated THM species when bromide is not present in the water (the natural log of 1.0 is 0). The definition of X_6 could be improved by adding stoichiometric coefficients to Fe, Mn, and NH_3. This was not determined, however, until after the modeling effort and this improvement has not yet been tested.

The development of an appropriate regression equation consisted of selecting the most significant variable forms from the list above and then performing a stepwise multiple linear regression analysis using the selected variable forms. The selection of the appropriate variable forms was done by developing a Pearson's Correlation matrix (Table A-3) for all of the above variable forms on the entire data base. 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.

In selecting independent variable forms for describing chloroform (Y_1) formation, only one occurrence of each of the controlling variables was desired. Table A-2 shows that the correlation coefficient between Y_1 and X_3 is higher ($r = 0.603$) than that between Y_1 and either X_1 ($r = 0.557$), X_2 ($r = 0.589$) or X_4 ($r = 0.303$). Therefore, X_3 was selected as the form of the independent variable incorporating TOC and UV-254. Because X_3 includes both UV-254 and TOC, no other variables were desired for describing these precursors. Similarly, X_5 was selected instead of X_6 to represent chlorine dose.

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TABLE A-2

VARIABLES DEFINED IN DEVELOPMENT OF TRIHALOMETHANE SPECIES

Dependent Variables

$$Y_1 = \ln\left(\frac{CHCl_3}{119.38}\right) \qquad Y_2 = \ln\left(\frac{CHBrCl_2}{163.83}\right)$$

$$Y_3 = \ln\left(\frac{CHBr_2Cl}{208.28}\right) \qquad Y_4 = \ln\left(\frac{CHBr_3}{252.73}\right)$$

where $CHCl_3$ is the chloroform concentration in $\mu g/L$, $CHBrCl_2$ is the dichlorobromomethane concentration in $\mu g/L$, $CHBr_2Cl$ is the chlorodibromomethane concentration in $\mu g/L$ and $CHBr_3$ is the bromoform concentration in $\mu g/L$. The constants used in the above equations are the molecular weights of the respective species.

Independent Variables

$$X_1 = \ln(TOC) \qquad X_2 = \ln(UV\text{-}254)$$

$$X_3 = \ln[(UV\text{-}254)(TOC)] \qquad X_4 = \ln\left(\frac{UV\text{-}254}{TOC}\right)$$

$$X_5 = \ln(Cl_2\ Dose) \qquad X_6 = \ln(Cl_2\ Dose - Fe - Mn - NH_3)$$

$$X_7 = \ln(t) \qquad X_8 = \ln(T)$$

$$X_9 = \ln(pH - 2.6) \qquad X_{10} = \ln(Br + 1)$$

$$X_{11} = \ln(Br) \qquad X_{12} = \ln\left(\frac{Br}{UV\text{-}254}\right)$$

$$X_{13} = \ln\left(\frac{Br}{TOC}\right)$$

where TOC is the total organic carbon concentration in mg/L, UV-254 is the UV absorbance at 254 nm in cm^{-1}, Cl_2 Dose is the free chlorine dose in mg/L, Fe is the iron concentration in mg/L, Mn is the manganese concentration in mg/L, NH_3 is the ammonia concentration in mg/L, t is the reaction time in hours, T is the temperature in degrees centigrade, pH is the pH of reaction and Br is the bromide ion concentration in mg/L.

TABLE A-3
PEARSON'S CORRELATION MATRIX FOR THM EQUATION VARIABLES

Variable Name	Variable Definition	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13
X1	Ln(TOC)	1.000	0.818	0.938	0.133	0.556	0.549	-0.006	-0.013	0.009	0.091	0.089	-0.260	-0.248
X2	Ln(UV254)	0.818	1.000	0.967	0.679	0.486	0.469	-0.009	-0.003	-0.238	0.041	-0.033	-0.445	-0.305
X3	Ln(UV254*TOC)	0.938	0.967	1.000	0.467	0.541	0.527	-0.008	-0.007	-0.139	0.066	0.020	-0.384	-0.294
X4	Ln(UV254/TOC)	0.133	0.679	0.467	1.000	0.128	0.107	-0.007	0.011	-0.421	-0.046	-0.170	-0.434	-0.207
X5	Ln(Cl2 dose)	0.556	0.486	0.541	0.128	1.000	0.997	0.115	0.266	0.191	0.278	0.265	0.035	0.072
X6	Ln(Cl2 Dose - Fe - Mn - NH3)	0.549	0.469	0.527	0.107	0.997	1.000	0.117	0.270	0.195	0.271	0.249	0.028	0.059
X7	Ln(Reaction Time)	-0.006	-0.009	-0.008	-0.007	0.115	0.117	1.000	0.036	0.043	0.041	0.035	0.035	0.037
X8	Ln(temperature)	-0.013	-0.003	-0.007	0.011	0.266	0.270	0.036	1.000	0.563	0.248	0.207	0.186	0.205
X9	Ln(pH - 2.6)	0.009	-0.238	-0.139	-0.421	0.191	0.195	0.043	0.563	1.000	0.255	0.294	0.362	0.283
X10	Ln(Br + 1.0)	0.091	0.041	0.066	-0.046	0.278	0.271	0.041	0.248	0.255	1.000	0.876	0.768	0.822
X11	Ln(Br)	0.089	-0.033	0.020	-0.170	0.265	0.249	0.035	0.207	0.294	0.876	1.000	0.910	0.943
X12	Ln(Br/UV254)	-0.260	-0.445	-0.384	-0.434	0.035	0.028	0.035	0.186	0.362	0.768	0.910	1.000	0.972
X13	Ln(Br/TOC)	-0.248	-0.305	-0.294	-0.207	0.072	0.059	0.037	0.205	0.283	0.822	0.943	0.972	1.000
Y1	Ln(CHCl3/119.38)	0.557	0.589	0.603	0.303	0.607	0.605	0.547	0.322	0.113	-0.101	-0.118	-0.351	0.301
Y2	Ln(CHCl2Br/163.8)	0.261	0.159	0.212	-0.059	0.527	0.513	0.494	0.377	0.379	0.611	0.715	0.575	0.608
Y3	Ln(CHClBr2/208.3)	-0.027	-0.166	-0.112	-0.252	0.250	0.233	0.222	0.260	0.400	0.769	0.921	0.894	0.905
Y4	Ln(CHBr3/252.7)	-0.131	-0.212	-0.186	-0.198	0.121	0.108	0.118	0.196	0.374	0.850	0.823	0.825	0.844

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Variables X_{10} to X_{13} define the variable forms for bromine incorporation. However, the selection of X_3, which contains UV-254 and TOC, makes it less desirable to select X_{12} or X_{13} since these forms contain UV-254 or TOC. Selection X_{12} or X_{13} would result in a multi-colinearity problem with X_3. Y_1 had a slightly higher correlation coefficient for X_{11} (r = -0.118) than X_{10} (r = -0.101), however, the choice of variable X_{10} ensures that the formation of chloroform will continue in the absence of bromide. A similar approach was followed to select independent variables for the other THM species.

The elimination of independent variables which are highly correlated with each other is important in avoiding multi-colinearity. This problem is minimized by using the correlation matrix. In this effort, however, the elimination of all such variables was not possible. For example, X_5 is highly correlated with X_1 (r = 0.56) because the chlorine dose used in the development of the database was based on the TOC concentration. Both of these variables are of prime importance in THM formation and, therefore, were considered in the equation in spite of the high correlation between them.

The stepwise multiple linear regression analysis described above was performed on the data base, resulting in the following equations:

$$CHCl_3 = 0.278[(UV\text{-}254)(TOC)]^{0.616}(Cl_2\ Dose)^{0.391}(t)^{0.265}(T)^{1.15}(pH-2.6)^{0.800}(Br+1)^{-2.23} \qquad \text{(A-7)}$$

[r = 0.941, adj r^2 = 0.884, SEE = 0.313, F = 713 (α < 0.001), n = 561]

$$CHBrCl_2 = 0.863[(UV\text{-}254)(TOC)]^{0.177}(Cl_2\ Dose)^{0.309}(t)^{0.271}(T)^{0.720}(pH-2.6)^{0.925}(Br)^{0.722} \qquad \text{(A-8)}$$

[r = 0.945, adj r^2 = 0.892, SEE = 0.360, F = 768 (α < 0.001), n = 561]

$$CHBr_2Cl = 2.57\left(\frac{UV\text{-}254}{TOC}\right)^{-0.184}(Cl_2\ Dose)^{-0.0746}(t)^{0.252}(T)^{0.570}(pH-2.6)^{1.35}(Br)^{2.08} \qquad \text{(A-9)}$$

[r = 0.962, adj r^2 = 0.926, SEE = 0.657, F = 1160 (α < 0.001), n = 561]

$$CHBr_3 = 61.4(UV\text{-}254)^{0.683}(Cl_2\ Dose)^{-0.176}(t)^{0.110}(T)^{-0.0596}(pH-2.6)^{1.89}\left(\frac{Br}{TOC}\right)^{1.79} \qquad \text{(A-10)}$$

[r = 0.810, adj r^2 = 0.652, SEE = 1.454, F = 176 (α < 0.001), n = 561]

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The number of data points (n), the correlation coefficient (r), the adjusted coefficient of determination (adj r^2), the standard error of estimate (SEE) and the F-statistic at significance level of α are shown beneath each equation.

An equation developed by regression analysis has strong descriptive capabilities if it shows a high correlation coefficient. The F values for Equations A-7 through A-10 are significant at the 99.9 percent confidence level as shown by α less than 0.001. The correlation coefficients, however, are highest for chloroform and gradually decrease with increasing bromine incorporation. This indicates a better quality of fit for the chloroform equation and relatively worse qualities of fit for the brominated species.

The use of Equations A-7 through A-10 is limited in the following respects:

- the equations were based on THM formation in untreated waters and the applicability of these equations to treated waters is unknown;
- the database used for developing the equations had waters primarily low in bromide, so the use of these equations for high bromide waters may be limited;
- the equations were based on data collected from thirteen waters (Amy, et. al., 1987) and, therefore, represent the best generalized method of simulating THM formation. While a generalized approach is needed for the purposes of this document, THM formation rates are site-specific due to variation in NOM characteristics. Users of these equations are, therefore, encouraged to develop site-specific parameter values instead of using the general parameter values shown; 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 are expected to underpredict bromine incorporation.

The same limitations apply to the use of Equations A-2 and A-4.

A.2.4 Calculation of Trihalomethane Formation Through Multiple Treatment Processes

The calculation of trihalomethane 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. This calculation would involve the use of Equations A-2

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and A-4 for total trihalomethanes and the use of Equations A-7 through A-10 for the individual trihalomethane species.

However, water quality conditions are not normally constant from the point of chlorine application to the end of the distribution system. An example of this is shown on Figure A-1, where chlorine is applied at time t_0 prior to Basin 1. The removal of NOM at time t_1 produces TOC and UV-254 levels in Basin 2 that are less than those in Basin 1. The THM formation in these basins is calculated as follows:

- TOC_1, $UV\text{-}254_1$ and t_1 are input into Equations A-2, A-4 and A-7 through A-10 to calculate the THM concentrations at t_1.
- TOC_2, $UV\text{-}254_2$ and t_1 are input into Equations A-2, A-4 and A-7 through A-10. The results are subtracted from the results obtained when TOC_2, $UV\text{-}254_2$ and t_2 are input into Equations A-2, A-4 and A-7 through A-10. These subtractions produce an estimate of THM formation in Basin 2.
- The estimate of THM formation in Basin 2 is added to the estimate of THM formation in Basin 1. A graphical representation of this procedure is shown in Figure A-1.

Similar procedures are followed for changes in other variables such as pH.

The calculation of THM formation in systems employing two points of chlorination is also an involved process. An example of this calculation is shown on Figure A-2. The THM formation in these basins is calculated as follows:

- Equations A-2, A-4 and A-7 through A-10 are used to calculate the THM concentrations at t_1.
- After calculating THM concentrations at t_1, the cumulative time was reset to zero and Equations A-2, A-4 and A-7 through A-10 are used to calculate THM formation in Basin 2. The cumulative time was <u>not</u> reset to zero in the example shown on Figure A-1.
- The estimate of THM formation in Basin 2 is added to the estimate of THM formation in Basin 1. A graphical representation of this procedure is shown in Figure A-2.

This calculation method is necessary because THM formation is based only on the chlorine dose and not on the chlorine residual. This is another limitation of the THM formation models.

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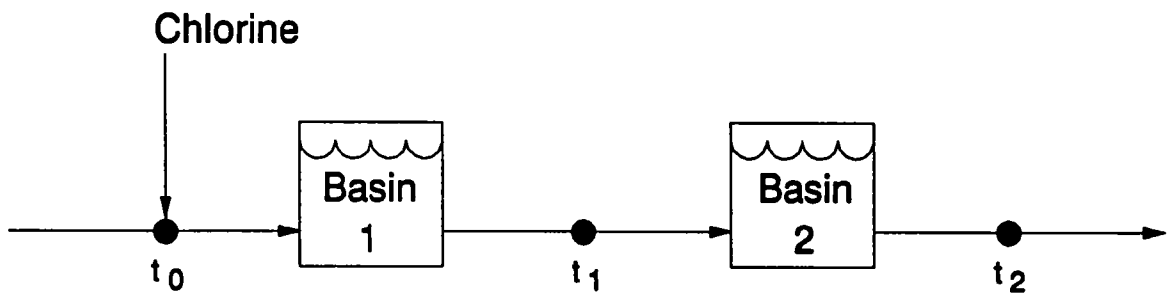
FIGURE A-1

CALCULATION OF TRIHALOMETHANE FORMATION



TOC(2) < TOC(1)
UV-254(2) < UV-254(1)
pH(2) = pH(1)
Br(2) = Br(1)
T(2) = T(1)

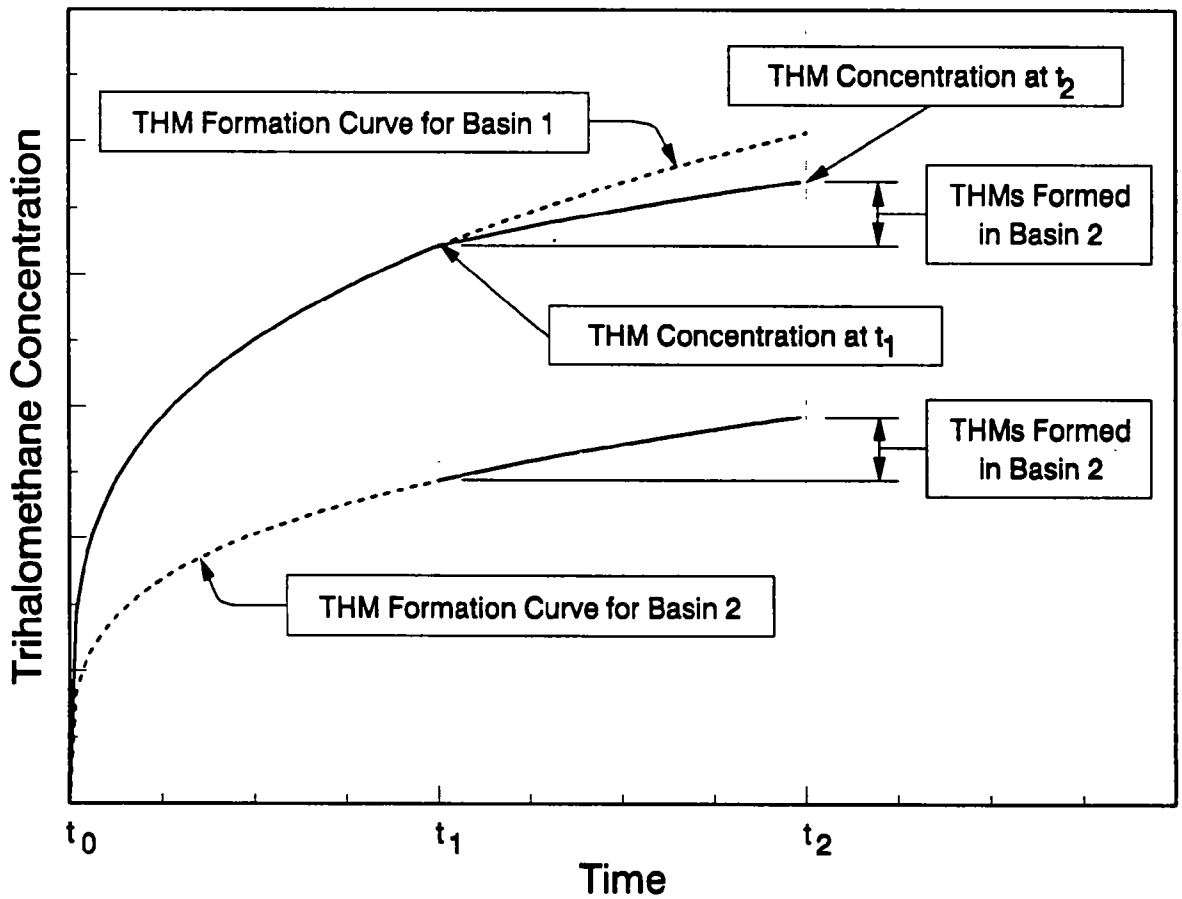
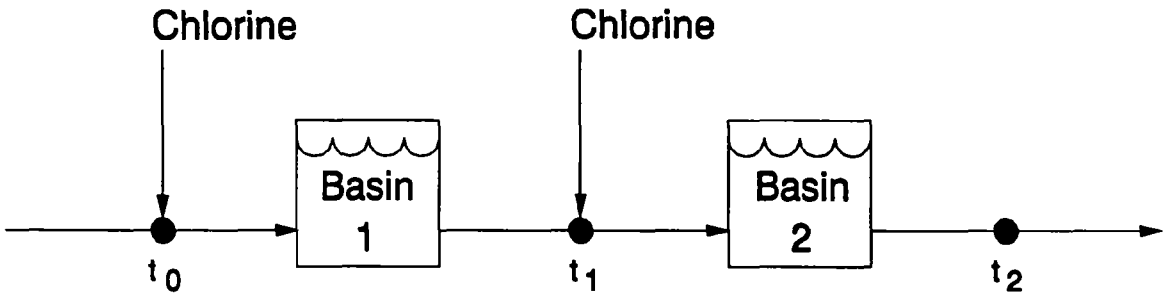


figure01

CALCULATION OF TRIHALOMETHANE FORMATION FOR TWO POINTS OF CHLORINATION



TOC(2) = TOC(1)
UV-254(2) = UV-254(1)
pH(2) = pH(1)
Br(2) = Br(1)
T(2) = T(1)

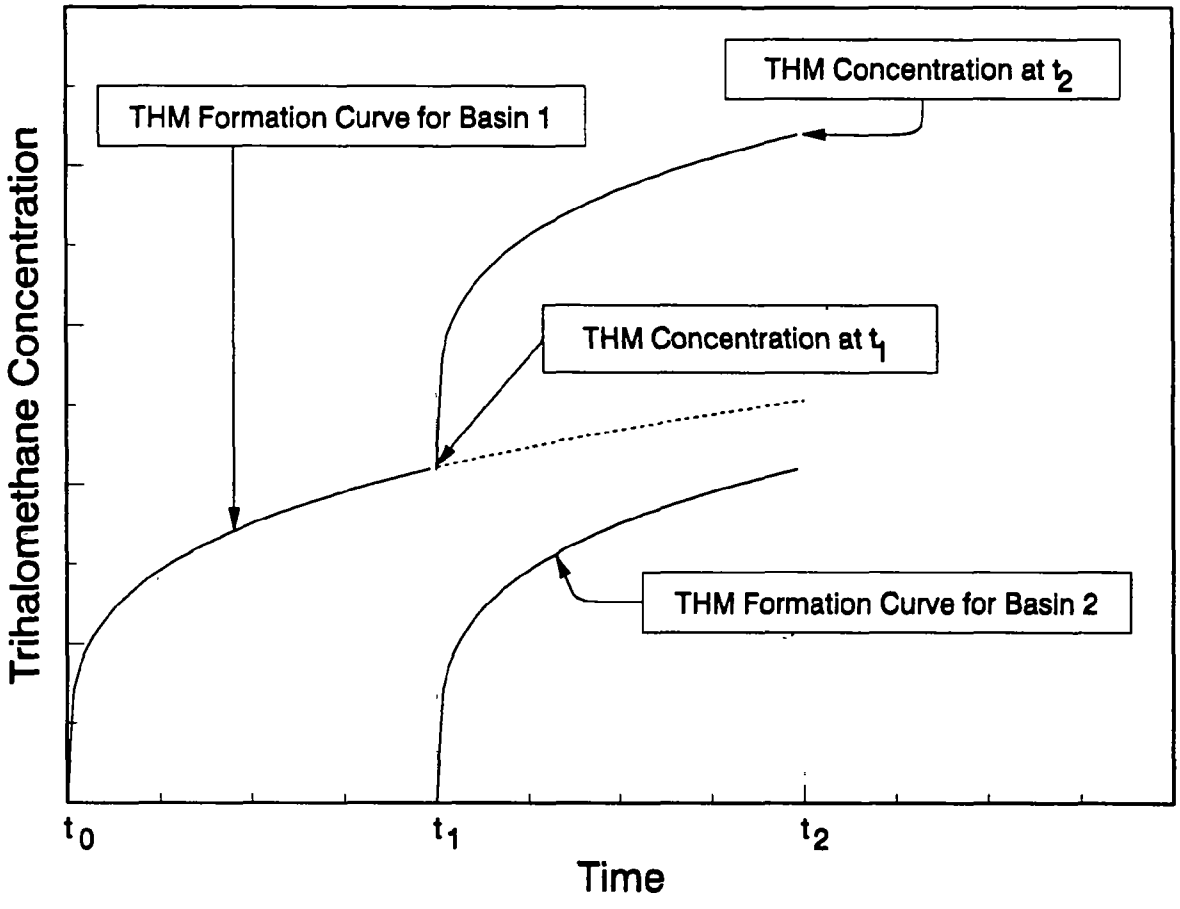


figure02

A.2.5 Trihalomethane Formation in the Presence of Chloramines

The formation of trihalomethanes is possible in the presence of a chloramine residual and has been observed (Hubbs and Holdren, 1986). This formation is possible for two reasons:

- 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 trihalomethanes depends on the rate of the forward reaction relative to the rate of the reverse reaction.

- 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 trihalomethane formation.

Studies have not been conducted to evaluate the conditions under which trihalomethane 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 trihalomethane formation during chloramination. Nevertheless, because trihalomethane formation is observed during chloramination, the model must account for it. A review of the data produced by Hubbs and Holdren (1986) indicates that trihalomethane formation observed during chloramination was approximately 10 percent of the formation observed during free chlorination. Bull and Kopfler (1991) used an estimate developed by Amy, et al. (1990) that trihalomethane formation in chloraminated waters "would approximate 20 percent of that observed if the same waters were chlorinated." Based on this review, the model assumes that the rate of trihalomethane formation during chloramination is 20 percent of the rate of trihalomethane formation during chlorination.

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A.3 EQUATIONS FOR HAA FORMATION

A.3.1 Equations Based on Utility Survey

A nationwide survey was conducted to evaluate DBP concentrations in treatment plant effluents (JMM and Metropolitan, 1989). During this survey, finished water samples were collected from 35 utilities nationwide and analyzed for THMs and other DBPs. Four samples were collected from each of the participating utilities representing four seasons. These data were statistically analyzed at the Illinois Institute of Technology to develop correlations between THMs and other DBPs.

The general relationship between HAA and THM concentrations took the following form (Haas, 1990):

$$f(DBP) = A + B(\text{Ln } CHCL_3) + C(\text{Ln } CHCl_2Br) + D(\text{Ln } CHClBr_2) + E(TOC) + F(pH) + G(CHBr_3 \text{ Class}) \quad \textbf{(A-11)}$$

Where:

A, B, C, D, and E are coefficients having the general format:

$$\text{Coefficient} = (\text{Constant}) + \left| x_1 \; x_2 \; x_3 \right| \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix}$$

Where:

$|x_1 \; x_2 \; x_3|$ = A vector of descriptor variables used to classify the disinfection category; and

$\begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix}$ = A vector of constants associated with each independent variable.

In this vector of coefficients, the first row (C_1) is multiplied by the value of x_1, the second row (C_2) is multiplied by the value of x_2 and the third row (C_3) is multiplied by the value of x_3. The sum of these three products would be the numerical value of the coefficient. In other words, whenever a column vector of coefficients appears in one of the regression equations, it is multiplied by the row vector $| x_1 \; x_2 \; x_3 |$ to determine the numerical value of the coefficient.

The values for x_1, x_2 and x_3 are determined from the following table and are a function of the disinfection practices of a given treatment plant:

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Descriptor Variables by Disinfection Type

Disinfection Group	x_1	x_2	x_3
Free Chlorine	1	0	0
Post-Ammoniation	0	1	0
Concurrent	0	0	1
Other	-1	-1	-1

Because many of the reported $CHBr_3$ concentrations were below detection limit, the regression analysis used a variable called "Br_3 Class". This variable was based on coding into classes spaced on a logarithmic scale. In this manner, the large number of bromoform observations below detection limits could be included in the regression without biasing the results. The values of Br_3 Class are listed in Table A-4. As shown in the table, all observations having a bromoform concentration less than 0.101 μg/L (the detection-limit used for the survey samples) were assigned a value of 1 for Br_3 Class. All observations having a bromoform concentration greater than 0.101 μg/L but less than 0.126 μg/L were assigned a value of 2 for Br_3 Class, and so on. The class boundaries increased by a factor of 1.25 until all observations were included, with the highest value of Br_3 Class corresponding to the highest observed bromoform concentration (81.6 μg/L) in the 35-Utility DBP Study data base.

The constants developed during this regression analysis are listed in Table A-5 for the various HAA species. The example below illustrates the use of this model to predict the concentration of DCAA for a utility in which the only disinfectant employed was free chlorine.

Given: $[CHCl_3]$ = 16.69 μg/L
$[CHBr_3]$ = 7.21 μg/L (Br_3 Class = 21)
[TOC] = 4.01 mg/L
pH = 7.63

Further: For free chlorine, $x_1 = 1$, $x_2 = 0$, and $x_3 = 0$.

$$(DCAA)^{1/3} = 1.33006 + \begin{vmatrix} 100 \end{vmatrix} \begin{vmatrix} 0.66865 \\ 0.64799 \\ 1.24804 \end{vmatrix} + 0.32686\ Ln(CHCl_3) - 0.00887\ (Br_3\ Class)$$

$$+ TOC \begin{vmatrix} 100 \end{vmatrix} \begin{vmatrix} 0.17166 \\ 0.01770 \\ -0.01272 \end{vmatrix} + pH \begin{vmatrix} 100 \end{vmatrix} \begin{vmatrix} -0.14785 \\ -0.08143 \\ -0.15625 \end{vmatrix} \qquad \textbf{(A-12)}$$

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TABLE A-4

VALUES OF THE INDEPENDENT VARIABLE "Br_3 CLASS"

Upper Class Boundary for $CHBr_3$ ($\mu g/L$)	Value of Variable "Br_3 Class"	Number of Observations in Class
0.101	1	46
0.126	2	4
0.158	3	2
0.197	4	2
0.247	5	4
0.308	6	1
0.385	7	3
0.482	8	3
0.602	9	7
0.753	10	5
0.941	11	5
1.176	12	9
1.470	13	6
1.837	14	3
2.296	15	4
2.871	16	3
3.588	17	1
4.485	18	1
5.607	19	1
7.008	20	4
8.760	21	3
10.950	22	1
13.688	23	0
17.110	24	5
21.388	25	2
26.734	26	3
33.418	27	3
41.773	28	5
52.216	29	0
65.270	30	3
81.587	31	1

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TABLE A-5

CONSTANTS FOR DBP REGRESSION ANALYSIS

	DCAA^(1/3)	ln(TCAA)	ln(MBAA)	ln(DBAA)	ln(MCAA)
CONSTANT	1.33006	2.47537	-2.05187	-1.27803	-0.63410
C1	0.66865				
C2	0.64799				
C3	1.24804				
L CHC13	0.32686	1.07748			
L BrC12					
L Br2C1					
TOC				0.07401	0.20800
pH		-0.42038			
Br3 Class	-0.00887		0.08289	0.13276	
LC13*TOC					
Br3Class*TOC					
LBr2C1*pH					
C1 LC13		-0.10960			
C2 LC13		-0.32806			
C3 LC13		0.29479			
C1 LBrC12			0.29841	0.13349	
C2 LBrC12			0.31497	0.44408	
C3 LBrC12			-0.88464	0.10853	
C1 LBr2C1			-0.24591		
C2 LBr2C1			-0.22422		
C3 LBr2C1			0.53450		
C1 TOC	0.17166				0.06587
C2 TOC	0.01770				0.00956
C3 TOC	-0.01272				-0.18197
C1 pH	-0.14785	-0.00733			
C2 pH	-0.08143	0.10439			
C3 pH	-0.15625	-0.07219			
C1 Br3Class				-0.02820	
C2 Br3Class				-0.05424	
C3 Br3Class				-0.00925	

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Simplification of the above equation results in:

$$(DCAA)^{1/3} = 1.33006 + 0.66865 + (0.32686)(LnCHCl_3) + (-0.00887)(Br_3\ Class) + (0.17166)(TOC) + (-0.14785)(pH),$$

and

$$DCAA = 12.1\ \mu g/L\ (predicted)$$

A.3.2 Equations Based on Laboratory Studies

The American Water Works Association (AWWA) Technical Advisory Workgroup (TAW) for D/DBP sponsored a laboratory study to examine the formation of THMs and HAAs as a result of chlorination. Data used for developing HAA predictive equations were derived from two experimental studies as described below:

- In the D/DBP TAW database, kinetic experiments were conducted on raw water samples from eight (8) utilities across the country. Each water sample was subjected to a single dose of chlorine and a single incubation temperature of 20°C. The chlorine dose was selected to maintain a free residual of 0.2 to 0.5 mg/L at the end of the 96-hour reaction time. Samples were collected at ten different reaction times over the 96-hour period and analyzed for HAAs. A series of additional experiments were conducted on two of the eight water samples to briefly investigate the impact of pH, chlorine dose, and temperature on the reaction kinetics. The entire database contains 172 observations on HAA formation.

- In the D/DBP TAW coagulation database, raw water samples from eighteen utilities were coagulated at different coagulant doses and at different coagulation pH values. The treated water was filtered through a 8.0 um filter paper. The filtered water sample were pH adjusted to 8.0, and was chlorinated at a 1:1 chlorine to TOC ratio, and were incubated at 20°C for sixteen hours. Formation of HAAs was measured at the end of the 16-hour reaction time. This database contained 71 observations on HAA formation.

These laboratory observations on HAA formation were used to develop regression equations correlating various HAA species with the water quality parameters. The equations for MCAA, DCAA, TCAA, MBAA, and DBAA are shown in Tables A-6 to A-10. These tables also include the boundary conditions relevant to each of the equations (JMM, 1992).

A.3.3 Calculation of HAA Formation

Calculation of HAA formation in the model utilizes one of the two sets of empirical equations outlined above. The user is given a choice to select which set of equations to use.

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TABLE A-6

MCAA EQUATION

TIME > 12 hours:

MCAA = $1.634 \bullet (TOC)^{0.753} \bullet (BR+0.01)^{-0.085} \bullet (PH)^{-1.124} \bullet (CL2DOSE)^{0.509} \bullet (TIME)^{0.300}$

BOUNDARY CONDITIONS

PARAMETER	MIN	MAX	MEAN	STANDARD DEVIATION
CL_2DOSE/Br	9.8	819.9	196.4	211.3
CL_2DOSE/TOC	1.0	2.3	1.5	0.4
TOC (mg/L)	2.8	11.0	4.3	1.8
UV-254 (cm^{-1})	0.050	0.382	0.127	0.073
BR (mg/L)	0.01	0.43	0.14	0.14
PH	5.6	9.0	7.5	0.8
CL2DOSE (mg/L)	3.0	25.3	6.9	4.9
TIME (hr)	15.8	105.0	55.0	27.5
TEMP (°C)	13.0	20.0	19.4	1.9
MCAA (μg/L)	1.2	22.0	6.0	4.8

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TABLE A-7

DCAA EQUATION

$$DCAA = 0.605 \bullet (TOC)^{0.291} \bullet (UV\text{-}254)^{0.726} \bullet (BR+0.01)^{-0.568} \bullet (CL2DOSE)^{0.480} \bullet (TIME)^{0.239} \bullet (TEMP)^{0.665}$$

BOUNDARY CONDITIONS

PARAMETER	MIN	MAX	MEAN	STANDARD DEVIATION
CL_2DOSE/Br	9.8	819.9	202.3	214.3
CL_2DOSE/TOC	1.0	2.3	1.6	0.4
TOC (mg/L)	2.8	11.0	4.4	1.9
UV-254 (cm^{-1})	0.050	0.382	0.131	0.077
BR (mg/L)	0.01	0.43	0.13	0.14
PH	5.6	9.0	7.5	0.8
CL2DOSE (mg/L)	3.04	25.30	7.3	5.2
TIME (hr)	0.1	105.0	27.4	32.6
TEMP (°C)	13.0	20.0	19.5	1.8
DCAA (μg/L)	1.9	251.0	36.6	38.4

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TABLE A-8

TCAA EQUATION

$$TCAA = 87.182 \bullet (TOC)^{0.355} \bullet (UV\text{-}254)^{0.901} \bullet (BR+0.01)^{-0.679} \bullet (PH)^{-1.732} \bullet (CL2DOSE)^{0.881} \bullet (TIME)^{0.264}$$

BOUNDARY CONDITIONS

PARAMETER	MIN	MAX	MEAN	STANDARD DEVIATION
CL_2DOSE/Br	9.8	819.9	202.3	214.3
CL_2DOSE/TOC	1.0	2.3	1.6	0.4
TOC (mg/L)	2.8	11.0	4.4	1.9
UV-254 (cm^{-1})	0.050	0.382	0.131	0.077
BR (mg/L)	0.01	0.43	0.13	0.14
PH	5.6	9.0	7.5	0.8
CL2DOSE (mg/L)	3.04	25.30	7.3	5.2
TIME (hr)	0.1	105.0	27.4	32.6
TEMP (°C)	13.0	20.0	19.5	1.8
TCAA (μg/L)	1.7	485.0	72.6	90.1

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TABLE A-9

MBAA EQUATION

$$MBAA = 0.176 \bullet (TOC)^{1.664} \bullet (UV\text{-}254)^{-0.624} \bullet (BR)^{0.795} \bullet (PH)^{-0.927} \bullet (TIME)^{0.145} \bullet (TEMP)^{0.450}$$

BOUNDARY CONDITIONS

PARAMETER	MIN	MAX	MEAN	STANDARD DEVIATION
CL_2DOSE/Br	9.8	192.0	39.0	50.4
CL_2DOSE/TOC	1.0	2.0	1.4	0.4
TOC (mg/L)	3.0	5.9	3.8	0.9
UV-254 (cm^{-1})	0.050	0.110	0.077	0.018
BR (mg/L)	0.05	0.43	0.24	0.13
PH	7.0	9.0	8.1	0.5
CL2DOSE (mg/L)	3.0	10.3	5.4	2.5
TIME (hr)	0.1	103.5	31.3	33.6
TEMP (°C)	13.0	20.0	19.4	2.0
MBAA (μg/L)	0.5	4.6	1.8	0.9

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TABLE A-10

DBAA EQUATION

$$DBAA = 84.940 \bullet (TOC)^{-0.620} \bullet (UV\text{-}254)^{0.651} \bullet (BR)^{1.073} \bullet (CL2DOSE)^{-0.200} \bullet (TIME)^{0.120} \bullet (TEMP)^{0.657}$$

BOUNDARY CONDITIONS

PARAMETER	MIN	MAX	MEAN	STANDARD DEVIATION
CL_2DOSE/Br	9.8	280.0	41.1	59.9
CL_2DOSE/TOC	1.0	2.0	1.4	0.4
TOC (mg/L)	3.0	5.9	3.7	0.9
UV-254 (cm^{-1})	0.050	0.170	0.080	0.025
BR (mg/L)	0.02	0.43	0.24	0.13
PH	5.6	9.0	8.1	0.6
CL2DOSE (mg/L)	3.0	10.3	5.2	2.4
TIME (hr)	0.1	103.5	27.6	32.8
TEMP (°C)	13.0	20.0	19.4	2.0
DBAA (μg/L)	0.6	31.0	11.0	7.9

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The application of the equations presented in Section A.3.2 to the treatment plant parameters for calculation of HAA concentrations follow the same techniques described in Section A.2.4 for THMs. The application of the equations presented in Section A.3.2 to the treatment plant parameters is based on statistical correlations and illustrated in Section A.3.2.

A.4 EQUATIONS FOR REMOVAL OF NATURAL ORGANIC MATTER

A.4.1 Alum Coagulation, Flocculation, Clarification and Filtration

Many investigators have evaluated the impacts of alum dose and coagulation pH on the removal of natural organic matter (NOM) at a bench-scale level (Kavanaugh, 1978; Young and Singer, 1979; Semmens and Field, 1980; Chadik and Amy, 1983; Knocke, et al., 1986; Hubel and Edzwald, 1987). In general, these studies have found that the removal of NOM can be optimized by maintaining certain pH ranges during coagulation, flocculation and clarification.

Despite extensive bench-scale testing, a complete field-scale assessment of pH and coagulant dose impacts has not been published to-date. Therefore, an effort was made to develop a model that described the removal of TOC and UV-254 in alum coagulation, flocculation, clarification and filtration plants. TOC and UV-254 were selected to quantify the NOM so that compatibility with the THM formation model was assured.

Removal of NOM by alum coagulation was based on full-scale process data collected in three studies (Montgomery and Metropolitan, 1989; Singer, 1988; and Edzwald, 1984). The complete field-scale database includes 45 data points obtained from the 17 treatment plants shown on Figure A-3. Characteristics of the database are shown in Table A-11 and indicate that the database covers a wide range of raw water qualities and treatment conditions. Median TOC and UV-254 removals in this database were 26 and 68 percent, respectively.

A multiple regression analysis was employed to analyze the influence of raw water TOC (TOC_0), alum dose, coagulation pH (pH_c), temperature and chloride on finished water TOC (TOC_f) in these 17 treatment plants. Because alum dose, TOC and chloride data were lognormally distributed, the natural logarithm of these variables was used for this analysis. Neither temperature nor chloride had a statistically significant impact on TOC_f in this data

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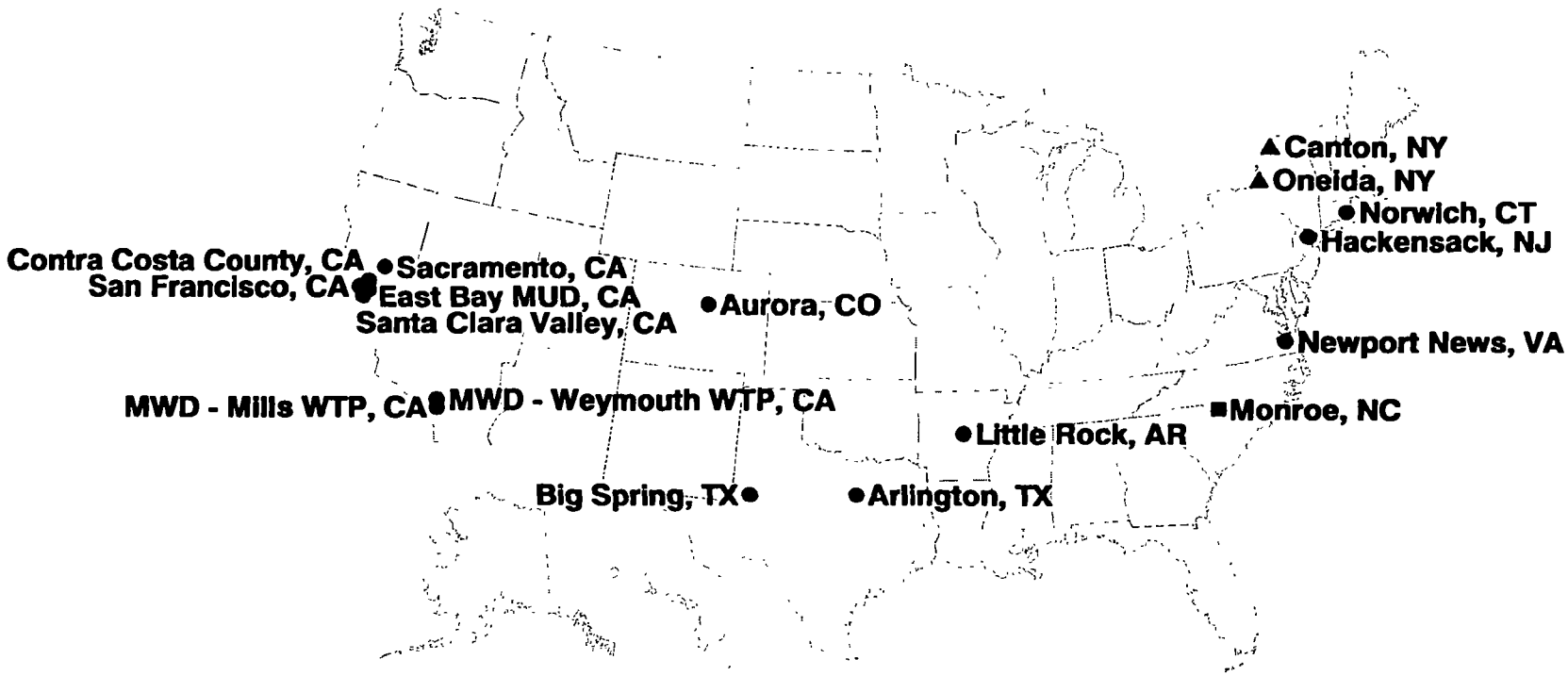
figure03

ALUM COAGULATION TREATMENT PLANT LOCATIONS



REFERENCES

▲ Edzwald, 1984 ■ Singer, 1988 ● JMM and MWD, 1989

FIGURE A-3

TABLE A-11

CHARACTERISTICS OF FIELD-SCALE ALUM COAGULATION DATABASE

	Distribution	Range	Median
Raw Water Quality			
TOC (mg/L)	lognormal	1.11 - 12.1	2.78
UV-254 (cm^{-1})	lognormal	0.019 - 0.84	0.111
pH	normal	6.3 - 9.0	7.7
Alkalinity (mg/L as $CaCO_3$)	lognormal	5.8 - 149	52
Hardness (mg/L as $CaCO_3$)	lognormal	10 - 550	93
Temperature (°C)	normal	2 - 31	18
Turbidity (NTU)	lognormal	0.4 - 26	2.4
Chloride (mg/L)	lognormal	1 - 640	20
Finished Water Quality			
TOC (mg/L)	lognormal	0.78 - 6.3	1.98
UV-254 (cm^{-1})	lognormal	0.002 - 0.095	0.037
Turbidity (NTU)	lognormal	0.04 - 0.61	0.16
Coagulation pH	normal	5.5 - 8.0	7.15
Alum Dose	lognormal	1.5 - 55	11

base. The apparent lack of significance between temperature and TOC removal is in agreement with the results of bench-scale studies performed by Knocke, et al. (1986).

The regression analysis was conducted a second time without temperature and chloride. Because both the intercept and slope of the relationship between ln(alum dose) and $\ln(TOC_f)$ are likely to depend on $\ln(TOC_0)$ and pH_c, several interactive variables were also included in the analysis (Kleinbaum and Kupper, 1978). Without the interactive variables, the resulting model would have indicated that the slope of the relationship between ln(alum dose) and $\ln(TOC_f)$ was independent of pH_c and $\ln(TOC_0)$. The variables examined in this analysis were those shown in Table A-12.

A stepwise variable selection procedure was used to select the most statistically significant of the independent variables and include them in an equation describing the performance of the 17 treatment plants in the data base. The resulting equation and its associated statistics are as follows:

$$\begin{aligned}\ln(TOC_f) = & -0.16 + 1.16[\ln(TOC_0)] \\ & -0.45[\ln(alum\ dose)] \\ & -0.070[\ln(TOC_0)][\ln(alum\ dose)] \\ & +0.057(pH_c)[\ln(alum\ dose)]\end{aligned} \qquad \text{(A-13)}$$

$[r^2 = 0.968,\ \text{adj } r^2 = 0.965,\ \text{SEE} = 0.087,\ F = 297\ (\alpha < 0.001),\ n = 44]$

An analysis was performed to determine the differences between finished water TOC levels predicted by Equation A-13 and those observed in the 17 treatment plants. Figure A-4 shows that 60 and 90 percent of the predicted finished water TOC levels were within 0.2 and 0.4 mg/L, respectively, of the observed concentration. In addition, 90 percent of the predicted values differed from observed values by less than 12 percent.

A sensitivity analysis of Equation A-13 is shown in Figures A-5 and A-6. These figures indicate the following:

- TOC removal increases with increasing alum dose, however, the magnitude of the increase becomes smaller as alum dose increases. This is consistent with observations described in the literature.

- TOC removal increases with decreasing coagulation pH down to pH 5.5. This is also in agreement with the literature. The range of coagulation pH levels in the database, however, did not allow for the determination of an optimal coagulation pH.

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TABLE A-12

VARIABLES DEFINED IN DEVELOPMENT OF NOM REMOVAL BY ALUM COAGULATION

Dependent Variable:	$\ln(TOC_f)$
Independent Variables:	$\ln(TOC_0)$
	ln(alum dose)
	pH_c
	$\ln(TOC_0)$ * ln(alum dose)
	$\ln(TOC_0)$ * pH_c
	ln(alum dose) * pH_c
	$\ln(TOC_0)$ * ln(alum dose) * pH_c

Notes:

TOC_f = Filtered water total organic carbon in mg/L
TOC_0 = Raw water total organic carbon in mg/L
alum dose = alum dose in mg/L as $Al_2(SO_4)_3 \bullet 14\ H_2O$
pH_c = pH of coagulation

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figure04

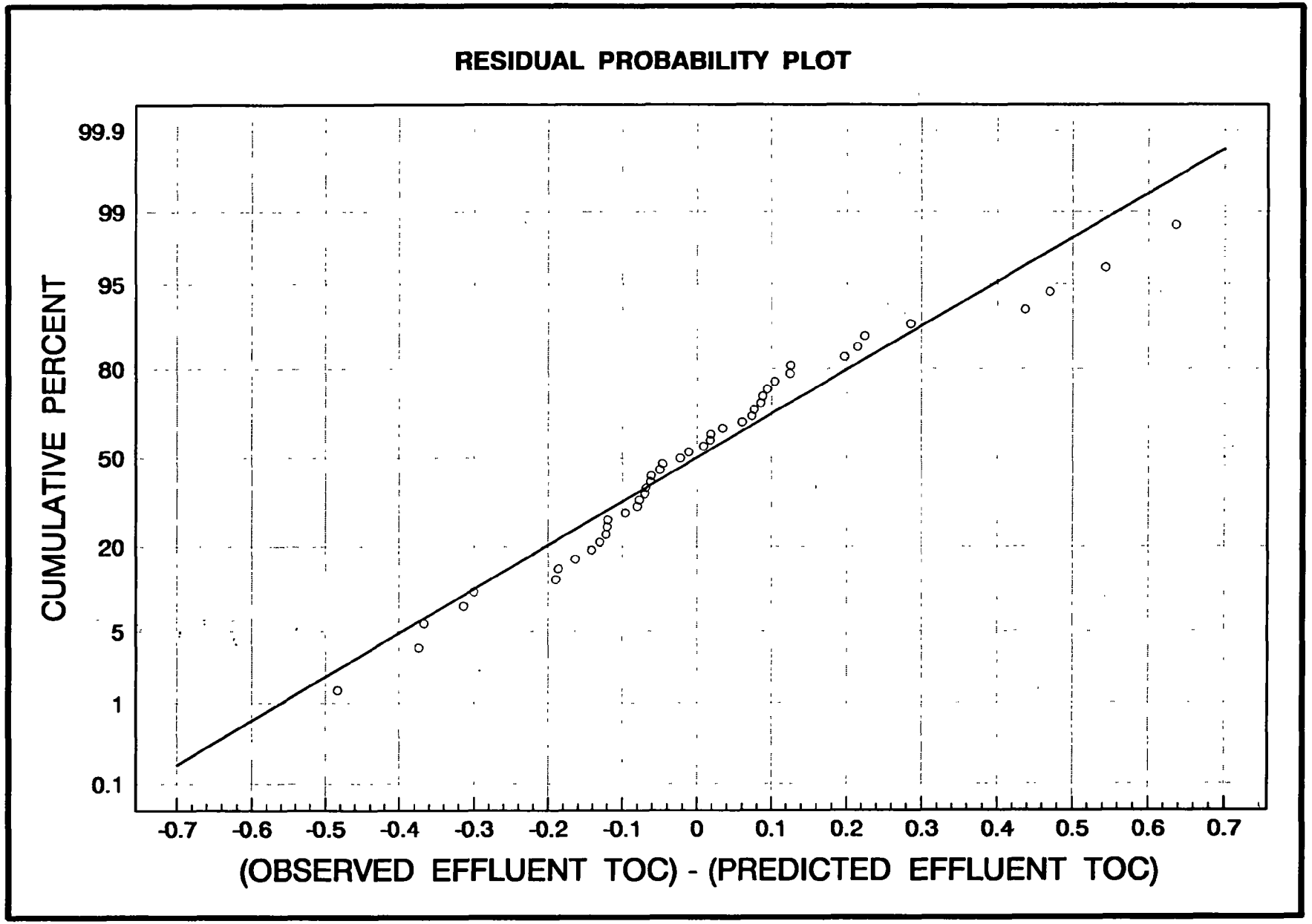

FIGURE A-4

figure05

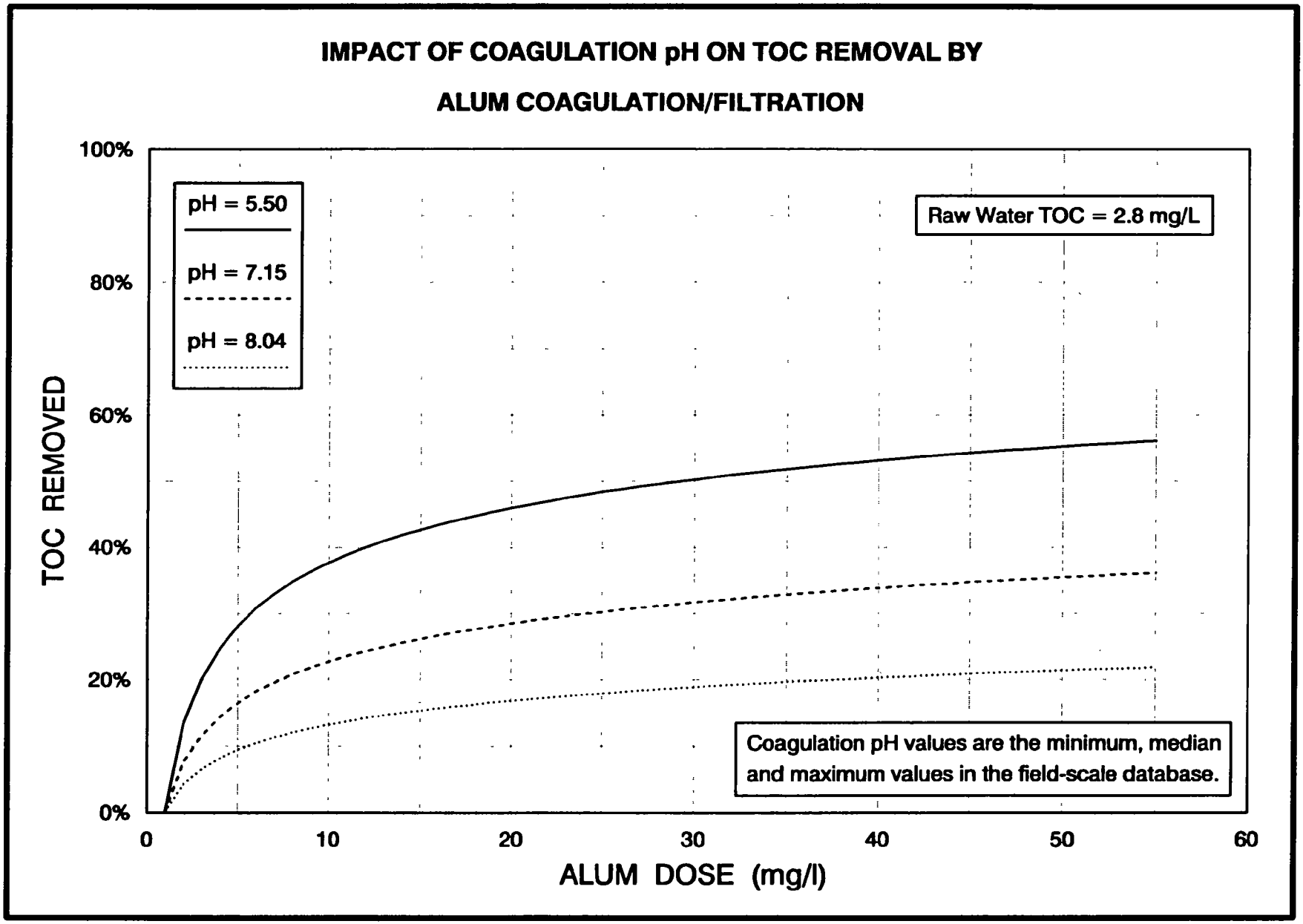

FIGURE A-5

figure06

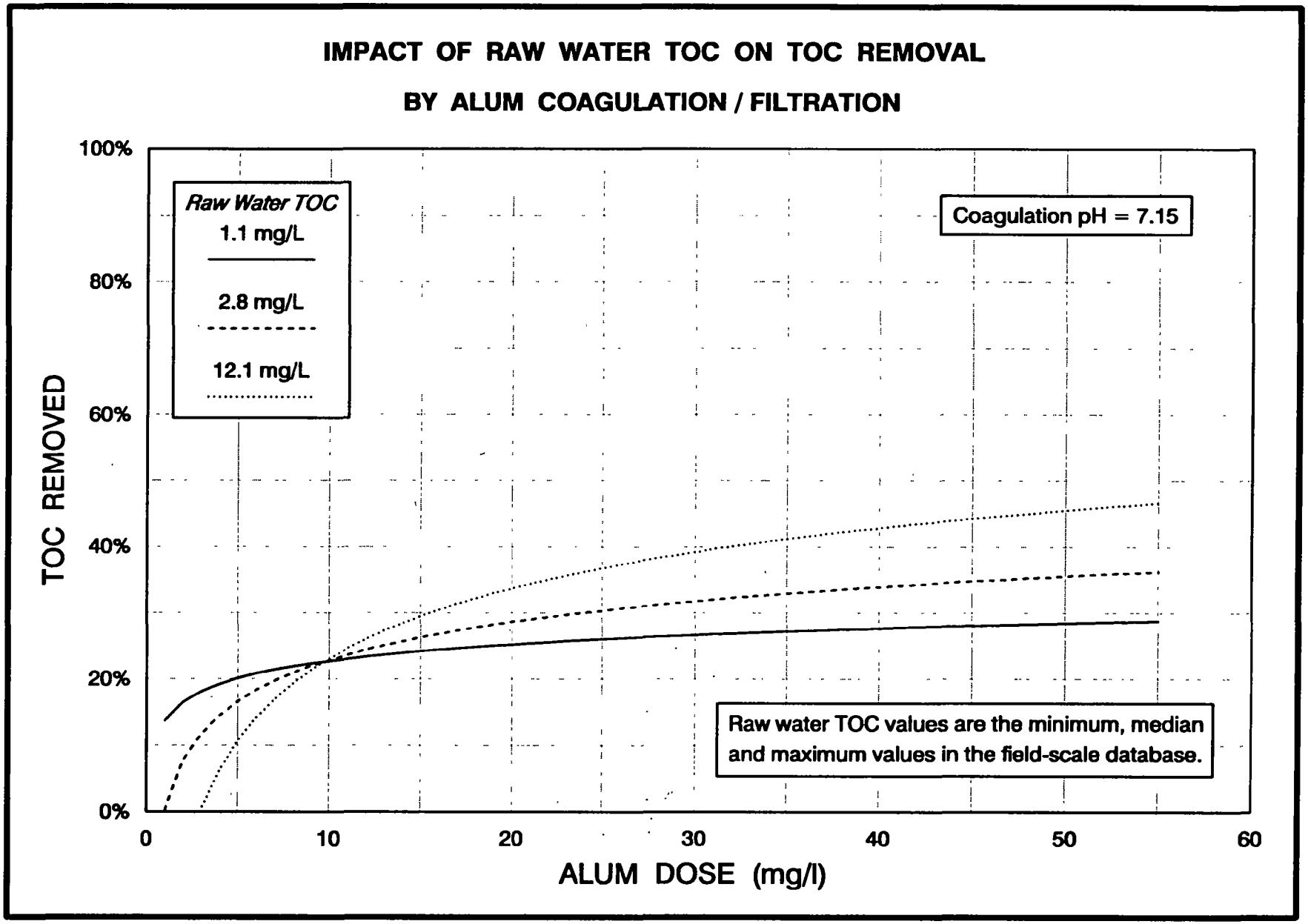

FIGURE A-6

- At alum doses greater than 10 mg/L, TOC removal increases with increasing raw water TOC levels.

- At pH 5.5, the maximum possible removal of TOC is approximately 55 percent for a water with a median TOC of 2.8 mg/L. Because the curves shown on Figure A-5 were developed from a regression analysis, the maximum possible removal of 55 percent is the expected average. Some utilities will observe greater removals while others will observe lower removals.

A database developed by USEPA's Technical Support Division (Fair, 1990) was used to develop a relationship for UV-254 removal. Using similar techniques to those used for TOC removal, the following equation was developed:

$$\begin{aligned} \ln(UV\text{-}254_f) = & -4.64 + 0.879[\ln(UV\text{-}254_0)] \\ & -0.185[\ln(alum\ dose)] \\ & +0.564(pH_c) \end{aligned} \qquad \textbf{(A-14)}$$

$$[r^2 = 0.733,\ \text{adj } r^2 = 0.702,\ \text{SEE} = 0.299,\ F = 23.8\ (\alpha < 0.001),\ n = 30]$$

where $UV\text{-}254_0$ is the raw water UV-254 in cm^{-1} and $UV\text{-}254_f$ is the filtered water UV-254 in cm^{-1}. The basis for selecting the USEPA database for this equation is described elsewhere (Harrington, et al., 1991).

A lower quality of fit was obtained for Equation A-14 when compared with Equation A-13. This lower quality of fit can be expected because the removal of UV-254 may also occur as a direct result of oxidation processes conducted during the coagulation, flocculation, clarification and filtration processes. An evaluation of this phenomenon has not been conducted to date.

A.4.2 Ferric Coagulation, Flocculation, Clarification 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 following raw water sources and geographical locations were represented:

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- San Diego, California (140 observations);
- Central Arizona Project Water, Arizona (46 observations);
- Clermont, Ohio (9 observations);
- Akron, Ohio (9 observations);
- Elizabethtown, New Jersey (6 observations); and
- Omaha, Nebraska (5 observations).

Summary statistics of this database are shown in Table A-13. The ability of the ferric coagulation equations to simulate NOM removal for the general case is not expected to be as good as the alum coagulation equations because fewer waters were included in the analysis and because the results may be skewed by the large number of observations from two sources.

Using similar techniques to those used for developing the alum coagulation equations, the following equations were developed for ferric salt coagulation:

$$\begin{aligned}\log_{10}(TOC_f) = \; & 0.316 + 0.891[\log_{10}(TOC_0)] \\ & -0.018[\log_{10}(FeCl_3\ dose)] \\ & -2.31\left(\frac{1}{pH_c}\right)\end{aligned} \tag{A-15}$$

[adj r^2 = 0.742, F = 200 (α < 0.001), n = 213]

$$\begin{aligned}\log_{10}(UV\text{-}254_f) = \; & 0.228 + 1.025[\log_{10}(UV\text{-}254_0)] \\ & -0.033[\log_{10}(FeCl_3\ dose)] \\ & -2.37\left(\frac{1}{pH_c}\right)\end{aligned} \tag{A-16}$$

[adj r^2 = 0.796, F = 247 (α < 0.001), n = 195]

where $FeCl_3$ dose is the ferric salt dose in mg/L as $FeCl_3 \cdot 6\ H_2O$.

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TABLE A-13

SUMMARY STATISTICS FOR FERRIC CHLORIDE DATABASE

Parameter	Mimimum	Maximum	Mean	Standard Deviation
Raw Water DOC (mg/L)	2.7	9.0	4.8	1.7
Raw Water UV-254 (1/cm)	0.044	0.720	0.080	0.08
Raw Water pH	6.0	10.8	8.1	0.7
$FeCl_3$ Dose (mg/L)	0.3	75	15.8	14.8
Treated Water DOC (mg/L)	1.9	8.9	3.9	1.3
Treated Water UV-254 (1/cm)	0.010	0.420	0.050	0.04
Treated Water pH	5.6	10.8	7.4	0.9

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A.4.3 Precipitative Softening, Clarification and Filtration

Full-scale data, including all of the parameters required for modeling, have been compiled for only twelve precipitative softening plants. TOC, UV-254, lime dose and total hardness values were available for most of the treatment plants. Seven of the plants reported calcium and magnesium hardness values in addition to total hardness.

Nine field-scale observations were available for these seven plants (Table A-14). Four observations were collected from four plants in the database developed by USEPA's Technical Support Division (Fair, 1990), three observations were collected from one plant in the database developed by Metropolitan and Montgomery (1989), and two observations were collected from two plants recently evaluated by Malcolm Pirnie, Inc. (1991)

Using similar techniques to those used for developing the coagulation equations, the following equations were developed for precipitative softening:

$$\begin{aligned}\ln(TOC_f) = \; & 1.09[\ln(TOC_0)] \\ & -0.0862[\ln(\Delta Ca)] \\ & -0.0482[\ln(\Delta Mg)]\end{aligned} \qquad \text{(A-17)}$$

[r^2 = 0.984, adj r^2 = 0.978, SEE = 0.217, F = 120 ($\alpha < 0.0001$), n = 9]

$$\begin{aligned}\ln(UV\text{-}254_f) = \; & 0.923[\ln(UV\text{-}254_0)] \\ & -0.0758[\ln(\Delta Ca)] \\ & -0.198[\ln(\Delta Mg)]\end{aligned} \qquad \text{(A-18)}$$

[r^2 = 0.989, adj r^2 = 0.986, SEE = 0.366, F = 183 ($\alpha < 0.0001$), n = 9]

where

ΔCa = Raw Water Calcium Hardness (mg/L as $CaCO_3$)
+ Calcium Hardness from Lime Addition (mg/L as $CaCO_3$)
- Finished Water Calcium Hardness (mg/L as $CaCO_3$)

and

ΔMg = Raw Water Magnesium Hardness (mg/L as $CaCO_3$)
- Finished Water Magnesium Hardness (mg/L as $CaCO_3$)

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TABLE A-14

CHARACTERISTICS OF FIELD-SCALE PRECIPITATIVE SOFTENING DATABASE

	Range	Median
Raw Water Quality		
TOC (mg/L)	2.2 - 19.0	4.6
UV-254 (cm^{-1})	0.030 - 0.697	0.123
pH	6.9 - 8.4	7.8
Alkalinity (mg/L as $CaCO_3$)	68 - 295	182
Calcium Hardness (mg/L as $CaCO_3$)	64 - 300	168
Magnesium Hardness (mg/L as $CaCO_3$)	0 - 183	28
Total Hardness (mg/L as $CaCO_3$)	98 - 360	247
Temperature (°C)	9 - 29	23
Turbidity (NTU)	0.1 - 10	2.2
Finished Water Quality		
TOC (mg/L)	1.7 - 9.5	2.9
UV-254 (cm^{-1})	0.010 - 0.232	0.060
Removals		
Calcium Hardness (mg/L as $CaCO_3$)	100 - 602	262
Magnesium Hardness (mg/L as $CaCO_3$)	0 - 90	16
Total Hardness (mg/L as $CaCO_3$)	104 - 644	346
Softening pH	8.9 - 11.3	10.2
Lime Dose (mg/L as $CaCO_3$)	109 - 394	228
Soda Dose (mg/L as Na_2CO_3)	0 - 9.4	0

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Because of the lack of data available for the development of the above equations, an extensive survey of field scale precipitative softening plants is recommended.

A.4.4 Granular Activated Carbon

TOC breakthrough curves for alum coagulated, settled and filtered water were described by the general logistic function (Clark, et al., 1986; Clark, 1987). This function is represented by the following equation:

$$TOC_f = \left[\frac{(TOC_0)^{n-1}}{1 + Ae^{-rt}}\right]^{\frac{1}{n-1}} \qquad \text{(A-19)}$$

where TOC_f is the finished water TOC, TOC_0 is the influent TOC, 1/n is the slope of the Freundlich isotherm and t indicates the time since the beginning of the adsorption process. The two constants of the logistic function, A and r, can be determined by the procedure discussed by Clark (1987).

The logistic function parameters, A and r, are a function of empty bed contact time (EBCT), the type of GAC used and water quality factors such as pH and ionic strength. A modified form of this equation is not developed at this time to account for these other factors. The existing database on granular activated carbon (GAC) adsorption of NOM should be evaluated to determine if Equation A-19 can be modified to reflect a general case. In the meantime, the model assumes that the Jefferson Parish, Louisiana case is representative of the general case, because this appears to be a median case when compared with results from other utilities. For instance, TOC removal was higher at Jefferson Parish than at Manchester, NH, Miami, FL and Metropolitan. TOC removal was lower at Jefferson Parish, however, than at Philadelphia, PA, Cincinnati, OH and Shreveport, LA.

The parameters reported for the Jefferson Parish case are as follows:

$$r = 0.0743(EBCT)^{-0.429} \qquad \text{(A-20)}$$

$$A = 0.757(EBCT)^{1.35} \qquad \text{(A-21)}$$

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$$\frac{1}{n} = 0.316 \qquad \text{(A-22)}$$

The model uses Equations A-19 through A-22 to calculate a running average TOC removal based on the EBCT and the regeneration frequency. Running average removals are of interest because USEPA plans to regulate DBPs on a running annual average basis. The model, therefore, is 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 the algorithm, the running average TOC is calculated as follows:

$$\overline{TOC_f} = \frac{\sum_{t=1}^{RF} \left\{ \left[\frac{(TOC_0)^{n-1}}{1 + Ae^{-nt}} \right]^{\frac{1}{n-1}} \right\}}{RF} \qquad \text{(A-23)}$$

where RF is the regeneration frequency.

Because a sufficient database was not available to develop a separate equation for UV-254 removal, the model assumes that UV-254 removal is equivalent to TOC removal on a percentage basis. Because UV-254 is a surrogate measure of the more adsorbable humic, non-polar fraction of organic material, this assumption is conservative. UV-254 removal would be expected to exceed that of TOC, which is comprised of both non-polar and polar (less adsorbable) organic material.

A.4.5 Membrane Processes

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). Relevant water quality characteristics from these studies are shown in Table A-15. Data from these three studies were combined and analyzed for relationships between nominal molecular weight cutoff (MWC) and removal of natural organic parameters. The best relationship obtained for dissolved organic carbon (DOC) removal was:

[adj r^2 = 0.886, n = 44]

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TABLE A-15

CHARACTERISTICS OF BENCH-SCALE, CONTINUOUS FLOW MEMBRANE STUDIES

	Range	Median
Raw Water Quality		
TOC (mg/L)	3.4 - 25.1	8.9
pH	5.8 - 7.9	7.2
Alkalinity (mg/L as $CaCO_3$)	20 - 338	97
Total Hardness (mg/L as $CaCO_3$)	152 - 352	231
Permeate Water Quality		
TOC (mg/L)	0.2 - 16.2	2.0
pH	5.9 - 7.7	6.8
Alkalinity (mg/L as $CaCO_3$)	7 - 343	48
Total Hardness (mg/L as $CaCO_3$)	4 - 365	122
Operating Parameters		
Molecular Weight Cutoff	50 - 40,000	400
Operating Pressure (psi)	50 - 190	130
Recovery (%)	45 - 86	76
Product Flux (gpd/sf)	9 - 57	26

$$\ln\left[\left(\frac{DOC_0}{DOC_f}\right) - 1\right] = 0.986 + 2.59[\ln(DOC_0)] - 0.385[\ln(MWC)][\ln(DOC_0)] \quad \text{(A-24)}$$

where DOC_f and DOC_0 are the product water and feed water DOC levels, respectively. This equation had an adjusted R^2 of 0.886 and was based on 44 observations from 6 different waters. Data for UV-254 removal were not reported in either study and, therefore, the model assumes that UV-254 and DOC are removed to the same extent in membrane systems.

A.5 EQUATIONS FOR ALKALINITY AND pH ADJUSTMENT

A.5.1 General

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):

$$Alkalinity = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad \text{(A-25)}$$

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:

$$[HCO_3^-] = \alpha_1 C_{T,CO_3} \quad \text{(A-26)}$$

$$[CO_3^{2-}] = \alpha_2 C_{T,CO_3} \quad \text{(A-27)}$$

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Where:

$$C_{T,CO_3} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad \text{(A-28)}$$

$$\alpha_1 = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad \text{(A-29)}$$

$$\alpha_2 = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad \text{(A-30)}$$

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 25°C 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):

$$\ln\left(\frac{K_1}{K_1^\circ}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T^\circ} - \frac{1}{T}\right) \quad \text{(A-31)}$$

where ΔH° is the standard enthalpy change of the dissociation of carbonic acid to bicarbonate, T° is the standard temperature of 298°K (25°C) and K_1° is the value of the equilibrium constant at T°. Solving Equation A-31 for K_1 produces the following:

$$K_1 = \exp\left\{\left[\frac{\Delta H^\circ}{R}\left(\frac{1}{T^\circ} - \frac{1}{T}\right)\right] - \ln K_1^\circ\right\} \quad \text{(A-32)}$$

Equations A-31 and A-32 assume that ΔH° is independent of temperature.

Using Equation A-32, the following equations were developed for K_1 and K_2:

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$$K_1 = \exp\left\{\left[\left(\frac{7700\ \frac{J}{mole}}{8.314\ \frac{J}{°K \cdot mole}}\right)\left(\frac{1}{298.15°K} - \frac{1}{T}\right)\right] - 14.5\right\} \qquad \text{(A-33)}$$

$$K_2 = \exp\left\{\left[\left(\frac{14900\ \frac{J}{mole}}{8.314\ \frac{J}{°K \cdot mole}}\right)\left(\frac{1}{298.15°K} - \frac{1}{T}\right)\right] - 23.7\right\} \qquad \text{(A-34)}$$

Equations A-33 and A-34 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:

$$[OH^-] = \frac{K_w}{[H^+]} \qquad \text{(A-35)}$$

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

$$\log_{10}(K_w) = \frac{-4470.99}{T} + 6.0875 - 0.01706T \qquad \text{(A-36)}$$

where T is the temperature in degrees Kelvin.

Based on Equations A-25 through A-30 and on Equation A-35, Equation A-25 can be rewritten as follows:

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

$$= \left(\frac{K_1[H^+] + K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)C_{T,CO_3} + \frac{K_w}{[H^+]} - [H^+] \qquad \text{(A-37)}$$

As shown by this equation, alkalinity is dependent on $[H^+]$, C_{T,CO_3} and several equilibrium constants. The equilibrium constants are dependent on temperature. Therefore, any change in alkalinity, C_{T,CO_3} or temperature will produce a change in $[H^+]$. Because pH is equal to $-\log_{10}[H^+]$, any change in alkalinity, C_{T,CO_3} or temperature will produce a change in pH.

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

$$Alkalinity = C_B - C_A \qquad \text{(A-38)}$$

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 A-38 can also be written as follows:

$$\begin{aligned} Alkalinity = {} & C_B' + 2[Ca^{2+}] + [CaOH^+] \\ & + 2[Mg^{2+}] + [MgOH^+] + [NH_4^+] \\ & - C_A' - [OCl^-] \end{aligned} \qquad \text{(A-39)}$$

where:

$$[CaOH^+] = \frac{[Ca^{2+}]K_{Ca^{2+}\sim CaOH^+}}{[H^+]} \qquad \text{(A-40)}$$

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$$[MgOH^+] = \frac{[Mg^{2+}]K_{Mg^{2+} \leftrightarrow MgOH^+}}{[H^+]} \tag{A-41}$$

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

$$= \exp\left[\frac{-72320 \frac{J}{mole}}{\left(8.314 \frac{J}{mole \cdot {}^\circ K}\right)(T)}\right] \tag{A-42}$$

and

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

$$= \exp\left[\frac{-65180 \frac{J}{mole}}{\left(8.314 \frac{J}{mole \cdot {}^\circ K}\right)(T)}\right] \tag{A-43}$$

Using Equations A-40 and A-41, Equation A-39 can be rewritten as follows:

$$\begin{aligned} Alkalinity = C_B' &+ [Ca^{2+}]\left(2 + \frac{K_{Ca^{2+} \leftrightarrow CaOH^+}}{[H^+]}\right) \\ &+ [Mg^{2+}]\left(2 + \frac{K_{Mg^{2+} \leftrightarrow MgOH^+}}{[H^+]}\right) \\ &+ [NH_4^+] - C_A' - [OCl^-] \end{aligned} \tag{A-44}$$

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

$$C_{T,Ca} = [Ca^{2+}] + [CaOH^+] + [Ca(OH)_{2\,(aq)}] \tag{A-45}$$

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where:

$$[Ca(OH)_{2\,(aq)}] = \frac{[Ca^{2+}]K_{Ca^{2+} \sim Ca(OH)_{2\,(aq)}}}{[H^+]^2} \tag{A-46}$$

and

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

$$= \exp\left[\frac{-159800\frac{J}{mole}}{\left(8.314\frac{J}{mole \cdot {}^\circ K}\right)(T)}\right] \tag{A-47}$$

Combining Equations A-40, A-45 and A-46, the following relationship is obtained:

$$[Ca^{2+}] = \frac{C_{T,Ca}}{1 + \frac{K_{Ca^{2+} \sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} \sim Ca(OH)_{2\,(aq)}}}{[H^+]^2}} \tag{A-48}$$

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

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^+] + [Mg(OH)_{2\,(aq)}] \tag{A-49}$$

where:

$$[Mg(OH)_{2\,(aq)}] = \frac{[Mg^{2+}]K_{Mg^{2+} \sim Mg(OH)_{2\,(aq)}}}{[H^+]^2} \tag{A-50}$$

and

Combining Equations A-40, A-49 and A-50, the following relationship is obtained:

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

$$= \exp\left[\frac{-159760 \frac{J}{mole}}{\left(8.314 \frac{J}{mole \cdot {}^{\circ}K}\right)(T)}\right] \tag{A-51}$$

$$[Mg^{2+}] = \frac{C_{T,Mg}}{1 + \frac{K_{Mg^{2+} \leftrightarrow MgOH^{+}}}{[H^{+}]} + \frac{K_{Mg^{2+} \leftrightarrow Mg(OH)_{2(aq)}}}{[H^{+}]^{2}}} \tag{A-52}$$

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

$$C_{T,OCl} = [HOCl] + [OCl^{-}] \tag{A-53}$$

where:

$$[HOCl] = \frac{[OCl^{-}][H^{+}]}{K_{HOCl \leftrightarrow OCl^{-}}} \tag{A-54}$$

and

$$K_{HOCl \leftrightarrow OCl^{-}} = \exp\left\{\left[\left(\frac{13800 \frac{J}{mole}}{8.314 \frac{J}{{}^{\circ}K \cdot mole}}\right)\left(\frac{1}{298.15^{\circ}K} - \frac{1}{T}\right)\right] - 17.5\right\} \tag{A-55}$$

Combining Equations A-53 and A-54, the following relationship is obtained:

$$[OCl^{-}] = \frac{C_{T,OCl}}{1 + \frac{[H^{+}]}{K_{HOCl \leftrightarrow OCl^{-}}}} \tag{A-56}$$

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

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$$C_{T,NH_3} = [NH_4^+] + [NH_3] \tag{A-57}$$

where:

$$[NH_3] = \frac{[NH_4^+]K_{NH_4^+ \sim NH_3}}{[H^+]} \tag{A-58}$$

and

$$K_{NH_4^+ \sim NH_3} = \exp\left\{\left[\left(\frac{52210 \ \frac{J}{mole}}{8.314 \ \frac{J}{°K \cdot mole}}\right)\left(\frac{1}{298.15°K} - \frac{1}{T}\right)\right] - 21.4\right\} \tag{A-59}$$

Combining Equations A-57 and A-58, the following relationship is obtained:

$$[NH_4^+] = \frac{C_{T,NH_3}}{1 + \frac{K_{NH_4^+ \sim NH_3}}{[H^+]}} \tag{A-60}$$

Combining Equations A-44, A-48, A-52, A-56 and A-60, the following expression may be written:

The model calculates $[H^+]$ based on the equality of Equations A-37 and A-61. 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.

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

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$$
\begin{aligned}
Alkalinity = {} & C_B' - C_A' \\
& + \frac{C_{T,Ca}\left(2 + \dfrac{K_{Ca^{2+}\sim CaOH^+}}{[H^+]}\right)}{1 + \dfrac{K_{Ca^{2+}\sim CaOH^+}}{[H^+]} + \dfrac{K_{Ca^{2+}\sim Ca(OH)_{2(aq)}}}{[H^+]^2}} \\
& + \frac{C_{T,Mg}\left(2 + \dfrac{K_{Mg^{2+}\sim MgOH^+}}{[H^+]}\right)}{1 + \dfrac{K_{Mg^{2+}\sim MgOH^+}}{[H^+]} + \dfrac{K_{Mg^{2+}\sim Mg(OH)_{2(aq)}}}{[H^+]^2}} \\
& + \frac{C_{T,NH_3}}{1 + \dfrac{K_{NH_4^+\sim NH_3}}{[H^+]}} - \frac{C_{T,OCl}}{1 + \dfrac{[H^+]}{K_{HOCl\sim OCl^-}}}
\end{aligned}
\tag{A-61}
$$

phase is equivalent to the molar quantity of carbonate ions leaving the aqueous phase. Therefore, the model assumes the following:

$$C_{Ca,ppt} = C_{CO_3,ppt} \tag{A-62}$$

where $C_{Ca,ppt}$ is the concentration of precipitated calcium in equilibrium with the aqueous phase and $C_{CO_3,ppt}$ is the concentration of precipitated carbonate in equilibrium with the aqueous phase. These concentrations are related to dissolved phase concentrations and Equation A-62 can be rewritten as follows:

$$C_{Ca} - C_{T,Ca} = C_{CO_3} - C_{T,CO_3} \tag{A-63}$$

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

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

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$$[Ca^{2+}][CO_3^{2-}] = K_{so,CaCO_3} \tag{A-64}$$

where

$$K_{so,CaCO_3} = \exp\left\{\left[\left(\frac{-12530\ \frac{J}{mole}}{8.314\ \frac{J}{°K \cdot mole}}\right)\left(\frac{1}{298.15°K} - \frac{1}{T}\right)\right] - 19.1\right\} \tag{A-65}$$

Based on Equations A-27, A-29 and A-44, Equation A-64 can be rewritten as follows:

$$K_{so,CaCO_3} = \left(\frac{C_{T,Ca}}{1 + \frac{K_{Ca^{2+} \sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} \sim Ca(OH)_{2(aq)}}}{[H^+]^2}}\right)\left(\frac{K_1K_2C_{T,CO_3}}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) \tag{A-66}$$

Solving Equation A-66 for $C_{T,Ca}$ yields the following:

$$C_{T,Ca} = \frac{K_{so,CaCO_3}\left(1 + \frac{K_{Ca^{2+} \sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} \sim Ca(OH)_{2(aq)}}}{[H^+]^2}\right)}{C_{T,CO_3}\left(\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)} \tag{A-67}$$

Solving Equation A-63 for C_{T,CO_3} and substituting Equation A-67 for $C_{T,Ca}$ yields the following:

$$C_{T,CO_3} = C_{CO_3} - C_{Ca} + \frac{K_{so,CaCO_3}\left(1 + \frac{K_{Ca^{2+} \sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+} \sim Ca(OH)_{2(aq)}}}{[H^+]^2}\right)}{C_{T,CO_3}\left(\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right)} \tag{A-68}$$

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Multiplying each term in Equation A-68 by C_{T,CO_3} yields:

$$0 = C_{T,CO_3}^2 - C_{T,CO_3}(C_{CO_3} - C_{Ca}) - K_{so,CaCO_3}\left(\frac{1 + \frac{K_{Ca^{2+}\sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+}\sim Ca(OH)_{2(aq)}}}{[H^+]^2}}{\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}}\right) \quad \text{(A-69)}$$

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

$$C_{T,CO_3} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{(A-70)}$$

where

$$a = 1 \quad \text{(A-71)}$$

$$b = C_{Ca} - C_{CO_3} \quad \text{(A-72)}$$

and

$$c = -K_{so,CaCO_3}\left(\frac{1 + \frac{K_{Ca^{2+}\sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+}\sim Ca(OH)_{2(aq)}}}{[H^+]^2}}{\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}}\right) \quad \text{(A-73)}$$

The model calculates C_{T,CO_3} from Equations A-70 through A-73 when

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$$K_{so,CaCO_3} < \left(\frac{C_{T,Ca}}{1 + \frac{K_{Ca^{2+}\sim CaOH^+}}{[H^+]} + \frac{K_{Ca^{2+}\sim Ca(OH)_{2(aq)}}}{[H^+]^2}} \right) \left(\frac{K_1 K_2 C_{T,CO_3}}{[H^+]^2 + K_1[H^+] + K_1 K_2} \right) \tag{A-74}$$

After calculating C_{T,CO_3}, the model calculates $C_{T,Ca}$ from Equation A-63. The calculated values of C_{T,CO_3} and $C_{T,Ca}$ are substituted into the alkalinity expressions in Equations A-37 and A-61.

The model uses Equation A-63 and Equations A-70 through A-73 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:

$$\frac{[Mg^{2+}]}{[H^+]^2} = K_{so,Mg(OH)_2} \tag{A-75}$$

where

$$K_{so,Mg(OH)_2} = \exp\left\{ \left[\left(\frac{-113960 \ \frac{J}{mole}}{8.314 \ \frac{J}{°K \cdot mole}} \right) \left(\frac{1}{298.15°K} - \frac{1}{T} \right) \right] + 38.8 \right\} \tag{A-76}$$

Based on Equation A-52, Equation A-75 can be rewritten as follows:

$$K_{so,Mg(OH)_2} = \frac{C_{T,Mg}}{[H^+]^2 + [H^+]K_{Mg^{2+}\sim MgOH^+} + K_{Mg^{2+}\sim Mg(OH)_{2(aq)}}} \tag{A-77}$$

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Solving Equation A-77 for $C_{T,Mg}$ yields the following:

$$C_{T,Mg} = K_{so,Mg(OH)_2}\left([H^+]^2 + [H^+]K_{Mg^{2+}\sim MgOH^+} + K_{Mg^{2+}\sim Mg(OH)_{2(aq)}}\right) \tag{A-78}$$

The model calculates $C_{T,Mg}$ from Equation A-78 when

$$K_{so,Mg(OH)_2} < \frac{C_{T,Mg}}{[H^+]^2 + [H^+]K_{Mg^{2+}\sim MgOH^+} + K_{Mg^{2+}\sim Mg(OH)_{2(aq)}}} \tag{A-79}$$

The model uses Equation A-78 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.

Calculating pH Changes

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 A-37 to be equivalent to the alkalinity calculated by Equation A-61. The flowchart shown in Figure A-7 provides a detailed description of this procedure.

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

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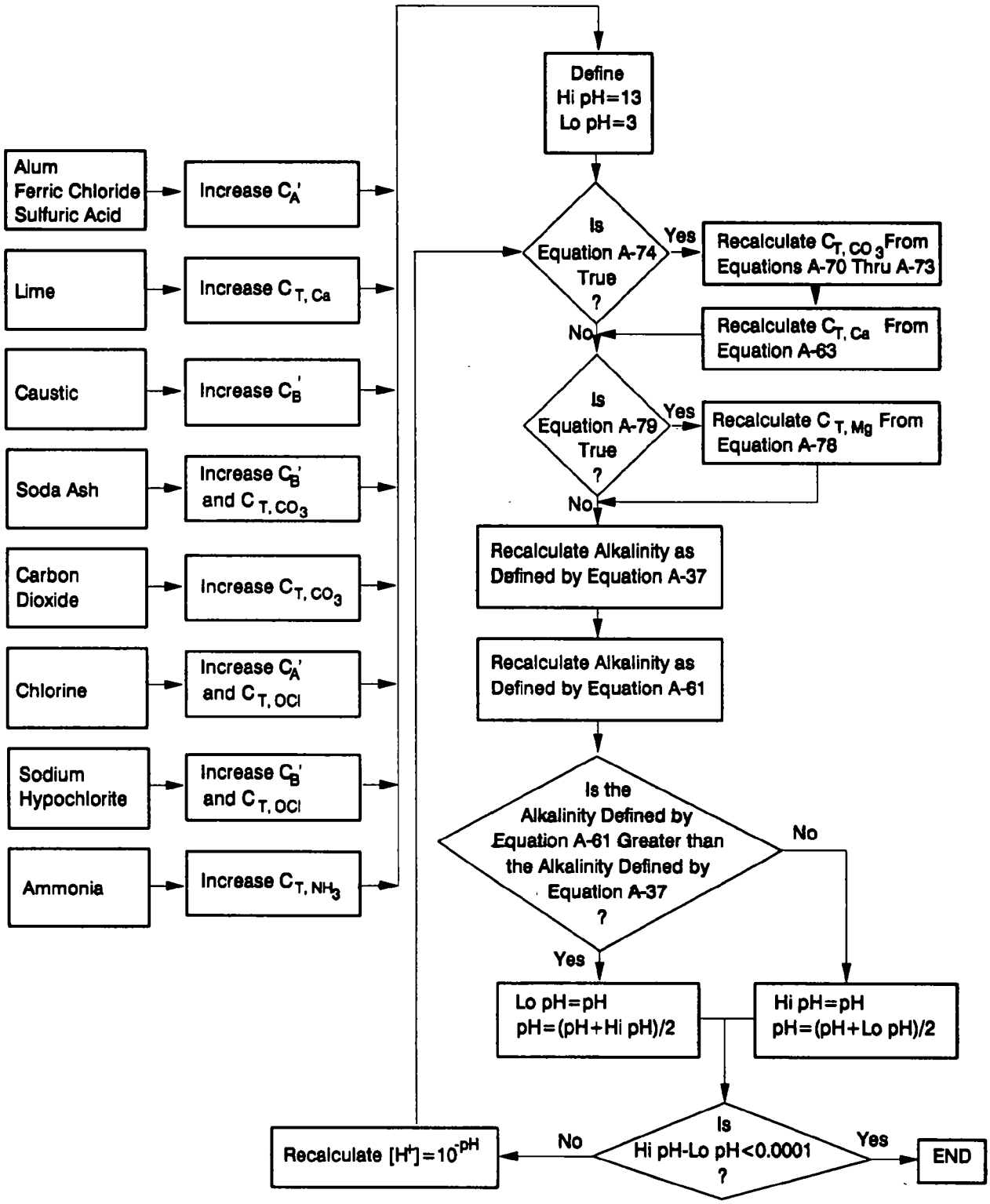
FIGURE A-7

ALGORITHM FOR CALCULATING PH CHANGES



figa-7

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 paper 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.

A.5.2 Alum Coagulation, Flocculation, Clarification and Filtration

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

$$Al_2(SO_4)_3 \bullet 14\,H_2O \rightarrow 2\,Al^{3+} + 3\,SO_4^{2-} + 14\,H_2O \qquad \text{A-80)}$$

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 A-61). 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°C). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.3 Ferric Coagulation, Flocculation, Clarification and Filtration

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

$$Fe_2(SO_4)_3 \bullet H_2O \rightarrow 2\,Fe^{3+} + 3\,SO_4^{2-} + H_2O \qquad \text{(A-81)}$$

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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 A-61). 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°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:

$$FeCl_3 \cdot 6\,H_2O \rightarrow Fe^{3+} + 3\,Cl^- + 6\,H_2O \qquad \text{(A-82)}$$

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 A-61). 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.

A.5.4 Precipitative Softening, Clarification and Filtration

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

$$Ca(OH)_{2\,(s)} \rightarrow Ca^{2+} + 2\,OH^- \qquad \text{(A-83)}$$

Therefore, when one mole of lime is added to one liter of water, $C_{T,Ca}$ increases by one mole per liter (see Equations A-74 and A-61). If the condition described by Equation A-74 is met

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(this is the objective in precipitative softening), C_{T,CO_3} is recalculated with Equations A-70 through A-73 and $C_{T,Ca}$ is recalculated with Equation A-63. If the condition described by Equation A-74 is not met, however, C_{T,CO_3} does not change and $C_{T,Ca}$ increases by one mole per liter (see Equation A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.5 Chlorine Addition

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

$$Cl_{2(g)} + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad \text{(A-84)}$$

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 A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.6 Sodium Hypochlorite Addition

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

$$NaOCl \rightarrow Na^+ + OCl^- \qquad \text{(A-85)}$$

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 A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

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A.5.7 Potassium Permanganate Addition

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

$$KMnO_4 \rightarrow K^+ + MnO_4^- \qquad \text{(A-86)}$$

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:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad \text{(A-87)}$$

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 A-86 and A-87 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 A-86 and A-87 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.

A.5.8 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:

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$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \quad \text{(A-88)}$$

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 A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.9 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:

$$NaOH \rightarrow Na^+ + OH^- \quad \text{(A-89)}$$

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 A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.10 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:

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+} + 2\,OH^- \quad \text{(A-90)}$$

Therefore, when one mole of lime is added to one liter of water, $C_{T,Ca}$ increases by one mole per liter (see Equations A-74 and A-61). If the condition described by Equation A-74 is met (this is not the objective when using lime for pH adjustment), C_{T,CO_3} is recalculated with Equations A-70 through A-73 and $C_{T,Ca}$ is recalculated with Equation A-63. If the condition described by Equation A-74 is not met, however, C_{T,CO_3} does not change and $C_{T,Ca}$ increases

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by one mole per liter (see Equation A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.11 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:

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \qquad \text{(A-91)}$$

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,CO_3} is increased by one mole per liter (see Equations A-74 and A-61). If the condition described by Equation A-74 is met, C_{T,CO_3} is recalculated with Equations A-70 through A-73 and $C_{T,Ca}$ is recalculated with Equation A-63. The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.12 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,CO_3} is increased by one mole per liter (see Equation A-37). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.13 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:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{(A-92)}$$

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Therefore, when one mole of ammonium hydroxide is added to one liter of water, C_{T,NH_3} increases by one mole per liter (see Equation A-61). The iterative procedure described above is used to obtain a new value for $[H^+]$ and, hence, pH.

A.5.14 Membrane Processes

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,CO_3} and $(C_B' - C_A')$ through a membrane process determine the alkalinity and pH of the permeate water. In an effort to predict pH changes through membrane processes, removals of hardness, alkalinity and C_T reported by Taylor, et al. (1987, 1989) were studied to determine their relationships with molecular weight cutoff (MWC), recovery and operating pressure.

The best relationship obtained for hardness removal was:

$$\ln\left[\left(\frac{TH_0}{TH_f}\right) - 1\right] = 13.1 - 0.0568(Recovery) - 0.261[\ln(MWC)][\ln(TH_0)] \quad \text{(A-93)}$$

$$[\text{adj } r^2 = 0.876,\ n = 25]$$

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 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 A-93.

The best relationship obtained for alkalinity removal was:

$$\ln\left[\left(\frac{ALK_0}{ALK_f}\right) - 1\right] = 7.50 - 0.421[\ln(MWC)][\ln(ALK_0)] + 0.00338[\ln(MWC)][\ln(ALK_0)](Pressure) - 0.000145(Pressure)(Recovery)[\ln(MWC)] \quad \text{(A-94)}$$

$$[\text{adj } r^2 = 0.893,\ n = 17]$$

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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 best relationship obtained for removal of total carbonates was:

$$\ln\left[\left(\frac{C_{T,CO_3,0}}{C_{T,CO_3,f}}\right) - 1\right] = 5.88 - 0.00451[\ln(MWC)](Pressure) - 0.0171[\ln(MWC)](Recovery) + 0.000082(Pressure)(Recovery)[\ln(MWC)] \quad \text{(A-95)}$$

$$[\text{adj } r^2 = 0.783,\ n = 15]$$

where $C_{T,CO_3,0}$ is the feed water total carbonate concentration in mg/L as calcium carbonate, $C_{T,CO_3,f}$ 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,CO_3} calculated by Equations A-94 and A-95 are used in combination with Equation A-37 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 A-37 to be equivalent to the alkalinity calculated by Equation A-94. Once the new value of $[H^+]$ is obtained, Equation A-61 is used in combination with the new values of $C_{T,Ca}$ and $C_{T,Mg}$ (calculated by Equation A-93) to calculate a new value for the quantity $(C_B' - C_A')$.

A.6 CHLORINE AND CHLORAMINE DECAY

A.6.1 Background

Rate equations for calculating the decay of chlorine and chloramines were developed by Dharmarajah, et al. (1991) through funding provided by the AWWA D/DBP TAW. The experimental design consisted of collecting raw water samples from 16 utilities nationwide and observing the decay of chlorine and chloramines under laboratory conditions. The

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equations which resulted from this effort are described in the following sections. The equations for chloramine decay were modified for use in the WTP program as described in Section A.6.3.

A.6.2 Chlorine Decay

Experimental observations suggested that the free chlorine residual decayed rapidly for the first 5 hours after the addition of chlorine. The decay rate decreased for the remainder of the experiment (120 hours). The decay during the first 5 hours was modeled as a second order reaction with respect to chlorine concentration while the decay after 5 hours was modeled as a first order reaction. The decay constants were correlated with raw water quality parameters by multiple, stepwise regression analyses similar to those described above. The following were the final equations for decay of free chlorine:

<u>For $(Cl_2)_0$:(TOC) ≥ 1.0 mg Cl_2/mg TOC</u>

<u>For 0 hours < t < 5 hours</u>

$$\frac{1}{(Cl_2)_t} = \frac{1}{(Cl_2)_1} + k_1 t \qquad \text{(A-96)}$$

where $(Cl_2)_1$ is calculated from:

$$\ln\left[(Cl_2)_0 - (Cl_2)_1 - 7.6(NH_3\text{-}N)\right] = -0.620 + 0.522\left\{\ln\left[\frac{(Cl_2)_0}{TOC}\right]\right\} + 0.302[\ln(UV\text{-}254)] + 0.842[\ln(TOC)] \qquad \text{(A-97)}$$

and $(Cl_2)_0$ is the applied chlorine dose.

<u>For 5 hours < t < 120 hours</u>

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$$\frac{(Cl_2)_t}{(Cl_2)_2} = \exp(-k_2 t) \tag{A-98}$$

where:

$$(Cl_2)_2 = \frac{1}{[\exp(-5k_2)]\left[\frac{1}{(Cl_2)_1} + (5k_1)\right]} \tag{A-99}$$

<u>For $(Cl_2)_0$:(TOC) < 1.0 mg Cl_2/mg TOC</u>

<u>For 0 hours < t < 120 hours</u>

$$\frac{(Cl_2)_t}{(Cl_2)_1} = \exp(-k_3 t) \tag{A-100}$$

Where $(Cl_2)_1$ is calculated by Equation A-97. The difference between the applied chlorine dose, $(Cl_2)_0$, and $(Cl_2)_1$ is considered the instantaneous chlorine demand.

The equations used to determine the chlorine decay rate constants, k_1, k_2 and k_3, are as follows:

$$\begin{aligned} \ln[(Cl_2)_0(k_1)] = & -2.44 - 1.57\left\{\ln\left[\frac{(Cl_2)_0}{TOC}\right]\right\} \\ & + 0.799[\ln(UV\text{-}254)] \\ & + 0.422(pH) \end{aligned} \tag{A-101}$$

$$\begin{aligned} \ln(k_3) = & -1.67 + 1.00[\ln(UV\text{-}254)] \\ & + 2.73[\ln(TOC)] \end{aligned} \tag{A-103}$$

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$$\ln(k_2) = -2.31 - 2.12\left\{\ln\left[\frac{(Cl_2)_0}{TOC}\right]\right\} + 1.27[\ln(UV\text{-}254)] - 0.842[\ln(TOC)] + 0.471(pH) \quad \text{(A-102)}$$

The boundary conditions for these experiments were:

- $(Cl_2)_0$:(TOC) = 0.5 to 4.0
- TOC = 2.0 to 13.9 mg/L
- UV-254 = 0.049 to 0.489 cm^{-1}
- pH = 6.4 to 8.4
- $(Cl_2)_0$ = 1.0 to 41.6 mg/L

Temperature was not varied in these experiments and bromide spiking was not performed (ambient bromide concentrations were not reported).

A.6.3 Chloramine Decay

Dharmarajah, et al. (1991), also developed rate equations to describe the decay of chloramine concentration. These equations, however, were found to predict chloramine formation under certain water quality conditions, particularly when a water with an alkalinity greater than 150 mg/L as calcium carbonate was chloraminated with a chlorine to ammonia ratio of 4:1. The prediction of chloramine formation occurred both within and outside the boundary conditions of the chloramine decay experiments. Because the prediction of chloramine formation is not desirable, USEPA funded Malcolm Pirnie to develop a new set of equations from the data collected by Dharmarajah, et al. (1991). The revised set of equations is as follows:

For $0 \leq t \leq 10$ hours

The decay over this time period was modeled as a generalized m^{th} order reaction with a rate constant k_1. The differential form of the equation is as follows:

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$$\frac{d[NH_2Cl]}{dt} = -k_1[NH_2Cl]^m \qquad \text{(A-104)}$$

The integrated form of the equation is as follows:

$$[NH_2Cl] = \left\{[NH_2Cl]_0^{1-m} + (m - 1)k_1 t\right\}^{\frac{1}{1-m}} \qquad \text{(A-105)}$$

Statistical analyses of the experimental data yielded the following correlations for the order and the rate constant:

$$m = 19.72[NH_2Cl]^{0.0977} \qquad \text{(A-106)}$$

[r = 0.23, r^2 = 0.05, adj r^2 = 0.03, F = 2.08]

$$k_1 = (1.86 \times 10^{-12})[NH_2Cl]^{-25.3}(TOC)^{1.08}(UV\text{-}254)^{3.83}[H^+]^{1.01} \qquad \text{(A-107)}$$

[r = 0.91, r^2 = 0.83, adj r^2 = 0.81, F = 44.9]

The low quality of fit for Equation A-106 indicates that the reaction order is not a strong function of initial chloramine concentration for the initial portion of the decay curve.

<u>For t > 10 hours</u>

The decay over this time period was modeled as a first order reaction with a rate constant k_2. The residual chloramine concentration, $[NH_2Cl]_{10}$, calculated by the above equations at ten hours is used as the initial concentration for this set of equations. The differential form of the equation is as follows:

$$\frac{d[NH_2Cl]}{d(t - 10)} = -k_2[NH_2Cl] \qquad \text{(A-108)}$$

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The integrated form of the equation is as follows:

$$[NH_2Cl] = [NH_2Cl]_{10}\exp\left[-k_2(t - 10)\right] \quad \textbf{(A-109)}$$

Statistical analyses of the experimental data yielded the following correlation for the rate constant:

$$k_2 = 0.424(TOC)^{-0.187}(UV\text{-}254)^{0.376}[H^+]^{0.227} \quad \textbf{(A-110)}$$

$$[r = 0.74,\ r^2 = 0.55,\ \text{adj } r^2 = 0.51,\ F = 16.9]$$

The boundary values for the chloramine decay experiments were:

- Cl_2:TOC = 0.5, 1.0 and 3.0
- Cl_2:NH_3 = 2.0 to 4.0 (42 of 54 tests were conducted at Cl_2:NH_3 = 4.0)
- TOC = 1.3 to 10.5 mg/L
- UV-254 = 0.039 to 0.401 cm^{-1}
- NTU = 0.22 to 31.6 NTU
- Alkalinity = 7 to 290 mg/L as $CaCO_3$
- pH = 6.5 to 8.6
- Cl_2 Dose = 0.7 to 31.5 mg/L

Temperature was not varied in these experiments and bromide spiking was not performed (ambient bromide concentrations were not reported).

A.6.4 Modeling Chlorine and Chloramine 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:

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$$C_f = C_i + tr \tag{A-111}$$

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 Nth CFSTR is given by the following set of equations:

$$C_{1f} = C_{1,i} + t_1 r_1 \tag{A-112}$$

$$C_{2,i} = C_{1f} \tag{A-113}$$

$$C_{2f} = C_{2,i} + t_2 r_2 \tag{A-114}$$

$$\vdots$$

$$C_{N,i} = C_{N-1f} \tag{A-115}$$

$$C_{Nf} = C_{N,i} + t_N r_N \tag{A-116}$$

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 A-112 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 A-113 is used to obtain $C_{2,i}$. Equation A-114 can then be used to calculate $C_{2,f}$ from known values of t_2 and r_2. The process is repeated through Equation A-116 until $C_{N,f}$ is calculated.

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In Equations A-112 through A-116, 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:

$$r_N = -kC_{Nf} \tag{A-117}$$

Integrated forms of this differential equation are shown above as Equations A-98, A-100 and A-109. For a second order decay process, r_N is given by the following expression:

$$r_N = -kC_{Nf}^2 \tag{A-118}$$

An integrated form of this differential equation is shown above as Equation A-98. For an mth order decay process, r_N is given by the following expression:

$$r_N = -kC_{Nf}^m \tag{A-119}$$

An integrated form of this differential equation is shown above as Equation A-105.

In order to use a set of equations such as those defined by Equations A-112 through A-116, 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:

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$$F = \frac{C_{Nf}}{C_{1,i}}$$
$$= 1 - \exp\left(\frac{-Nt}{t_m}\right)\left[1 + \frac{Nt}{t_m} + \frac{1}{2!}\left(\frac{Nt}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt}{t_m}\right)^{N-1}\right] \quad \text{(A-120)}$$

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:

$$0.1 = 1 - \exp\left(\frac{-Nt_{10}}{t_m}\right)\left[1 + \frac{Nt_{10}}{t_m} + \frac{1}{2!}\left(\frac{Nt_{10}}{t_m}\right)^2 + \cdots + \frac{1}{(N-1)!}\left(\frac{Nt_{10}}{t_m}\right)^{N-1}\right] \quad \text{(A-121)}$$

Using this equation, the theoretical value of t_{10}:t_m can be calculated for any value of N by using an iteration procedure. The results of such an analysis are presented in Figure A-8 and are compared with data obtained from actual treatment plant basins and filters (Teefy and Singer, 1990).

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:

$$t_{theo} = \frac{V}{Q} \quad \text{(A-122)}$$

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

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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 shown on Figure A-8. Therefore, the selected value of N is based on the t_{10}:t_m ranges listed in Table A-16.

Once the value of N is selected from Table A-16, Equations A-112 through A-116 are used in conjunction with the appropriate rate equations to calculate chlorine and chloramine decay in the basin or filter of interest.

A.7 DETERMINATION OF INACTIVATION RATIO

A.7.1 Background

The Surface Water Treatment Rule (SWTR) requires specific levels of disinfection for surface water and ground water sources. For surface water systems (or ground water systems under the direct influence of surface water), the minimum disinfection requirement is based on the removal and/or inactivation of Giardia. For ground water sources, the disinfection requirement is based on the removal and/or inactivation of viruses. The value of the inactivation ratio determines whether a system meet the inactivation requirements of the SWTR.

A.7.2 Calculating Inactivation Ratios

The inactivation ratio is defined as follows:

$$IR = IR_1 + IR_2 + IR_3 + \ldots\ldots \qquad \textbf{(A-123)}$$

where:

$$IR_i = \frac{CT\ value\ achieved\ through\ process_i}{CT\ value\ needed\ for\ inactivation\ requirement} \qquad \textbf{(A-124)}$$

The achieved CT value is calculated as follows:

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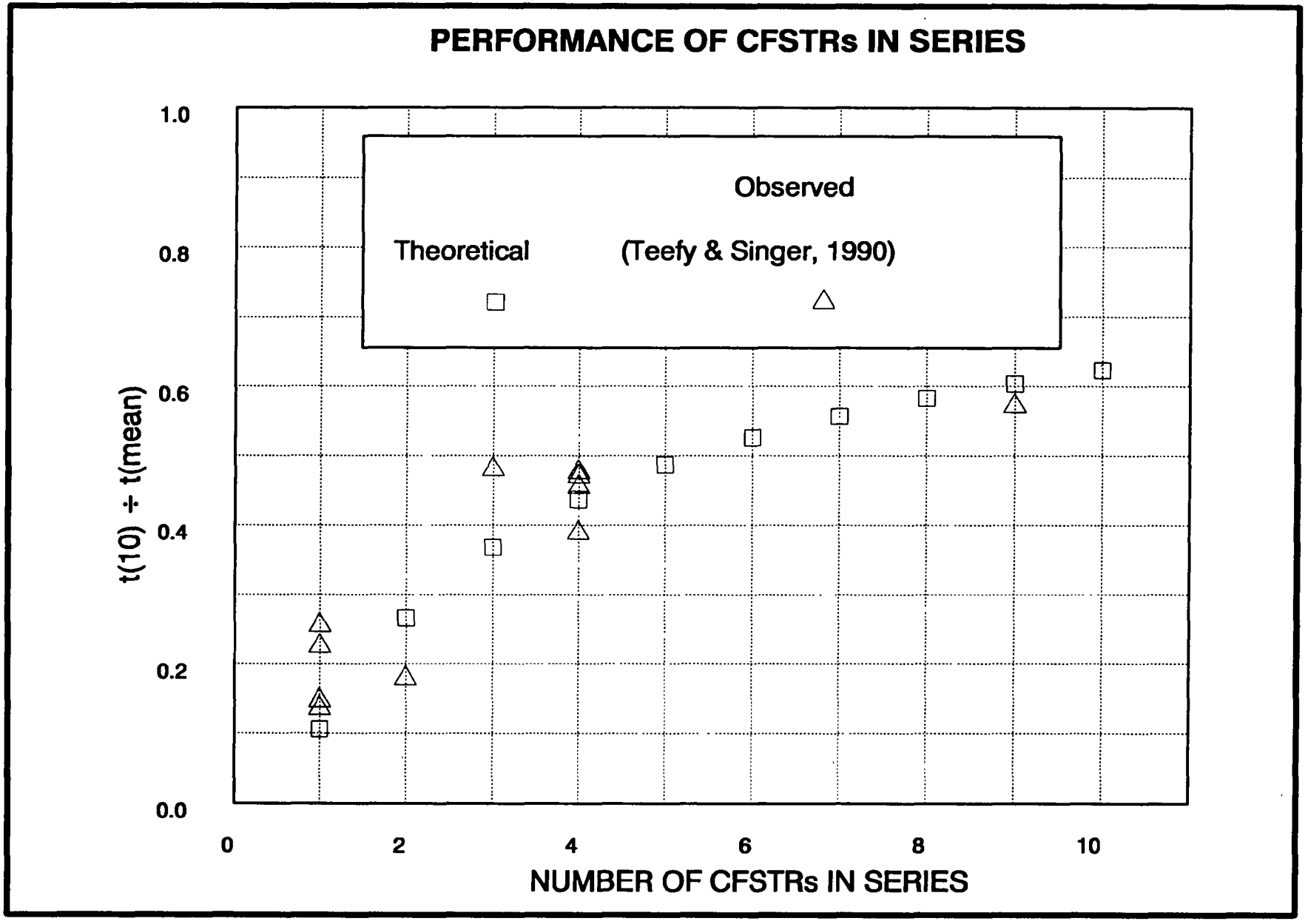
PERFORMANCE OF CFSTRs IN SERIES
Observed
Theoretical
(Teefy & Singer, 1990)
t(10) ÷ t(mean)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
NUMBER OF CFSTRs IN SERIES

FIGURE A-8

TABLE A-16

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

$$CT_{Achieved} = (Residual)(t_{theo})\left(\frac{t_{10}}{t_{theo}}\right) \qquad \text{(A-125)}$$

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). Tables A-17 to A-18 present the CT requirements for ground water systems using chlorine or chloramines, respectively, as the primary disinfectant. Table A-19 presents the CT requirements for surface water systems using chloramines as the primary disinfectant. For surface water systems using chlorine as the primary disinfectant, the required CT value can be estimated from the following equation (Clark and Regli, 1991):

$$CT_{req'd} = 0.36(Cl_2)^{0.15}(pH)^{2.69}(T)^{-0.15}\left[-\log_{10}\left(\frac{N}{N_0}\right)\right] \qquad \text{(A-126)}$$

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 A-126 calculates values of $CT_{req'd}$ that are within 10 percent of the values listed in the SWTR Guidance Manual.

Equation A-126 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).

The required log inactivation is given as follows:

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TABLE A-17

CT VALUES FOR INACTIVATION OF VIRUSES BY FREE CHLORINE

	Log Inactivation					
	2.0		3.0		4.0	
	pH		pH		pH	
Temperature (°C)	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-18

CT VALUES FOR INACTIVATION OF VIRUSES BY CHLORAMINE

	Temperature (°C)					
Inactivation	**<=1**	**5**	**10**	**15**	**20**	**25**
2-log	**1,243**	**857**	**643**	**428**	**321**	**214**
3-log	**2,063**	**1,423**	**1,067**	**712**	**534**	**356**
4-log	**2,883**	**1,988**	**1,491**	**994**	**746**	**497**

Note: CT values apply for systems using combined chlorine where chlorine is added prior to ammonia in the treatment sequence.

TABLE A-19

CT VALUES FOR INACTIVATION
OF GIARDIA CYSTS BY CHLORAMINE pH 6-9

	Temperature (°C)					
Inactivation	<=1	5	10	15	20	25
0.5-log	635	365	310	250	185	125
1-log	1,270	735	615	500	370	250
1.5-log	1,900	1,100	930	750	550	375
2-log	2,535	1,470	1,230	1,000	735	500
2.5-log	3,170	1,830	1,540	1,250	915	625
3-log	3,800	2,200	1,850	1,500	1,100	750

$$log\ inactivation = -\log_{10}\left(\frac{N}{N_0}\right) \quad \text{(A-127)}$$

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 as follows:

Daily Average Giardia Cyst Concentration/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
100-1,000[1]	6-log	7-log
1,000-10,000[1]	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.

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. Therefore, a surface water plant with a 3-log (99.9%) removal/inactivation requirement would only be required to achieve a 0.5-log inactivation.

It is anticipated that all ground water systems will be required to achieve a 4-log removal/inactivation of viruses. According to the SWTR, a 2.0-log removal credit is given

[1] Recent surveys (Le Chevallier, et al., 1991) of the occurrence of Giardia in surface water supplies indicate that Giardia concentrations in some supplies exceed the maximum range (10-100) specified by the USEPA in the SWTR. Therefore, linear extrapolation of the CT criteria were made to include 6- and 7- log removal/inactivations for higher raw water Giardia concentrations.

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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

The flowchart shown in Figure A-9 provides a detailed description of how the model calculates the inactivation ratio through a given treatment process (i.e., a basin or filter).

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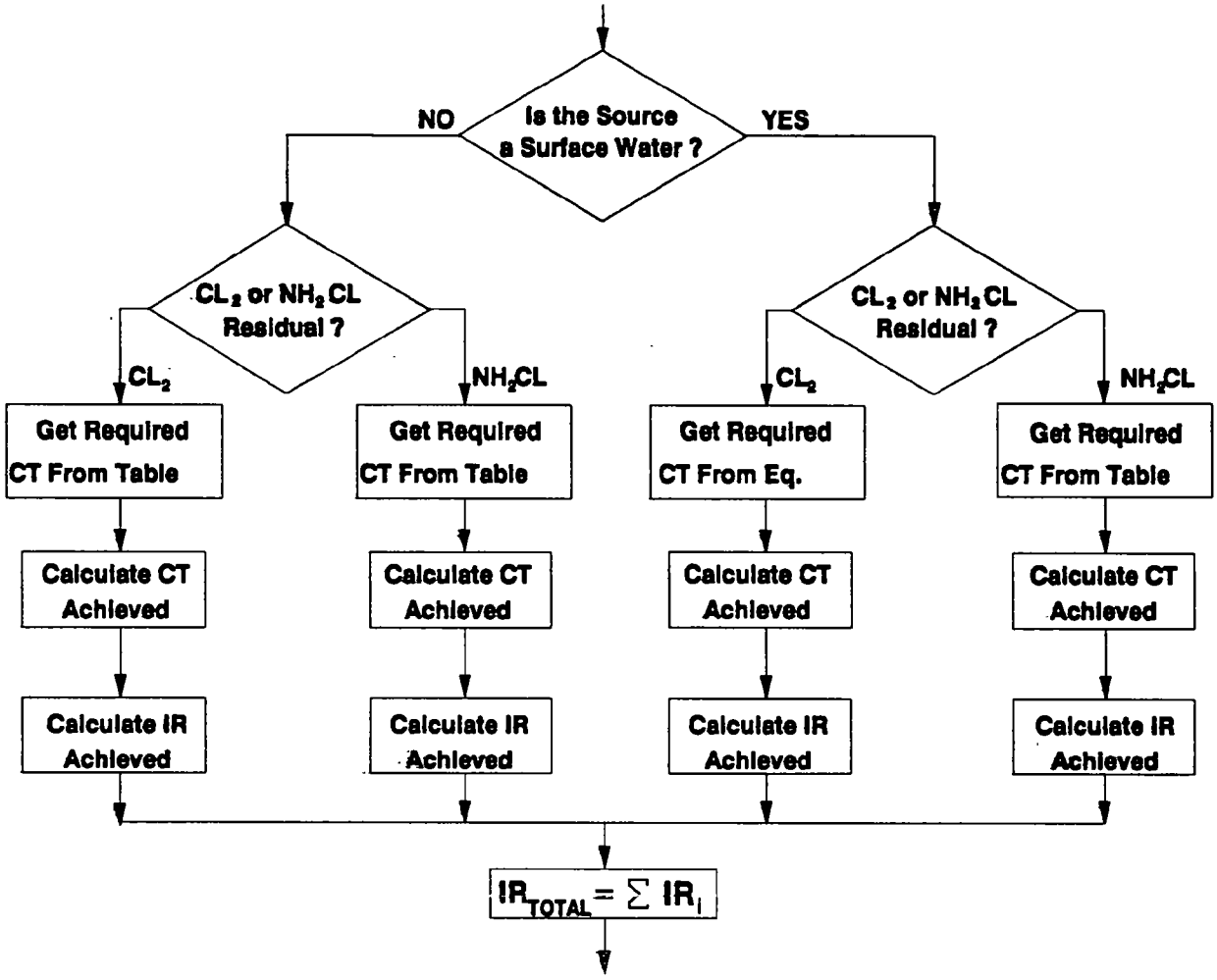
FIGURE A-9

ALGORITHM FOR CALCULATING INACTIVATION RATIOS



FIGA-9.DRW

APPENDIX B

RESULTS OF MODEL VERIFICATION EFFORTS

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B.1 INTRODUCTION

The model verification process presented in this Appendix is based upon an evaluation of SDWA impacts on the member agencies of the Metropolitan Water District of Southern California (Metropolitan). The overall project, completed in June 1990, included the following major elements:

- modifying the model by incorporating new equations for chlorine and chloramine decay, and individual THM species formation;
- performing a preliminary model verification using a 35 Utility Survey (Montgomery and Metropolitan, 1989);
- collecting data from member agency plants for 1)further model verification, and for 2)providing baseline conditions for sequential process modifications to meet projected scenarios resulting from the SDWA Amendments; and
- evaluating the process and economic impacts of the SDWA Amendments on the member agency plants.

This effort was funded solely by Metropolitan and, accordingly, the validation effort presented here includes only Metropolitan's member agency plants. *This member agency database is not likely representative of all drinking water supplies in the United States. Therefore, it is strongly recommended that the model be further verified with a database that is more representative of nationwide treatment plants.* Nonetheless, this work is the most complete verification to-date, and for that reason, is described here.

B.2 VERIFICATION OF MODEL PREDICTIONS

B.2.1 Introduction

Verification was performed in October 1990 to determine the relative accuracy of predictions not only for THM formation, but also for NOM surrogates (i.e. TOC, UV-254) that impact the prediction of THM formation. It is important to note that the modeling effort described here is based solely on the prediction of THMs, and does not include other DBPs (e.g. haloacetic acids) that may be regulated as a part of the D/DBP Rule.

In the subsequent discussion, verification is a term used when comparing predicted and measured results with fixed equations described in Appendix A. Calibration defines modifying the predictive equations using measured data. When modeling, it is inappropriate

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to verify results with measurements used to calibrate the model, because this results in an "internal" data set that biases the comparison of predicted and measured values.

Predicted and measured results were compared using two data sets:

- a nationwide survey of 35 utilities (Montgomery and Metropolitan, 1989); and
- a survey of member agencies of the Metropolitan Water District of Southern California (Malcolm Pirnie and Metropolitan, 1991).

The 35 Utility Survey was selected initially because these plants would have the most complete data available for comparing measured and predicted values. The THM model had not been compared at that time with an external database, and the 35 Utility Survey provided the opportunity to identify limitations in model calculations and predictions on a preliminary basis. Upon review of the preliminary verification results from the 35 utility data set, model limitations were identified, and in some instances, relationships were recalibrated with results from the 35 utility data set.

While the preliminary verification with the 35 utility data set was being performed, data were being collected from Metropolitan's member agency treatment plants. As both data and model limitations became evident through preliminary verification, the data collection from the member agency plants was focused on ensuring that critical values (e.g. unit process detention times) were collected. The model was then verified using the member agency data.

This section summarizes:

- preliminary verification results from the 35 utility database;
- identification of model limitations; and
- verification results from the member agency treatment plants.

B.3 PRELIMINARY VERIFICATION RESULTS FROM THE 35 UTILITY DATABASE

B.3.1 Database Compilation

The 35 Utility Survey was initially performed to determine the spatial and temporal distribution of DBPs in treated drinking waters throughout the U.S. Treated water samples were collected over four seasons (the first season, spring, did not include a complete database for modeling purposes) in calendar years 1988 and 1989 and were analyzed for a

host of physical and chemical parameters, of greatest interest being the DBPs other than THMs. THMs, haloaectonitrites (HANs), haloketones (HKs), chloropicrin, HAAs and cyanogen chloride were measured for all of the utilities, and some additional DBPs that are expected to occur based upon individual treatment processes employed also were measured (e.g. chlorite and chlorate for utilities using chlorine dioxide).

In a meeting among Malcolm Pirnie, Inc., Metropolitan staff, and James M. Montgomery Consulting Engineers, Inc. (JMM, consultant to the D/DBP TAW), it was determined that the 35 Utility Survey would be a reasonable external data set for initial verification efforts. As such, compilation of additional data necessary to run the model became a portion of the scope of work to be performed by JMM for the D/DBP TAW.

Malcolm Pirnie, Inc. provided JMM with the data input requirements for the model, so that JMM could determine the extent of data gaps in the survey and update the database as necessary. Over a three month period, JMM contacted the 35 utilities, updated the database as required, and transmitted those results to Malcolm Pirnie, Inc.. Upon completion, JMM and Malcolm Pirnie, Inc. reviewed the results and determined those utilities which had data sets that would be most applicable for verification based upon:

- the type of plant operation (i.e. continuous or batch treatment);
- the nature of the treatment processes and the ability to simulate those processes with the existing model (e.g. chlorine dioxide is currently not an available unit process in the model, and the database for lime softening had not been compiled at the time of model verification); and
- the degree of confidence in the information provided.

Of the original 35 utilities, 20 were selected for model verification. Table B-1 summarizes the coagulation type, primary disinfectant type and location, and residual disinfectant type for the utilities used in the preliminary verification step. The table is arranged in order by primary and secondary disinfectant. Plants using the same disinfectants are listed in order of no treatment, coagulation with polymers, alum coagulation, and ferric coagulation. Throughout the presentation of the preliminary verification results, the plants are ordered in this manner.

B.3.2 Model Assumptions

The raw water quality and operational data collected from the data compilation effort were used as the basis for developing the input files for the individual utility treatment

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TABLE B-1

LIST OF UTILITIES IN 35-PLANT SURVEY

Utility	Primary Disinfection		Residual	Coagulation/Softening			
No.	Type	Location	Disinfectant	Alum	Iron	Polymer	Lime (1)
1	Cl2	Post-Air	Cl2				
24	Cl2	Pre & Post	Cl2				
33	Cl2	Only trtmnt	Cl2				
34	Cl2	Only trtmnt	Cl2				
3	Cl2	Post	Cl2	X			
8	Cl2	Pre	Cl2	X			
15	Cl2	Pre & Post	Cl2	X			X
17	Cl2	Pre & Post	Cl2	X			X
22	Cl2	Post	Cl2	X			X
35	Cl2	Pre	Cl2				X
2	Cl2	Post	NH2Cl			X	
5	Cl2	Pre	NH2Cl	X			
6	Cl2	Pre & Post	NH2Cl	X			
7	Cl2	Pre	NH2Cl	X			
14	Cl2	Pre & Post	NH2Cl	X			
18	Cl2	Pre & Post	NH2Cl	X			
12	Cl2	Pre	NH2Cl	X			X
13	Cl2	Pre & Post	NH2Cl	X			X
4	NH2Cl	Pre	NH2Cl	X			
10	NH2Cl	Pre	NH2Cl	X			

Notes: 1. For some utilities lime is added for pH adjustment.

TABB-1 WK1

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plants. As a part of the data gathering effort, baffling characteristics for clearwells were requested. None of the utilities, however, had performed tracer tests to determine actual detention times in the unit processes. Therefore, it was assumed that t_{mean} : $t_{theoretical}$ for basins and filters were 0.7 and 0.9, respectively. These ratios were based upon studies performed to assess these ratios for specific baffling characteristics and basin configurations (Hudson, 1981; Malcolm Pirnie, Inc. 1990) and are required when verifying actual plant performance.

B.3.3 Preliminary Verification Results

The preliminary verification was performed for complete water quality data sets for summer, fall and winter seasons. Measured and predicted values were compared for :

- TOC;
- pH;
- chlorine residual; and
- TTHMs.

B.3.4 Comparison of TOC Predictions

Table B-2 summarizes predicted and measured TOC removals for the utilities evaluated. In general, the predicted and measured results compared well; predicted values were within 10 percent of the measured values 70 percent of the time (n=60). It was noted that the finished water TOC measured at Utility 33 in the summer and fall was up to 40 percent less than the raw water, although there is no coagulation at this Utility. The model did not predict any removal of TOC under these conditions.

The good comparison between the predicted and measured values, to some extent, could be expected. The 35 Utility Survey was a subset of the database used to prepare the predictive equations for TOC removal (see Section A.4.1 in Appendix A) and, therefore, the model was not verified with a completely external database in this preliminary step. Verification with external data is described in Section B.4.2 and elsewhere (Harrington, et al., 1991).

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TABLE B-2

COMPARISON OF MEASURED AND PREDICTED TOC; 35 UTILITY SURVEY

Utility No.	TOTAL ORGANIC CARBON CONCENTRATION (mg/L)								
	Summer 1988			Fall 1988			Winter 1988		
	Raw Water	Finished Water		Raw Water	Finished Water		Raw Water	Finished Water	
		Measured	Predicted		Measured	Predicted		Measured	Predicted
1	0.8	0.8	0.8	1.1	0.8	1.1	1.0	0.9	1.0
24	0.6	0.7	0.6	0.7	0.6	0.7	0.7	0.7	0.7
33	5.4	3.1	5.4	5.2	3.9	5.2	3.5	3.5	3.5
34	2.6	2.6	2.6	2.9	2.8	2.9	3.3	3.3	3.3
3	3.2	1.6	1.8	2.7	1.7	1.6	3.2	1.9	2.0
8	1.6	1.4	1.4	1.5	1.4	1.3	1.7	1.4	1.4
15	1.3	1.1	1.2	1.2	1.1	1.2	1.4	1.0	
17	3.0	2.0	1.9	2.8	2.0	1.9	3.2	1.9	2.0
22	5.5	3.8	3.8	4.4	3.6	3.0	4.0	3.4	2.6
35	3.1	3.1	3.1	3.0	3.1	3.0	3.5	3.4	3.5
2	2.4	2.3	2.2	2.9	2.2	2.8	2.5	2.0	2.3
5	5.4	3.8	4.4	5.3	4.2	4.2	5.5	4.4	4.0
6	4.5	3.7	3.2	3.9	3.1	2.8	4.9	2.9	2.9
7	2.8	2.6	2.6	2.8	2.7	2.5	2.7	2.6	2.7
14	2.6	1.9	1.8	2.9	2.7	2.2	3.9	2.4	2.5
18	1.8	1.4	1.4	2.7	2.4	2.5	1.9	1.7	1.7
12	2.6	1.7	2.1	2.2	1.7	1.5	2.8	1.8	1.9
13	1.1	0.8	0.8	1.5	1.1	1.1	1.5	1.0	1.1
4	2.8	2.5	2.6	2.7	2.4	2.5	2.7	2.4	2.5
10	4.6	3.8	3.5	4.9	3.7	3.9	5.3	4.2	4.0

Notes: 1. Blank cells indicate missing data.

TABB-2 WK1
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B.3.5 Comparison of pH Predictions

Table B-3 compares measured and predicted values for pH over the 3 seasons. The pH was not predicted reliably under the following circumstances:

- The raw water for Utility 3 has low alkalinity, and the model did not predict the measured finished water pH of between 4.6 and 4.8. The finished water sample was collected prior to pH adjustment before distribution at this utility while the model was used to predict pH after this adjustment;

- For utilities with no treatment other than free chlorination (Utilities 1, 24, 33, and 34), the extent of pH depression predicted by the model was dependent upon the alkalinity and the chlorine dose. The measured values did not always reflect this relationship. For example, the measured finished water pH for Utility 33 was 6.8 (raw water pH 8.2), while the predicted value from the model in this buffered water remained at 8.2. The example cited here indicates that the predicted values from the model more closely approximate expectations based upon water chemistry; and

- Finished water pH in plants that add lime (Utilities 12, 13, 15, 17, 22, and 35) were not predicted as well as in plants that do not add lime. This is a direct result of the preliminary nature of the lime softening unit process in the model, at the time of verification and that recarbonation is not included in the current model version. Also, the kinetics of CaO dissolution and CO_2 exchange are slow when lime is added. Therefore, the predicted values for pH were consistently lower than the measured values.

For the remaining utilities, the pH was generally predicted within 0.5 units. The above factors, however, indicated that it was important to document exactly where pH adjustment was performed in the plant, and that lime softening was a process that could not be evaluated accurately at the time of model verification.

B.3.6 Comparison of Measured and Predicted Chlorine Residual

Table B-4 summarizes the comparison of measured and predicted values for free and total chlorine residual from the 35 Utility Survey. This verification work was performed prior to the development of the chloramine decay equations shown in Section A.6. The verification effort identified the following:

- free chlorine decay (hence, residual) was predicted better than chloramine decay. In some instances, chloramine residual increased through the treatment system, as a result of water quality parameters that were outside of the boundary values used during the chloramine modeling effort (see Utility 7); and

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TABLE B-3

COMPARISON OF MEASURED AND PREDICTED pH; 35 UTILITY SURVEY

Utility No.	pH								
	Summer 1988			Fall 1988			Winter 1988		
	Raw Water	Finished Water		Raw Water	Finished Water		Raw Water	Finished Water	
		Measured	Predicted		Measured	Predicted		Measured	Predicted
1	7.4	7.4	7.3	7.2	7.5	7.2	8.3	7.7	7.1
24	7.1	7.6	6.8	7.2	8.2	6.9	7.2	7.5	6.8
33	8.2	6.8	8.2	7.3	6.9	6.6	7.4	7.0	6.7
34	7.3	7.1	7.2	6.7	6.7	6.7	7.1	NA	6.9
3	6.3	4.6	6.7	6.7	4.8	7.4	6.5	4.8	7.4
8	7.7	8.2	9.0	7.6	8.5	9.1	7.9	9.0	9.3
15	9.0	9.0	7.2	9.0	9.1	7.7		9.1	
17	7.0	8.7	4.7	6.5	8.7	5.8	6.9	9.1	5.3
22	7.7	8.7	6.9	7.8	8.5	7.0	7.5	8.3	6.8
35	7.0	8.0	6.9	7.2	8.5	7.1	7.3	8.6	7.1
2	8.6	7.5	7.3	8.6	7.6	7.3	8.4	7.6	7.4
5	8.2	8.1	8.3	8.1	8.2	8.3	6.9	8.1	6.9
6	7.6	8.1	7.8	7.2	7.0	7.5	7.2	6.9	7.3
7	8.2	8.2	8.6	8.3	8.0	8.7	8.4	8.2	8.4
14	7.8	7.2	6.8	7.8	7.2	7.2	7.8	7.1	6.8
18	7.9	7.2	7.3	8.4	7.9	7.1	7.4	7.8	7.3
12	8.2	8.4	7.5	8.1	8.6	8.1	8.0	8.5	8.6
13	7.2	8.6	7.4	7.1	7.1	7.5	7.6	8.9	7.8
4	8.4	8.5	7.9	7.8	8.5	8.3	8.0	8.4	8.5
10	7.9	7.3	7.4	8.3	7.2	7.2	8.1	NA	7.7

Notes: 1. Blank cells indicate missing values.

TABB-3.WK1
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TABLE B-4

COMPARISON OF MEASURED AND PREDICTED CHLORINE RESIDUAL; 35 UTILITY SURVEY

Utility No.	Summer 1988				Fall 1988				Winter 1988			
	Measured		Predicted		Measured		Predicted		Measured		Predicted	
	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total	Free	Total
1	1.0	1.1	0.8	0.8	0.8	0.9	0.9	0.9	1.2	1.3	1.2	1.2
24	0.6	0.7	1.9	1.9	0.8	0.8	1.3	1.3	0.6	0.7	1.7	1.7
33	3.4	3.6	3.7	3.7	2.7	3.1	2.1	2.1	2.5	2.8	2.4	2.4
34	0.7	0.9	1.3	1.3	0.6	0.7	1.0	1.0	0.7	0.7	0.2	0.2
3	0.7	1.7	2.2	2.2	0.6	1.3	1.2	1.2	0.6	1.1	1.2	1.2
8	0.8		1.3	1.3	0.8	0.9	1.1	1.1	0.7	0.9	1.2	1.2
15	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4		0.4		
17	1.0	1.0	4.1	4.1	1.0	1.0	1.0	1.0	1.1	1.1	1.3	1.3
22	0.6		2.2	2.2	0.4		0.8	0.8	0.3		1.1	1.1
35	1.1	1.2	1.3	1.3	1.2	1.3	0.9	0.9	1.1		1.0	1.0
2	0.0	1.9	0.0	2.3	0.0	2.0	0.0	1.6	0.0	2.2	0.0	1.8
5	0.2	2.5	0.0	3.7	0.5	2.5	0.0	3.6	1.2	2.5	0.0	3.6
6	1.5	3.0	0.5	0.5	0.9	1.3	0.0	18.1	0.6	1.0	0.0	3.2
7	0.0	1.5	0.0	19.5	0.0	1.5	0.0	24.8	0.0	1.5	0.0	19.8
14	0.1	1.4	0.2	0.2	0.2	1.8	0.0	3.6	0.2	1.6	0.0	3.8
18	0.0	1.1	0.0	1.0	0.0	1.3	0.0	1.2	0.1	1.3	0.0	1.0
12	0.1	1.1	0.0	0.6	0.1	0.7	0.0	0.2	0.2	0.9	0.0	0.0
13	0.5	0.5	1.2	1.2	0.3	0.4	1.2	1.2	0.3	0.3	1.4	1.4
4	0.0	1.5	0.0	2.0	0.0	1.5	0.0	2.0	0.0	1.6	0.0	2.7
10	0.1	3.3	0.0	6.2	0.1	3.3	0.0	6.5	0.1	4.5	0.0	6.5

Notes: 1. Blank cells indicate missing values.

TABB-4 WK1
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- upon review with JMM, it appeared that there may have been some confusion in the measured values reported for some utilities.

The THM formation equations are based upon chlorine dose, not residual. From a modeling standpoint, however, the prediction of chlorine and chloramine decay are important. A desired disinfectant residual in the distribution system is selected during alternative treatment evaluation, and the decay determines the dosage at the plant. This dosage impacts THM formation.

B.3.7 Comparison of Measured and Predicted THMs

Table B-5 summarizes the measured and predicted THM values for individual compounds, as well as the TTHMs, in the summer sampling effort. Because THM formation increases with temperature, the summer results are expected to exhibit the highest THM concentrations. Higher concentrations of THMs during summer are also expected to result in larger absolute differences between the measured and the predicted concentrations of THMs. The following are noted:

- in general, predicted values for TTHMs are lower than measured values. This may result from the difficulties that arise in predicting actual free chlorine contact times in treatment processes, which strongly influence the predicted THM formation. JMM indicated that accessing accurate information on flowrates at the time of the sampling was difficult, and this parameter, along with the actual:theoretical detention time ratios, strongly impact the prediction of THMs; and

- predictions for the brominated species become poorer when the bromide concentration in the raw water increases and the extent of bromine incorporation increases .

A review of the sensitivity of THM predictions to variations in the independent variables indicated that the estimated detention times have a significant effect on predicted THMs. Because the water quality data were collected over four quarters in 1988, JMM attempted to access accurate operational information for the dates when the samples were collected. In a meeting between Metropolitan and Malcolm Pirnie, Inc. it was decided that the preliminary verification had served its purpose and that it was not necessary for JMM to attempt to refine the operational input values. Model limitations and sensitivities had been determined, and a more accurate database incorporating water quality data and

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TABLE B-5

COMPARISON OF MEASURED AND PREDICTED THM; 35 UTILITY SURVEY: SUMMER 1988

Utility	THM (ug/L)									
	CHCl3		CHCl2Br		CHClBr2		CHBr3		Total	
No.	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.
1	0.9	2.2	2.0	3.4	3.1	1.7	1.9	0.8	7.9	8.1
24	0.4		0.5		4.2		34.8		39.9	0.0
33	41.8	15.4	2.2	0.8	0.0	0.0	0.0	0.0	44.0	16.2
34	36.0	25.0	9.0	2.1	1.2	0.0	0.1	0.0	46.3	27.1
3	4.1	7.7	1.7	1.5	0.3	0.1	0.0	0.0	6.1	9.3
8	18.1	6.5	7.0	3.3	2.0	0.5	0.1	0.1	27.2	10.4
15	25.0	1.9	1.9	0.6	0.1	0.0	0.0	0.0	27.0	2.5
17	85.0	15.3	5.0	1.9	0.2	0.0	0.0	0.0	90.2	17.2
20	64.2	16.2	10.7	3.4	1.1	0.1	0.0	0.0	76.0	19.7
22	56.1	29.2	4.2	2.5	0.2	0.0	0.1	0.0	60.6	31.7
35	34.7	15.6	2.9	0.9	0.1	0.0	0.0	0.0	37.7	16.5
2	66.7	81.0	18.1	29.8	4.5	7.2	0.3	2.5	89.6	120.5
5	15.4	17.5	15.0	8.5	10.2	3.2	1.5	0.1	42.1	29.3
6	70.3	48.3	22.0	15.0	5.2	2.3	0.2	0.2	97.7	65.8
7	12.0	15.2	20.5	16.3	24.3	13.4	6.2	1.2	63.0	46.1
14	13.2	10.3	36.7	31.3	48.8	75.1	15.7	12.0	114.4	128.7
18	5.1	0.9	1.6	0.3	0.2	0.0	0.7	0.0	7.6	1.2
12	4.7		12.6		28.3		25.8		71.4	0.0
13	20.1	2.0	3.1	0.9	0.3	0.1	0.0	0.0	23.5	3.0
4	2.7	5.7	3.5	8.9	2.4	14.8	0.5	1.5	9.1	30.9
10	1.0		3.8		8.6		29.8		43.2	0.0

Notes: 1. Blank cells indicate missing values.

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operational practices needed to be developed for verification. The ongoing member agency data collection effort provided potential for this database.

The following subsections describe first a summary of model limitations, and then verification with the member agency database.

B.4 VERIFICATION RESULTS FROM THE MEMBER AGENCY DATABASE

B.4.1 Database Compilation

After the model limitations were understood and addressed to the extent permitted by the scope of work, the improved model was tested against the member agency database. The experience gathered from the preliminary verification with the 35 Utility Survey and a better understanding of the model data needs at the time of member agency data collection helped create a more complete database. This effort included visits to some of the member agency plants to gather supplemental samples. For these reasons, it was hoped that the database enhancement, along with the improved model from the preliminary verification with the 35 Utility Survey, would improve the overall model prediction. A complete set of input parameters were available for 19 of the member agency plants.

As described previously, the contact time with free chlorine has a strong impact on THM prediction. Malcolm Pirnie, Inc. had performed tracer studies at two of the member agency plants as part of another study (Malcolm Pirnie, Inc. 1990). Because many of the member agencies had similar basin designs, these previous studies were useful in the overall evaluation.

B.4.2 Verification Results

Comparisons were made for the following parameters:

- TOC concentration;
- UV absorbance; and
- TTHM concentrations.

Comparison of Measured and Predicted TOC

Figure B-1 illustrates measured and predicted values for TOC in treated water from the 19 member agency plants evaluated, for both alum and ferric chloride coagulation. There are two relationships presented on this figure:

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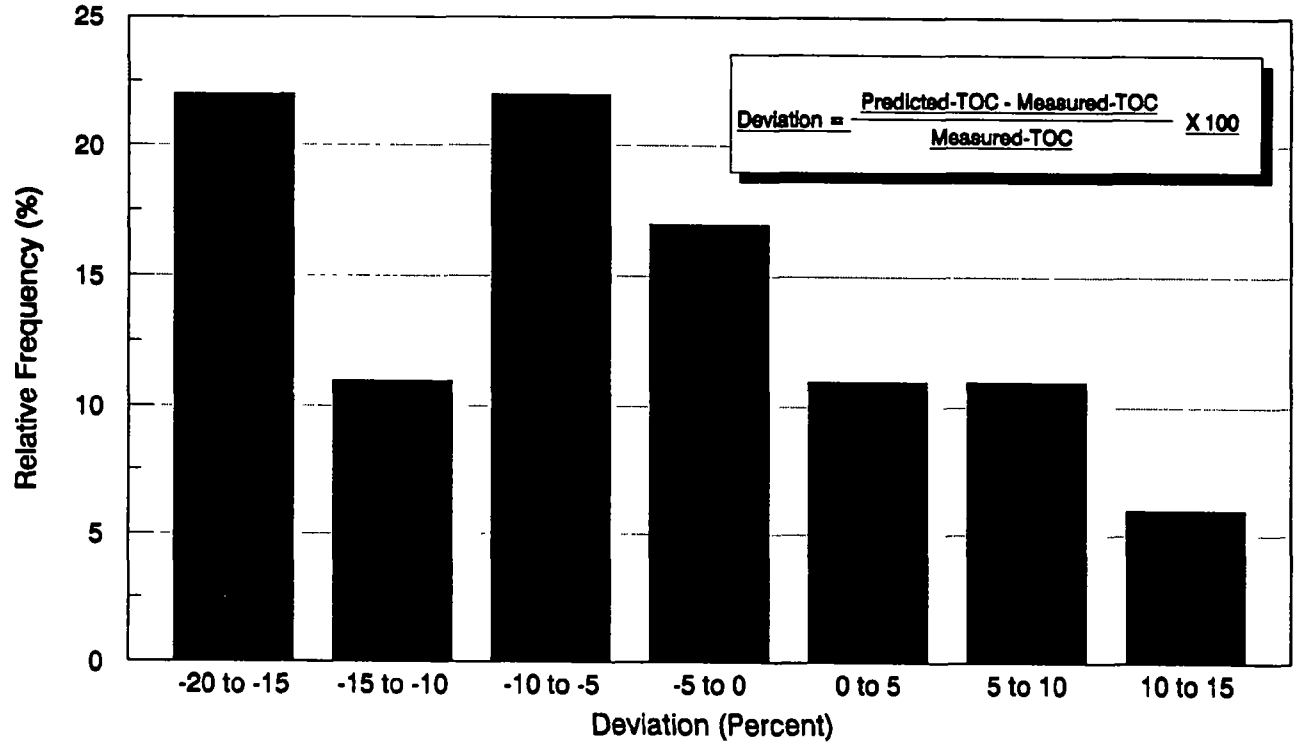
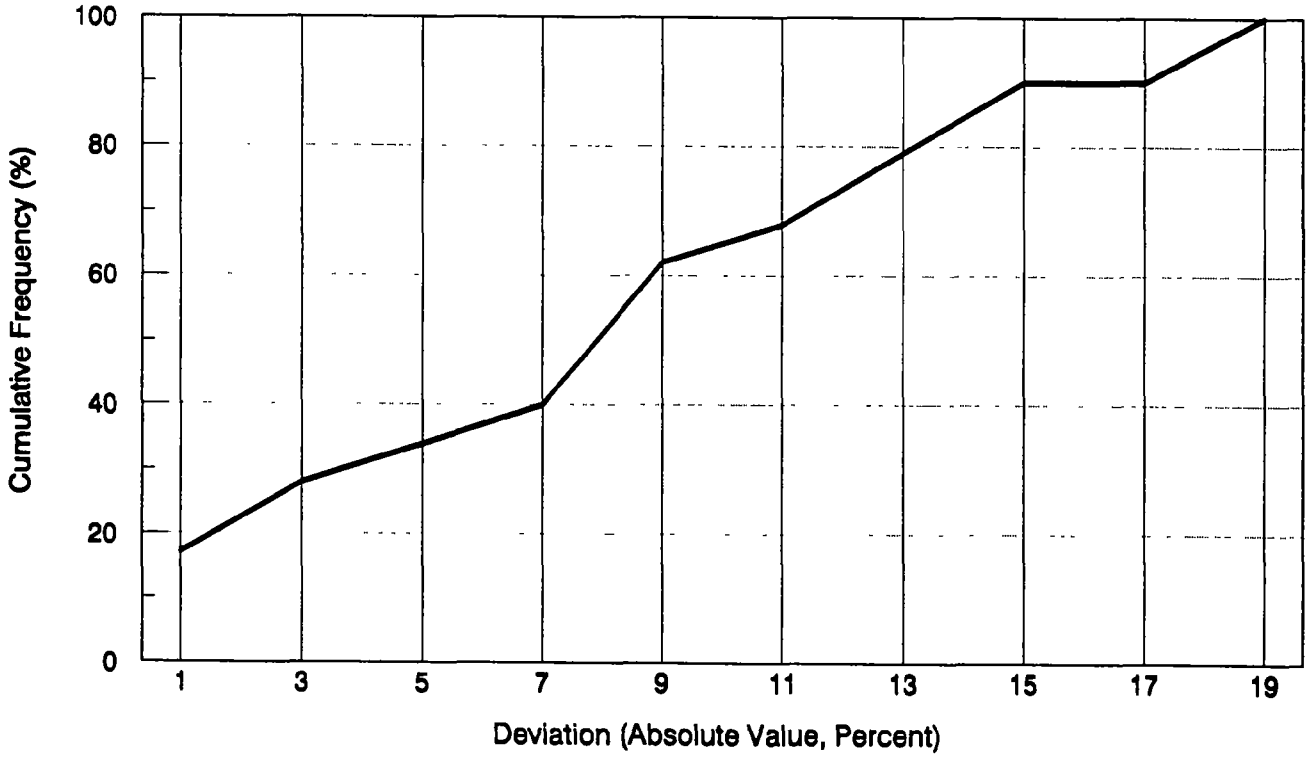
FIGURE B-1

Statistical Comparison of Measured and Predicted TOC Values
Metropolitan Member Agency Plants





- a cumulative frequency showing the absolute value of the percent deviation between measured and predicted values; and

- a histogram illustrating the relative frequency of percent deviation between measured and predicted values. In this relationship, negative values indicate that the model predicted lower TOC values than were measured (overpredicted removals), and positive values indicate that the predicted TOC concentrations were higher than measured (underpredicted removals).

These results indicate that approximately 65 percent of the predictions were within 10 percent of the measured values. All of the predictions were within 19 percent of the measured values. For the member agency plants evaluated, the model appears to overpredict TOC removal (70 percent showed higher removal and 30 percent showed lower removal than observed). The central tendency was to underpredict finished water TOC by 5 to 10 percent.

From a standpoint of predicting THM formation, overpredicting TOC removal will translate to lower predicted TTHMs. Considering the variation in treatment processes, the use of two different coagulants employing separate equations for predicting removal, and the analytical error associated with sample analyses, the predicted values compare well with measured values.

Comparison of Measured and Predicted UV Absorbance

Figure B-2 illustrates the comparison for measured and predicted UV-absorbance at 254 nm. In this relationship, UV-254 data were available for only 19 of the 32 member agency plants. This comparison indicates:

- approximately 50 percent of the predicted values deviate less than 20 percent from the measured values;

- the model tends to predict higher UV-254 values (i.e. underpredicts removals), as evidenced by the relative frequency of positive percent deviation in the histogram (56 percent showed lower removal and 44 percent showed higher removal than measured); and

- the central tendency of the model was to overpredict finished water UV-254 by 10 percent.

The spread of the deviation between predicted and measured values is greater than for the TOC prediction, in this instance towards underprediction of UV-254 reduction. One

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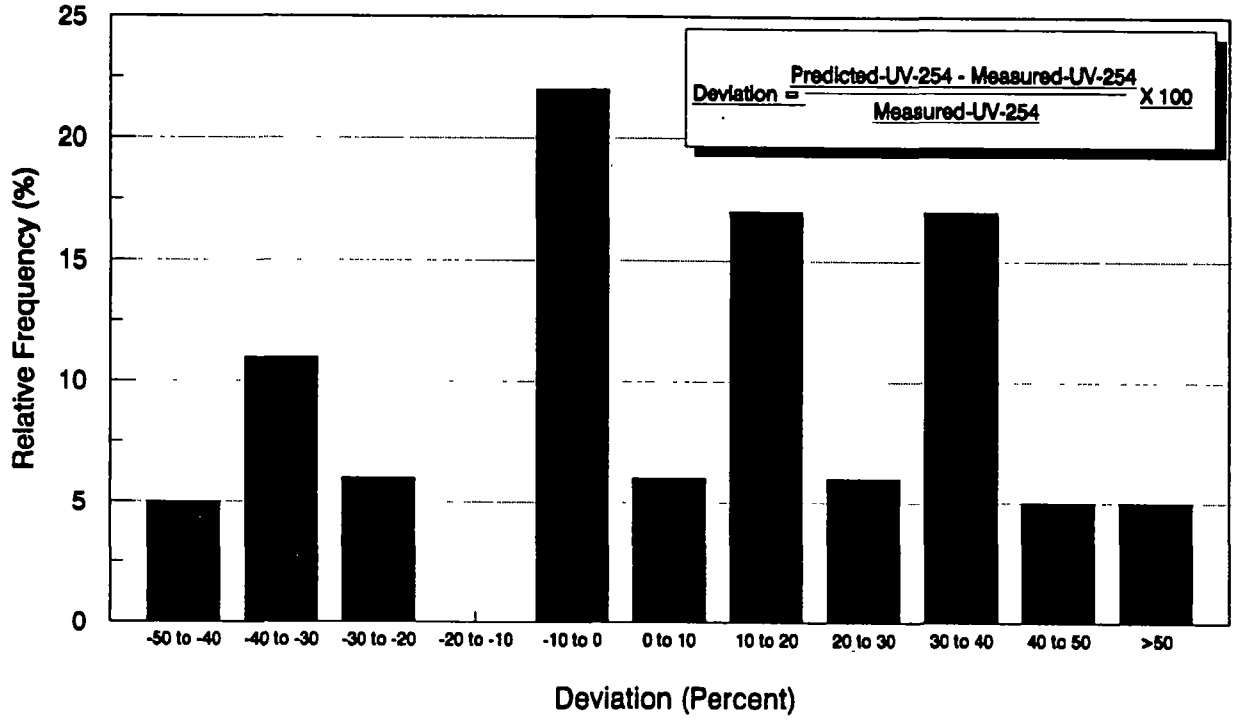
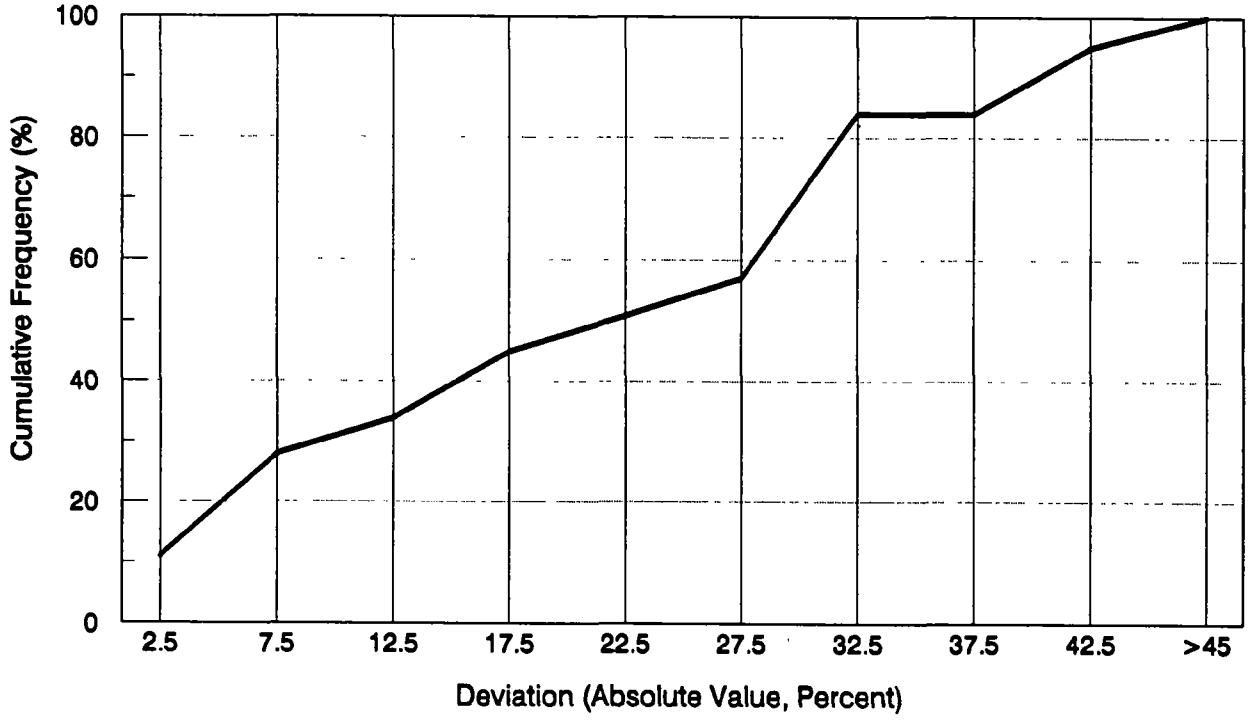
Statistical Comparison of Measured and Predicted UV-254 Values
Metropolitan Member Agency Plants





factor that might contribute to the larger spread in UV-254 predictions is that chlorination is known to impact UV-254 values without any change in TOC concentration.

The underprediction of reduction in UV-254 corresponds to a relatively higher prediction for TTHMs. This offsets the trend discussed previously for overprediction of TOC removal.

Comparison of Measured and Predicted Values for TTHM

Measured and predicted values of TTHM were compared for the following cases:

- simulated distribution system for 19 member agency data set; and
- a modified data set of SDS-THM for plants treating raw waters with < 0.30 mg/L bromide (17 of the 19 plants).

Figure B-3 illustrates a comparison of measured and predicted simulated distribution system (SDS) values for TTHM. The relationship indicates that:

- 50 percent of the predicted values deviate 20 percent or less from the measured values;
- 80 percent of the predicted values deviate 40 percent or less from the measured values;
- the remaining 20 percent of the values deviate between 40 and 85 percent of the measured values; and
- there is a general trend to underpredict TTHM formation. This underprediction could not be traced to any one dependent variable, such as consistently predicting lower pH values than measured (thereby underpredicting TTHMs).
- the central tendency was to underpredict TTHMs by 20 to 30 percent.

Considering the compounding errors in predicting dependent variables such as TOC and pH, in this level of accuracy may be expected. From the verification work performed previously, however, the member agency data set was reviewed to determine how the prediction might be improved. Figure B-4 illustrates a comparison of the cumulative frequency of deviation in predicted and measured values for two data subsets:

- all SDS observations for TTHM; and

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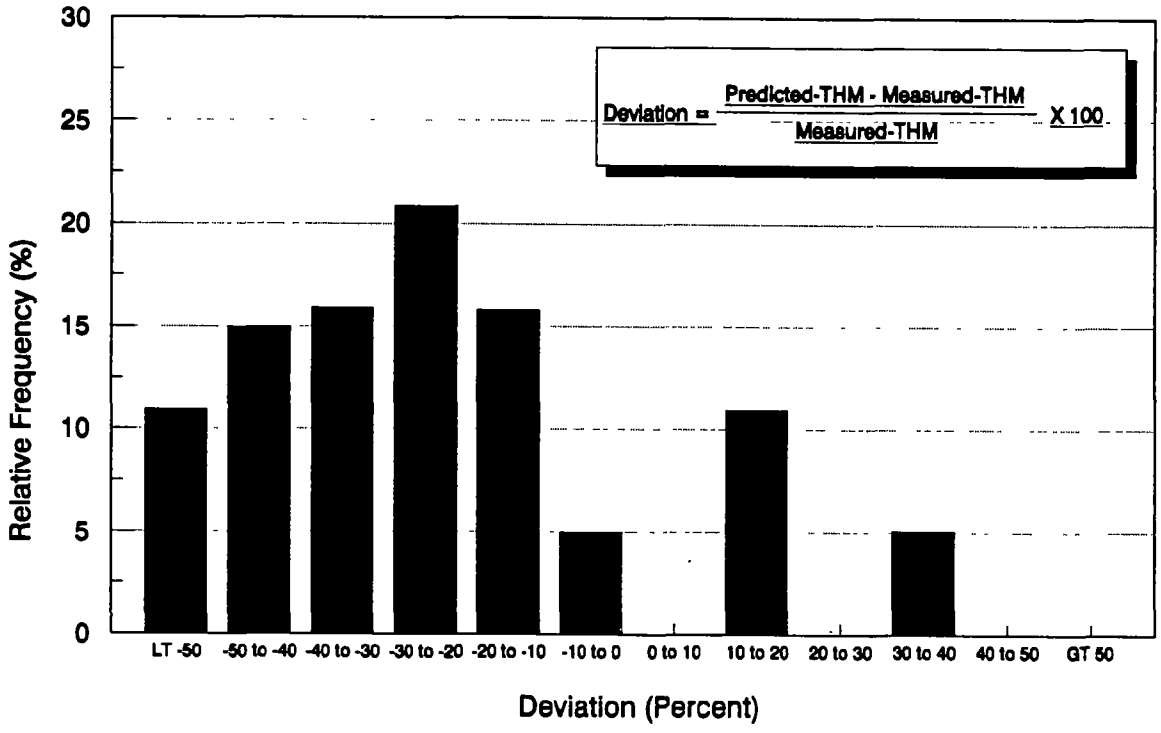
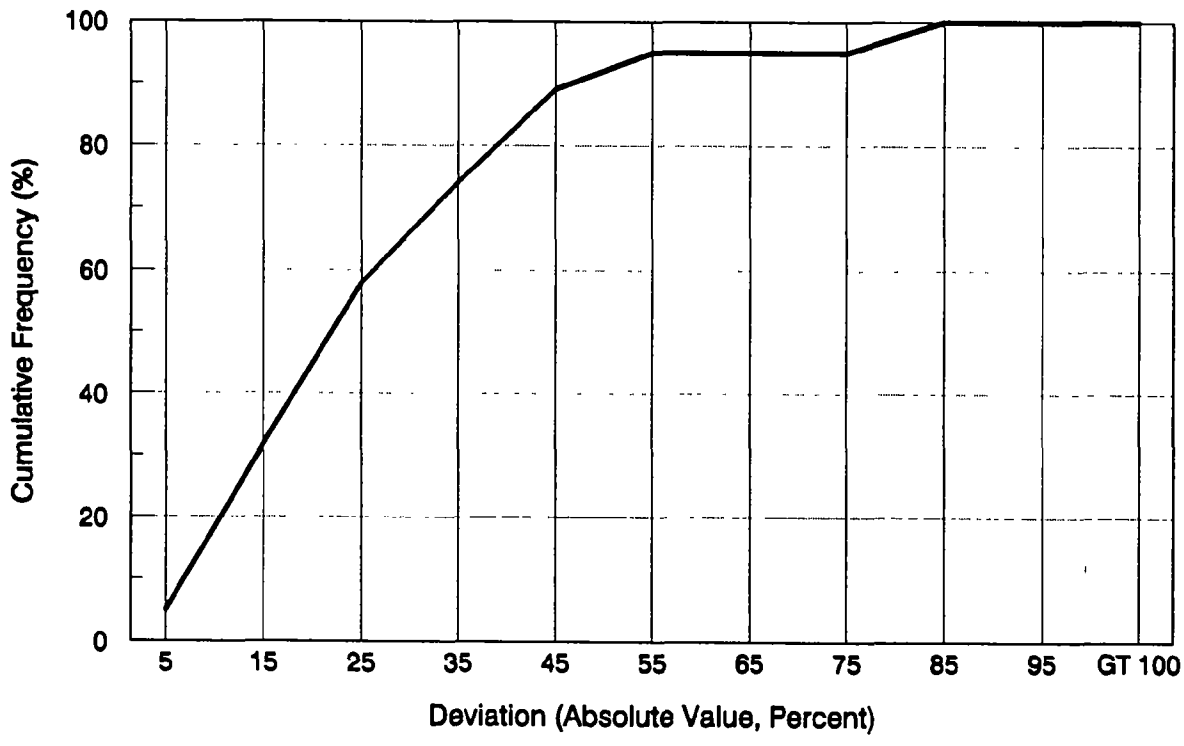
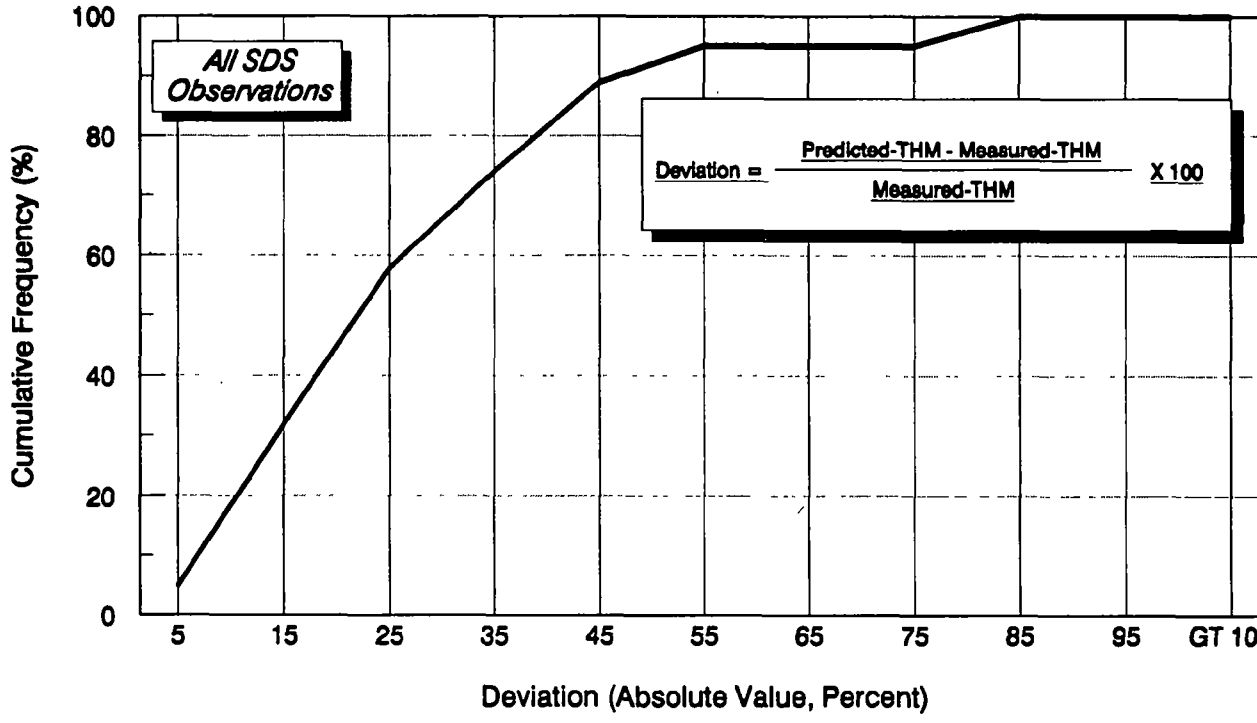
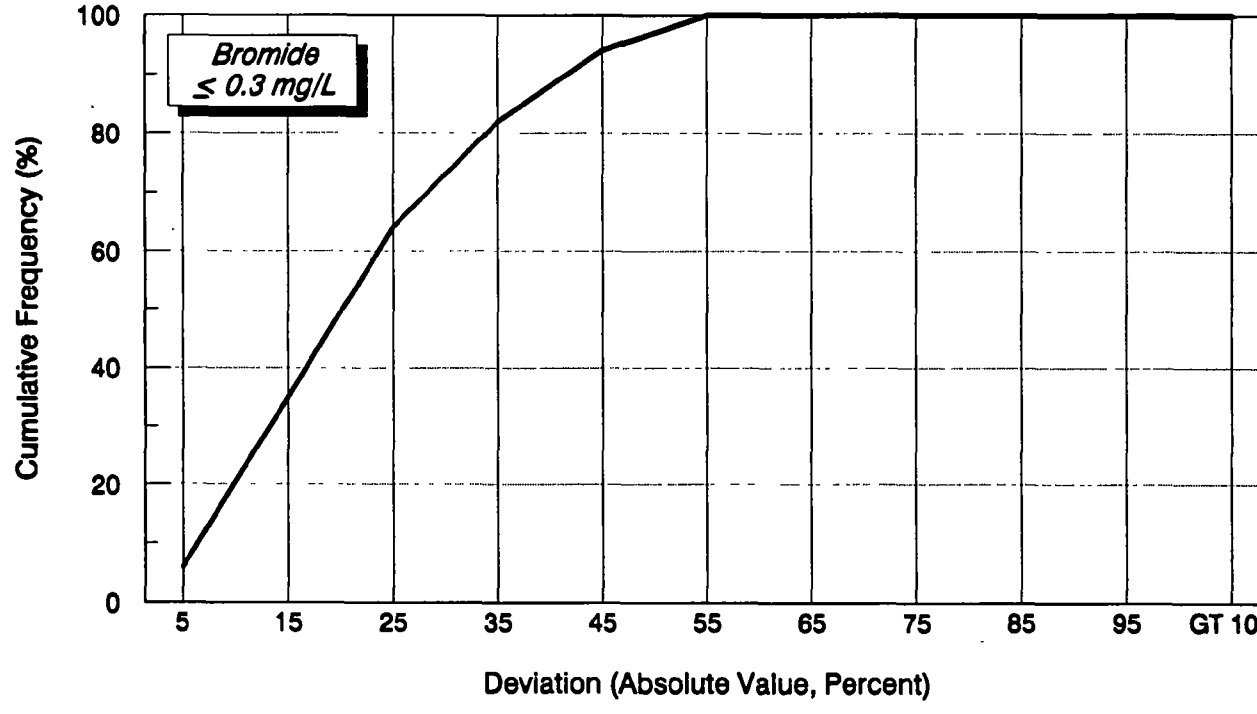
Statistical Comparison of Measured and Predicted SDS-THM Metropolitan Member Agency Plants





Evaluation of SDS-THM Predictions
Effect of Bromide on Prediction





- SDS-TTHM for the member agency plants treating raw water with bromide concentrations < 0.30 mg/L.

The results from this comparison illustrate improvement in prediction. For the data set with bromide concentrations < 0.30 mg/L bromide:

- approximately 50 percent of the predicted values deviate less than 20 percent from the measured values;
- 80 percent of the predicted values deviate less than 35 percent of the measured values; and
- all of the values deviate less than approximately 50 percent of the measurements, compared to 85 percent of the predictions within 50 percent when all data were included.

This indicates that the bromide containing waters (Br^- > 0.30mg/L) were responsible for the most significant deviation in TTHM prediction.

B.4.3 Summary of Observations

The degree of prediction outlined above represents the best that can be performed with the model at this time. Model predictions for SDS-THM were expected to improve when using the Metropolitan member agency database as compared to the 35 Utility Survey, because of greater confidence in the actual disinfectant contact times for the member agency plants. However, the member agency database is a small subset of utility water qualities throughout the country, and does not necessarily represent the central tendency for all waters in the United States.

At this time, the major limitation is in the prediction of brominated THM formation for high bromide waters. This can be attributed to an understanding that the THM formation equations are based upon a database (Amy et al, 1987) that contains:

- limited values for higher bromide waters. Bromide spiking was performed, but the impact of higher bromide on increased formation of brominated species cannot be predicted with certainty; and
- THM measurements performed at a Cl_2:TOC ratio of 3 to 1. Recent studies (Krasner, 1991; Symons, 1991) indicate that at lower Cl_2:TOC ratios (e.g. 1 to 1.5), which are more typical of plant operation and provide a chlorine residual of 0.5 to 1.0 mg/L after a specified holding time (24 to 72 hours), bromine incorporation increases.

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Together, these factors indicate that the model may underpredict SDS-THM measurements for member agency plants with bromide concentrations exceeding 0.3 mg/L and Cl_2:TOC dosages between 1.0 and 1.5.

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APPENDIX C

SAMPLE SURVEY QUESTIONNAIRE

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TABLE C-1

SAMPLE SURVEY QUESTIONNAIRE

Utility Name: _____

Utility Address: _____

Contact person: _____

Phone #: _____

FAX #: _____

Water Treatment Plant name and address:

_____

Source of raw water:

	Yes/No	% of Total Supply
Groundwater	_____	_____
Lake/Reservoir	_____	_____
Purchased (from other utility):	_____	_____
	Total =	100 %

Design hydraulic capacity: _____

Average Flow: _____

Range of flow rates: _____

Peak Hourly Flow: _____

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TABLE C-1 (continued)

Schematic of the Plant Processes Including the Locations of Chemical Addition

Please attach a schematic drawing of your plant.

Unit Process Basins

	Dimensions (feet)			Baffling Characteristics (yes/no)		
Unit Process	Length	Width or Diameter	Depth	Inlet	Outlet	Intermediate
Rapid Mix						
Flocculation						
Sedimentation						
Filtration						
Clear Well						
On-Site Storage						

Please note any other basins or large pipelines/conduits in the treatment process train or any other dimensions which will affect water detention time:

_____

_____

_____

_____

Have any tracer studies conducted to determine the actual detention times? If yes, please attach or explain results.

_____

_____

_____

_____

_____

Please state any nonconventional treatment process operations, such as operating the plant in a batch or semi-batch mode, non-continuous operations, etc..

_____

_____

_____

_____

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TABLE C-1 (continued)

Chemical Addition

	Chemical	Annual Average Dose (ppm)	Range of Dosages (ppm)		
			Minimum	Average	Maximum
Pretreatment					
Rapid mix					
Flocculation					
Sedimentation					
Filtration					
Disinfection					
Softening					
Recarbonation					
Other					

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TABLE C-1 (continued)

Advanced Unit Treatment Processes

Does the treatment plant use:	Yes/No	If yes:
Granular activated carbon?		Empty bed contact time = Regeneration frequency =
Aeration or Air Stripping?		Air-to-water ratio = Diffused, mechanical, or packed tower?
Ion Exchange?		Media type is: Contact time = Regeneration frequency =
Membranes?		Membrane type = Moleculer weight cutoff = Recovery =

Water Quality

	Raw Water		Finished Water	
	Annual Average	Range	Annual Average	Range
pH				
Alkalinity (mg/L as CaCO3)				
Turbidity (NTU)				
Color (Standard Color Units)				
Total Organic Carbon (mg/L, ppm)				
Temperature (C)				
UV-Absorbance (1/cm)				
Bromide (mg/L or ppm)				
Chloride (mg/L or ppm)				
Calcium Hardness (mg/L as CaCO3)				
Total Hardness (mg/L as CaCO3)				
Ammonia (mg/L)				

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TABLE C-1 (continued)

Disinfection and Disinfection By-Products

Disinfectant Residual in the Treatment Plant

	After Rapid Mix	After Settling	After Filters	Filtered Water
Free Chlorine (ppm)				
Total Chlorine (ppm) (Chloramines)				
Chlorine Dioxide (ppm)				
Ozone (ppm)				

Disinfectant Residual in the Distribution System

	Finished Water		Distribution System	
	Annual Average	Range	Annual Average	Range
Free Chlorine (ppm)				
Combined Chlorine (ppm)				
Chlorine Dioxide (ppm)				
Trihalomethanes				
Total (ppb)				
Chloroform (ppb)				
Dichlorobromomethane (ppb)				
Dibromochloromethane (ppb)				
Bromoform (ppb)				
Haloacetic Acids				
Total (ppb)				
Monochloroacetic Acid (ppb)				
Dichloroacetic Acid (ppb)				
Trichloroacetic Acid (ppb)				
Monobromoacetic Acid (ppb)				
Dibromoacetic Acid (ppb)				
Other DBPs (if any measured)				
Estimated Detention Time in the Distribution System (days)				

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