# Dissertation

## Development, Testing and Application of a Real-time Sensing Network for Monitoring Chemical Contamination Events in a Drinking Water Distribution System

Submitted by

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY SEONGHO CHO ENTITLED DEVELOPMENT, TESTING, AND APPLICATION OF A REAL-TIME DISTRIBUTED SENSING NETWORK FOR MONITORING INTENTIONAL AND UN-INTENTIONAL CONTAMINATION EVENTS IN A DRINKING WATER DISTRIBUTION SYSTEM BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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# ABSTRACT OF DISSERTATION


**Development, Testing and Application of a Real-time Sensing Network for Monitoring Chemical Contamination Events in a Drinking Water Distribution System**

Routine on-line monitoring which detects the change of water quality by both chemicals and biofilm of drinking water distribution systems offers potential in eliminating the danger of purposeful contamination events.

One of the objectives of this research was to evaluate online UV254 as a surrogate for TOC analysis to detect contaminants in the distribution system. UV254 has a lower cost than on-line TOC analysis or grab sampling techniques. Seven contaminants were monitored by measuring common water quality parameters such as conductivity, pH, chlorine residual, turbidity, TOC, and UV254. Results indicate that the seven chemical contaminants can be detected at relatively low concentrations with routine on-line monitoring. Some (aldicarb, sodium fluoroacetate, sodium cyanide) of the seven chemical contaminants can be detected below a concentration that will cause significant health impacts.

Because of the insensitivity of the turbidimeter, the indigenous biofilm in the presence of toxic chemicals may provide an effective, indirect surrogate response with either turbidity or UV254. The hypothesis is that, if toxic chemicals are added to the distribution system, the biofilm would die and slough off to an extent that would change the UV254 absorbance and light scattering of the water so that relatively inexpensive monitors could detect the event. This hypothesis was proven to be correct and turbidity was found to be an excellent indirect monitor for intentional contamination events.

The real-time data collected by the cost effective MSU (Micro Sensor Unit) network can be used to predict the behavior and spread of substances throughout the water system. $H_2O$ Map software that can model the hydraulic and chemical characteristics of a distribution system was used to study the CSU facility. Several intentional contamination scenarios were simulated at different points to determine the optimum location and number of MSUs. The results of this modeling showed that there was a probability of detection of greater than 60% at 2 hours and 80% at 4 hours with 5 MSUs in the CSU system.

The results of this research indicate that low cost, reliable, bulk water quality monitors can provide significant chemical detection in a public water distribution system.

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# Chapter 1
# INTRODUCTION

The terrorist attack of September 11, 2001, has brought a new age to American water utilities. Once recognized as among the safest water supply utilities in the world, following September 11th the security of America's water supply has been a concern to the U.S. Environmental Protection Agency (USEPA), to water utilities, and to the associations that represent and serve them.

Concerns about the security of drinking water distribution systems date as far back as approximately 300 B.C. during the construction of Aqua Appia, one of the aqueducts of the Roman Empire. The Romans were concerned that their water supply systems could be rendered useless by enemy action (Herschel, 1973).

If a terrorist were to attack a water system, hundreds of thousands of people could be impacted at once. However these systems have not been a focus for security improvements because they have not been attacked in the past. Water system security concerns focus on the possibility of actual contamination of drinking water because this scenario could have a rapid and deleterious effect on public health. What is new is the increased awareness and concern due to the tragic events of September 11, 2001. Drinking water systems were identified almost immediately as a potential target for further attacks (Rose, 2002).

In most water systems such as drinking water and waste water plants a significant number of water quality parameters are currently monitored at the plant. This is required for compliance and maintenance of water quality as the water enters the distribution system. In the distribution system, water quality is usually monitored through grab samples with an analysis turn-around time of hours to days (National Research Council,

2002). Water distribution networks are uniquely vulnerable because of their accessibility to those it serves and the geographic area that it reaches. A contaminant can be injected into any water distribution system node using a pump or a mobile pressurized tank, capable of overcoming the system pressure. Long term actions that a utility should consider taking include the use of early warning monitoring systems in the distribution system that will detect changes in chemical characteristics of the water (DeNileon 2001, Clark and Deininger 2000).

In this study, a novel method for detecting significant distribution system contamination events in real-time using commonly available monitoring equipment was developed, tested and documented. The significant contribution of this work would be the development of the capability for timely response and mitigation to expedite the return of the water system back to service, and to inform the public health agencies so that they can help in disease diagnosis if remedial action is not taken quickly enough. Results of this research are also applicable to the detection of common inadvertent contamination events such as backflow, line breaks, iron from heavily tuberculated cast-iron mains, and sloughed-off biofilm, to name a few.

The overall goal of this research is to evaluate commonly used water distribution tools for their potential to provide guidance in security applications. These tools include water distribution modeling software and basic water quality instruments. Other tools that could be used for security issues include the monitoring equipment already in use (turbidimeters, conductivity meters, pH probes, chlorine analyzers, TOC, UV 254, etc).

The dissertation is organized into separate chapters based on different hypotheses and objectives. Chapter 3 describes the testing of a surrogate on-line instrument for TOC

analysis, UV absorbance at 254 nm (UV254). In this chapter, we describe the testing of an instrument that has a significantly lower overall cost than on-line TOC with a range of potential chemical contaminants. Chapter 4 includes additional routine instrument testing (pH, conductivity, turbidity, chlorine residual) with an expanded set of potential chemical contaminants. This chapter uses existing instruments that are being sold for distribution system security applications and evaluates them with a wide range of chemical contaminants to study their effectiveness. These existing instruments have several disadvantages that are the focus of the research in Chapters 5 and 6.

One of the disadvantages of the existing instruments is that turbidity, although inexpensive and easy to use, will not detect dissolved compounds. In Chapter 5, we studied the use of turbidity to detect the sloughing of indigenous biofilm due to the presence of hazardous chemicals. We examine the biofilm's response to different chemical contaminants and the potential for using turbidity and UV254 for indirect chemical contaminant detection.

Another disadvantage of existing distribution system security instruments is the initial cost and the operations and maintenance complexity. In Chapter 6, we describe the development and testing of a relatively low-cost instrument that is easy to use and maintain. Due to these characteristics, the instrument is more likely to be deployed at multiple locations in a distribution system. To determine the impact of multiple spatial deployments, water distribution system hydraulic software was used to model the transport of the contaminants with different scenarios. The CSU campus water distribution system is used to determine the optimum number and location for detector instrument installation.

# Chapter 2
# HYPOTHESES, RESEARCH OBJECTIVES, AND LITERATURE REVIEW

## 2.1 Hypotheses

The research that will be presented in this dissertation is designed to address the five hypotheses below:

2.1.1 UV 254 monitoring of distribution system water can be a cost-effective sensitive alternative to on-line TOC analysis for detecting chemical contaminants.

2.1.2 The use of routine instruments that measure bulk water quality parameters (pH, conductivity, turbidity, TOC, UV254 and chlorine residual) can be effective for detecting potential intentional chemical contaminants in a drinking water distribution system.

2.1.3 Biofilm in the distribution system will die and slough off the pipes when exposed to hazardous levels of intentional contaminants and provide a measurable secondary response to contamination events.

2.1.4 Bulk water quality instruments that are lower cost than existing instruments can be developed and be effective at detecting the presence of chemical contaminants.

2.1.5 Water distribution system hydraulic modeling can be used to optimize sensor number and placement based on probability of detection of chemical contaminants.

## 2.2 Objectives

There are five objectives which are addressed in this research. They include that comparing UV and TOC instruments, developing monitoring methods and detection limits of chemicals, using biofim test as indirect detecting chemical contaminants, and developing micro sensor units and simulating $H_2O$ Map software.

2.2.1 Compare two water quality instruments in a pilot scale drinking water distribution system for the effectiveness in detecting chemical agents.

This point is mainly focused on comparing accurate and cost effective water quality instruments to detect significant chemical disturbances in a drinking water distribution system. The two water quality instruments are UV 254 and Total Organic Carbon (TOC) and will be used to measure the amount of organic carbon compounds in the water distribution system. Detailed information is presented in Chapter 3.

2.2.2 Use routine real-time monitoring instruments and develop monitoring methods and detection limits for potential chemical agents.

The main objective of this research was to develop monitoring methods for the real time detection of significant chemical contaminants, which disturb water quality in a drinking water distribution system. The primary objective was accomplished by combining routine monitoring instruments that are readily available. The research provides needed information to interpret real-time distribution system monitoring that has begun or will be implemented in the future. Detailed information is presented in Chapter 4.

2.2.3 Determine the efficacy of indirectly detecting intentional chemical contamination in the distribution system through biofilm sloughing-caused turbidity response.

Increasing the signal to noise ratio of the contaminant instrument response may lie in taking advantage of biofilms that are a natural part of drinking water distribution systems. Toxic chemicals will be introduced from different sources to the pilot scale distribution system that has a steady-state indigenous biofilm. The indirect turbidity response to the sloughing of biofilm will be measured in a continuous flow system. The concentration of biofilm associated with the pipe surface will be quantified before and after the contamination events. Detailed information is presented in Chapter 5.

2.2.4 Evaluate the efficacy and cost-effectiveness of routine monitoring instruments for detecting intentional contamination of the distribution system.

It is not cost effective to install preexisting water quality instruments at every place in the distribution system. $H_2OMap$ modeling will help to optimize sensor placement, provide emergency response scenarios and help make decisions. Detailed information is presented in Chapter 6.

2.2.5 Install security sensors across CSU campus, collect data for a minimum of three months and determine / demonstrate trends in water quality associated with system operation. It is important to rapid detect significant system disturbances such as potential security incidents, isolate and intervene before a major catastrophe occurs. Micro-Sensor networks allow the system operators to identify problem areas to get grab samples. The real-time data collected by Syndromic Common Operating Picture for the Enterprise (SCOPE) can be used to model behavior and spread of substances throughout the water system using standard water plant modeling software. We did collect and analyze data from at least 5 sensors installed across campus. Detailed information is presented in Chapter 6.

## 2.3 Literature Review

Following is a review of literature that is specific to significant components of this research effort. These components include demonstrating a valid need for this research, establishing a credible threat contaminant list to be used in the research, the use of biofilm test to simulate microbiological conditions in a distribution system, and simulating $H_2O$ Map software to optimize Micro Sensor Unit (MSU) placement. In addition, additional topics will be presented in the literature review that is of significant importance in distribution system security monitoring, namely: using SCOPE-$H_2O^{TM}$ to collect data from MSU, explaining water quality instrument, SCADA system, and TOC and UV analyzer explanation.

### 2.3.1 Chemicals

For chemical contaminants, Khan et al. (2000) use the following criteria to prioritize contaminant credibility: already known to be weaponized, available to potential terrorists, likely to cause major morbidity or mortality, potential of causing public panic and social disruption, and requires special action for public health preparedness. They list the following as priority chemical agents: arsenic, pesticides, and cyanides. The National Research Council [40] addresses morbidity and mortality, or toxicity, and focuses on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents and are persistent in water. The US Army Center for Health Promotion and Preventive Medicine listed sodium fluoroacetate as priority potential chemical threat agents [41]. The following specific chemical compounds were used in this investigation.

**Dicrotophos**

Dicrotophos emits toxic fumes of phosphorus and nitrogen oxides when heated to decomposition. In two human poisoning cases, symptoms such as cramps, nausea, vomiting, diarrhea, dyspnea, and general weakness occurred when exposed to spray, and loss of pulse and respiration occurred when ingested. In both cases, atropine and pralidoxime relieved the symptoms and the patients showed improvement.

**Sodium Arsenate**

Sodium arsenate is a pentavalent form of inorganic arsenic. It is a heptahydrate, which normally exists as colorless crystals with no discernible odor. Inorganic arsenical compounds have been classified as Class A oncogens, demonstrating positive oncogenic effects based on sufficient human epidemiological evidence.

**Cycloheximide**

Actidione (Cycloheximide) is an antibiotic that acts as an inhibitor of protein synthesis in eukaryotes but not prokaryotes. Cycloheximide is an odorless, white, crystalline powder used in hospital and research laboratories as an antibiotic, a protein synthesis inhibitor, or a plant growth regulator. Cycloheximide also has broader agricultural use as a fungicide, but such use is being discontinued due to the recent findings of birth defects at low doses in animals. Cycloheximide can irritate the skin and also may cause cancer.

**Sodium Cyanide**

Sodium cyanide is a product of a series of reactions involving sodium carbonate, limestone, carbon, and oxygen from the air. Sodium cyanide and potassium cyanide are both white solids with a bitter, mild almond-like odor in damp air.

**Glyphosate** [54]

The other chemical name of Glyphosate ($C_3H_8NO_5P$) is N-(phosphonomethyl) glycine and it is a colorless crystal at room temperature. The water solubility is 12,000 mg/L. It is a broad-spectrum, nonselective systemic herbicide used for control of annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. It is an acid and its salts are moderately toxic compounds in EPA toxicity class II. It is generally distributed as water-soluble concentrates and powders.

**Nicotine**

Nicotine is usually obtained from *Nicotiana tabacum*. Nicotine is one of the more than 4,000 chemicals found in the smoke from tobacco products such as cigarettes, cigars, and pipes. Nicotine is a naturally occurring colorless liquid that turns brown and acquires the odor of tobacco when exposed to air. The immediate effects of nicotine include increased blood pressure and heart rate, thickening of blood, narrowing of arteries, decrease in skin temperature, increase in respiration, and stimulation of the central nervous system, vomiting, and diarrhea.

**Aldicarb**

Aldicarb is directly toxic through oral, dermal, and inhalation routes. It is toxic through secondary poisoning – when plants systemically exposed are consumed or when exposed insects, rodents, and birds are consumed by predators and scavengers. Aldicarb is highly soluble in water, soluble in acetone, zylene, ethyl, ether, toluene, and other organic solvents, and is highly mobile in soil. Levels of aldicarb in drinking water exceeding the health advisory level of 10 ppb established by the Office of Drinking Water at EPA have been recorded in couple states in U.S.

**Dichlorvos** [51]

The other chemical name of Dichlorvos ($C_4H_7C_{l2}O_4P$) is 2,2-dichlorovinyl dimethyl phosphate and it is a colorless to amber liquid with a mild chemical odor. The water solubility is 10,000 mg/L. Dichlorvos is an organophosphate compound used to control household, public health, and stored product insects. It is highly toxic, because it may cause cancer and there is only a small margin of safety for other effects. Dichlorvos is used to treat a variety of parasitic worm infections in dogs, livestock, and humans.

**Sodium Fluoroacetate**

Sodium fluoroacetate, also commonly known as compound 1080, sodium monofluororacetate, fratol, furatol, ratbane, and yasoknock, is a rodenticide. Fluoroacetic acid differs from the fluoroacetate ion that makes up sodium fluoroacetate only in the addition of a hydrogen atom, $C_2H_3FO_2$ or as a more protonated form. Sodium fluoroacetate is a deadly human poison by ingestion. Fluoroacetate poisoning results in a lethal accumulation of citric acid, which in turn causes violent convulsions and death from cardiac failure or respiratory arrest.

**Dicamba** [53]

The other chemical name of Dicamba ($C_8H_6C_{l2}O_3$) is 3,6-dichloro-O-anisic acid and it is an odorless, white crystalline solid. The technical acid is a pale buff crystalline solid. The water solubility is 6500 mg/L. It is a benzoic acid herbicide. It is used in pastures, range land, and non-crop areas such as fence-rows and roadways to control weeds with combination with a phenoxyalkanoic acid or other herbicide. It is has classified this toxicity class III (slightly toxic) by EPA because of its irritating, corrosive effect on skin and eyes.

**Potassium Ferricyanide** [55]

The other chemical name of Potassium Ferricyanide ($K_3Fe(CN)_6$) is Potassium ferricynate; tripotassium hexacyanoferrate; Ferrate (3-), hexacyano, tripotassium

Bright red, crystalline powder. It is odorless and Slowly soluble in 2.5 parts cold water. It is also stable. Very little information on the toxicity of potassium ferricyanide was found in the available literature. Exposure of the general population to potassium ferricyanide occurs primarily through its use in photographic processing, particularly in home and school darkrooms.

**Arsenic Trioxide** [52]

Arsenic trioxide is one of the arsenites found in nature and is produced mainly from by-products of copper smelting. Arsenic trioxide ($As_2O_3$) is a white or transparent solid in the form of glassy, shapeless lumps or a crystalline powder that resembles sugar. It has no odor or taste. The effect of arsenic trioxide may cause a burning sensation to the nose, mouth, and eyes and cause coughing, shortness of breath, headache, sore throat, and dizziness. The solubility is low in water. OSHA PEL (permissible exposure limit) is 10 $\mu g/m^3$ and NIOSH IDLH (immediately dangerous to life or health) is 5 mg $As/m^3$.

### 2.3.2 $H_2O$ Map

There are four major capabilities for the modeling and analysis of water distribution systems by $H_2O$Map (MWH soft, Inc., Pasadena, CA). $H_2O$Map can construct an accurate representation of the distribution system, attributes required for analysis. It may perform several different types of hydraulic and water quality network simulations. It offers many powerful GIS and mapping functions. Also it allows information to be easily exchanged with other applications such as CAD, spreadsheets, and relational databases. It has many tools to analyze model results such as annotating/labeling, color-coding, graphing, contouring, profiling, reporting, and animation.

Modeling water quality in water distribution systems has become a widely accepted tool in support of water supply planning, operations and research (Frazey, 2004). Models can provide a picture of how water moves throughout the distribution system. One of the emerging abilities of models is to help utilities understand how the system will respond due to either accidental or intentional contamination. Specifically, as applied to water system security, models have been used to examine three different time frames. First, they have been used as planning tools to assess vulnerabilities of the systems for various events. Second, they are used as a real-time tool during actual events for assistance in formulating responses. Third, they have been used for investigating events that occurred in the past.

**Water Quality Simulations (initial constituent, bulk reaction, wall reaction)**

There are three water quality simulations that these models can complete: water age, source tracing, and chemical constituent.

Water age is a function that calculates the age of the water in the network, computed at any node. The models compute this characteristic based on EPANET calculations, which is performed under constant hydraulic conditions and is a simple, non-specific measure of the overall quality of delivered water. This analysis tracks the percent of water over time that reaches any node in the network from an original specified node. The specified node can be any node in the network. The information required for age analysis is pipe velocity and flow rate; therefore, no reaction coefficients are required (Haestad Methods, 2002).

The trace function determines the fraction of water that originates from a specified node over time, again with the calculations based on EPANET. EPANET treats the source node as a constant source of non-reacting constituent, entering the network at the node with a concentration of 100 (Rossman, 2000). The analysis can be useful for analyzing systems with two or more raw water sources, thus showing how the water blended over time (Rossman, 2000). It can only be performed using the EPS method with input information of pipe velocity and flow rate (Haestad Methods, 2002).

The final water quality analysis is the chemical constituent. A constituent is defined as any substance for which the growth or decay can be adequately described through bulk and wall reaction coefficients (Haestad Methods, 2002). This type of analysis determines the concentration of the constituent at all nodes and links in the system. The constituent can be anything from chlorine to fluoride to an unwanted contaminant. This analysis determines the concentration of the constituent at all nodes and links in the system (Haestad Method, 2002). The source of the constituent can be

from the main treatment works, well head or satellite facility, or unwanted contaminant intrusion and either conservative or reactive species can be modeled.

This analysis can only be performed using the EPS (Expanding Period Simulation). The following must be input into the model for chemical constituent:

- Initial Constituent: the initial concentration of the constituent at the beginning of the analysis.
- Bulk Reaction: reaction rate used to model reactions of the constituent within the bulk flow.
- Wall Reaction: reaction rate constant for the material reacting along the pipe wall.

The constituent analysis is based on the principles of conservation of mass and reaction kinetics. There are three processes used to conduct this calculation (MWH Soft, Inc., 2002):

- Advection in pipes: This is based on that fact that the constituent will travel down the pipe with the same average velocity as the fluid carrying it. While traveling, the constituent will react, either growing or decaying. Longitudinal dispersion is usually not an important transport mechanism under most operating conditions meaning there is no intermixing of mass between adjacent parcels of water traveling down a pipe.
- Mixing at Junctions: The mixing is assumed to be complete and instantaneous.
- Mixing at Tanks: There are several different types of mixing in tanks. These different types of mixing are discussed under tank mixing.

**Mode of contaminant entry**

Another similarity between these distribution models is the mode of entry for the contaminant. The models allow any node in the system to serve as the source for a chemical constituent. Each modeling program allows several different methods to introduce the contaminant into the system. These are explained below (Haestad Methods, 2002; MWH Soft, Inc., 2002; Rossman, 2000).

- Concentration: This method fixes the concentration of any external inflow entering the system at a node. An example would be a reservoir or a negative demand located at a junction.
- Flow Paced Booster: This method adds a fixed concentration to the flow resulting from the mixing of all inflow to the node from other points in the network.
- Setpoint booster: This fixes the concentration of any flow leaving the node. This can be used as long as the concentration resulting from all inflow to the node is below the setpoint.
- Mass Booster: This is used to add a fixed mass flow to the flow entering the node from other points in the network.

**Tank mixing**

Tank mixing is another item that impacts the contaminant character with in the system. Again, the models complete this calculation based on EPANET methods, which includes complete mixing, two-compartment mixing, first in/first out plug flow, and last in/last out plug flow. These are described more in detail below.

- Completely mixed: This assumes that all water entering the tank is completely and instantaneously mixed with the water already in the tank. This is a reasonable assumption for many tanks operating under fill-and-draw conditions providing sufficient momentum flux imparted to inflow (Rossman, 2000).
- Two-compartment mixing: this assumes that the tank storage is divided into two completely mixed compartments. Inflow and outflow are assumed to take place in the first compartment. The second compartment receives over-flow from the first, and this overflow is completely mixed. The inlet and outlets of the tanks are in the first compartment. As new water enters, it completely mixes with the first compartment and overflow is sent to the second compartment. When water leaves the first compartment, it receives an equivalent amount of water from the second compartment. Based on this information, the second compartment can have dead zones (Rossman, 2000).
- First in/first out plug flow model: this model assumes there is no mixing of water during the time it is in the tank. Water parcels are effectively stacked on one another, moving through the tank in a segregated fashion where the first parcel to enter is the first parcel to leave. This is most appropriate for baffled tanks that operate with simultaneous inflow and out flow (Rossman, 2000).

- Last in/last out plug flow model: this model assumes that no water mixing occurs in the tank. Water parcels still stack up one on top of another and the last parcel to enter is the first to leave from the bottom of the tank. This is most appropriate for tall, narrow standpipes that have an inlet/outlet pipe at the bottom and low momentum inflow (Rossman, 2000).

**Chemistry modeling**

The water models use the EPANET calculation methods for modeling chemical reactions. The EPANET method can model bulk and wall reactions, in regards to decay or growth. The bulk reactions used by these programs include: simple first-order decay, first-order saturation growth, two-component second order decay, Michealis-Menton Decay kinetics, or zero-order growth (Rossman, 2000).

**Bulk flow reactions**

The programs model reactions in the bulk flow with n-th order kinetics. The instantaneous rate of reaction is assumed to be concentration-dependent according to:

$R = K_b C^n$

Where:

- R = rate of reaction (mass/volume/time)
- $K_b$ = a bulk reaction rate coefficient $K_b$ has units of concentration raised to the (1-n) power divided by time.
- C = reactant concentration (mass/volume)
- n = reaction order

There are other special case equations, described below. These equations are based on three parameters used to characterize bulk rates ($K_b$, $C_L$, and n). Table 2-1 summarized the parameters and gives examples of a constituent that each would model.

**Table 2-1** Summary of model parameters and examples

| Model | Parameters | Examples |
|---|---|---|
| First-Order Decay | $C_L = 0$, $K_b < 0$, $n = 1$ | Chlorine |
| First-Order Saturation Growth | $C_L > 0$, $K_b > 0$, $n = 1$ | Trihalomethanes |
| Zero-Order Kinetics | $C_L = 0$, $K_b <> 0$, $n = 0$ | Water Age |
| No Reaction | $C_L = 0$, $K_b = 0$ | Fluoride Tracer |

The special case equations are discussed below. These equations are based on EPANET.

- First Order Decay ($C_L = 0$, $K_b < 0$, $n = 1$)

$$R = K_b C$$

This can be used for the decay of many different substances, including chlorine.

- First Order Saturation Growth ($C_L > 0$, $K_b > 0$, $n = 1$)

$$R = K_b (C_L - C)$$

This can adequately model the growth of disinfection by-products where the ultimate formation is limited by the amount of reactive precursor there is in the water.

- Two Component Second Order Decay ($C_L \neq 0$, $K_b < 0$, $n = 2$)

$$R = K_b C (C - C_L)$$

This equation assumes that substance A will react with B in some unknown ratio, which will produce product P. Based on the reaction, the rate that A disappears is proportional to the product of A and B remaining.

- Michaelis-Menton Decay Kinetics ($C_L > 0$, $K_b < 0$, $n < 0$)

$$R = \frac{K_b C}{C_L - C}$$

The programs will use the Michaelis-Menton Decay Kinetics when a negative reaction order n is specified, shown above for a decay reaction, but this is only a special case. The above is for decay reactions, but for growth the denominator becomes $C_L + C$. This equation is used frequently to describe enzyme-catalyzed reactions and microbial growth. Mathematically, it produces first order behavior at low concentrations and zero-order behavior at higher concentrations. For decay reactions, $C_L$ must be set at a higher value than the initial concentration present (Rossman, 2000).

This equation was applied by Koechling (Frazey, 2004) to model chlorine decay in a number of different waters. It was found that $C_L$ and $K_b$ could be related to the organic content of the water and that its ultraviolet absorbance is as follows.

$$K_b = -0.32UVA^{1.365}\frac{(100UVCA)}{DOC}$$

$$C_L = 4.98UVA - 1.91DOC$$

Where:

- UVA = ultraviolet absorbance at 254 nm (1/cm)
- DOC = dissolved organic carbon concentration (mg/L)
- Note that these expressions apply only for values of $C_L$ and $K_b$ used with Michaelis-Menton kinetics
- Zero Order Growth ($C_L = 0$, $K_b = =10$, $n = 0$)

R = 1.0

This is a special case that can be used to model the water age. For each unit of time, the concentration, or age, increased by one unit. There is a relationship between the bulk rate constant at one temperature ($T_1$) related to another temperature ($T_2$). This is often expressed using the van't Hoff-Arrehnius equation of the form:

$$K_{b2} = K_{b1}\theta^{T_2-T_1}$$

Where: θ is a constant.

Use of the equation discussed above is predicated on some knowledge of the reaction coefficients. If the reaction coefficients are unknown, they will need to be measured in the lab or estimated with empirical relationships.

**Wall reactions**

Substantial water quality changes can occur at or near the pipe wall interface. Wall reactions can be complicated, as they depend on temperature as well as pipe material and age. As metal pipes age, their roughness tends to increase with encrustation and tuberculation of corrosion products on accumulating on the pipe walls. This in turn produces a lower Hazen-Williams C-factor or a higher Darcy-Weisbach roughness coefficient that results in greater frictional head loss through the pipe. Dissolved substances are transported to the pipe wall and react with materials such as the biofilm or corrosion products (e.g. iron oxides) on or near the wall. Several variables will influence this reaction. One of these is the area available for the reactions, which is simply the surface area per unit volume. Another variable is the rate of mass transfer between the fluid and the wall. The factor is represented by a mass transfer coefficient. The value of this mass transfer coefficient depends on the reactive substance's molecular diffusivity as well as the Reynolds number of the flow. The wall reaction rate can be considered to be dependent on the concentration in the bulk flow by using an expression of the form:

$$R = (A/V)K_w C^n$$

Where:

- $K_w$ = a wall reaction rate coefficient
- (A/V) = the surface area per unit volume within a pipe (equal to 4 divided by the pipe diameter).

The programs limit the choice of wall reaction order to either 0 or 1, so the units of $K_w$ are either mass/area/time or length/time, respectively. The $K_w$ value must be supplied by the modeler. The first-order $K_w$ values can have a wide range; anywhere form 0 to 5 ft/day. The value should be adjusted to account for any mass transfer limitations in the moving reactants and products occurring between the wall and bulk flow. The programs do this automatically based on the substance's given molecular diffusivity and on the Reynolds number of the flow.

The programs can make the pipe $K_w$ a function of the roughness coefficient. Note that WaterCAD does not have these calculations listed in the manual. The equations are listed below.

**Table2-2** Formula of headloss and wall reaction

| Headloss Formula | Wall Reaction Formula |
|---|---|
| Hazen-Williams | $K_w = F/C$ |
| Darcy-Weisbach | $K_w = -F/\log(e/d)$ |
| Chezy-Manning | $K_w = Fn$ |

Where C = Hazen-Williams C-factor, e = Darcy-Weisbach roughness, d = pipe diameter, n= Manning roughness coefficient, and F = wall reaction – pipe roughness coefficient.

The value for F must be developed from site-specific field measurements. It will have a different meaning depending on which head loss equation is chosen. This method requires only F to allow wall reaction coefficients to vary within the network.

Pipe wall reactions can also be expressed by using the following set of equations.

- First Order rate

$$r = \frac{2k_w k_f C}{R(k_w + k_f)}$$

Where:

- $k_w$ = wall reaction rate constant (length/time)
- $k_f$ = mass transfer coefficient (length/time)
- R = pipe radius

This would be representative in situations where chlorine is the limiting reactant. This might occur with reactions that involve complex organic compounds, or those found in exocellular enzymes and metabolic products produced by biofilm on the pipe wall (MWH Soft, Inc., 2004).

- Zero Order kinetic reaction

For this equation, the rate cannot exceed the mass transfer rate, thus the equation becomes:

$$r = MIN(k_w k_f C)(2/R)$$

Where kw now has units of mass/area/time.

The mass transfer rates are normally expressed by the Sherwood number, which is a dimensionless number (Sh):

$$k_f = Sh\frac{D}{d}$$

Where:

- D = the molecular diffusivity of the species being transported (length$^2$/time)
- d = pipe diameter.

When the flow is fully developed laminar, the average Sherwood number through the pipe is expressed by the following:

$$Sh = 3.65 + \frac{0.068(d/L)\,\mathrm{Re}\,Sc}{1 + 0.04[(d/L)\,\mathrm{Re}\,Sc]^{2/3}}$$

Where:

- Re = Reynolds number
- Sc = Schmidt number (kinematic viscosity of water divided by the diffusivity of the chemical)

When the flow is turbulent, the following empirical correlation is used (Notter and Sleicher, 1971):

$$Sh = 0.0149\,\mathrm{Re}^{0.88}\,Sc^{1/3}$$

Where all the values are the same as for the above equations.

MWH states that the zero-order model would be representative when chlorine immediately oxidizes some reductant (i.e.a ferrous compound) and the rate is then dependent on how quickly the reductant is made by the pipe. Based on this, this mechanism would apply mostly to corrosion-induced reactions (MWH Soft, Inc., 2004).

### 2.3.3 SCOPE

SCOPE-$H_2O$™ is a complete solution for Real-Time Water Distribution System Monitoring. SCOPE-$H_2O$™ monitors the water throughout the city distribution system using Micro-Sensor Networks. A number of Micro-Sensor Units are spatially distributed throughout the water distribution system to detect contamination, corrosion build-up and stagnation points. This allows for early pre-emption by taking corrective action.

The SCOPE$H_2O$ platform has many benefits, including:

- Sensor network approach yields coverage of an entire city, not just single points
- Cost effective due to relatively inexpensive sensors which are optimized for detecting contamination events

The overall goals and results of the SCOPE-MSU System are shown in Table 2-3. There were 5 different goals and each goal was completed. Several chemicals which are recommended by EPA were used for this test and MSU detected these chemicals. Multiple MSUs were installed across the campus and data communications and collection were verified. Using SCOPE, real-time data were collected and imported into Excel for archiving and analysis.

**Table 2-3** SCOPE $H_2O$ System Goals

| Goal | Result |
|---|---|
| Ensure detection sensors properly detect chemical contaminants, bio-film buildup, corrosion, etc. | Demonstrated detection of EPA contaminants, other chemicals, pipe bio-film buildup, corrosion agents. |
| Demonstrate straightforward installation and communication scenarios. | Multiple installation scenarios demonstrated on CSU campus, labs, and local businesses. Zigbee and Ethernet communication solutions tested and verified. |
| View real-time and archived data using SCOPE dashboards and reports. Export data to other applications. | Verified proper operation of SCOPE monitoring dashboards. Reports generated, data imported into Excel. |
| Demonstrate complete system operation including detection, interdiction, and resolution of events. | Complete system demonstrated over campus wide setting. System used exclusively for contaminant and bio-film buildup tests. |
| Show the system is reliable and requires minimal maintenance. | Minimal maintenance required for initial test units. Almost no data dropouts encountered during 3 month test. Limited recalibrations required. |

In Figure 2-1, the flow chart of the use of a SCOPE-MSU system is shown. MSU that were installed multiple locations (Environmental Lab, Engineering Research Center, Colorado State University Main campus, and Commercial sites) were used to test this system In addition, the MSUs were used to do chemical injection tests, biofilm tests and to provide data for modeling.

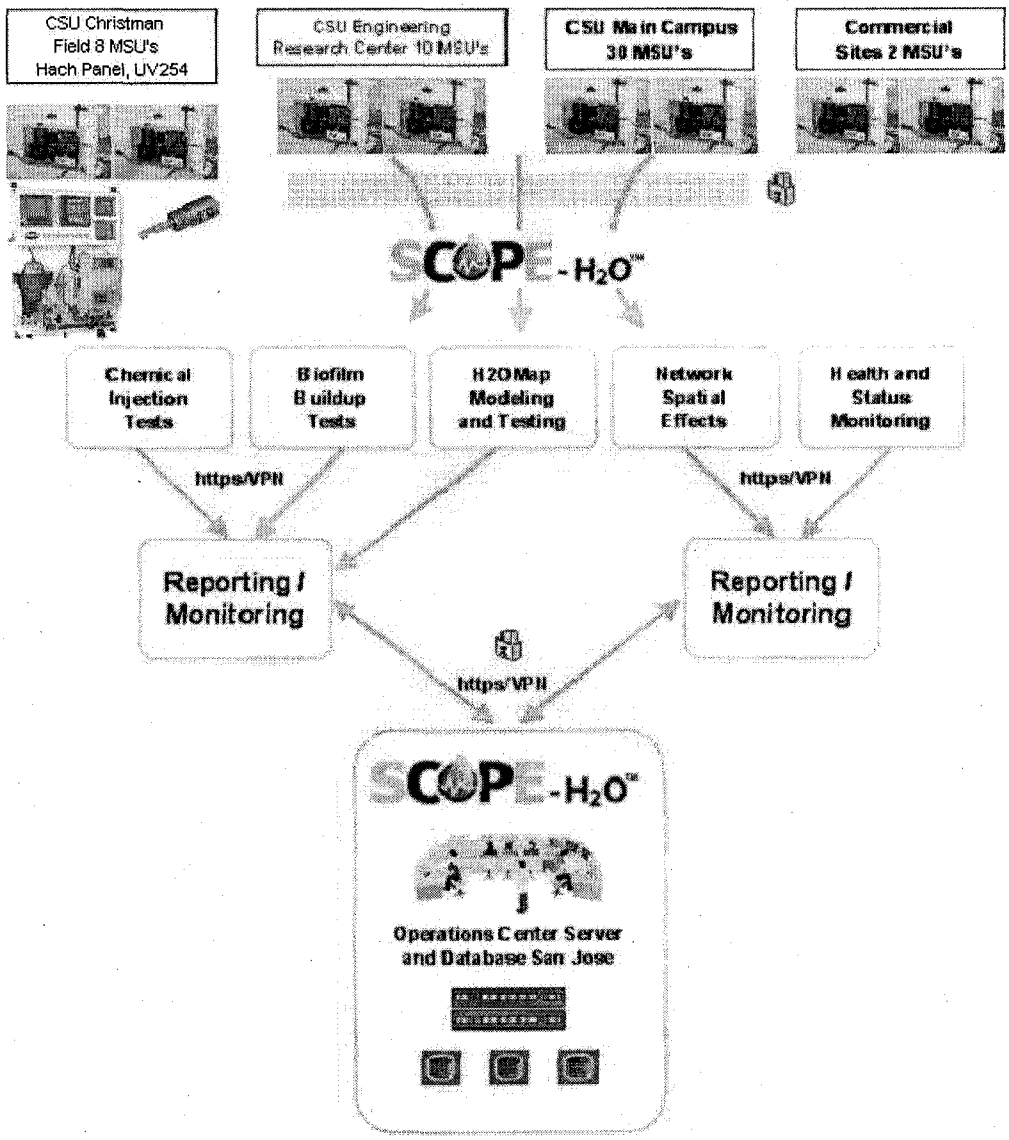



**Figure 2-1** Flow Chart of SCOPE-$H_2O$™

### 2.3.4 SCADA

SCADA stands for Supervisory Control and Data Acquisition. The term SCADA refers to a central system that monitors and controls a complete site or a system spread out over a long distance or a large-scale, distributed measurement system. It is normal to use Supervisory Control and Data Acquisition (SCADA) technology to monitor/control chemical, physical or transport processes, in municipal water supply systems. SCADA systems include the means for connecting instruments to other system components, including input/output signal hardware, controllers, Human Machine Interface (HMI), networks, communication, Remote Terminal Unit (RTU) or a Programmable Logic Controller (PLC),and software as demonstrated in Figure2-2.

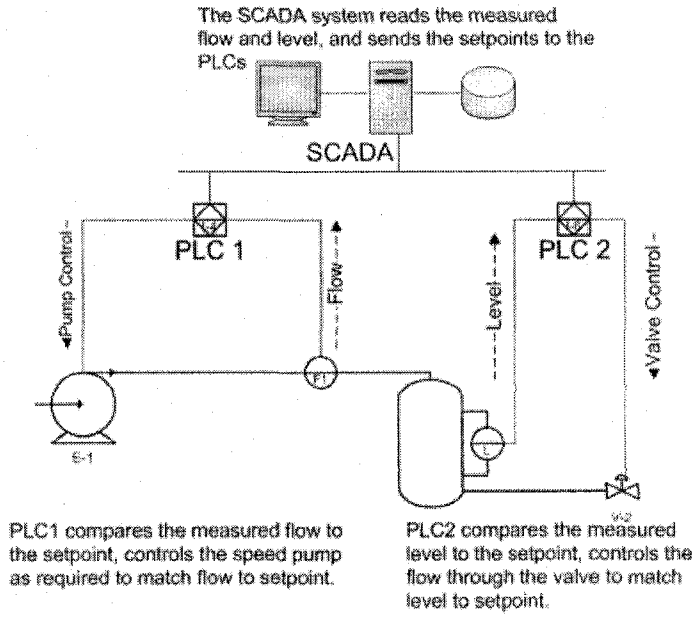



**Figure 2-2** Diagram of SCADA System [50]

Monitoring instruments are connected to remote telemetry units or programmable logic controllers to convert instrument outputs to appropriate units, compare the instrument responses to programmed criteria, generate alarms if required, and send control signals to other equipment. The host computer polls the PLCs and RTUs for data and in some systems, analyzes this data and provides specified information to system operators. SCADA [50]

A HMI device presents process data to enable a human operator, to control the process. PLC does provide automated, pre-programmed control over a process. The RTU connects to physical equipment, and reads status data such as the open/closed status from a switch or a valve, reads measurements such as pressure, flow, voltage or current.

### 2.3.5 Biofilm

**A. Introduction of microorganism in distribution system**

Biofilm is recognized as indigenous in a normal aquatic system and can exist in all distribution systems containing properly treated, but non-sterile, water [31]. Living microorganisms and nutrients enter drinking water distribution systems with raw water during water treatment failures or from pipe breaks or leaks, backflow, and cross-connections [32]. Microbiological contamination also can occur via uncovered storage tanks and during water main installation and repair [33].

**B. Definition of biofilm**

For a number of years, biofilm was generally regarded as "cells immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin." A more-universal definition – "matrix-enclosed bacterial populations adherent to each other and/or to surfaces or interfaces" – is better suited to all ecological, industrial, and medical situations, and in 1995, biofilm was defined as, "microbial cells, attached to a substratum, and immobilized in a three-dimensional matrix of extracellular polymers enabling the formation of an independent functioning ecosystem, homeostatically regulated" [35].

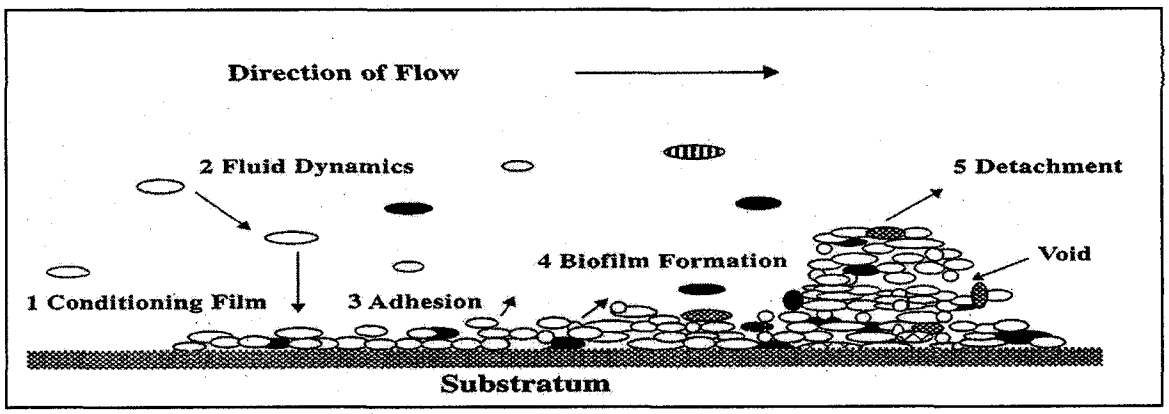



**Figure 2-3** Biofilm Formation Diagram (from Precival et al., 2000)

**C. Process of biofilm formation**

While biofilm formation is considered to be complex, it can be summarized as a five-stage process [35]

a. Development of a surface-conditioning film: A clean, uncontaminated surface can be conditioned by the transport medium, i.e. water, containing organic substances and microbial cells in as little as 15 minutes.

b. Events that bring the organisms into close proximity with the surface: Transport of organisms to the surface can be through laminar flow or turbulent flow. Temperature and gravity typically dictate the speed of flow.

c. Adhesion, either reversible or irreversible sorption: Reversible adhesion is an initial, weak attachment of microbial cells to a surface. Irreversible adhesion establishes a permanent bonding of the microorganisms with the surface and requires mechanical or chemical treatment for removal.

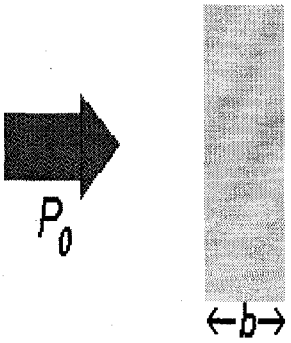
d. Growth and division of the organisms with the colonization of the surface, microcolony formation and biofilm formation: There are a number of parameters that affect the development of biofilm, such as temperature, hydrodynamic conditions, nutrient availability, roughness, and pH.

e. Detachment: The five means of biofilm detachment include: erosion of single cells, sloughing of clusters, abrasion, human intervention, and predator grazing. Erosion is the removal of small particles of biofilms. Sloughing is a random and discrete process, the detachment of large particles of biofilm. Abrasion is caused by the collision of solid particles, human intervention involves detachment of the biofilm by chemical or physical means, and predator grazing is the consumption of biofilms by organisms.

### 2.3.6 UV & TOC

**A. Beer's Law**

Many compounds (usually organic) absorb ultraviolet (UV) or visible light. The diagram below shows a beam of monochromatic radiation of radiant power $P_0$, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P. The amount of radiation absorbed may be measured in a number of ways; however transmittance and absorbance are the primary methods. Transmittance (T) = P / $P_0$, % Transmittance (%T) = 100 T. Absorbance is described as follows;




$A = \log_{10} P_0 / P, \rightarrow A = \log_{10} 1 / T, \rightarrow A = \log_{10} 100 / \%T, \rightarrow A = 2 - \log_{10} \%T$

Absorbance can be calculated directly from percentage transmittance data using the last equation.

**B. Beer Lambert Law**

Beer Lambert Law states that the absorbance (A) is proportional to the concentration (c) of the absorbing species, and to the length of the path (b) of the electromagnetic radiation through the sample containing the absorbing species.

A=ebc

The proportionality constant e is the absorptivity of the species at the wavelength.

**C. UV254 correlation to TOC**

Spectrophotometry measures the absorbance of light by dissolved chemical compounds and correlates this with the concentration of the compounds. Chemical compounds absorb light at certain frequencies that represent the energy required to excite an electron to a greater energy state. Since the absorption of light is related to the electron density, compounds with electron-rich functional groups will absorb more light than compounds without these groups.

**D. Advantages of UV254 over TOC**

Measuring UV-254 and correlating it with TOC is much simpler than measuring TOC directly, and as shown in this paper, the correlation can be shown to be practicably accurate. Response time gains can also been seen using UV254, since the measrument is made *in-situ* within the sample chamber. No waste is generated by the UV254 measurement technique, allowing deployment into areas where a sanitary drain is not provided. Finally, the cost of UV254 instruments, while high, is much less than on-line TOC analyzers. For example, the Optek AF45 Single Wavelength UV Absorption Sensor has a list price of around $8000, nearly ¼ the list price of the on-line TOC units. The Optek unit used in this study reads directly in CU (concentration units) which according to the Optek factory, directly correlates to absorbance (A). The Optek on-line UV254 unit is shown below.

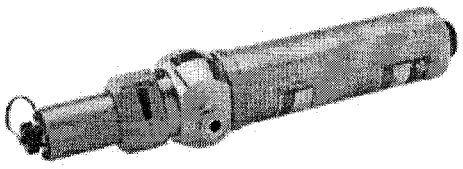


**Figure 2-4** UV 254 AF45

# Chapter 3
## Using UV254 as a TOC Surrogate for Intentional Contaminant Detection in Drinking Water Distribution Systems

Seongho Cho, Kenneth Carlson, Kenneth Stutzman

***Presented at AWWA Water Distribution System Analysis Conference, Cincinnati, OH August 29, 2006***

**Abstract**

Detecting chemical contaminants in water distribution systems has traditionally been accomplished by grab sampling techniques or more recently, using high-end process analyzers such as TOC (total organic carbon). The method presented in this paper uses an online UV254 analyzer to detect chemical contamination events. The results of the introduction of seven "particularly hazardous" chemicals and four baseline chemicals are presented, along with laboratory analysis of each, demonstrating the viability of using UV254 for quickly investigating and detecting contamination events at a much lower cost than with traditional instruments or grab sampling techniques.

**Keywords**

UV254, Total Organic Carbon, TOC, Drinking Water Distribution Systems

## 3.1 Introduction

Due to increased concerns about terrorist activity, the importance of early detection of chemical contaminants in drinking water distribution systems has become a topic of great interest. Well controlled and secured water treatment facilities have been mandated by federal, state and local governments for well over 50 years, and have been a key factor in ensuring water remains safe. Yet one remaining portion of the water supply, the distribution system, remains mostly unmonitored. This highly complex series of pipes, tanks, and pumps distribute water from water treatment facilities to end users, including homes, schools, offices, and hospitals.

### 3.1.1 Background

The security of water distribution systems has recently been the spotlight of many studies and news stories showing current systems are vulnerable, and are overdue for an attack. Even government agencies acknowledge issues with the water distribution system as shown in a letter from the Florida Department of Environmental Protection (DEP) to water plant owners and operators

We live in a new era. We must be much more vigilant and responsive about the security of our water supply systems to protect the public. Incidents, that in the past may have been viewed as acts of mischief and vandalism, now need to be fully investigated and managed seriously (Gelting et al. 2004).

To date, the majority of the dollars spent on homeland security related to water projects have been on physical security measures at water treatment facilities such as fences, cameras and security guards. While these are important security steps, most water plant experts agree that these measures will not protect against even the simplest

threats to the distribution system, and that real-time monitoring is critical for identifying threat events. While testifying before congress in 2001, Jeffrey J. Danneels, department manager Security Systems and Technology Center for Sandia National Laboratories states:

Monitoring the distribution pipelines and storage reservoirs will provide continuous feedback on water quality to detect malevolent contamination, allowing parts of the distribution system to be isolated in the event of an attack (Danneels 2001).

### 3.1.2 Water Distribution System Susceptibility

The susceptibility of water distribution systems to attack dates back to the early Egyptian and Roman times when armies literally "choked" the enemy by diverting water from aqueducts or poisoning the influent stream with chemicals like cyanide. These tactics are still a concern today, and in-fact, have been specifically covered in modern day treaties of war. Earlier this year the topic was again brought to the forefront by tapes recovered by the United States forces in Iraq where Iraq's then Deputy Prime Minister Tariq Aziz was quoted as saying to Saddam Hussein:

Sir, the biological is very easy to make. It's so simple that any biologist can make a bottle of germs and drop it into a water tower and kill 100,000. This is not done by a state. No need to accuse a state. An individual can do it (2006 ABC News).

A similar plot was uncovered in February of 2002 in Rome, Italy:

Italian police have been investigating whether the US Embassy in Rome was the object of a plot to poison the city's water, a scheme uncovered with the arrest of four Moroccans in possession of large quantities of cyanide, and who are suspected of working for al Qaeda. Media reports said that the suspects, aged 30 to 40, had been

followed by police for days, and were found with around 10 pounds of cyanide, maps of Rome highlighting the city's water supply and of the US Embassy building, and about 100 counterfeit resident permits. At least two of the men were also illegal immigrants (WaterTechOnline 2002).

Easy accessibility to a broad array of off-the-shelf chemicals and recipes for creating poisons from these chemicals on the internet compounds the problem. A trip to the local hardware store yields an interesting lot of drain cleaners, polishes, acids, bases, and caustics, many combinations of which yield results that are poisonous and even lethal in small quantities.

Threats like these show an impending attack is real, and if water suppliers are not prepared, could have devastating effects on end users and ultimately the economies of the United States, Europe and the world.

### 3.1.3 Grab Sampling Techniques

The current system for ensuring water distribution system safety (and compliance to EPA guidelines) is based on grab sampling techniques. In this method, lab technicians collect samples from various areas throughout a city. This is typically done a routine basis (for example every 7 or 30 days). In most cases, the samples are capped, held at a constant temperature in an ice chest, and returned to a water quality laboratory for analysis. For some measurements such as dissolved oxygen, the samples are stabilized in place with a chemical reagent, and then returned to the lab. The samples are normally analyzed in a first in, first out scheme, with a turn around time of 24-48 hours. From these samples, a table of detected contaminants is produced, which is sent to water users on an annual basis.

**Figure 3-1** Grab Sampling Techniques in the field and laboratory

More sophisticated systems may use an on-line sampler such as the American Sigma 900 MAX series for automatically capturing a sample, then storing it a temperature conditioning holding area. The same process is repeated as above, however the sampler can be triggered to automatically capture water samples based on a predefined event, such as a change in pH for example.

**Figure 3-2** A sample of Automated Samplers

Another popular grab sampling approach is to perform lab measurements in the field using portable test equipment. Cyanide measurements, for example, can be easily done using a portable colorimeter such as the CHEMetric V-2000. Using pre-packaged, sealed reagent vials, this device offers free cyanide measurements in the range of 0ppm to 0.4ppm.

**Figure 3-3** Hand Held Colorimeter for Cyanide Measurements

### 3.1.4 On-Line TOC Analyzers

Grab sampling procedures result in a best case scenario of 4 or 5 sample points per month, not nearly enough to capture any real security threat. As a result, an on-line detection sensor that can cover a broad array of chemicals has been long sought after. One such line of instruments, on-line Total Organic Carbon Analyzers (TOC), has showed great promise in filling this gap. Borrowed from the semiconductor and power industries, TOC analyzers automate several complex steps and combine the answer into a simple, easy to understand part per million (PPM) result.

In water treatment facilities, TOC gives a general idea as to the effectiveness of organic removal in the water treatment process, and is typically reported as a ratio of influent to effluent. Similarly, for pharmaceutical and semiconductor industry applications, TOC measurements ensure pure water is used as the basis for drug and wafer manufacturing operations.

The best known on-line analyzers are the Hach (Loveland CO) AstroTOC UV and Sievers 900. These units automate a very complex process of "combusting" the organic fraction sample in a furnace, then analyzing the remaining carbon dioxide which is directly proportional to the amount of organic carbon in the sample.

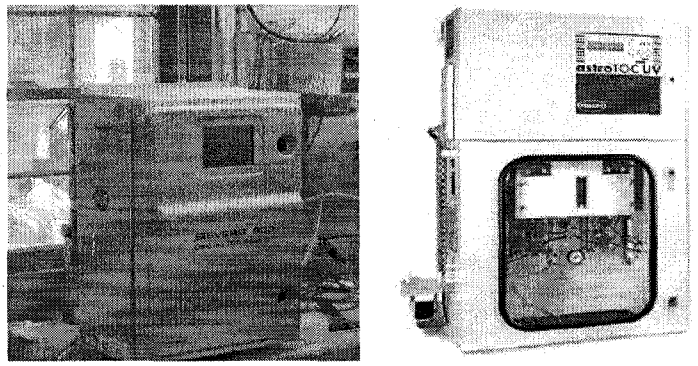



**Figure 3-4** On-Line TOC Analyzers

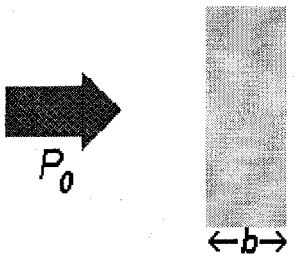
Although on-line TOC analyzers automate the process, they are extremely complex instruments, and thus are not ideally suited for out-of-plant installations such as remote water distribution sites. In addition, a supply of laboratory grade nitrogen is required, as are multiple liquid reagents causing very high Operation & Maintenance (O&M) costs for water treatment plant operators. Finally, on-line TOC analyzers are expensive, starting around $30,000 list price (Hach Company) and reaching over $50,000 for higher end models, such as making wide distribution of such instruments nearly impossible.

### 3.1.5 UV254 as a TOC Surrogate

In this study, the hypothesis is that UV254 can be used as a TOC surrogate. The physics behind this hypothesis are described in the following section.

(1) Beer's Law [5]

Many compounds (usually organic) absorb ultraviolet (UV) or visible light. The diagram below shows a beam of monochromatic radiation of radiant power $P_0$, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P. The amount of radiation absorbed may be measured in



a number of ways; however transmittance and absorbance are the primary methods.

Transmittance (T) = $P / P_0$, % Transmittance (%T) = 100 T

Absorbance is described as follows;

$A = \log_{10} P_0 / P, \rightarrow A = \log_{10} 1 / T, \rightarrow A = \log_{10} 100 / \%T, \rightarrow A = 2 - \log_{10} \%T$

Absorbance can be calculated directly from percentage transmittance data using the last equation.

(2) Beer Lambert Law [6]

Beer Lambert Law states that the absorbance (A) is proportional to the concentration (c) of the absorbing species, and to the length of the path (b) of the electromagnetic radiation through the sample containing the absorbing species.

A=ebc

The proportionality constant e is called the absorptivity of the species at the wavelength.

(3) UV254 correlation to TOC [7]

Spectrophotometry measures the absorbance of light by dissolved chemical compounds, which can be correlated to the concentration of the compounds. Chemical compounds absorb light at certain frequencies that represent the energy required to excite an electron to a greater energy state. Since the absorption of light is related to the electron density, compounds with electron-rich functional groups will absorb more light than compounds without these groups. Since this characteristic is analogous to the chlorine reactivity of a compound, researchers have shown that a concentration normalized absorbance at ultraviolet (UV) wavelengths can be an indicator of organic matter and hence TOC in water sample. Specific UV absorbance (SUVA) is calculated as the UV absorbance at 254nm divided by the dissolved organic carbon concentration

(UV254/DOC) and has been used as an indicator of the fraction of humic substances (plant derived) in water. The greater the SUVA, the higher the fraction of humic, hydrophobic, chlorine-reactive Natural Organic Matter (NOM) in a water.

(4) Advantages of UV254 over TOC [8]

Measuring UV-254 and correlating it with TOC is much simpler than measuring TOC directly, and as shown in this study, the correlation has notable accuracy. Response time gains are also achieved using UV254, since the measurement is made in-situ within the sample chamber. No waste is generated by the UV254 measurement technique, allowing deployment into areas where a sanitary drain is not provided. Finally, the cost of UV254 instruments, while high, is much less than on-line TOC analyzers. For example, the Optek AF45 Single Wavelength UV Absorption Sensor has a list price of around $8000, nearly ¼ the list price of the on-line TOC units. The Optek unit used in this study reads directly in CU (concentration units) which according to the Optek factory directly correlates to absorbance (A). The Optek (Specification will be on appendix) on-line UV254 unit is shown below.

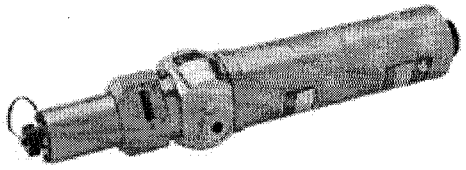


**Figure 3-5** On-Line UV254 Analyzer

## 3.2 Methods and Materials

### 3.2.1 Bench Scale Distribution System Setup

A bench scale distribution system was setup for examining the correlation between UV254 to TOC. Because the chemicals selected for contamination are toxic volatile materials, the bench scale distribution system was built near a ventilation hood. The discharged hazardous waste was then collected under the ventilation hood and sent to a hazardous disposal service. Two inch PVC pipe was selected for the pipe loop material to simulate real world conditions as closely as possible.

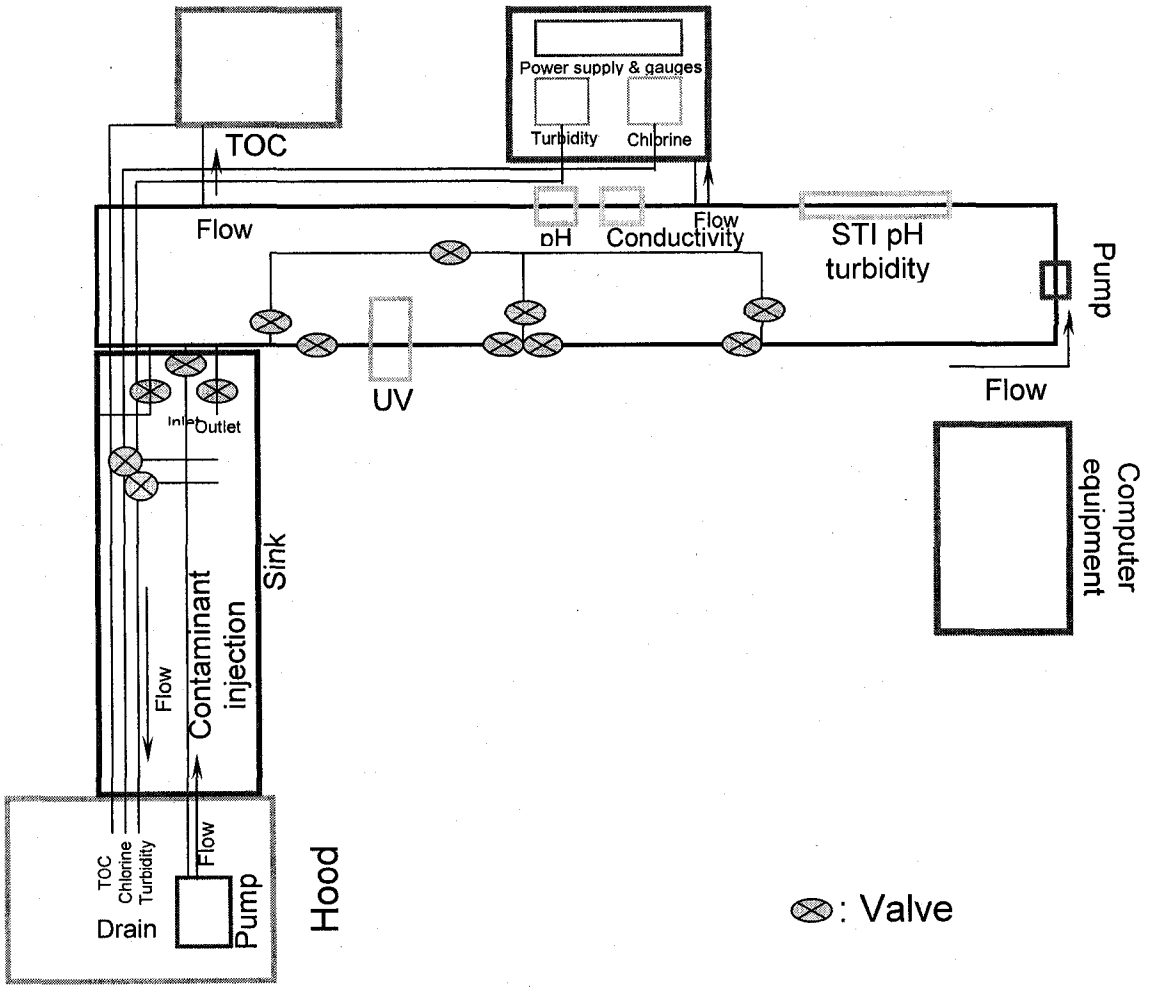



**Figure 3-6** Bench scale distribution system schematic drawing

### 3.2.2 Characterization and calibration of instruments

The UV254 characterization was part of a larger ongoing test, so multiple instruments were installed on the pipe loop. This paper examines only the results of the UV254 and TOC instruments, however all instruments are documented in this section.

The instruments used to measure pH, conductivity, turbidity, chlorine residual, TOC, and UV will detect both organic and inorganic chemicals. These instruments also detect changes in water quality by acute toxicity. Two different groups of instrument were used for this test due to character of the test. One is for batch analysis and the other is for on-line analysis. The on-line instruments required a two hour warm up period before readings were considered valid. On-line instruments that measure pH and chlorine residual were calibrated against bench top analytical equipment on a daily basis. The TOC panel, turbidimeter, and conductivity probe were all calibrated before they were placed in service. The UV254 system was calibrated by the manufacturer at the factory, so no additional calibration was necessary. Table 3-1 summarizes the analytical instruments that were used in this test.

**Table 3-1** Analytical instruments used in this test

| Parameter/ Measurement | Instrument | Method Used |
|---|---|---|
| **Batch analysis** | | |
| pH | Fischer Scientific AR-25 | Standard Method 4500-H |
| Conductivity | ECTestr Low Conductivity Meter | Standard Method 2510-B |
| Turbidity | Hach DR/3000 Spectrophotometer | Nephelometry USEPA Method 181.1 |
| Chlorine Residual | Hach Spectrophotometer | DPD colorimetric Standard Method 4500-C1G |
| TOC | Astro autoTOC 1950plus | UV/persulfate oxidation |
| **On-line analysis** | | |
| Flow | Cole-Parmer | Rotameter |
| pH | Hach EC 310 | Standard Method 4500-H |
| Conductivity | GLI C53 Conductivity Analyzer | Standard Method 2510-B |
| Turbidity | Hach 1720D/L | Nephelometry USEPA Method 181.1 |
| Chlorine Residual | Hach CL-17 | DPD colorimetric Standard Method 4500-C1G |
| TOC | Astro autoTOC 1950 plus | UV/persulfate oxidation |
| UV | Optek AF45 Sensor | UV absorbtion |

### 3.2.3 Baseline water quality data

**Figure 3-7** Bench scale distribution system photo

A city tap water connection was connected to a shut off valve, check valve and pressure regulator, which was set to 6 PSI. This regulator was then connected to the two-inch PVC pipe loop containing the following equipment (Figure 3-6): Using data logger software from Hach Company, baseline data was collected every 30 sec. The first 20,000 data points were used to define the baseline of the distribution system, and to estimate the three standard deviations from the mean. It was also used to give an explanation for 99.96% of the random variability from statistic concept. Anything outside of 99.96% represents an anomaly, and was addressed consequently. For example, 4 data samples out of 10,000 chances that the anomaly is a false positive. To determine a limit of detection, the standard deviation data from baseline test was also used to compare beaker test data to the 3-sigma values. This result will provide the first indication on the potential of using water quality parameters as surrogates to detect a contamination event.

Before contaminants were injected with the peristaltic pump, a 2-hour baseline was reestablished to ensure that contaminant-instrument response was comparable to water quality just previous to introduction of the contaminants. After the 120 minute baseline was established, the PVC pipe loop system was ready to test the contaminants. In this mode there were two different influents to the system including the tap water from the local distribution system, and one of the seven different contaminants that were pumped in using a peristaltic pump under the ventilation hood. The effluents were from the bench scale distribution system and to the two panels.

### 3.2.4 Contaminant selection

Two groups of contaminants were selected four of which were non-toxic, while the remaining seven were toxic for human being.

To investigate potential correlation between TOC and UV254 measurements, the four non-toxic chemicals were implemented. The four chemicals selected were formic acid, acetic acid, trichloro acetic acid, and potassium hydrogen phthalate. These chemicals contained organic carbon so they would be detected by the two methods. The chemicals chosen were weak acids and bases which could be drained from the PVC pipe loop, without requiring hazardous waste disposal. These served as an initial indicator to test toxic chemicals.

The next set of seven chemicals was selected as toxic "credible threat contaminants." Several key properties were identified for selecting these chemicals. These were (1) high toxicity, (2) high water solubility, (3) chemical and physical stability, (4) a lack of taste, color and odor, (5) and a low chance of detection with normal analytical methods. According to Khan et al. (2000), the criteria of chemical contaminants are as follows: (1) already used in chemical weapons, (2) available to potential terrorists, (3) likely to cause major morbidity or mortality, (4) potential of causing public panic and social disruption, and (5) requiring special action for public health preparedness. They list the following as priority chemical agents: arsenic, pesticides, and cyanides. The National Research Council (2002) addresses morbidity and mortality, or toxicity, by focusing on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents, and are persistent in water. The US Army Center

for Health Promotion and Preventive Medicine listed sodium cyanide and fluoroacetate as priority potential chemical threat agents (Burrows et al., 1997).

Thus the seven toxic contaminants that were used in this research included: aldicarb, nicotine, sodium fluoroacetate, sodium arsenate, sodium cyanide, cycloheximide, and dicrotophos. According to the criteria specified above, all are considered very credible water threat contaminants.

### 3.2.5 Beaker test

For this test, four different desired stock concentrations of seven contaminants were measured using an analytical scale, and mixed with tap water. Using five different bench top analytical instruments in Table 3-1, the beaker tests were conducted. The distribution system experiments used on-line instrument.

Baseline water was collected from the PVC pipe loop after 10 days of initial run time. This was done after the collection of 20,000 data points on the on-line instruments. To obtain tap water only data (no chemical), tap water was added to a beaker, and the parameters were measured using bench top analytical equipment. Then the contaminants were added to the tap water in the beakers in increasing concentrations, and readings were noted from the bench top analytical equipment. The difference between the readings with and without contaminants was recorded, and the change in the water quality parameters was determined.

In addition to the standard analytical bench top instruments, an HP 8452A diode array spectrophotometer was used to characterize each chemical across a wide array of wavelengths (approximately 200 to 800nm). This data was used to ensure there would be adequate response at the regions of interest (254nm).

The beaker tests were then repeated with DI water instead of tap water, to two different solvents which are DI water and tap water were used to obtain compared data.

### 3.2.6 Bench scale distribution system tests

During this test, two different data sets were collected (with and without contaminants). The influent to the system for the first test was tap water from the local distribution system. The effluent was from the 2 in pipe loop, which stands for distribution system, to the instrument panels, to the instrument connected on distribution system, and the non-hazardous waste water effluent from the panels and TOC.

During the second data collection (with contaminants), a 100-minunte baseline was used to ensure that instrument response was compared to water quality just previous to introduction of the contaminants. After 100-minute baseline was established, the system was ready to inject one of the seven different contaminants. Each contaminant was pumped into the PVC pipe loop just after the flow regulator from the local distribution system. The effluent was from the 2 in pipe loop, which stands for distribution system, to the instrument panels, to the instrument connected on distribution system. The hazardous waste was redirected with the use of valves and collected under the ventilation hood for proper disposal.

Initially it was noted that the increased flow and turbulence in the system stirred up particulate matter which had settled in the PVC piping, so the peristaltic pump that re-circulates the system water was turned on and the on-line equipment allowed stabilizing for several hours. After the monitoring equipment had returned to steady state, and had shown consistent readings, the 100-minutes baseline data collection began.

## 3.3 Results and Discussion

The focus of this research is on detecting contamination events in the distribution system real-time using water quality parameters that will change significantly in the event of contamination. The parameters that will be used in this study to detect changes in drinking water quality include chlorine residual, turbidity, pH, conductivity, UV, and TOC, however only the results of UV254 and TOC are presented in this paper.

### 3.3.1 Baseline

For over one week, the water quality in the distribution system was collected every 30 seconds to obtain baseline data, utilizing on-line analytical equipment. Over 20,000 data points per every two weeks were collected between July-October 2005 and first two months 2006. Over 16,000 of the data points were collected during a one-week period in January 2006.

The baseline provided valuable information to determine what is "normal" in the distribution system relative to the time that the data was collected. To decide detection limit for contaminant, $\sigma$ data from the on-line baseline was used in union with the beaker test data. This was used as the first signal on the prospective of using water quality parameters as surrogates to detect a contamination occurrence. The relationship between baseline drinking water quality conditions and timeframe that the data was collected is shown in Table 3-2.

**Table 3-2** On-line monitoring baseline water quality results

| Time | pH | Conductivity (μS/cm) | Turbidity (NTU) | Chlorine (mg/L) | TOC (mg/L) | UV (CU) |
|---|---|---|---|---|---|---|
| Minimum | 7.7 | 81 | 0.079 | 0 | 0.008 | 1.005 |
| Average | 8.02 | 103 | 0.094 | 0.23 | 1.308 | 1.024 |
| Maximum | 8.13 | 157 | 0.223 | 0.31 | 2.648 | 1.064 |
| $\sigma$ | 0.05 | 8 | 0.024 | 0.04 | 0.154 | 0.01 |
| $3\sigma$ | 0.15 | 23 | 0.072 | 0.11 | 0.462 | 0.03 |

If the baseline data does not fit to a normal distribution, then there is a reasonable question which is "what exactly is the significance of three-sigma?" Three-sigma is the assumption that 99.96% of the baseline data under normal conditions will fall within x-bar plus or minus three-sigma valid. The percentage of baseline data points per parameter that is compromised in the x-bar plus or minus three-sigma shows in Table 3-3. As Table 3-3 demonstrates, it is fair to state that any data point outside of x-bar plus or minus three-sigma represents an anomaly.

**Table 3-3** Percentage of baseline data points falling within average +/- 3σ

| PH | Conductivity (μS/cm) | Turbidity (NTU) | Chlorine (mg/L) | TOC (mg/L) | UV (CU) |
|---|---|---|---|---|---|
| 99.02 % | 99.99 % | 94.92 % | 99.40 % | 99.09 % | 98.52 % |

Figure 3-8 shows time series plots of more than 20,000 baseline data set. The difference and common in time series plots figure is that every parameter behaves differently with respect to time, and that the values of the parameters are in a constant state of flux. Because the baseline water quality data is always changing, the baseline water quality in real-time distribution systems is important. To detect a contaminant event, the on-line analysis must have an established baseline data to compare the suspect data. This is significant relative to the time that the comparison is taking place. Without the timely baseline data, the potential exists to inaccurately determine that an anomalous event has or hasn't taken place. Descriptive statistics and determining anomalous events however, could prove very useful.

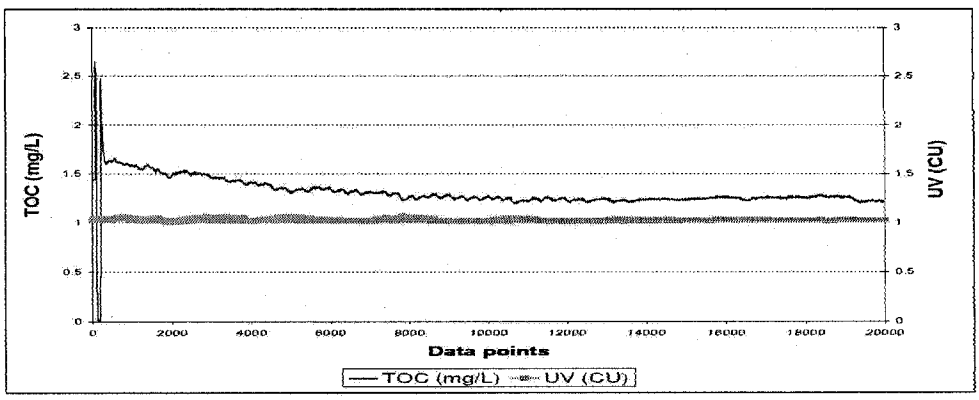



**Figure 3-8** Baseline water quality time series plot

### 3.3.2 Contaminants

A) Aldicarb

Aldicarb is directly toxic through oral, dermal, and inhalation; it is toxic when plants systemically exposed are consumed and secondary poisoning occurs when exposed prey items, such as insects, rodents, and birds, are consumed by preators and scavengers.

B) Cycloheximide

Cycloheximide is an odorless, white, crystalline powder used in hospital and research laboratories as an antibiotic, a protein synthesis inhibitor, or a plant growth regulator. Cycloheximide also has broader agricultural use as a fungicide, but this use is being discontinued due to the recent findings of birth defects at low doses in animals.

C) Dicrotophos

Dicrotophos emits toxic fumes of phosphorus and nitrogen oxides when heated to decomposition. In two human poisoning cases, symptoms such as cramps, nausea, vomiting, diarrhea, dyspnea, and general weakness occurred when exposed to spray, and loss of pulse and respiration occurred when ingested. In both cases, atropine and pralidoxime relieved the symptoms and the patients showed improvement.

D) Nicotine

Nicotine is one of the more than 4,000 chemicals found in the smoke from tobacco products such as cigarettes and pipes. Nicotine is a naturally occurring colorless liquid that turns brown and acquires the odor of tobacco when exposed to air.

E) Sodium Arsenate

Sodium arsenate is a pentavalent form of inorganic arsenic. It is a heptahydrate, which normally exists as colorless crystals with no discernible odor. Inorganic arsenical compounds have been classified as Class an oncogens, demonstrating positive oncogenic effects based on sufficient human epidemiological evidence.

F) Sodium Cyanide

Sodium cyanide is a product of a series of reactions involving sodium carbonate, limestone, carbon, and oxygen from the air. Sodium cyanide and potassium cyanide are both white solids with a bitter, mild almond-like odor in damp air.

G) Sodium Fluoroacetate

Sodium fluoroacetate, also known as compound 1080, sodium monofluororacetate, fratol, furatol, ratbane, and yasoknock, is a rodenticide that has been previously used in the U.S. to control gophers, squirrels, coyotes, and prairie dogs, and is presently banned.

### 3.3.3 Toxicity of water calculations

The information on the toxicity of the water contaminants that were used in this research effort shows in Table 3-4. The minimum concentration in a glass of water to reach $LD_{50}$ (lethal dose for 50% of the population) is based on a 60kg person drinking a 0.5L glass of water. In addition, physical and chemical properties of these same contaminants are provided.

**Table 3-4** Properties of interest for credible threat chemical contaminants

| Property | Aldicarb | Cyclo-Heximide | Dicro-tophos | Nicotine | Sodium Arsenate | Sodium Cyanide | 1080 |
|---|---|---|---|---|---|---|---|
| Human Oral $LD_{50}$ (mg/kg) | 0.8[15] | 2 (rat) | 12.7 (rat) | 10 (mouse) | 20[16] | 3-7[14] | 2-5[14] |
| Min Concentration in glass of water to reach min human oral $LD_{50}$ (mg/L) | 96 | 240 | 1,524 | 1,200 | 2,400 | 360 | 240 |
| Life-Threatening Toxicity (mg/L) | NA | NA | NA | NA | 14[18] | 48[18] | 60[17] |
| CAS number | 116-06-3 | 66-81-9 | 141-66-2 | 54-11-5 | 7778-43-0 | 143-33-9 | 62-74-8 |
| Chemical Formula | $C_7H_{14}N_2O_2S$ | $C_{15}H_{23}NO_4$ | $C_8H_{16}NO_5P$ | $C_{10}H_{14}N_2$ | $Na_2HAsO_4$ | NaCN | $C_2H_2FO_2Na$ |
| Molecular Weight | 190.25 | 281.35 | 237.21 | 162.23 | 185.9 | 49.01 | 100.03 |
| Soluble in Water | 0.6g/100 mL | 2-5g/100mL | Miscible | Miscible | 61g/100mL | 37g/100 mL | Extremely |
| Stability in Water | Stable | Stable | Stable in glass container | Stable in glass container | Stable | Stable | $t_{1/2}$ = 2-6 days in water |

### 3.3.4 Beaker tests

Beaker tests were conducted before the contaminants were introduced into the bench scale distribution system. There are several objectives to obtain during the beaker tests; these are (1) determining which parameters would be most influenced by specific contaminants, (2) determining a fairly accurate minimum concentration of contaminants in a controlled environment that would change water quality, and (3) anticipating concentrations that would be pumped into the distribution system.

### 3.3.5 Non-Toxic Chemical Beaker Tests

Initially, four concentrations of the four non-toxic chemicals were run as grab samples through the bench top TOC analyzer, and scanned with the HP 8452A diode array spectrophotometer. The 8452A device characterizes each chemical over a wide array of wavelengths (approximately 200 to 800 nm). The concentrations were 1, 3, 5, 7 and 10ppm. There was no TOC grab sample data for four non-toxic chemicals.

A) Formic Acid

Formic Acid was best detected at 10ppm around 200 nm; however trace amounts were also detected at lower concentrations.

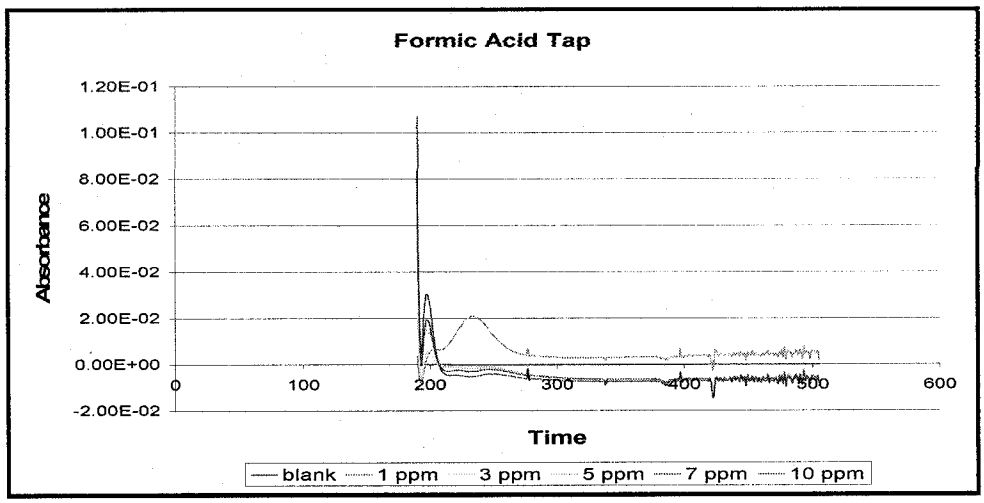



**Figure 3-9** Formic Acid with tap water absorbance vs. wavelength

B) Acetic Acid

All concentrations of Acetic Acid were easily detected around 200 nm.

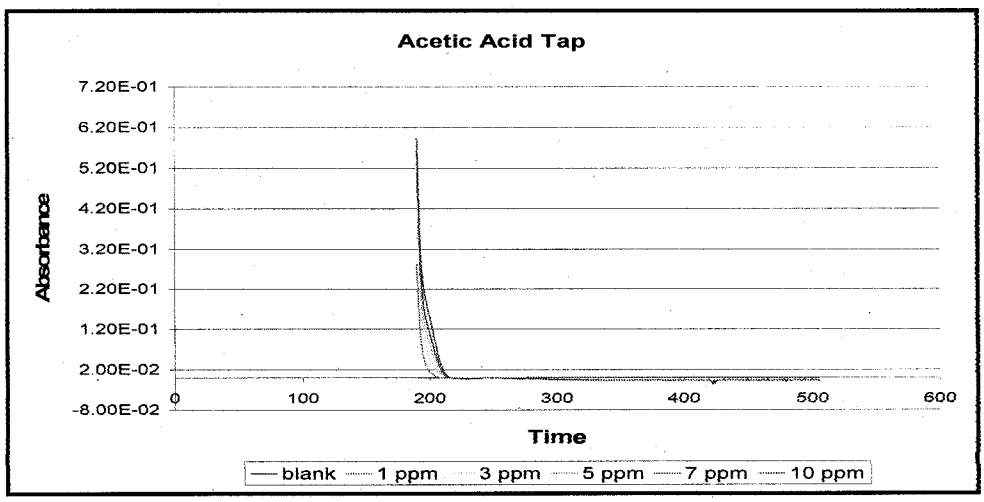



**Figure 3-10** Acetic Acid with tap water absorbance vs. wavelength

C) Trichloro Acetic Acid

All concentrations of Acetic Acid were detected around 200 nm. The 1ppm solution was almost not detected, however.

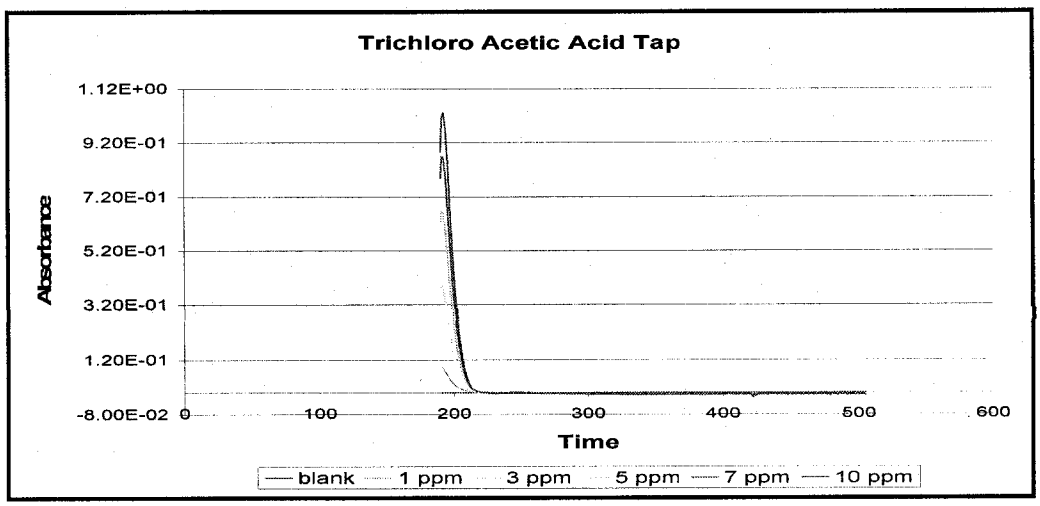



**Figure 3-11** Trichloro Acetic Acid with tap water absorbance vs. wavelength

D) Potassium Hydrogen Phthalate

All five concentrations of Potassium Hydrogen Phthalate were detected around 200 nm.

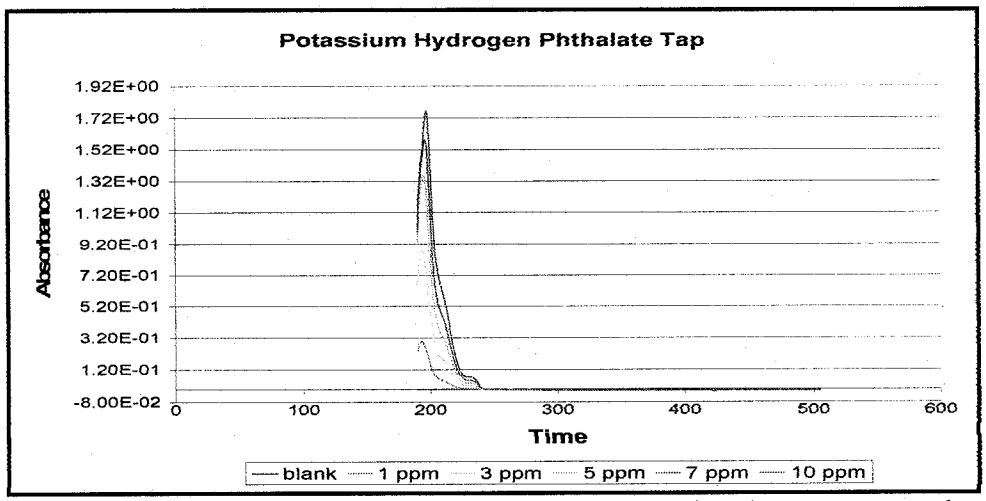



**Figure 3-12** Potassium Hydrogen Phthalate with tap water absorbance vs. wavelength

Acetic Acid has the highest absorbance peak data, and the other three chemicals have similar peak data. Out of three chemicals, Potassium Hydrogen Phthalate was easily detected due to the Carbon amount.

### 3.3.6 Toxic Chemical Beaker Tests

Next, four concentrations of the seven toxic chemicals were run as grab samples through the AstroTOC analyzer, and scanned with the HP 8452A diode array spectrophotometer on the bench. The results are shown below.

A) Aldicarb

Aldicarb has strong UV peaks at approximately 200nm for the 5 concentrations noted. The maximum peak was around 0.68A for the 10ppm concentration. There is also a smaller secondary peak around 250 nm for higher concentrations (7 and 10ppm). The blank also showed an unusual response below approximately 250nm. The TOC analyzer had good increasing responses to all concentrations.

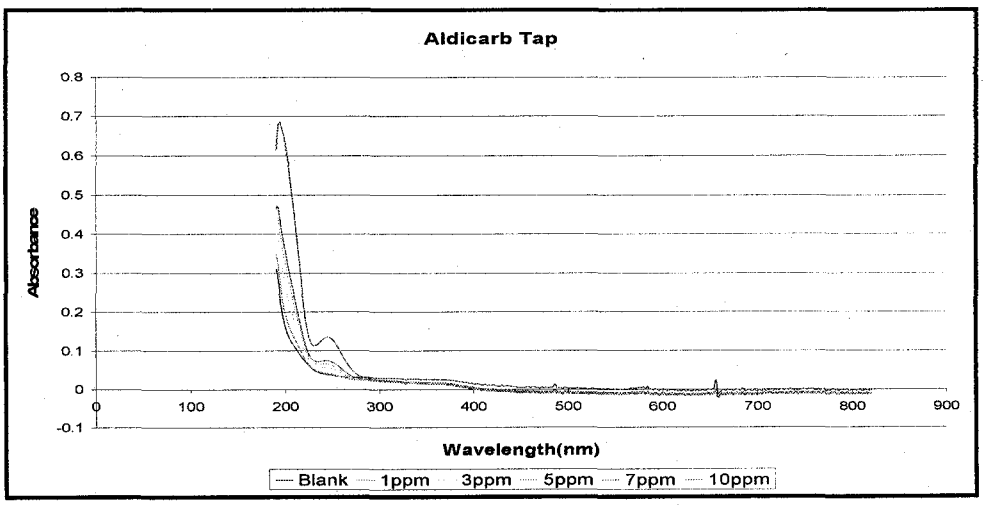



**Figure 3-13** Aldicarb with tap water absorbance vs. wavelength

**Table 3-5** Aldicarb ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Aldicarb | 0 (1.03) | 0 |
| | 1 | 0.56 |
| | 2 | 1.12 |
| | 5 | 2.1 |
| | 10 | 4.07 |
| | 20 | 8.97 |
| | 40 | 8.97 |

B) Cycloheximide

Cycloheximide has a strong UV peak at approximately 200nm for the 5 tested. The maximum peak was approximately 0.47A for the 10ppm concentration. The TOC concentration showed good responses above the 1ppm level, but tapered off above 4ppm.

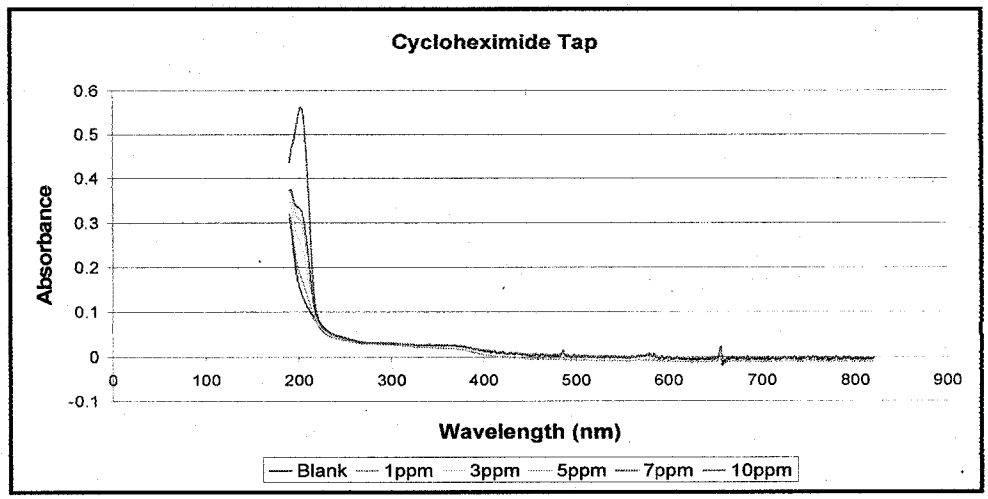



**Figure 3-14** Cycloheximide with tap water absorbance vs. wavelength

**Table 3-6** Cycloheximide ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Cycloheximide | 0 (1.03) | 0 |
| | 1 | 0.45 |
| | 4 | 1.63 |
| | 6 | 1.64 |
| | 8 | 1.63 |

C) Dicrotophos

Dicrotophos has a strong UV peak at approximately 200nm for the 5 tested.

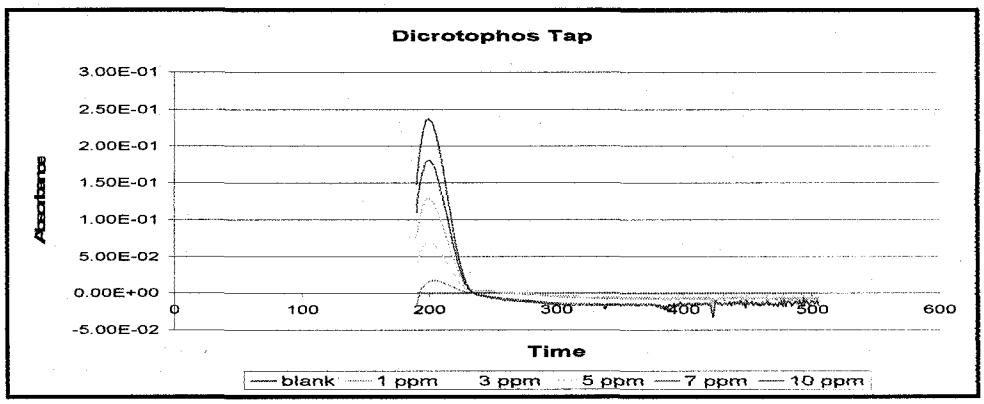



**Figure 3-15** Dicrotophos with tap water absorbance vs. wavelength

Dicrotophos also has a strong TOC response, with responses over 40ppm.

**Table 3-7** Dicrotophos ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Dicrotophos | 0 (1.03) | 0 |
| | 1 | 0.48 |
| | 2 | 0.76 |
| | 5 | 1.85 |
| | 10 | 3.25 |
| | 20 | 6.04 |
| | 40 | 8.97 |

D) Nicotine

No test data was available for the benchtop absorbance scan of Nicotine; however the TOC response was excellent for all samples, with increasing ppm for each higher concentration.

**Table 3-8** Nicotine ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Nicotine | 0 (1.25) | 0 |
| | 1 | 0.7 |
| | 4 | 2.86 |
| | 10 | 6.83 |
| | 20 | 8.75 |

E) Sodium Cyanide

Sodium Arsenate has a strong UV peak at approximately 200nm for the 5 concentrations tested. The maximum peak was 0.35A at 10ppm. All concentrations down to 1ppm were nearly at the peak absorbance, indicating Sodium Cyanide can be detected at very low concentrations. The grab sample TOC data also shows increasing responses to Sodium Arsenate for all concentrations.

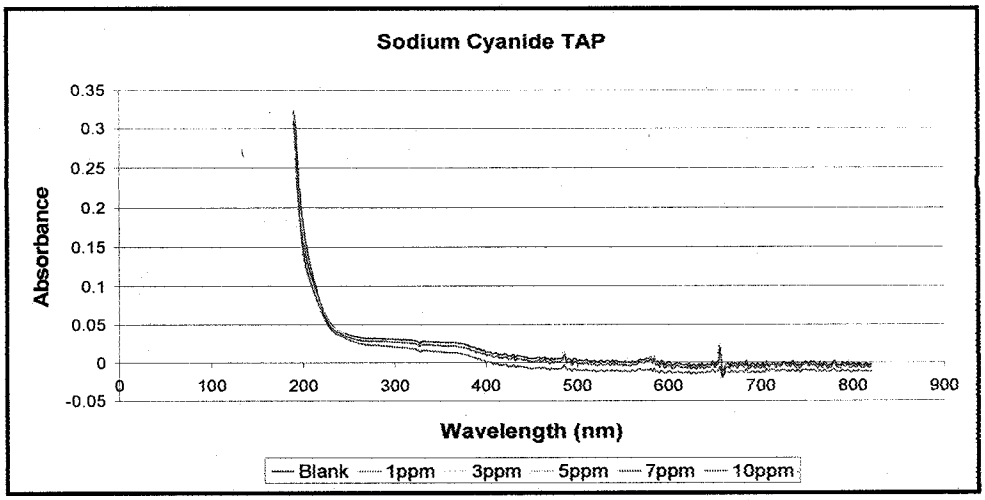



**Figure 3-16** Sodium Cyanide with tap water absorbance vs. wavelength

**Table 3-9** Sodium Cyanide ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Sodium Cyanide | 0 (1.03) | 0 |
| | 1 | 0.13 |
| | 2 | 0.27 |
| | 4 | 0.6 |
| | 6 | 1.01 |
| | 8 | 1.21 |
| | 12 | 1.86 |
| | 24 | 3.65 |

F) Sodium Arsenate

Sodium Arsenate has a strong UV peak at approximately 200nm for the 5 concentrations tested. The maximum peak was 0.35A at 10ppm. No grab sample TOC data was available for Sodium Arsenate.

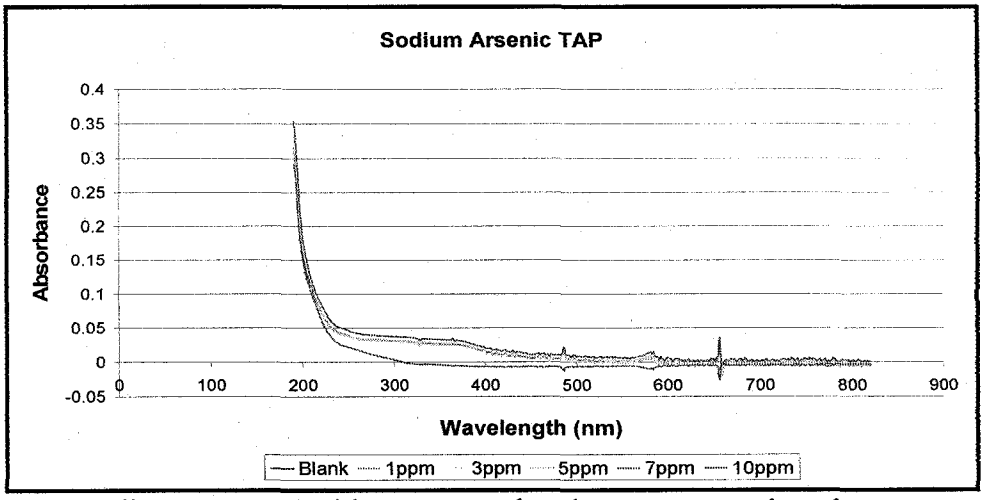



**Figure 3-17** Sodium Arsenate with tap water absorbance vs. wavelength

G) Sodium Fluoroacetate

Like Sodium Cyanice, Sodium Arsenate has a strong UV peak at approximately 200nm for the 5 concentrations tested with all concentrations yielding nearly the same peak absorbance. The maximum peak was 0.31A at 10ppm.

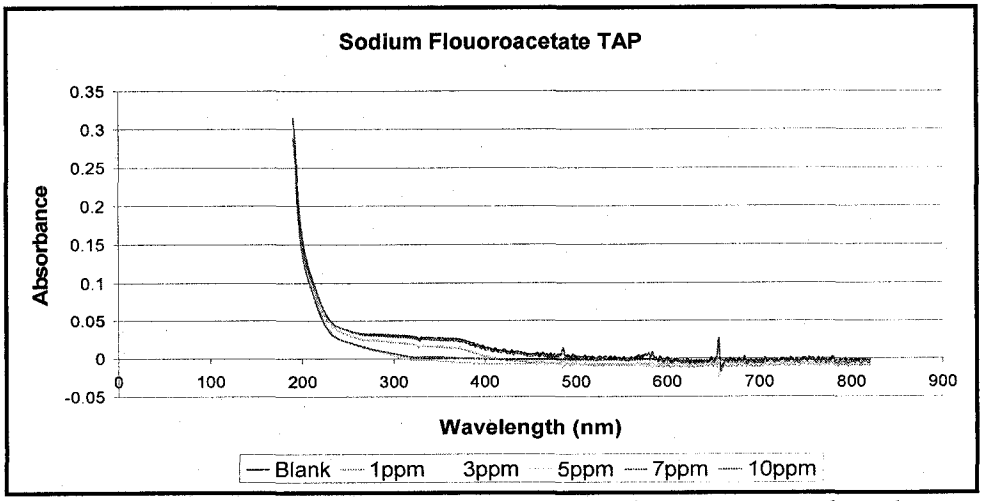



**Figure 3-18** Sodium Fluoroacetate with tap water absorbance vs. wavelength

The TOC response was also very good for Sodium Fluoracetate, with linearly increasing readings up to 40ppm.

**Table 3-10** Sodium Fluoroacetate ΔTOC vs. concentration

| Contaminant | Concentration (mg/L) | Δ TOC (mg/L) |
|---|---|---|
| Sodium Fluoroacetate (1080) | 0 (1.29) | 0 |
| | 1 | 0.29 |
| | 4 | 0.89 |
| | 10 | 2.75 |
| | 20 | 5.18 |
| | 40 | 8.71 |
| | 80 | 8.71 |

### 3.4 Bench scale distribution system tests

After the beaker tests, contaminants were pumped into the bench top distribution system in known, increasing concentrations. The contaminants were injected through 1/8" tubing into the 2" pipe loop, and then diluted due to mixing within the system before flowing through the instrument panels. At this point, the contaminant concentration flowing through the panels was an unknown. Because of this, the beaker tests needed to be performed to provide an indication of the concentration flowing through the on-line panels, similar to a calibration curve.

To establish a baseline condition, 100 minutes of data was collected. Each chemical was then injected at increasing concentrations using the peristaltic pump as noted in the methods section above. The pipe loop was flushed after each chemical was tested.

### 3.4.1 Non-Toxic Chemical Injections

Initially the four non-toxic acids were injected into the pipe loop at increasing concentrations of 1, 3, 5, and 10ppm. The results from the TOC analyzer and UV254 instrument from these injections are shown below.

A) Formic Acid

Both TOC and UV254 showed good responses in the pipe loop to Formic Acid above 5ppm.

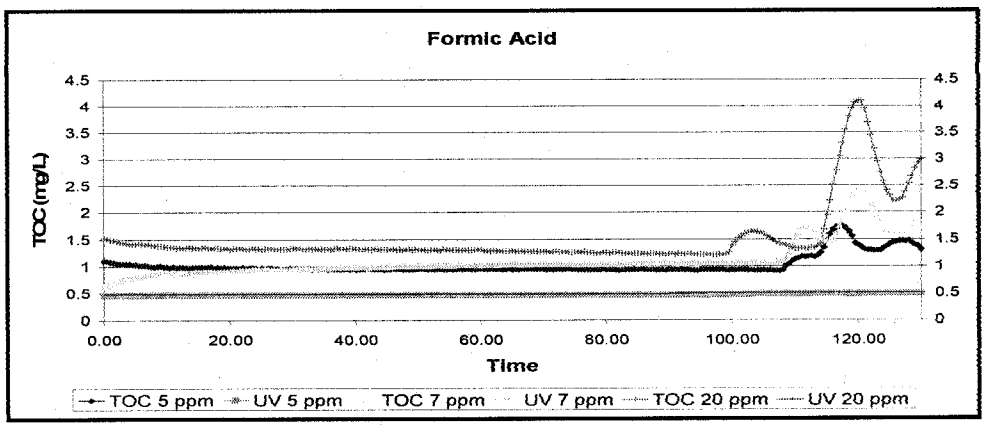



**Figure 3-19** Formic Acid TOC/UV loop data

B) Acetic Acid

Both TOC and UV254 showed good responses in the pipe loop to Acetic Acid above 3ppm.

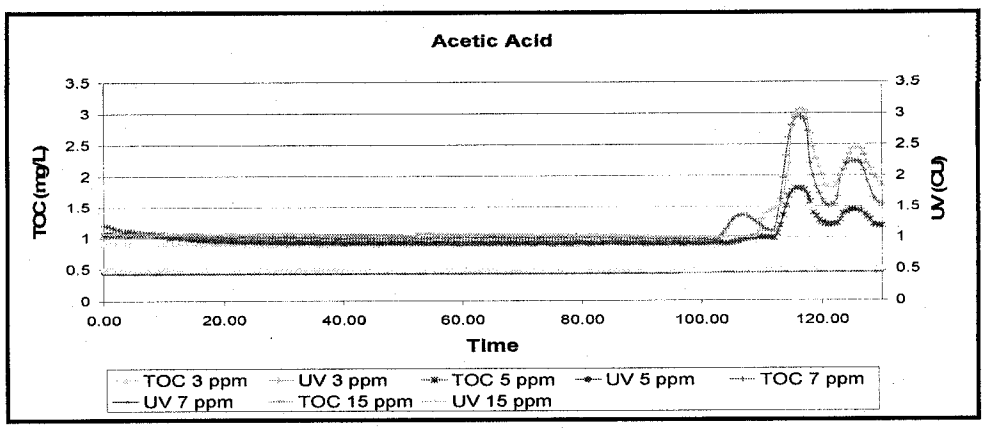



**Figure 3-20** Acetic Acid TOC/UV loop data

C) Trichloro Acetic Acid

Both TOC and UV254 showed good responses in the pipe loop to Trichloro Acetic Acid above 1ppm.

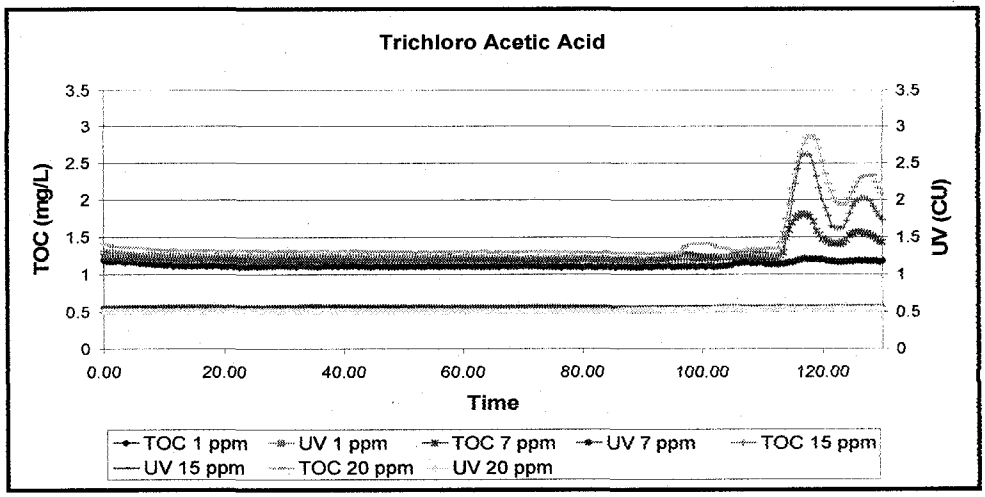



**Figure 3-21** Trichloro Acetic Acid TOC/UV loop data

D) Potassium Hydrogren Phthalate

Both TOC and UV254 showed good responses in the pipe loop to Potassium Hydrogen Phthalate Acid above 3ppm.

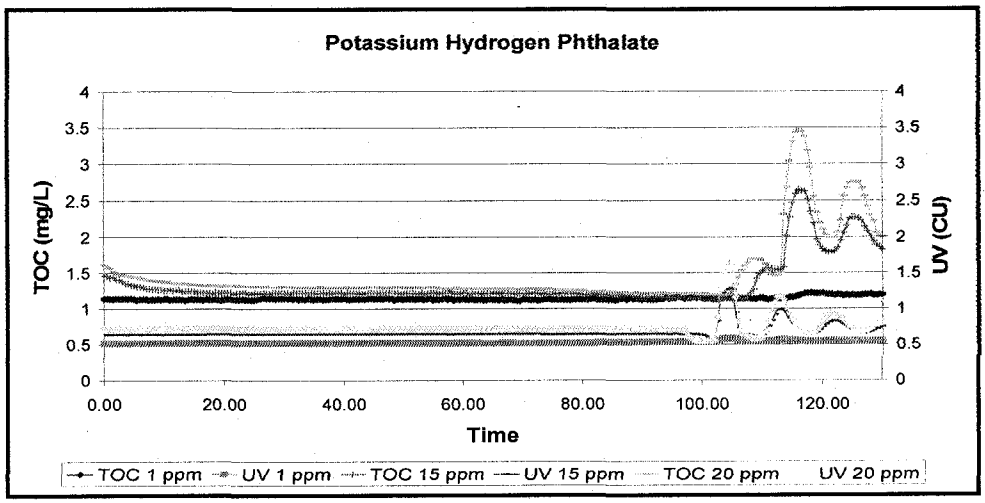



**Figure 3-22** Potassium Hydrogen Phthalate TOC/UV loop data

### 3.4.2 Toxic Chemical Injections

Next the seven toxic chemicals were injected into the pipe loop at increasing concentrations of 1, 3, 5 and 10ppm. The results from the TOC analyzer and UV254 instrument from these injections are shown below.

A) Aldicarb

Both TOC and UV254 showed good responses in the pipe loop to Alidcarb above 1ppm. The initial TOC sample showed unusual behavior for the first 160 minutes, indicating instrument warm up or that the pipe loop was not fully flushed of contaminates.

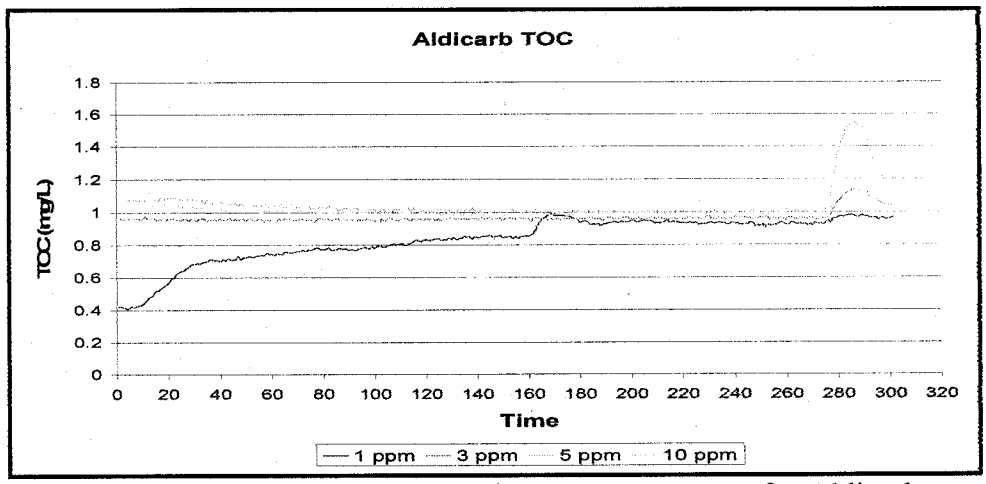



**Figure 3-23** TOC time series plot of on-line instrument response for Aldicarb

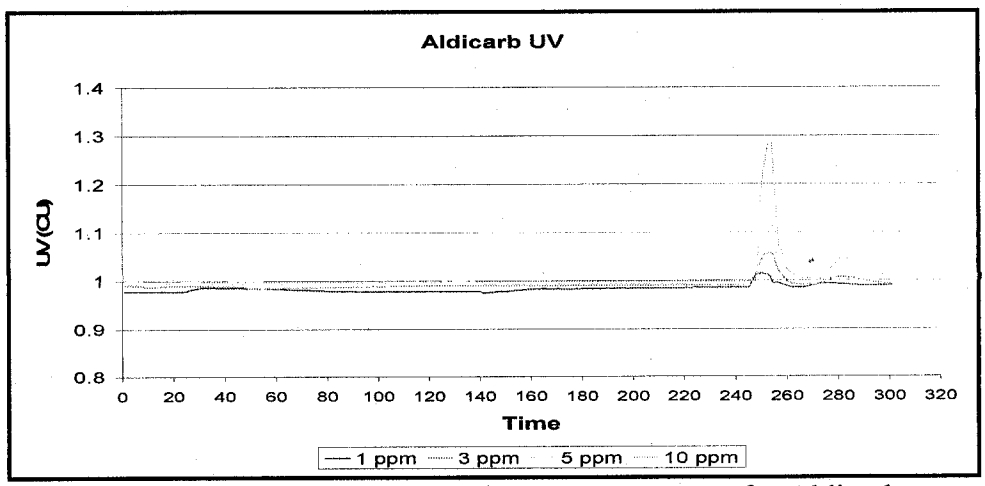



**Figure 3-24** UV time series plot of on-line instrument response for Aldicarb

B) Cycloheximide

Both TOC and UV254 showed good responses in the pipe loop to Cycloheximide for all concentrations tested. The initial TOC sample showed unusual behavior for the first 160 minutes, indicating instrument warm up or that the pipe loop was not fully flushed of contaminates.

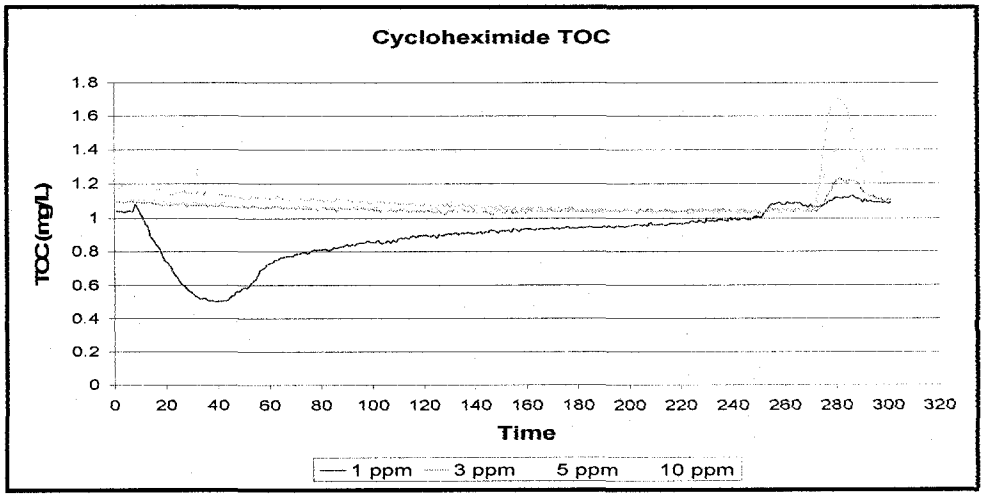



**Figure 3-25** TOC time series plot of on-line instrument response for Cycloheximide

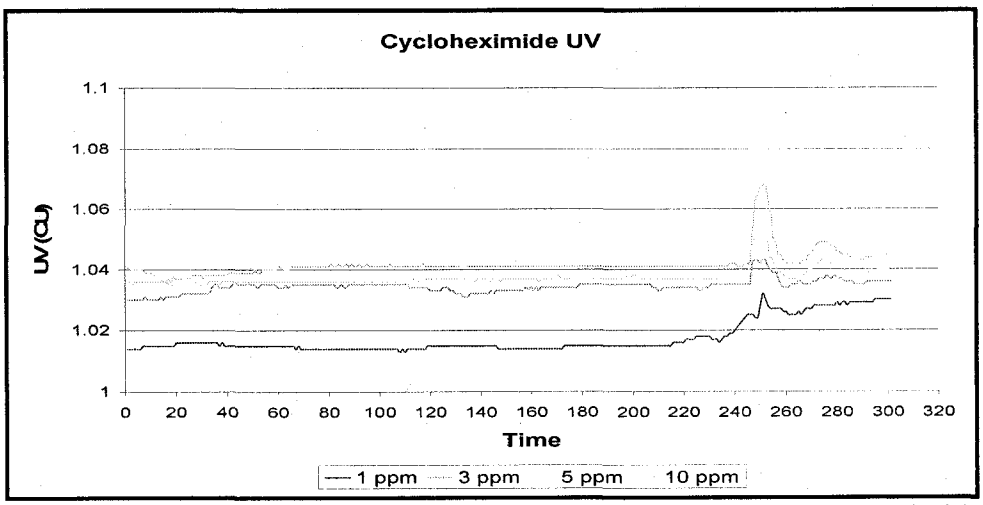



**Figure 3-26** UV time series plot of on-line instrument response for Cycloheximide

C) Dicrotophos

Dicroptphos is detected by TOC, with a maximum peak of 1.5 mg/L for the 10ppm injection. The 1ppm injection noted unusual behavior initially, indicating the water in the loop may have been agitated or not fully flushed of contaminates. UV254 showed similar response to TOC.

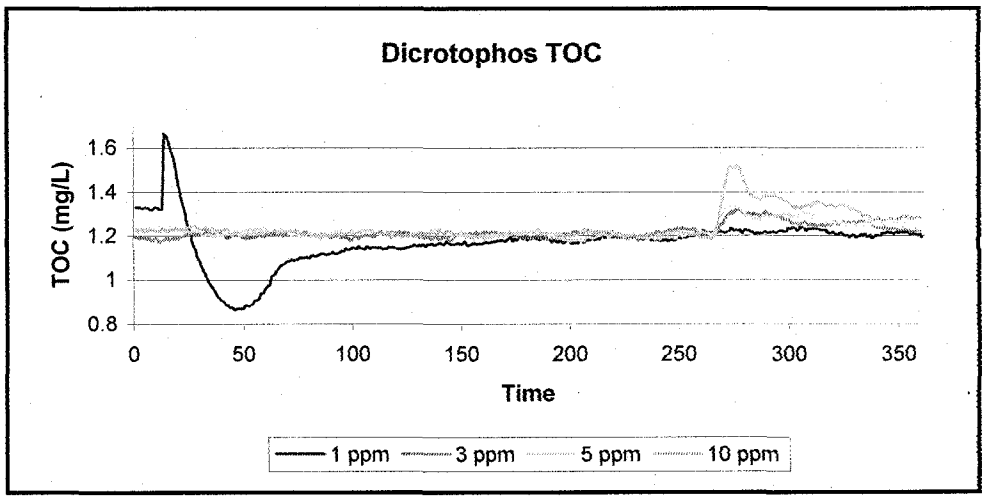



**Figure 3-27** TOC time series plot of on-line instrument response for Dicrotophos

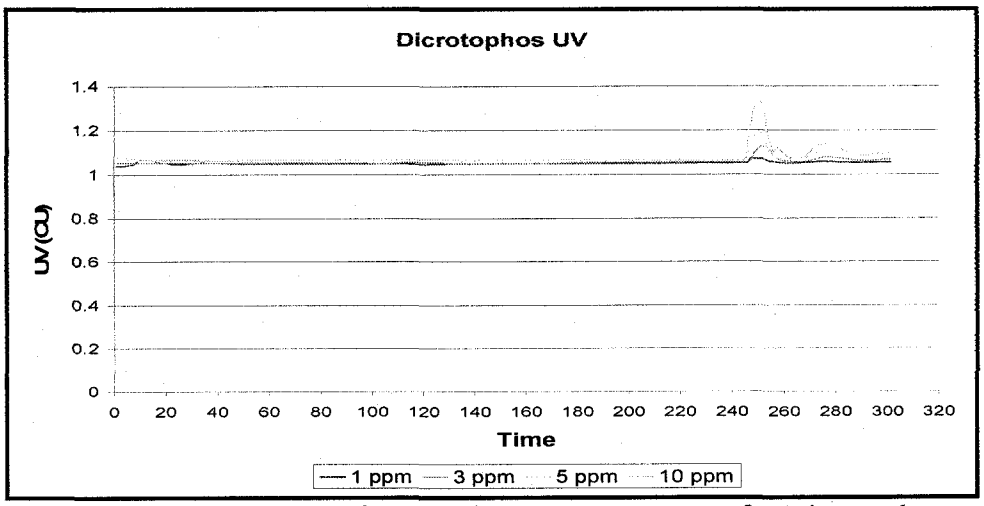



**Figure 3-28** UV time series plot of on-line instrument response for Dicrotophos

D) Nicotine

Nicotine showed a very strong response to both TOC and UV254 for nearly all concentrations.

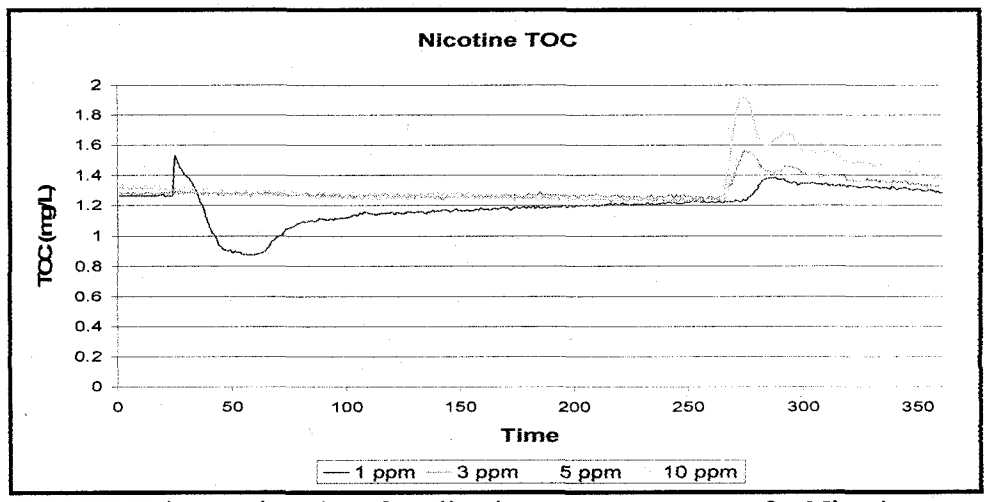



**Figure 3-29** TOC time series plot of on-line instrument response for Nicotine

Nicotine is also easily detected by UV254 at concentrations above 1ppm.

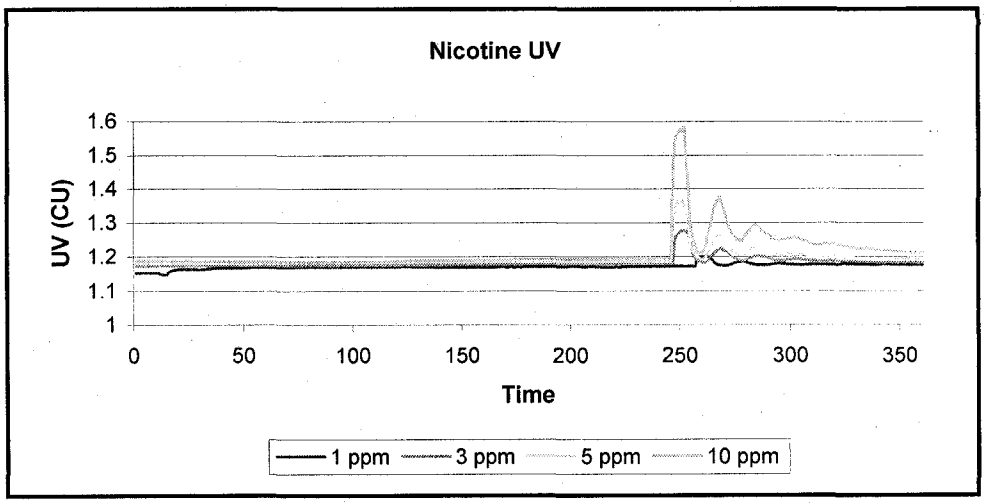



**Figure 3-30** UV time series plot of on-line instrument response for Nicotine

E) Sodium Arsenate

Sodium Arsenate showed a good response to the UV254 instrument; however the TOC analyzer only saw a small rise in readings. This is unusual because the bench-top devices both showed very good correlation with all concentrations of Sodium Arsenate. Sodium Arsenate doesn't have organic carbon. TOC and UV254 shouldn't have any response with these two devices.

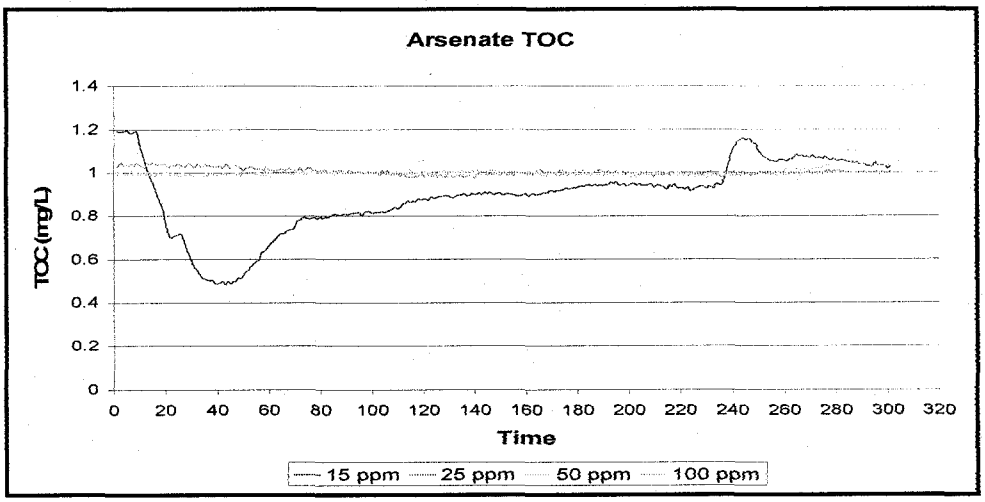



**Figure 3-31** TOC time series plot of on-line instrument response for Sodium Arsenate

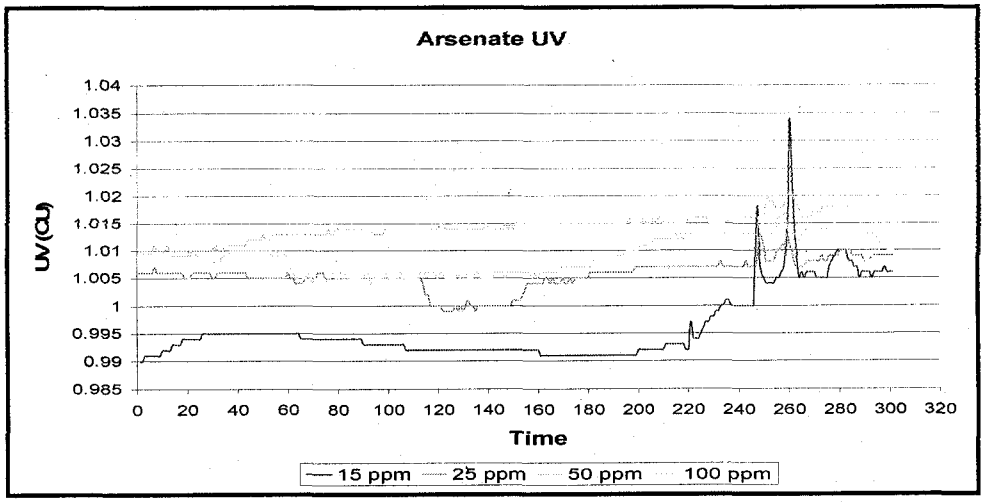



**Figure 3-32** UV time series plot of on-line instrument response for Sodium Arsenate

F) Sodium Cyanide

Sodium Cyanide showed good correlation in the pipe loop with both TOC and UV254. The 1ppm, sample, however, showed a usual response to TOC until the sample was injected.

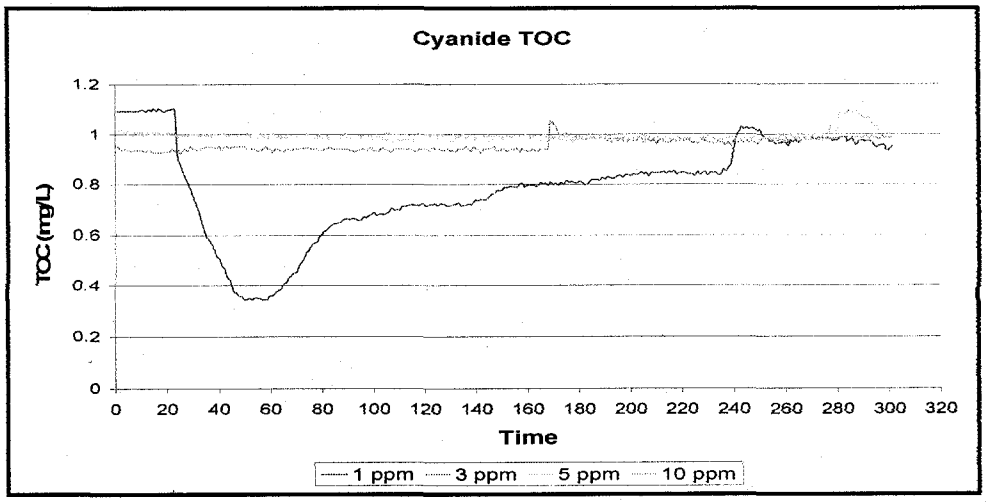



**Figure 3-33** TOC time series plot of on-line instrument response for Sodium Cyanide

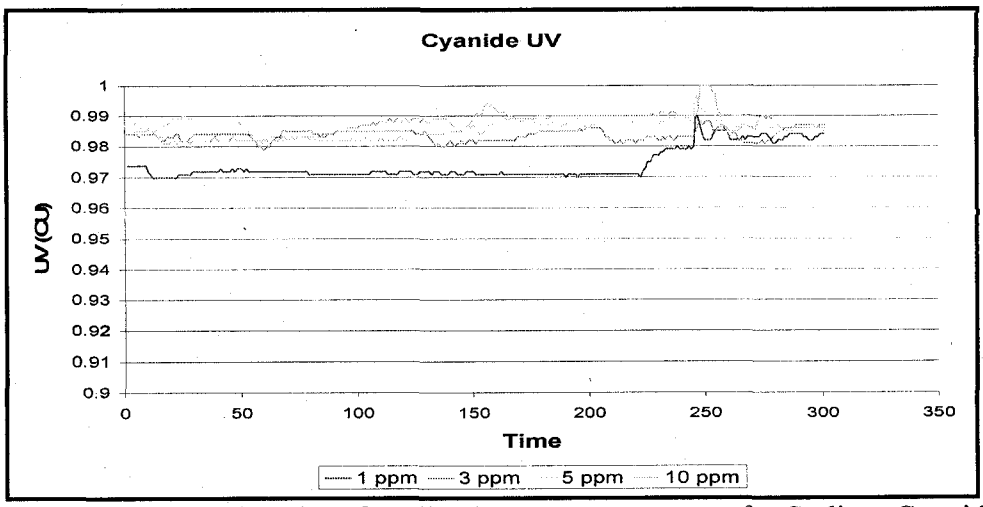



**Figure 3-34** UV time series plot of on-line instrument response for Sodium Cyanide

G) Sodium Fluoroacetate

Sodium Fluoroacetate (1080) was difficult to detect in the pipe loop for both the TOC and UV254 instruments. This is unusual because the bench-top devices both showed very good correlation with all concentrations of 1080.

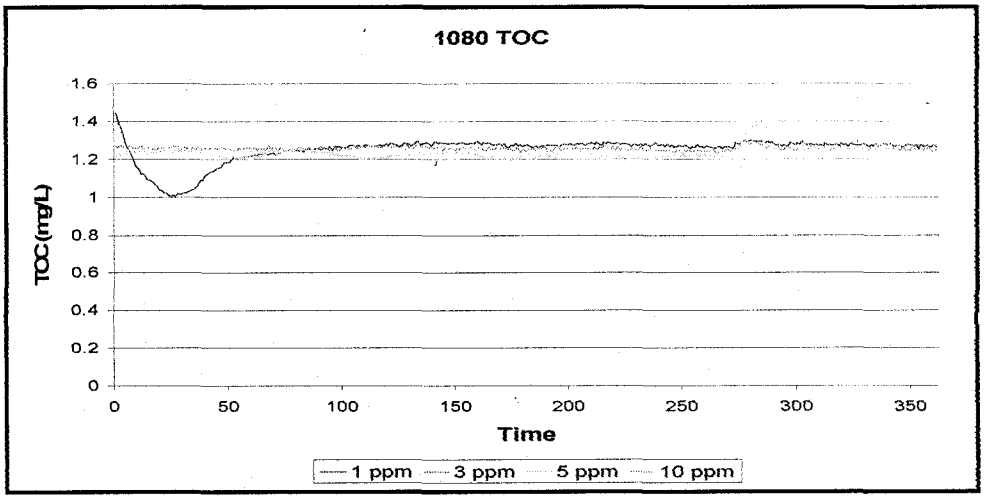



**Figure 3-35** TOC time series plot of on-line instrument response for Sodium Fluoroacetate

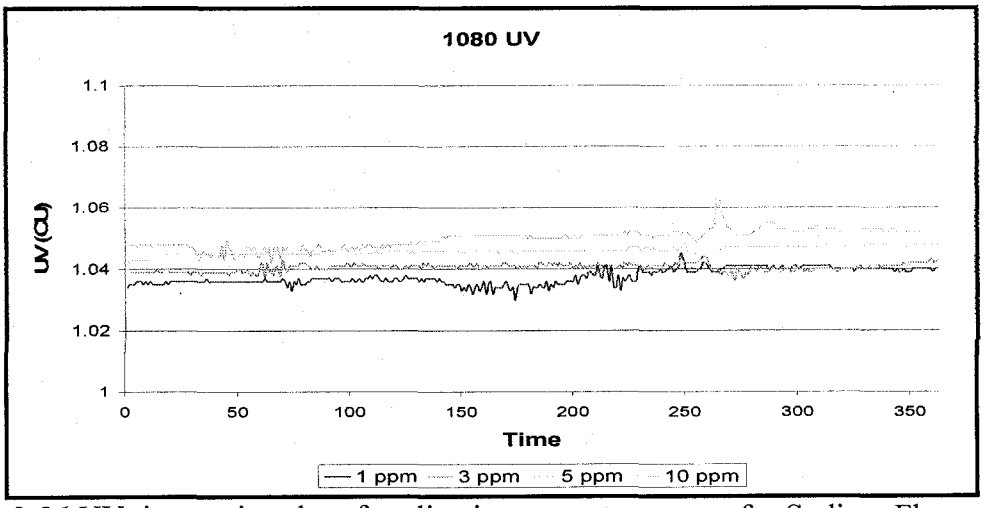



**Figure 3-36** UV time series plot of on-line instrument response for Sodium Fluoroacetate

### 3.4.3 Limit of Detection Results

The values in Table 3-11 indicate the lowest concentration that the contaminant was detected at using the water quality parameter. These values are the result of comparing the change in the water quality parameter to both the three-sigma value from the 100-minute baseline, and the published instrument error. Highlighted values indicate the lowest limit of detection, or a recommended water quality surrogate for detecting that contaminant. Sodium cyanide has good response with TOC analyzer; however the other parameters are recommended water quality surrogate for detection. Only two inorganic compounds TOC and UV are not highlighted.

**Table 3-11** Limits of detection for contaminants per water quality surrogate

| Contaminant | pH | Conductivity | Turbidity | Chlorine residual | TOC | UV |
|---|---|---|---|---|---|---|
| Aldicarb (mg/L) | 1 | >10 | 1 | 1 | 1 | 1 |
| Cycloheiximide (mg/L) | 3 | 3 | 3 | 3 | 1 | 1 |
| Dicrotophos (mg/L) | 1 | 3 | 1 | 3 | 1 | 1 |
| Nicotine (mg/L) | >10 | 3 | >10 | 1 | 1 | 1 |
| Sodium Arsenate (mg/L) | >100 | 25 | <15 | >100 | >100 | >30 |
| Sodium Cyanide (mg/L) | 1 | 5 | 1 | 1 | 5 | 3 |
| Sodium Fluoroacetate (mg/L) | 5 | 3 | 3 | 10 | 3 | 3 |

### 3.4.4 Response Time Results

The values in 3-12 indicate the lag time from injection that shows start, peak, and stop time. Start time represented the interval time from injection point to UV 254 parameter or TOC analyzer point. For aldicarb, for example it took approximately 15 minutes to arrive at TOC analyzer and 2 minutes to UV254.

Stop time showed the interval time between start points to returning to the 3 sigma value. Usually TOC took longer than UV owing to several reasons such as length of tubing to the TOC analyzer, burning and analysis time. For adlicarb, for example, it

took approximately 11 minutes for TOC stop and 7 min for UV254 stop. Peak time is calculated by dividing the start and stop interval time in half.

**Table 3-12** Lag time at different contaminants at 5ppm

| Contaminant | TOC start | TOC peak | TOC stop | UV start | UV peak | UV stop |
|---|---|---|---|---|---|---|
| Aldicarb (mg/L) | 15min | 5.5min | 11min | 2min | 3.5min | 7min |
| Cycloheiximide (mg/L) | 15min | 4.5min | 9min | 2min | 2.5min | 5min |
| Dicrotophos (mg/L) | 15min | 5min | 10min | 2min | 3.5min | 7min |
| Nicotine (mg/L) | 15min | 5.5min | 11min | 2min | 4min | 8min |
| Sodium Arsenate (mg/L) | No detection | | | 2min | 3min | 6min |
| Sodium Cyanide (mg/L) | 15min | 10min | 20min | 2min | 3min | 6min |
| Sodium Fluoroacetate (mg/L) | 15min | 5min | 10min | 2min | 2min | 4min |

Figures 3-23 through 3-36 represents the time series plots showing the on-line instrument response after the contaminants are injected with peristaltic pump into the distribution system at different concentrations. The beginning 100-minute data show baseline conditions. When the pump with 8.0 rpm turned on at t=100 minutes to inject contaminants, it took three and half minute to feed the one-liter of contaminant into the distribution system.

### 3.5 Conclusion

The object of this research was to test detection of chemical contaminants in a bench scale drinking water distribution system using UV254 as a surrogate of TOC. Overall, the UV254 instrument performed very well, sometimes even detecting events missed by the TOC analyzer.

The TOC instrument's maximum level is approximately 10.73mg/L. If the limit of detection is much lower than the specified concentration, then it would cause significant health impact. As can be seen, the TOC analyzer's limit of detection for dicrotophos was 0.96mg/L, significantly lower than using conductivity for sodium fluoroacetate (10.45mg/L). This result should be expected for organic contaminants, with molecules having more organic carbon being detected at lower concentrations than those having less.

Even though Sodium cyanide is an inorganic compound, cyanide elicited a significant instrument response from the TOC analyzer at a concentration well below the point of significant health impact. It is thought that the low-temperature UV-persulfate oxidation analysis method used in the TOC analyzer was not effective at purging the triple-bonded carbon-nitrogen molecule, so the carbon remained and was oxidized to carbon dioxide, and therefore detection as TOC was complete.

3 sigma values of all equipments was measured and used to decide detection limit which is based on 7 different chemicals' beaker test for each detection surrogate. Some of contaminants were not tested for human itself cause that no life threatening toxicity value was not obtained by test. 14 mg/L of sodium arsenate data was used as an indicator of detection for other contaminants which don't have this data.

Five of seven chemicals are organic compounds which is measured detected well at TOC analyzer and UV 254 analyzer. Through the beaker test of TOC and UV 254 showed the different tendency between organic and inorganic compounds. But sodium cyanide is an inorganic compound which has different results like organic contaminants. Measuring UV254 and correlating it with TOC is much simpler than measuring TOC directly, and the correlation for these chemcials has been shown to be practicably accurate.

In the bench scale distribution test, TOC and UV254 sometimes show results with more than one peak. Our assumption is that all injected contaminants were not diffused equally, and a residual in the loop caused the second peak. The remaining ratio of solution was detected as lower peaks and so on.

Overall UV254 and TOC correlate very well, and are sensible for detecting contamination events in water; however these work only for organic compounds even though there is an exception such as sodium cyanide. For inorganic compounds, another parameter such as free chlorine may be better at detecting contaminants.

In this research, a constant flow rate was used. For future research, the relationship between UV254 and flow rate should be further investigated. Also, biofilm growth on the optical surfaces of the UV254 analyzer should be studied to ensure sensor fouling is not an issue with the instrument.

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# Chapter 4
## Use of On-line Water Quality Analyzers for Monitoring Distribution System Security

Seongho Cho, Kenneth Carlson, Kenneth Stutzman

***Presented at AWWA Water Security Congress Conference, Washington D.C., September 12, 2006***

**Abstract**

While drinking water system security has always been an important issue for U.S. water treatment facilities, it has become key in the country's domestic security response to the catastrophic events of September 11, 2001 that framed the U.S. as a terrorist target. On-line monitoring of drinking water distribution systems offers potential in eliminating the danger of purposeful contamination that would, otherwise, be evident only through symptomatic events in the community served by the water system.

Seven credible drinking water chemical contaminants (aldicarb, cycloheximide, dicrotophos, nicotine, sodium arsenate, sodium cyanide, and sodium fluoroacetate) were measured at different dosing concentrations to determine their detectability in a drinking water distribution system model. These contaminants were monitored by measuring common water quality parameters such as conductivity, pH, chlorine residual, turbidity, total organic carbon (TOC), and UV254 as indicator analytes.

This investigation included:

1. Establishing a baseline for each water quality parameter

2. Determining laboratory instrument response to various concentrations of contaminant mixed with treated drinking water in benchtop containers

3. Using benchtop data to introduce appropriate contaminant concentrations into a bench-scale distribution system monitored by commercially available on-line water quality instruments

4. Determining detectability of specified contaminant concentrations in the bench-scale distribution system

Results indicate that the seven chemical contaminants can be detected at relatively low concentrations with routine monitoring. Some of the seven chemical contaminants can be detected below a concentration that will cause significant health impacts.

**Keywords**

Water Quality Instrument such as TOC and UV 254m, 7 chemicals, Drinking Water Distribution Systems

## 4.1. Introduction

Well-controlled and secured water treatment facilities have been mandated by federal, state and local governments for more than 50 years and have been key in ensuring that drinking water remains safe. Yet, a significant portion of the water supply, the distribution system, remains, for the most part, unregulated and unmonitored. This highly complex system of pipes, tanks, and pumps distribute water from treatment facilities to end users, including homes, schools, offices, and hospitals.

### 4.1.1 Background

Recently, studies and news stories have shown current water distribution systems are vulnerable and overdue for an attack. Governmental agencies acknowledge concern over water distribution system security, as reflected in a letter from the Florida Department of Environmental Protection (DEP) to water plant owners and operators:

We live in a new era. We must be much more vigilant and responsive about the security of our water supply systems to protect the public. Incidents, that in the past may have been viewed as acts of mischief and vandalism, now need to be fully investigated and managed seriously (Gelting et al. 2004).

The majority of the dollars spent on homeland security related to water projects has been applied to physical security measures such as fences, cameras and security guards at treatment facilities. Most water plant experts agree that these measures, while important security tools will not protect against even the simplest threats to the distribution system and that real-time monitoring is critical for identifying threat events. While testifying before Congress in 2001, Jeffrey J. Danneels, Manager of the Security Systems and Technology Center for Sandia National Laboratories stated:

Monitoring the distribution pipelines and storage reservoirs will provide continuous feedback on water quality to detect malevolent contamination, allowing parts of the distribution system to be isolated in the event of an attack (Danneels 2001).

### 4.1.2 Water Distribution System Susceptibility

The susceptibility of water distribution systems to attack dates back to the early Egyptian and Roman times when armies literally "choked" the enemy by diverting water from aqueducts or poisoning the influent stream with chemicals like cyanide. Such tactics are still a concern today, and, in fact, have been specifically addressed in modern day treaties of war. Earlier this year the topic was again brought to the forefront when tapes recovered by the United States forces in Iraq revealed Iraq's then Deputy Prime Minister Tariq Aziz informing Saddam Hussein:

Sir, the biological is very easy to make. It's so simple that any biologist can make a bottle of germs and drop it into a water tower and kill 100,000. This is not done by a state. No need to accuse a state. An individual can do it (2006 ABC News).

A similar plot was uncovered in February of 2002 in Rome, Italy:

Italian police have been investigating whether the US Embassy in Rome was the object of a plot to poison the city's water, a scheme uncovered with the arrest of four Moroccans in possession of large quantities of cyanide, and who are suspected of working for al Qaeda. Media reports said that the suspects, aged 30 to 40, had been followed by police for days, and were found with around 10 pounds of cyanide, maps of Rome highlighting the city's water supply and of the US Embassy building, and about 100 counterfeit resident permits. At least two of the men were also illegal immigrants (WaterTechOnline 2002).

These incidents show the threat of impending water system attack is real. Easy accessibility to a broad array of off-the-shelf chemicals and recipes on the internet for creating poisons from these chemicals compounds the problem. A trip to the local hardware store reveals a selection of drain cleaners, polishes, acids, bases, and caustics, many combinations of which yield results that are poisonous and even lethal in small quantities. If water suppliers are not prepared, malevolent and criminal contamination could have devastating effects on end users and even the economies of the United States, Europe and the world.

### 4.1.3 Routine Use of On-Line TOC Analyzers

Grab sampling routines typically result in a best-case scenario of four or five sample points per month, not nearly enough to detect any real security threat. As a result, an on-line sensor that can detect the presence of a broad array of chemicals has been long sought after. The on-line Total Organic Carbon (TOC) Analyzer has shown great promise in filling this gap. TOC analyzers automate several complex steps and combine signals into a simple, easy to understand part per million (PPM) result.

Originally applied in the semiconductor, power, and pharmaceutical industries, TOC analyzer readings ensure pure water is used as the basis for drug and wafer manufacturing operations. In water treatment facilities, the TOC measurement provides a general determination of the effectiveness of organic removal in the water treatment process and is typically reported as a ratio of influent to effluent.

The most popular on-line analyzers are the Hach (Loveland CO) AstroTOC UV TOC Analyzer and the Sievers® 900 TOC Analyzer. These units automate a very complex process of oxidizing or "combusting" the organic fraction sample in an integral

furnace and then analyzing the remaining carbon dioxide, which is directly proportional to the amount of organic carbon in the sample. Although on-line TOC analyzers automate the process, they are extremely complex instruments and thus are not ideally suited for out-of-plant installations such as remote water distribution sites. On-line TOC analyzers are expensive, with a list price starting at around $30,000 and topping $50,000 for higher end models. Further, ownership costs are very high because operation requires a supply of laboratory grade nitrogen and multiple liquid reagents.

### 4.1.4 UV254 as a TOC Surrogate

(1) How UV Absorbance Measurement Relates to TOC

UV-254 absorbance is determined by shining an ultraviolet light through 10 cm of water and measuring how much of the light is absorbed at a wavelength of 254 nm by natural organic material (NOM) in the water. While TOC is a measure of the total organic material in the water sample, UV254 readings correlate well with more complex TOC measurements and are a reliable indicator of TOC.

(2) The advantages of UV254 measurement over TOC [5]

Direct TOC measurement, which requires consumed reagents and high-purity nitrogen gas, is more complex and costly to monitor than UV254. The TOC analyzer itself is typically large, complicated to install, and requires operator maintenance and periodic tubing replacement. Some water utilities rely on the more practical UV254 measurement, which costs about 1/6 that of a TOC reading, as a surrogate measure of organic content and reliable trending indicator.

(3) Using TOC and UV for water quality monitoring [6]

Chemical compounds absorb light at certain wavelengths that represent the exact energy required to excite an electron to a greater energy state. Since the absorption of light is essentially related to the electron density, compounds with electron-rich functional groups will absorb more light than compounds without these groups. This characteristic also signals high chlorine reactivity, and researchers have shown that a concentration-normalized absorbance of ultraviolet (UV) wavelengths can be an indicator of NOM quality in a water sample.

A spectrophotometer measures the absorbance of light by dissolved chemical compounds, which can be correlated to the absorbance with the concentration of the compounds. Specific UV absorbance (SUVA), calculated as the UV absorbance at 254nm divided by the dissolved organic carbon concentration (UV254/DOC), has been used as an indicator of the fraction of humic substances (plant-derived) in water. The greater the SUVA, the higher the fraction of humic, hydrophobic, and chlorine-reactive Natural Organic Matters (NOM) in the water.

## 4.2 Methods and Materials

### 4.2.1 Bench-Scale Distribution System Design

The bench-scale distribution system design is shown in Figure 4-1. The toxicity of the volatile chemicals injected into the system required a ventilation hood, which also minimized exposure when the hazardous waste was collected at drain. Two-inch PVC piping, commonly used in municipal distribution systems, was used throughout the circulation loop, with one-inch pipe for drain from the pH, conductivity, chlorine and turbidity analyzers and 0.5-inch pipe draining the TOC analyzer.

An 8.0-rpm peristaltic installed at the ventilation hood injected the subject contaminant chemicals, while a 1.0-rpm pump positioned nine feet from the injection pump circulated the water through the system loop. The main line was ten feet long (from drain to wall-mounted analyzers). Flow rate was 700 ml/min.

This design incorporates two different influents, tap water from the municipal water distribution system and one of the seven contaminants injected with the peristaltic pump under the ventilation hood. Effluent from the circulating loop, when a specific contaminant presence constituted hazardous waste, was redirected from the drain with the use of valves and collected under the ventilation hood for treatment by a specific facility.

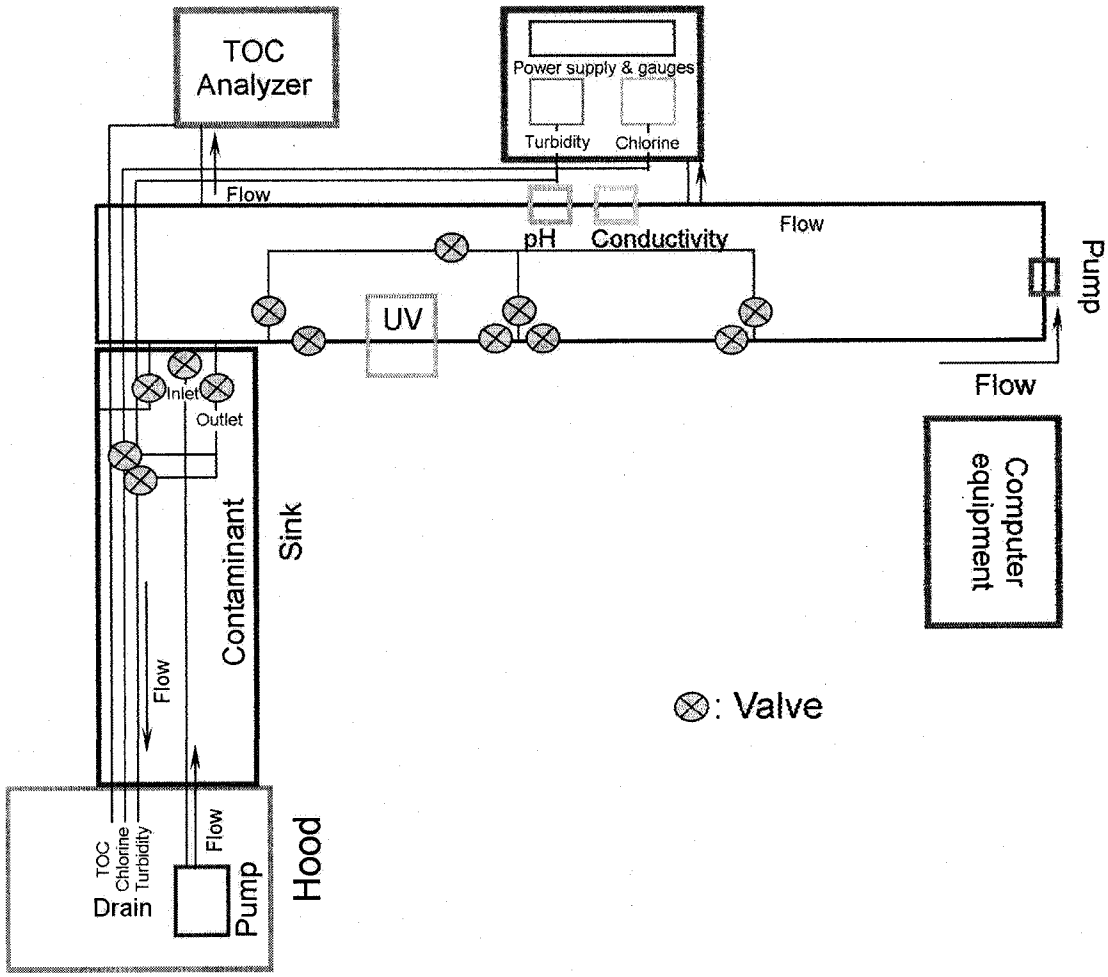


**Figure 4-1** Bench-Scale Distribution System Schematic

### 4.2.2 The character and calibration of instruments

The pH, conductivity, turbidity, chlorine residual, TOC, and UV analyzers are designed for direct measurement of concentration of organic and inorganic chemicals; yet, their trending can also signal water quality changes relating to acute toxicity. Two different groups of instruments were used, one for batch analyses and the other for on-line measurements. On-line pH and chlorine residual instruments were calibrated against bench-top equipment on a daily basis. The on-line TOC, turbidimeter, and conductivity instruments were all calibrated before they were placed in service. All on-line analyzers were allowed two hours to warm up before readings were considered valid, except for the UV system, which was calibrated at the manufacturer and did not require preparation or warm up time before deployment. Table 4-1 identifies the specific analytical instruments used in this investigation.

**Table 4-1** Analytical Instrument Used in Bench-Scale Water Distribution System Monitoring

| Parameter/ Measurement | Instrument | Method Used |
|---|---|---|
| **Batch analyses** | | |
| pH | Fischer Scientific AR-25 | *Standard Methods* 4500-H |
| Conductivity | ECTestr Low Conductivity Meter | *Standard Methods* 2510-B |
| Turbidity | Hach DR/3000 Spectrophotometer | Nephelometry USEPA Method 181.1 |
| Chlorine Residual | Hach Spectrophotometer | DPD colorimetric *Standard Methods* 4500-C1G |
| TOC | Hach AutoTOC 1950Plus TOC Analyzer | UV/persulfate oxidation |
| **On-line analyses** | | |
| Flow | Cole-Parmer | Rotameter |
| pH | Hach EC 310 | *Standard Methods* 4500-H |
| Conductivity | GLI C53 Conductivity Analyzer | *Standard Methods* 2510-B |
| Turbidity | Hach 1720D/L Turbidimeter | Nephelometry USEPA Method 181.1 |
| Chlorine Residual | Hach CL-17 Chlorine Analyzer | DPD colorimetric *Standard Methods* 4500-C1G |
| TOC | Hach AutoTOC 1950Plus TOC Analyzer | UV/persulfate oxidation |
| UV | Optek AF45 Single Wavelength UV Absorption Sensor | UV absorption |

### 4.2.3 Baseline water quality data

After instrument warm up, continuously running tap water circulating in the two-inch PVC pipe loop was automatically sampled for turbidity, chlorine residual, TOC, pH, conductivity, and UV absorption every 30 seconds over a span of 20,000 data points. Datalogging software (Hach Company) was used to define the normal tap water quality profile in this distribution system by determining mean and standard deviation (S.D.) for each parameter. Calculation of three standard deviations (3-sigma) from the mean identified the range of values defining random variability in which there is 99.96% probability an outlier data point is a false positive that reflects a true change in water quality from 'normal'.

### 4.2.4 Contaminant selection

Key properties of credible threat contaminants are:

- high toxicity
- high water solubility
- chemical and physical stability
- a lack of taste, color and odor
- a low chance of detection with normal analytical methods

According to Khan et al. (2000), chemical contaminants also possess these criteria:

- already used in chemical weapons
- available to potential terrorists
- likely to cause major morbidity or mortality
- potential of causing public panic and social disruption
- requiring special action for public health preparedness

Khan et al. list arsenic, pesticides, and cyanides as priority chemical agents. The National Research Council (2002) addresses morbidity and mortality, or toxicity, and focuses on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents and are persistent in water. The US Army Center for Health Promotion and Preventive Medicine listed sodium cyanide and fluoroacetate as priority potential chemical threat agents (Burrows et al., 1997).

There were two groups of contaminants used in this investigation, one a group of toxic chemicals with carbon atoms that would allow correlation between the TOC analyzer and the UV analyzer. The second group consisted of were weak acids and bases that are not considered hazardous waste and could be drained directly; this group

included formic acid, acetic acid, trichloro acetic acid, and potassium hydrogen phthalate. The following is a list of the specific chemical compounds used in this investigation.

**Aldicarb**

Aldicarb is directly toxic through oral, dermal, and inhalation routes. It is toxic through secondary poisoning – when plants systemically exposed are consumed or when exposed insects, rodents, and birds are consumed by predators and scavengers. Aldicarb is highly soluble in water, soluble in acetone, zylene, ethyl, ether, toluene, and other organic solvents, and is highly mobile in soil. Levels of aldicarb in drinking water exceeding the health advisory level of 10 ppb established by the Office of Drinking Water at EPA have been recorded in a few states in U.S.

**Cycloheximide**

Actidione (Cycloheximide) is an antibiotic that acts as an inhibitor of protein synthesis in eukaryotes but not prokaryotes. Cycloheximide is an odorless, white, crystalline powder used in hospital and research laboratories as an antibiotic, a protein synthesis inhibitor, or a plant growth regulator. Cycloheximide also has broader agricultural use as a fungicide, but such use is being discontinued due to the recent findings of birth defects at low doses in animals.

**Sodium Cyanide**

Sodium Cyanide (NaCN) is also known as cyanogran, cyanide of sodium, cymag, hydrocyanic acid sodium salt, and cyanobrik. Sodium cyanide is a product of a series of reactions involving sodium carbonate, limestone, carbon, and oxygen from the air. Sodium cyanide and potassium cyanide are both white solids with a bitter, mild almond-like odor in damp air.

**Sodium Arsenate**

Sodium arsenate is a pentavalent form of inorganic arsenic. It is a heptahydrate and normally exists as colorless crystals with no discernible odor. Inorganic arsenical compounds have been classified as Class A oncogens, demonstrating positive oncogenic effects based on sufficient human epidemiological evidence.

**Dicrotophos**

Dicrotophos is the E isomer of O, O-dimethyl-O-(3-dimethylamino-1-methy-3-oxo-1-propenyl) phosphate. Dicrotophos emits toxic fumes of phosphorus and nitrogen oxides when heated to decomposition. In two human poisoning cases, symptoms such as cramps, nausea, vomiting, diarrhea, dyspnea, and general weakness occurred on exposure to spray, and loss of pulse and respiration occurred when ingested.

**Nicotine**

Nicotine is usually obtained from *Nicotiana tabacum*. Nicotine is one of the more than 4,000 chemicals found in the smoke from tobacco products such as cigarettes, cigars, and pipes. Nicotine is a naturally occurring colorless liquid that turns brown and acquires the odor of tobacco when exposed to air.

**Sodium Fluoroacetate**

Sodium fluoroacetate, also commonly known as compound 1080, sodium monofluororacetate, fratol, furatol, ratbane, and yasoknock, is a rodenticide. Fluoroacetic acid differs from the fluoroacetate ion that makes up sodium fluoroacetate only in the addition of a hydrogen atom, $C_2H_3FO_2$ or as a more protonated form.

Table 4-2 lists information on the water contaminants used in this investigation, including physical, chemical, and toxicity properties.

**Table 4-2** Properties of Interest for Credible Threat Chemical Contaminants

| Property | Aldicarb | Cyclo-Heximide | Dicro-tophos | Nicotine | Sodium Arsenate | Sodium Cyanide | 1080 |
|---|---|---|---|---|---|---|---|
| Human Oral $LD_{50}$ (mg/kg) | 0.8[6] | 2 (rat) | 12.7 (rat) | 10 (mouse) | 20[8] | 3-7[7] | 2-5[7] |
| Min Concentration in glass of water to reach min human oral $LD_{50}$ (mg/L) | 96 | 240 | 1,524 | 1,200 | 2,400 | 360 | 240 |
| Life-Threatening Toxicity (mg/L) | NA | NA | NA | NA | 14[10] | 48[10] | 60[9] |
| CAS number | 116-06-3 | 66-81-9 | 141-66-2 | 54-11-5 | 7778-43-0 | 143-33-9 | 62-74-8 |
| Chemical Formula | $C_7H_{14}N_2O_2S$ | $C_{15}H_{23}NO_4$ | $C_8H_{16}NO_5P$ | $C_{10}H_{14}N_2$ | $Na_2HAsO_4$ | NaCN | $C_2H_2FO_2Na$ |
| Molecular Weight | 190.25 | 281.35 | 237.21 | 162.23 | 185.9 | 49.01 | 100.03 |
| Soluble in Water | 0.6g/100 mL | 2-5g/100mL | Miscible | Miscible | 61g/100mL | 37g/100 mL | Extremely |
| Stability in Water | Stable | Stable | Stable in glass container | Stable in glass container | Stable | Stable | $t_{1/2}$ = 2-6 days in water |

*Based on a 60-kg person drinking a 0.5-liter glass of water
NA: Not available
[6] see reference no. 6
[7] see reference no. 7
[8] see reference no. 8

### 4.2.5 Beaker test

The chemical contaminants, in powder or liquid form, were obtained commercially. After the three-sigma value was calculated for each parameter from the on-line monitoring period, beakers of tap water only were analyzed for each parameter with the benchtop instruments identified in Table 4-1. Several different target concentrations of each contaminant were prepared with tap water, added to the beakers sequentially, and again each parameter was measured with the benchtop instruments. Plotting instrument response against the baseline three-sigma value for each parameter identified the minimum contaminant concentration that resulted in a parameter reading outside the range of random variability. This value reflected the minimum detectable dose of contaminant that would reflect an abnormal – or unexplained – water quality profile shift.

### 4.2.6 Bench-scale distribution system tests

Prior to chemical introduction, tap water circulated through the bench-scale distribution system for one to two hours to stabilize flow, turbulence, and any particulate matter that may have settled in the piping since the baseline data collection period. Then, the system continued to flow and analyzers collected measurement of each parameter for 100 minutes to assure instrument response was comparable to the baseline collection period – that the influent tap water exhibited the same baseline profile as that collected previously. After this 100-minute period, each contaminant was injected at the minimum detectable dosage determined by beaker tests to result in a change in normal parameter range and at three higher dosages, with each dosage injected for approximately 30 minutes.

## 4.3 Results and Discussion

The focus of this investigation was the real-time detection of contamination events in the distribution system, either through direct measurement of a contaminant or detection of water quality baseline changes that signal an abnormal or possible contamination, event.

### 4.3.1 Baseline

The 20,000-data point baseline the information to determine what parameter values were "normal" in this distribution system with the influent received from the local water treatment facility during this time period. Table 4-3 provides as summary of baseline data collected.

**Table 4-3** On-Line Monitoring Baseline Water Quality Profile

| | pH | Conductivity (μS/cm) | Turbidity (NTU) | Chlorine (mg/L) | TOC (mg/L) | UV (Conc Units) |
|---|---|---|---|---|---|---|
| Minimum | 7.7 | 81 | 0.079 | 0 | 0.008 | 1.005 |
| Mean | 8.02 | 103 | 0.094 | 0.23 | 1.308 | 1.024 |
| Maximum | 8.13 | 157 | 0.223 | 0.31 | 2.648 | 1.064 |
| S.D. | 0.05 | 8 | 0.024 | 0.04 | 0.154 | 0.01 |
| three-sigma | 0.15 | 23 | 0.072 | 0.11 | 0.462 | 0.03 |

In a normal distribution of data points, 99.96% of the measurements will fall within x-bar (mean) plus or minus three standard deviations from the mean, or within the three-sigma range. The percentage of baseline data points for each parameter that were found to fall within the x-bar plus or minus three-sigma range is given in Table 4-4. Any data point outside of x-bar plus or minus three-sigma represents an anomaly.

**Table 4-4** Percentage of Baseline Data Points Falling Within Mean ± 3σ

| pH | Conductivity (μS/cm) | Turbidity (NTU) | Chlorine (mg/L) | TOC (mg/L) | UV (CU) |
|---|---|---|---|---|---|
| 99.02 % | 99.99 % | 94.92 % | 99.40 % | 99.09 % | 98.52 % |

Figures 4-2 through 4-4 graphs display time series plots of the more than 20,000-data point baseline for the six water quality parameters monitored on-line. It is evident that each parameter displays a range of variation, a normal profile, different than the other parameters.

It is important to note that the baseline water quality profile changes due to temperature, season, flow rate, customer demand, and water treatment plant operation. To reliably detect a contaminant event, the on-line analysis must have an established baseline data that represents the current distribution system conditions to properly identify suspect data. Without an appropriate baseline, there is a potential of inaccurately identifying an anomalous event – or missing one. Descriptive statistics prove very powerful, however, when the baseline data set is accurate.

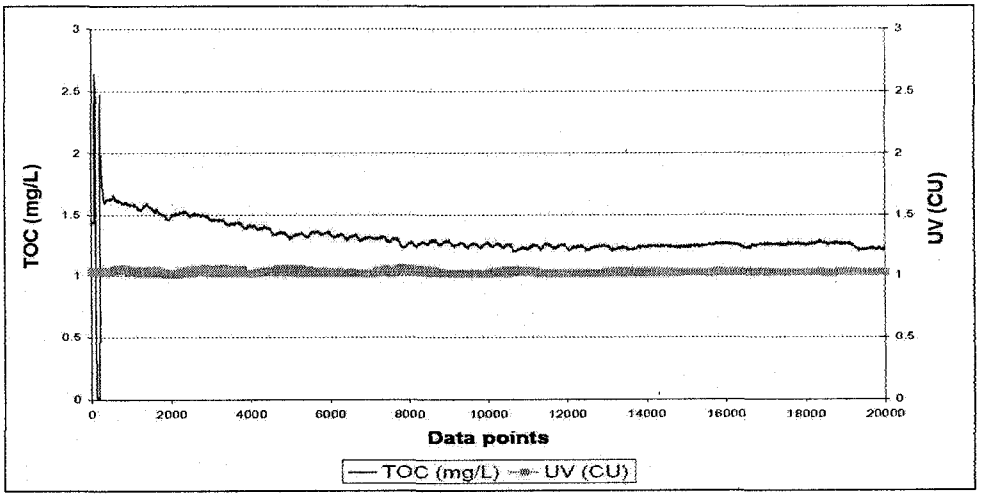


**Figure 4-2** TOC and UV Baseline Data

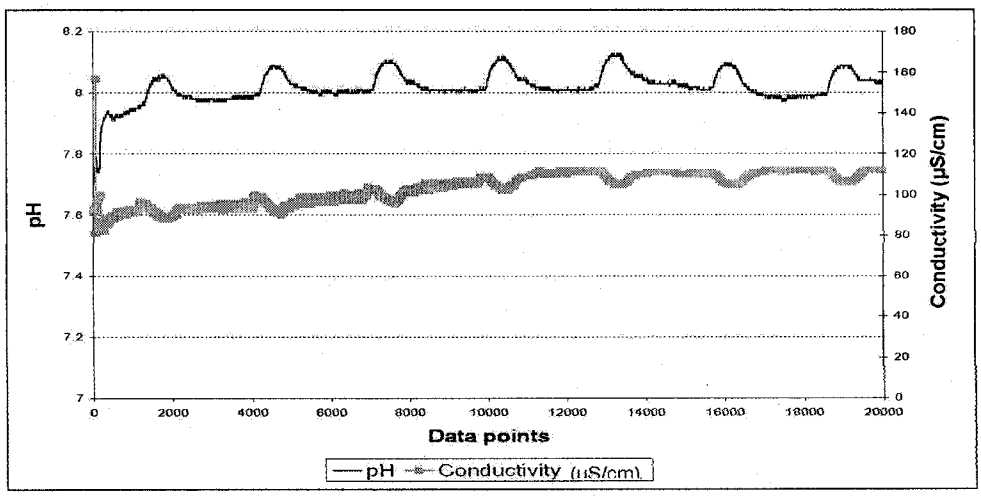


**Figure 4-3** pH and Conductivity Baseline Data

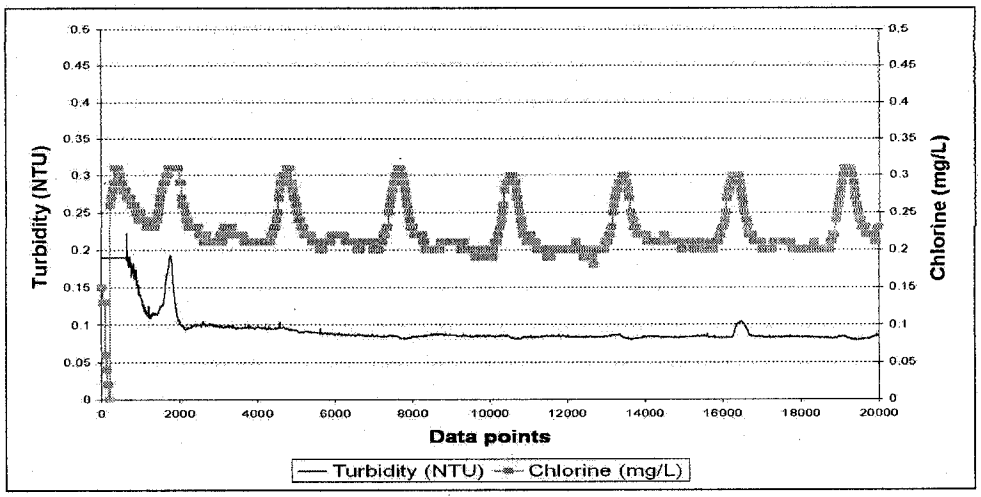


**Figure 4-4** Turbidity and Chlorine Baseline Data

### 4.3.2 Beaker tests

Objectives of the beaker tests were:

- to determine which of the six common water quality parameters would be most influenced by specific contaminants
- to determine, in a controlled environment, the minimum detectable concentration of contaminants that would change the normal water quality profile
- to determine the target contaminant concentrations that would be injected into the distribution system

Accordingly, the beaker tests, in effect, provided a calibration curve of contaminant concentrations to be injected into the bench-scale distribution system. Figures 4-5 through 4-8 illustrate the change in baseline water quality parameter values when a specific contaminant is added to tap water at specified concentrations.

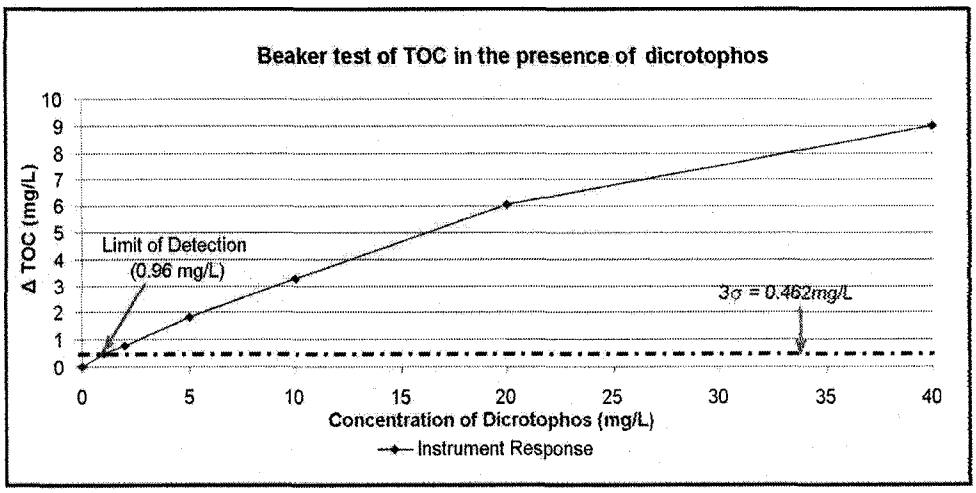


**Figure 4-5** TOC Response with Injection of Dicrotophos

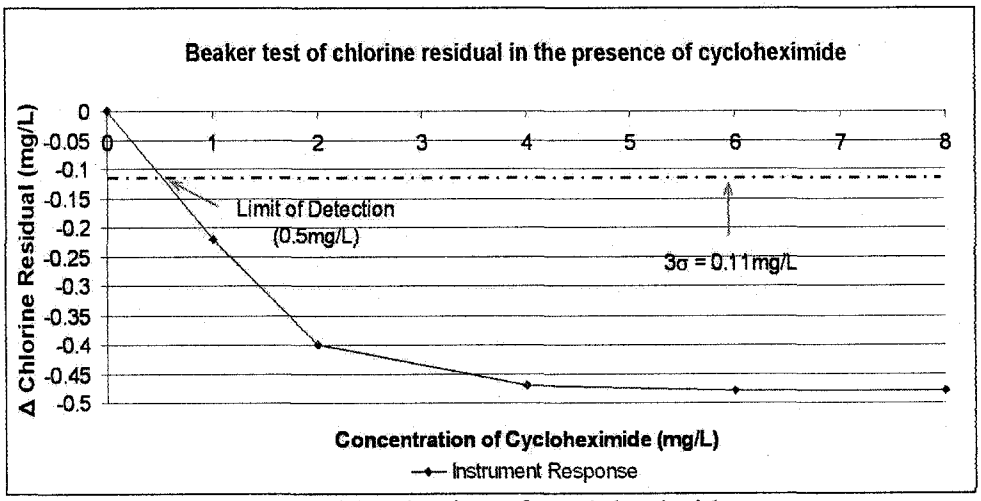


**Figure 4-6** Chlorine Response with Injection of Cycloheximide

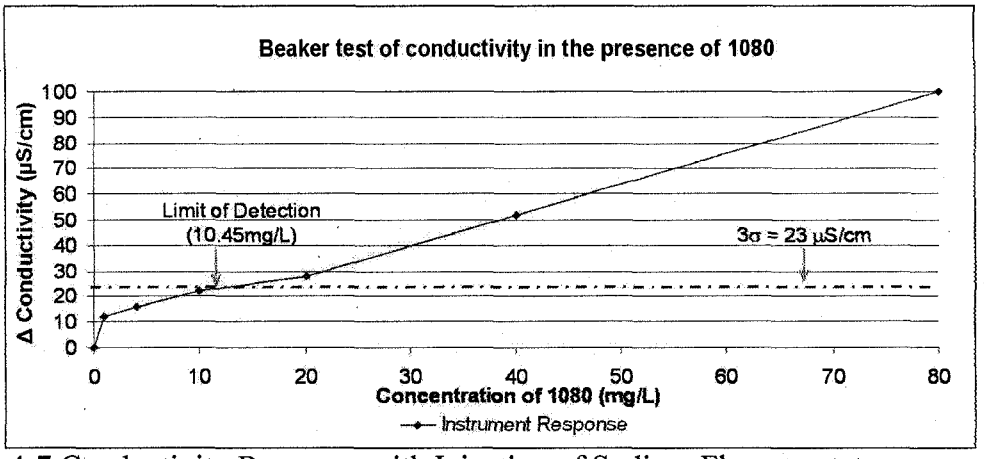


**Figure 4-7** Conductivity Response with Injection of Sodium Fluoroacetate

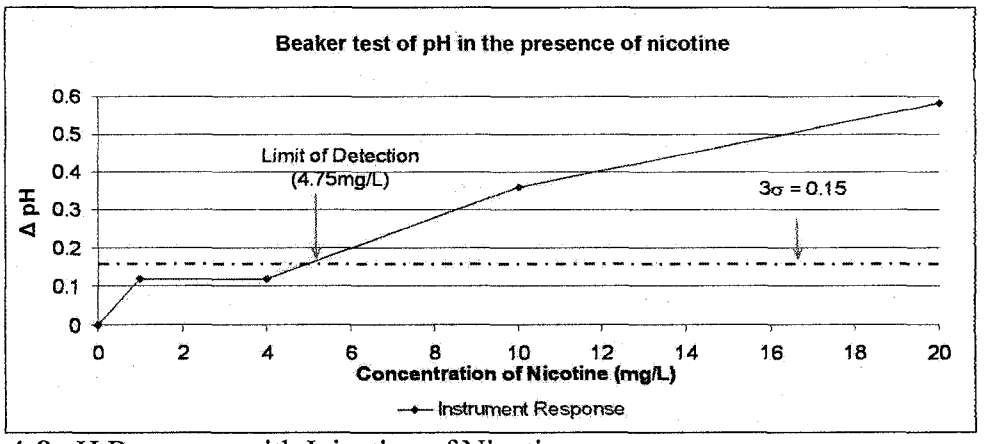


**Figure 4-8** pH Response with Injection of Nicotine

Figure 4-5 shows that TOC reading varied from normal water quality profile due to dicrotophos at a concentration as low as 0.96mg/L – a level low enough to signal contamination before adverse health effects would be noticed. Figure 4-6 shows conductivity response was not as critical in the presence of sodium fluoroacetate, with limit of detection of 10.45mg/L. This result would be expected for organic contaminants, which have molecules of more organic carbon that make them detectable at lower concentrations than those compounds that have less organic carbon.

Yet, while sodium cyanide is an inorganic compound, cyanide elicited a significant TOC response at a concentration well below the point of significant health

impact. It is proposed that the low-temperature UV-persulfate oxidation analysis method used in this TOC analyzer is not effective at purging the triple-bonded carbon-nitrogen molecule and the carbon that remained was oxidized to carbon dioxide and, therefore, was detected as TOC.

The results shown in Figures 4-5 and 4-6 suggest that on-line monitoring of common water quality parameters could detect contamination events at concentrations lower than those that would cause serious health effects. Figures 4-7 and 4-8 illustrate that more sophisticated techniques of data analysis are needed to reduce the limit of detection.

### 4.3.3 Bench-scale distribution system test

The values in 4-5 indicate the lowest contaminant concentration that resulted in a change from the normal water quality parameter profile. These values were derived from measurements recorded outside the water quality parameter baseline three-sigma value and the published instrument error. Shaded values indicate the lowest limit of detection and, therefore, a parameter that could be recommended as a water quality surrogate for detecting that contaminant. The TOC analyzer showed sensitive response to the presence of sodium cyanide; however, other parameters showed better response and potential as a surrogate for sodium cyanide detection.

**Table 4-5** Limits of Detection for Contaminants Determined by On-line Monitoring Data

| Contaminant | pH | Conductivity | Turbidity | Chlorine residual | TOC | UV |
|---|---|---|---|---|---|---|
| Aldicarb (mg/L) | 1 | >10 | 1 | 1 | 1 | 1 |
| Cycloheximide (mg/L) | 3 | 3 | 3 | 3 | 1 | 1 |
| Dicrotophos (mg/L) | 1 | 3 | 1 | 3 | 1 | 1 |
| Nicotine (mg/L) | >10 | 3 | >10 | 1 | 1 | 1 |
| Sodium Arsenate (mg/L) | >100 | 25 | <15 | >100 | >100 | >30 |
| Sodium Cyanide (mg/L) | 1 | 5 | 1 | 1 | 5 | 3 |
| Sodium Fluoroacetate (mg/L) | 5 | 3 | 3 | 10 | 3 | 3 |

Table 4-6 shows the lag time between contaminant injection and the start of analyzer response and the time from initial response to end of response, that is, the return of analyzer reading to within three-sigma of baseline. Peak time reflects half of that time period. The longer response time for the TOC analyzer, compared to the UV Analyzer, is due to further distance in the circulating loop from the inlet point and a longer analysis time. Response and return to normal baseline took approximately ten minutes for TOC analyzer and seven minutes for the UV analyzer.

**Table 4-6** Time for TOC and UV Analyzer Response to Contaminants at 5ppm

| Contaminant | TOC start | TOC Peak | TOC stop | UV start | UV peak | UV stop |
|---|---|---|---|---|---|---|
| Aldicarb (mg/L) | 15min | 5.5min | 11min | 2min | 3.5min | 7min |
| Cycloheiximide (mg/L) | 15min | 4.5min | 9min | 2min | 2.5min | 5min |
| Dicrotophos (mg/L) | 15min | 5min | 10min | 2min | 3.5min | 7min |
| Nicotine (mg/L) | 15min | 5.5min | 11min | 2min | 4min | 8min |
| Sodium Arsenate (mg/L) | No detection | | | 2min | 3min | 6min |
| Sodium Cyanide (mg/L) | 15min | 10min | 20min | 2min | 3min | 6min |
| Sodium Fluoroacetate (mg/L) | 15min | 5min | 10min | 2min | 2min | 4min |

Figures 4-9 through 4-14 illustrate on-line instrument measurements during the pre-injection 100-minute baseline and response after injection of different concentrations of selected contaminant at about 120 minutes of water circulation time. The 8.0-rpm feed pump injected the entire one liter of contaminant solution into the distribution system in about three and half minutes.

Of all the parameters measured, conductivity showed the most significant response to presence of sodium arsenate; conductivity also showed considerable response to cycloheximide, dicrotophos, nicotine, and sodium fluoroacetate.

There are couple contaminants whose presence significantly changed all of the water quality parameters at relatively low concentrations. These are cycloheximide, dicrotophos, and sodium cyanide. Aldicarb, nicotine, and sodium cyanide affected the

chlorine residual quickly. As expected, TOC responded less to the sodium contaminants (fluoroacetate, cyanide, and arsenate) than the four organic compounds that contained more carbon. Most of the organic compounds elicited significant changes in reading by the UV254 instrument, which appeared to be the best detector of these contaminants, while the turbidimeter appeared the least sensitive.

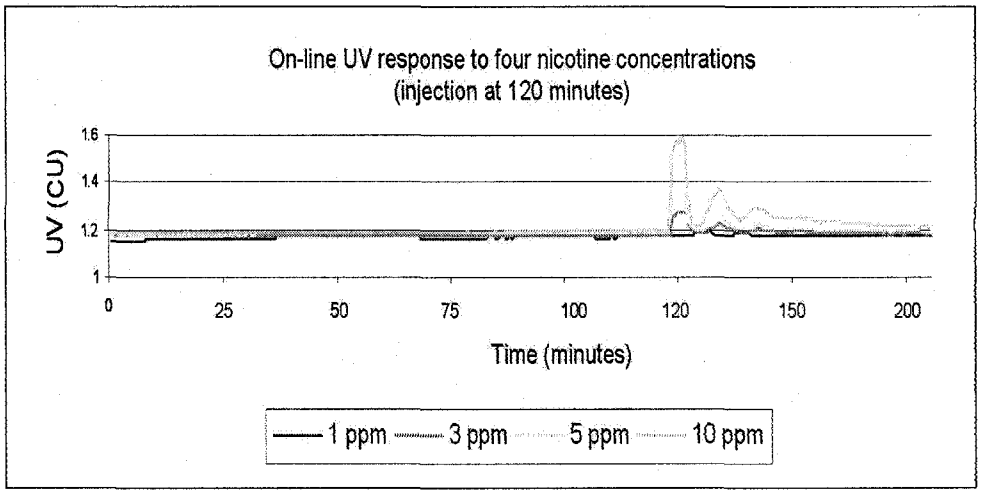


**Figure 4-9** Time Series Plot of UV Analyzer Response to Nicotine

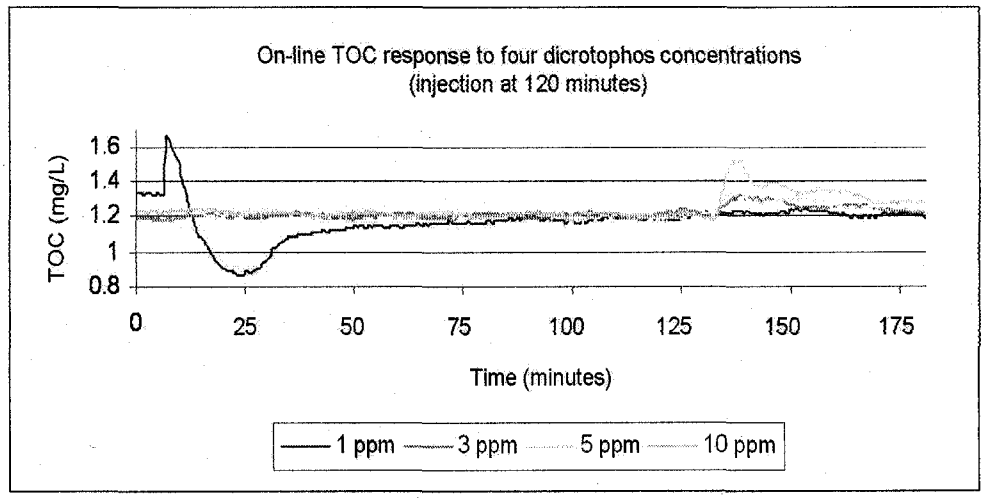


**Figure 4-10** Time Series Plot of TOC Analyzer Response to Dicrotophos

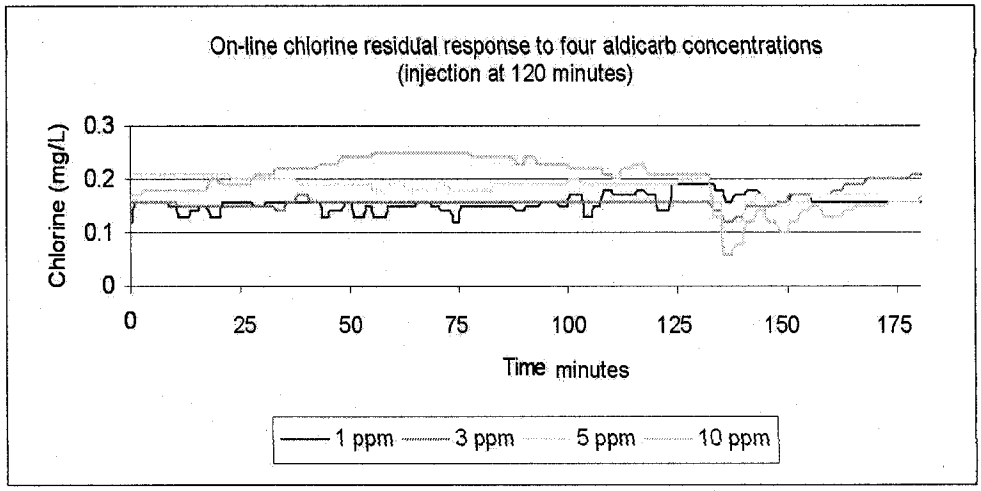


**Figure 4-11** Time Series Plot of Chlorine Analyzer Response to Aldicarb

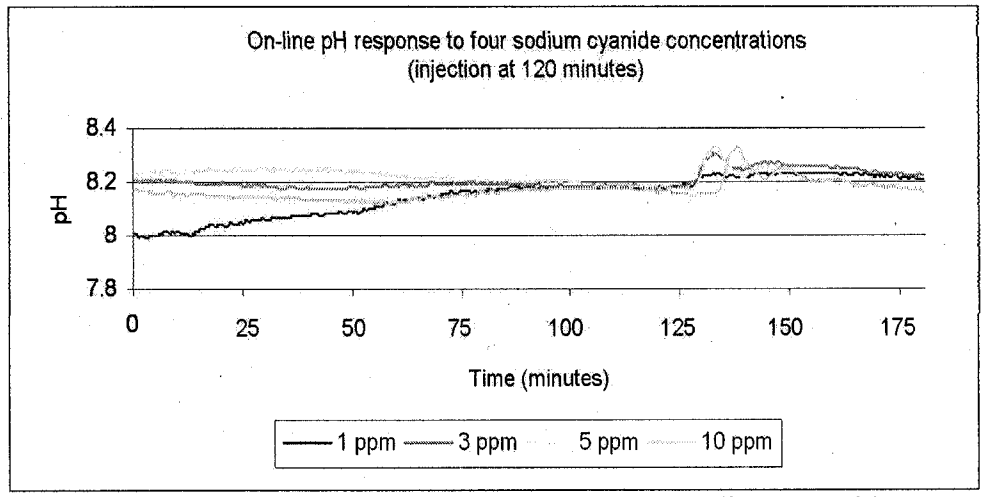


**Figure 4-12** Time Series Plot of pH Analyzer Response to Sodium Cyanide

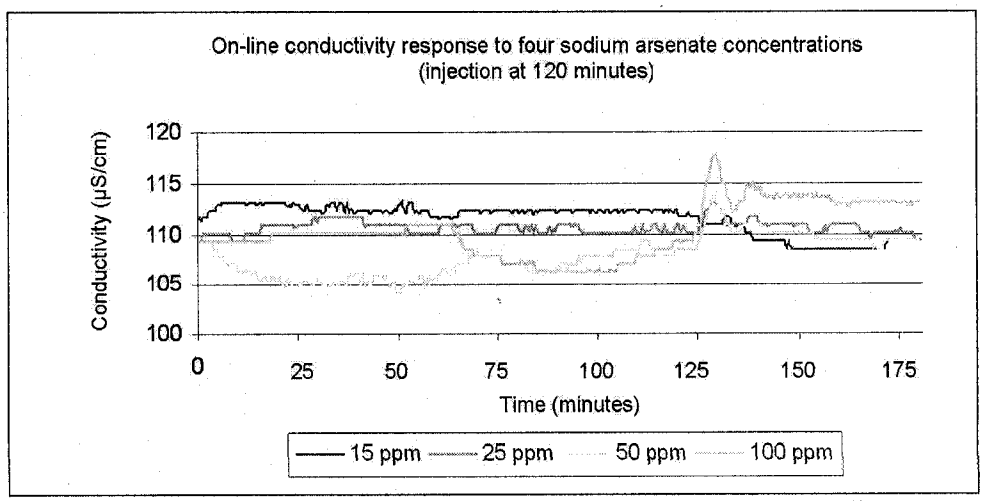


**Figure 4-13** Time Series Plot of Conductivity Analyzer Response to Sodium Arsenate

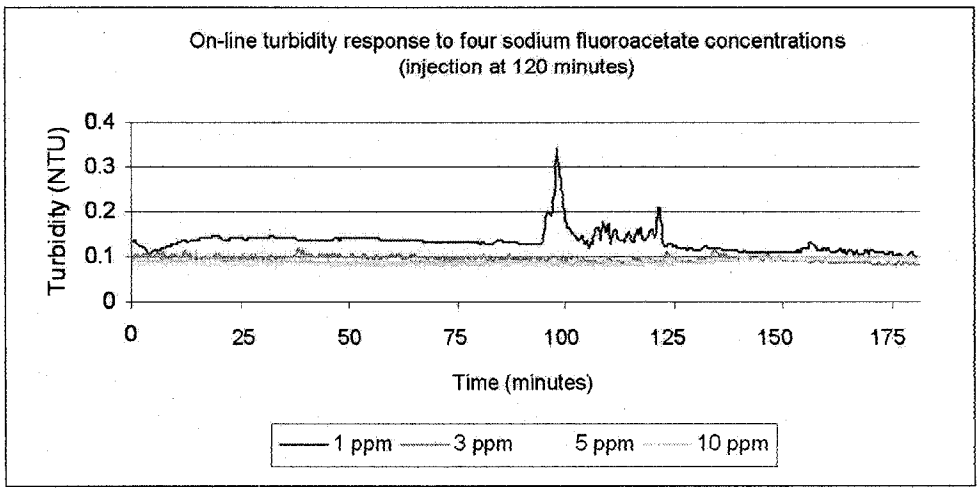


**Figure 4-14** Time Series Plot of On-line Turbidimeter Response to Sodium Fluoroacetate

## 4.4 Conclusion

Due to increased concern of terrorism, the early detection of chemical contaminants in drinking water distribution systems has become an issue of great interest. This study examined the detection of chemical contaminants in a bench-scale drinking water distribution system using common water quality parameters as surrogate indicators. Of the six on-line monitoring instruments used, the UV analyzer and the TOC analyzer provided response that correlated well to the organic compound contaminants present. TOC also showed response to the presence of inorganic sodium cyanide. Measuring UV254 and correlating it with TOC is much simpler than measuring TOC directly, and the correlation has been shown to be accurate.

The chlorine residual analyzer provided the best surrogate detection of the inorganic compound introduced to this distribution system. The on-line turbidimeter did not respond well to the presence of chemical contaminants in this study; however, future research will examine the use of turbidity to monitor the distribution system for the presence of biofilm.

## 4.5 References

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# Chapter 5
## Indirect Detection of Intentional Chemical Contamination in the Distribution System Using Low Cost Turbidity Sensors

Seongho Cho, Kenneth Carlson, Kenneth Stutzman

***Presented at AWWA Water Quality Technology Conference, Denver, CO November 6, 2006***

**Abstract**

Rapid detection of chemical contamination in the distribution system is essential in protecting public health, and using water quality surrogates to signal a contamination event offers the advantage of detecting a large number of chemicals. The concern over using surrogate parameters is whether they offer the ability to detect contaminants at concentrations low enough to prevent serious illness. The best candidates for water quality surrogates are generally thought to be chlorine residual and TOC, with conductivity, pH and turbidity being less sensitive to many chemical contaminants. All of these surrogate measurements have been in direct response to the chemical contaminant itself.

This paper describes research on how the indigenous biofilm in the presence of toxic chemicals may provide an effective, indirect surrogate response with either turbidity or UV254. Rotating annular bioreactors and pipe loops were used to quantify the effect that the biofilm has on the turbidity and UV254 measurements. The hypothesis is that, if toxic chemicals are added to the distribution system, the biofilm would die and slough off to an extent that would change the UV254 absorbance and light scattering of the water so that relatively inexpensive monitors could detect the event.

In previously documented work, three reactors with 20 PVC coupons in each were used to acclimate the biofilm for at least six weeks. The number of biofilm cells on each coupon was enumerated using automated fluorescence microscopy. The coupons were submersed into beakers with four potential chemical contaminants; aldicarb, cyanide, arsenate and fluoroacetate. The concentration of the contaminants was less than 1 mg/L, a concentration that was shown to be feasible to achieve in a distribution system in previous research. The turbidity was measured after 1, 8 and 48 minutes to determine the response time of the biofilm to the chemicals. In all cases, the turbidity significantly increased after one minute and in most cases continued to increase at the longer times.

The batch data indicate that turbidity may be a useful surrogate monitor for chemical contamination due to die-off of the indigenous biofilms. Biofilm slough-off and increased turbidity response occurred in the present study in which a commonly used turbidity monitor and a simple, inexpensive turbidity sensor monitored a simulated distribution system inoculated with five common industrial chemical contaminants. We will detail the results of the pipe loop study at the conference and describe the inexpensive turbidity monitor that has been developed.

**Keywords**

V254, Biofilm, Turbidimeter, 5 chemicals, Drinking Water Distribution Systems

## 5.1 Introduction

During the distribution of drinking water, bacterial regrowth as biofilm fueled by the presence of organic substances can lead to a deterioration of water quality, increased in corrosion, generation of bad tastes and odors, and proliferation of macroinvertebrates [1]. Studies in pilot-scale systems have shown that bacterial growth as biofilm within drinking water distribution systems can seriously affect the quality of drinking water [2]; therefore, to protect public health, it is essential to be able to rapidly detect changes in biofilm presence in the distribution system.

### 5.1.1 Introduction of microorganism in distribution system

Biofilm is recognized as indigenous in a normal aquatic system and can exist in all distribution systems containing properly treated, but non-sterile, water [3]. Living microorganisms and nutrients enter drinking water distribution systems with raw water during water treatment failures or from pipe breaks or leaks, backflow, and cross-connections [4]. Microbiological contamination also can occur via uncovered storage tanks and during water main installation and repair [5]. Even those water systems observing excellent sanitary practices for main breaks and repair experience contaminant entry into the distribution system [6].

### 5.1.2 Definition of biofilm

For a number of years, biofilm was generally regarded as cells immobilized at a substratum and frequently embedded in an organic polymer matrix of microbial origin. A more-universal definition – matrix-enclosed bacterial populations adherent to each other and/or to surfaces or interfaces – is better suited to all ecological, industrial, and medical situations, and in 1995, biofilm was defined as, microbial cells, attached to a substratum,

and immobilized in a three-dimensional matrix of extracellular polymers enabling the formation of an independent functioning ecosystem, homeostatically regulated [7].

### 5.1.3 Formation of biofilm

Biofilms can be found virtually anywhere a surface comes into contact with the water in a distribution system. In water distribution system pipelines, biofilms form when microbial cells attach to pipe surfaces and multiply to form a film or slime layer on the pipe. This growth is a complex and dynamic microenvironment, incorporating processes such as metabolism, growth and product formation, and finally detachment, erosion, or "sloughing" of the biofilm from the surface. The roughness of the pipe wall, usually a factor of the pipe material and condition, is a key condition influencing both attachment and detachment of biofilm. In fact, pipe material may have more influence on biofilm growth potential than the level of organic matter in the system.

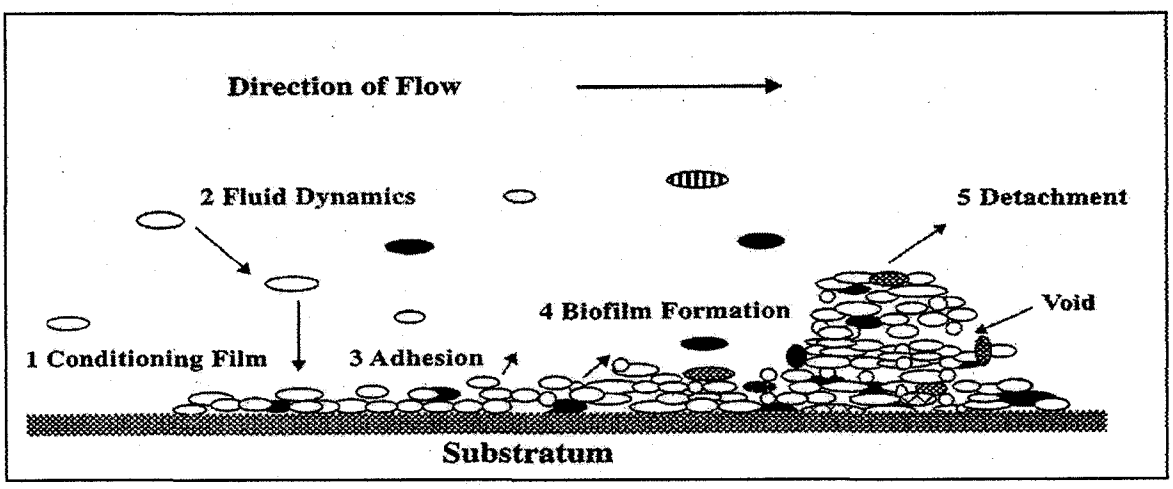



**Figure 5-1** Biofilm Formation Diagram (from Precival et al., 2000)

### 5.1.4 Process of biofilm formation

While biofilm formation is considered to be complex, it can be summarized as a five-stage process [7]

a. Development of a surface-conditioning film: A clean, uncontaminated surface can be conditioned by the transport medium, i.e. water, containing organic substances and microbial cells in as little as 15 minutes.

b. Events that bring the organisms into close proximity with the surface: Transport of organisms to the surface can be through laminar flow or turbulent flow. Temperature and gravity typically dictate the speed of flow.

c. Adhesion, either reversible or irreversible sorption: Reversible adhesion is an initial, weak attachment of microbial cells to a surface. Irreversible adhesion establishes a permanent bonding of the microorganisms with the surface and requires mechanical or chemical treatment for removal.

d. Growth and division of the organisms with the colonization of the surface, microcolony formation and biofilm formation: There are a number of parameters that affect the development of biofilm, such as temperature, hydrodynamic conditions, nutrient availability, roughness, and pH.

e. Detachment: The five means of biofilm detachment include: erosion of single cells, sloughing of clusters, abrasion, human intervention, and predator grazing. Erosion is the removal of small particles of biofilms. Sloughing is a random and discrete process, the detachment of large particles of biofilm. Abrasion is caused by the collision of solid particles, human intervention involves detachment of the biofilm by chemical or physical means, and predator grazing is the consumption of biofilms by organisms.

### 5.1.5 Factors affecting biofilm accumulation

Previous investigation assessed the impact of various factors on biofilm accumulation by measuring pseudo steady-state biofilm HPC (Heterotrophic Plate Count) levels [9]. The most significant factor was found to be the presence of disinfectant residual – increasing the free chlorine residual from 0 to 0.5 mg/L reduced biofilm HPC levels, measured in cfu/cm$^2$, by about four orders of magnitude. High chloramines residual (2.0 mg/L) also significantly suppressed biofilm HPC levels.

The presence of easily biodegradable organic matter (BOM) also was found to be significant, in that it influenced the impact of other factors such as flow velocity, shear force, temperature, pipe material, and substratum. In the absence of BOM, HPC increased with higher shear and remained unaffected by temperature change. In the presence of BOM, the temperature effect was important at lower shear stress. The condition leading to the highest levels of biofilm HPC was a high level of easily degradable BOM in the absence of a disinfectant. The fact that shear was important under some conditions indicates that mass transfer might be limited in some circumstances.

### 5.1.6 Measurement of biofilm formation

Biofilm control is recognized as an important part of the operation and maintenance of drinking water plants and distribution systems [1]. The classical approach to estimating biofilm growth in drinking water distribution system is to measure the biofilm formation rate. This process is laborious and time consuming because it requires frequent sampling in piping systems that are, typically, extensive and complex. To streamline the process, numerical models have been developed to help predict bioflim

growth [8]. Another possible means of determining biofilm growth rates is to estimate the release rate of bacteria from the bioflim.

### 5.1.7 Using turbidity to track biofilm, and distribution system, changes

Turbidity, technically, is a measure of the scatter of light by suspended particles in water; in practical terms, it is often thought of as a measure of the cloudiness of water. Turbidity is caused not only by total suspended solids (TSS) such as clay, silt, and organic matter but also by plankton and other microscopic organisms. While turbidity itself is not necessarily a health concern, higher levels of turbidity reflect particulate presence that can interfere with disinfection and provide a medium for microbial growth. [10]

This study looks at using turbidity to monitor the presence of detached biofilm which, of itself, can pose a health concern and also signals changes in the distribution system conditions. The investigators propose taking advantage of the fact that biofilm is a natural consequence of distribution system conditions and examining whether changes in distribution system conditions that alter biofilm integrity and result in detachment and sloughing of biomass – such as the introduction of toxic chemicals – might be signaled by increased turbidity levels in the system water.

## 5.2 Methods and Materials

**Figure 5-2** Bench-Scale Distribution System

### 5.2.1 Bench-Scale Distribution System Design

The bench-scale distribution system used in the study is shown in Figure 5-2. This design incorporates two different influents, tap water direct from the municipal water distribution system and tap water with one of five contaminants injected by an 8.0-rpm peristaltic pump. The toxicity of the volatile chemicals injected into the system required a ventilation hood, which also minimized exposure when the hazardous waste was collected at drain.

This continuously flowing loop system constructed with 3/4-inch PVC pipe throughout was utilized because it is more representative of an actual water distribution system than the rotating annular bioreactor (RAB) model used in other studies. The typical RAB test uses one liter of contaminant solution in a batch setup with test coupons representing system surfaces submersed into the beakers. In the current study, a PVC

coupon was inserted inline with the pipe to collect biofilm. Using Hach DR/3000 Spectrophotometer, the turbidity of RAB test was measured

Figure 5-3 details the bench-scale distribution system. The main system line (▬) was 21 feet long. Flow rate (▭) was 6 gal/hour in each pipe. Pipe unions built into the line allowed easy insertion and removal of the three coupons inserted in each pipe (▭) to accumulate biofilm. An ST-Infonox Micro Sensor (■) measuring pH, temperature, and turbidity, a Hach 1720 D on-line Turbidimeter, and an Optek UV 254nm Sensor monitored the continuously flowing water in the simulated distribution system. Valves (not shown in the diagram) allowed flow direction change between the pipe with tap water (▭) and the pipe with contaminated water (▬). Only contaminated water circulated through the UV and turbidity instruments was collected as waste water.

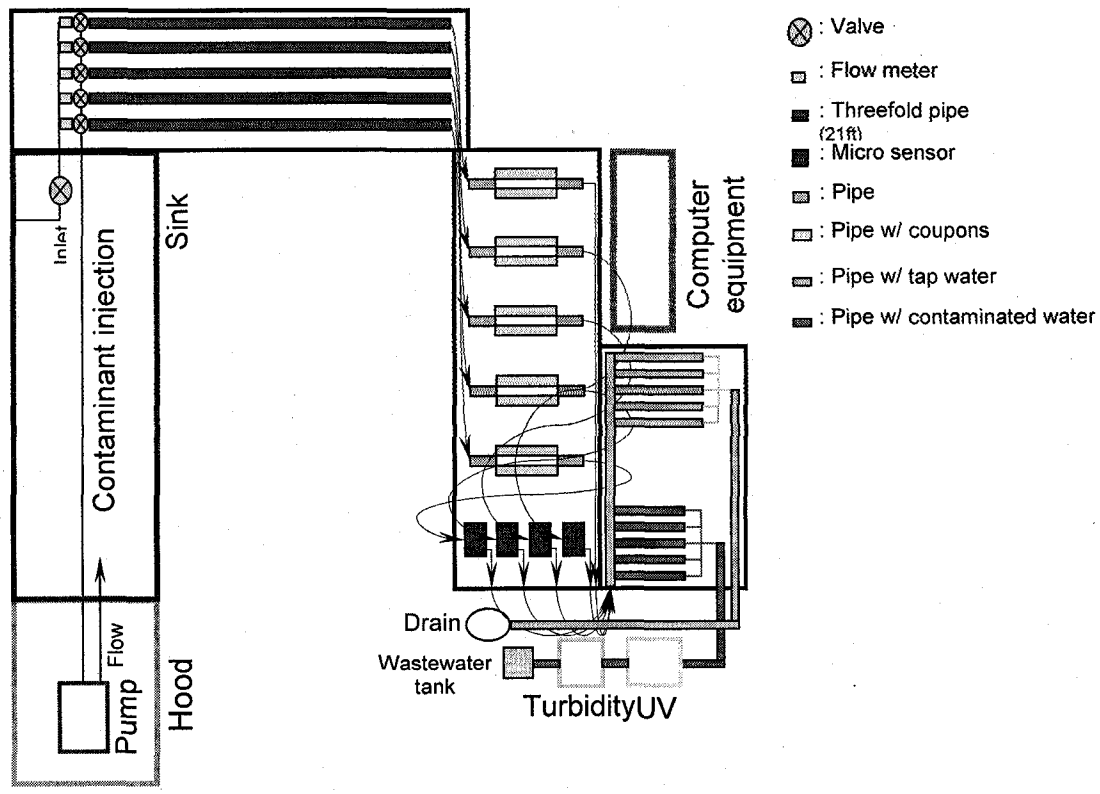



**Figure 5-3** Bench-Scale Distribution System Schematic drawing

### 5.2.2 Contaminant selection

Key properties of credible threat contaminants are:

- high toxicity
- high water solubility
- chemical and physical stability
- a lack of taste, color and odor
- a low chance of detection with normal analytical methods

According to Khan [11], chemical contaminants also possess these criteria:

- already used in chemical weapons
- available to potential terrorists
- likely to cause major morbidity or mortality
- potential of causing public panic and social disruption
- requiring special action for public health preparedness

The National Research Council [12] addresses morbidity and mortality, or toxicity, and focuses on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents and are persistent in water. The US Army Center for Health Promotion and Preventive Medicine listed sodium fluoroacetate as priority potential chemical threat agents [13]. The following specific chemical compounds were used in this investigation.

**Aldicarb**

Aldicarb is directly toxic through oral, dermal, and inhalation routes. It is toxic through secondary poisoning – when plants systemically exposed are consumed or when exposed insects, rodents, and birds are consumed by predators and scavengers. Aldicarb is highly soluble in water, soluble in acetone, zylene, ethyl, ether, toluene, and other organic solvents, and is highly mobile in soil. Levels of aldicarb in drinking water exceeding the health advisory level of 10 ppb established by the Office of Drinking Water at EPA have been recorded in couple states in U.S.

**Nicotine**

Nicotine is usually obtained from *Nicotiana tabacum*. Nicotine is one of the more than 4,000 chemicals found in the smoke from tobacco products such as cigarettes, cigars, and pipes. Nicotine is a naturally occurring colorless liquid that turns brown and acquires the odor of tobacco when exposed to air.

**Cycloheximide**

Actidione (Cycloheximide) is an antibiotic that acts as an inhibitor of protein synthesis in eukaryotes but not prokaryotes. Cycloheximide is an odorless, white, crystalline powder used in hospital and research laboratories as an antibiotic, a protein synthesis inhibitor, or a plant growth regulator. Cycloheximide also has broader agricultural use as a fungicide, but such use is being discontinued due to the recent findings of birth defects at low doses in animals.

**Sodium Arsenate**

Sodium arsenate is a pentavalent form of inorganic arsenic. It is a heptahydrate and normally exists as colorless crystals with no discernible odor. Inorganic arsenical compounds have been classified as Class A oncogens, demonstrating positive oncogenic effects based on sufficient human epidemiological evidence.

**Sodium Fluoroacetate**

Sodium fluoroacetate, also commonly known as compound 1080, sodium monofluororacetate, fratol, furatol, ratbane, and yasoknock, is a rodenticide. Fluoroacetic acid differs from the fluoroacetate ion that makes up sodium fluoroacetate only in the addition of a hydrogen atom, $C_2H_3FO_2$ or as a more protonated form.

### 5.2.3 Measurement of contaminant-instrument response

After the biofilm was established in the ¾ in PVC pipe for minimum 6-weeks and before contaminant injection, one coupon was removed from each pipe. This first coupon provided a baseline cell count (t=0). The other two coupons were taken from the pipe at after one and fifteen minutes following contaminant injection to determine biofilm response to chemical exposure.

Turbidity and UV were monitored prior to injection around three and half minutes and documented after one, fifteen minutes after contaminant injection to identify turbidity change from baseline. This comparison would provide the first indication that toxicity-induced sloughing might increase turbidity measurements in a distribution system.

### 5.2.4 Counting cells on the PVC coupon

Counting bacterial cells on the PVC coupon entailed staining of bacteria, preparing bacterial suspensions, and viewing the stained samples.

**Equipment needed**

- Epifluorescence microscope
- Optical Filters
    - excitation/emission = 480/500 nm for SYTO 9 (Nikon B-2A)
    - excitation/emission = 520/635 nm for propidium iodide (Nikon G-2E/C)
- Vortex
- Sterile 25mm Luer-Lock syringe filter holder (Life Sciences)
- 60ml Luer-Lock syringe.
- 5ml Luer-Lock syringe with needle.
- Sterile 25X200mm screw cap test tube.
- 10µl pipette
- 1000µl pipette
- Sterile Coupon scraping tool
- Forceps

**Materials needed**

- Live/Dead® *Bac*Light™ Bacterial viability kit L7012 containing:
    - SYTO 9 dye, 3.34mM, 300µL solution in DMSO
    - Propidium iodide, 20mM, 300µL solution in DMSO
    - *Bac*Light mounting oil, 10µL
- Sterile 0.85%NaCl solution
- 25 mm diameter 0.22 micron, black, polycarbonate membrane filter (Osmonics inc.)
- Sterile 2ml centrifuge tube

**Staining of bacteria**

For each of the three filter membranes:

1. Add 1.5µl of SYTO 9 and 1.5µl Propidium iodide in a 2ml centrifuge tube containing 1ml of sterile 0.85%NaCl solution.
2. Take up the stain solution into the 5ml syringe.
3. Slowly pass the stain solution through the filter holder containing the membrane filter.
4. Incubate filter holder containing filter and stain solution at room temperature in the dark for 15 minutes.
5. Pass an additional 5ml of sterile 0.85%NaCl solution through the filter holder to remove excess stain.
6. Place one drop of mounting oil on microscope slide.
7. With forceps remove the membrane filter from the holder and place on microscope slide.
8. Place one more drop of mounting oil onto filter surface and cover with cover slip.

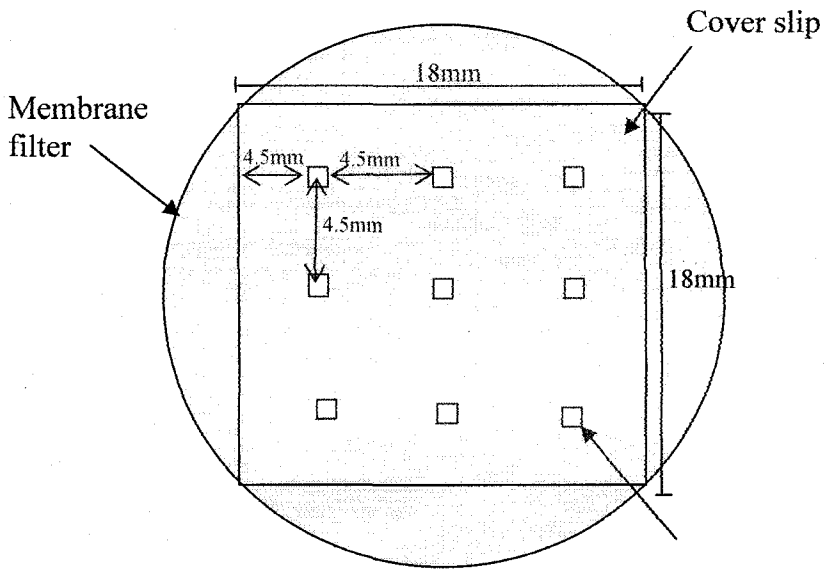
**Preparation of bacterial suspensions**

1. Place coupon in the large test tube containing 55ml solution containing 0.85%NaCl.
2. Use coupon scraping tool to gently scrape the biofilm from the coupon. Scrape up and down on the coupon 2 times on each side.
3. Remove the scraping tool and coupon from the test tube.
4. Vortex the test tube for 2 minutes to disperse the biofilm throughout the solution.
5. Poor the solution into a 60ml Luer-Lock syringe.

6. Attach the filter holder containing the 0.22 micron membrane filter to the syringe.
7. Filter all of the solution through the filter

**Viewing the samples**

1. View the slides using the 40X objective lens.




2. Capture images of 9 view fields on each filter from the following locations:
3. Upper left view field should be 4.5mm from the edges of the cover slip; this can be measured using the measurements at the edges of the stage. All other view fields should be spaced 4.5mm from other fields and the cover slip edges.
4. Each View field should have an image taken using both the B-2A and the G-2E/C optical filters.
5. When counting cells in each view field only well defined cells (cocci or bacilli), larger than approximately 1μm are to be counted.

Live cells fluoresced green, dead cells fluoresced red as indicated in Figure 5-4.

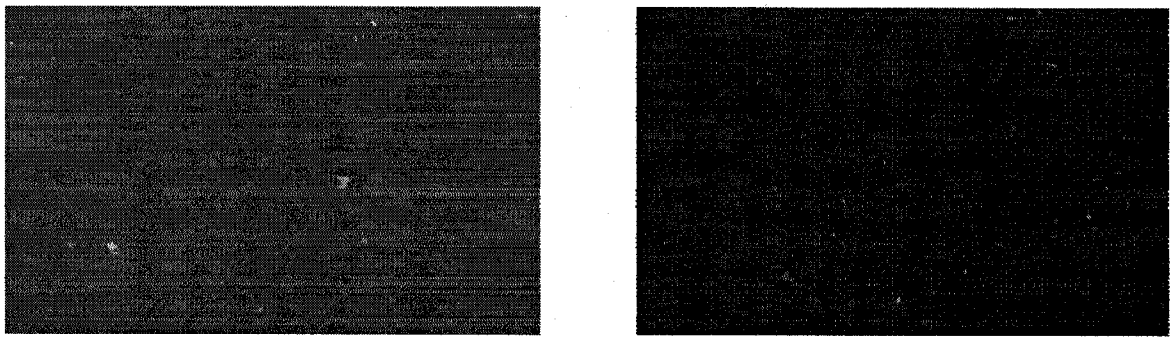


**Figure 5-4** Fluorescing Live (left) and Dead (right) Cells under UV Light

### 5.2.5 Determining log-removal of cells

To determine the log removal of cells from the coupons (y), the negative log was taken of the live cell count after exposure to the contaminant in the pipe at one minute and at 15 minutes ($c_t$), divided by the live cell count ($c_0$) before exposure to the contaminant.

$y = - \log (c_t/c_0)$

## 5.3 Results and Discussion

### 5.3.1 Documented Rotating Annular Bioreactors (RAB) Results

Figure 5-5 displays documented increase in turbidity after contaminants were added to the bioreactor at different concentrations. As shown, the turbidity increased markedly and quickly after the contaminants were added. It is expected that the reactors contained different quantities of biomass on the coupons, hence the differences in instrument response that did not necessarily correlate to the concentration of the contaminant. In cases where there is a decrease in turbidity after increased exposure time to the contaminant, it is thought that perhaps there was less biomass available on the coupon after initial exposure to the contaminant. [14]

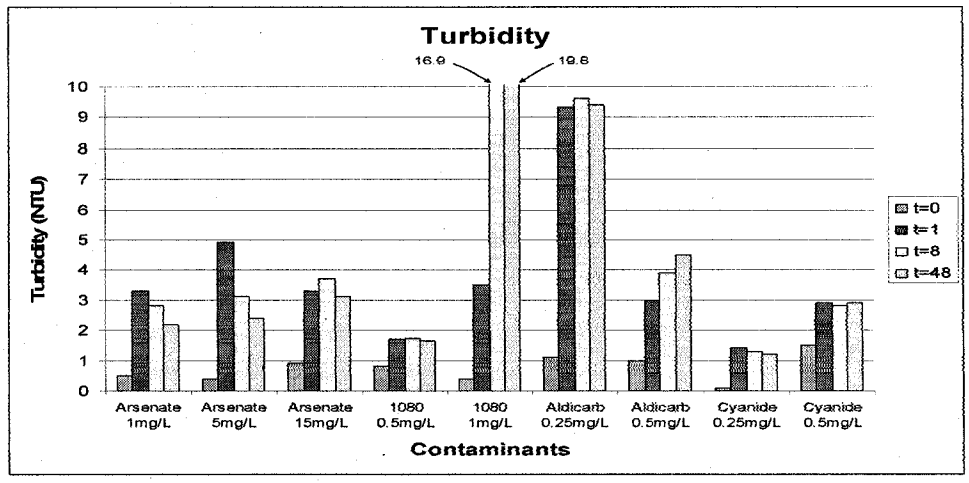



**Figure 5-5** Turbidity Response from Biofilm Exposure to Contaminants – RAB

To correlate the increased turbidity readings in the reactor water to coupon exposure to contaminants, the cells on the coupons were quantified before and after exposure to the contaminants. Figure 5-6 displays the log-removal of cells after exposure to the contaminants. The three t = 48 minute exposures that had log removal values of 2.0 were actually much larger, as the cell count for those three exposures were reduced to zero, making a log removal calculation impossible, or theoretically infinite, resulting in 100% removal. For comparison purposes, a log removal of one implies 90% removal, and a log removal of 0.5 provides 66% removal. The expected trend would be for an increased log removal of cells as the exposure time and contaminant concentration increases. In cases where this does not happen, consideration should be given to the variance in biomass on the individual coupons, remembering that one coupon was pulled at t = 0. [14]

Figure 5-6 clearly indicates a direct relationship between the concentration of the contaminant and cell removal for sodium arsenate and aldicarb. 1080 and sodium cyanide do not share a similar relationship between contaminant concentration and log removal rates, likely due to variance in cell counts per coupon. Again, in most cases, the

coupons were shown to be homogeneous, but when they weren't, it impacted the results. [14]

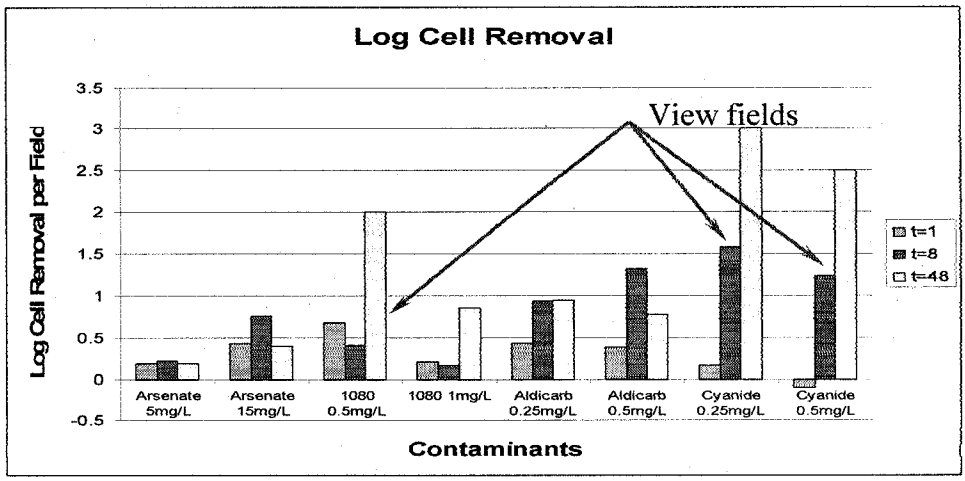



**Figure 5-6** Toxicity-Induced Cell Death per Contaminant Concentration – RAB

### 5.3.2 Bench-Scale Distribution System Results

Figures 5-7 through 5-9 display the change in turbidity measured by the on-line turbidimeter, UV absorption, and turbidity as signaled by the Micro Sensor Unit (MSU), respectively, after the contaminants were added to pipes at different concentrations. As shown, turbidity response to injection varied among contaminants. In most cases, the turbidity increased at t = 1 and decreased at t = 15 except after injection of 0.25ppm nicotine and 0.5ppm cycloheximide. It is expected that the coupons in the different pipes contained different quantities of biomass, hence the differences in instrument response that may not necessarily be correlated to the concentration of the contaminant. In cases where there is a decrease in turbidity after increased exposure time to the contaminant, it is thought that perhaps there was less biomass available on the coupon to be sloughed off after initial exposure to the contaminant.

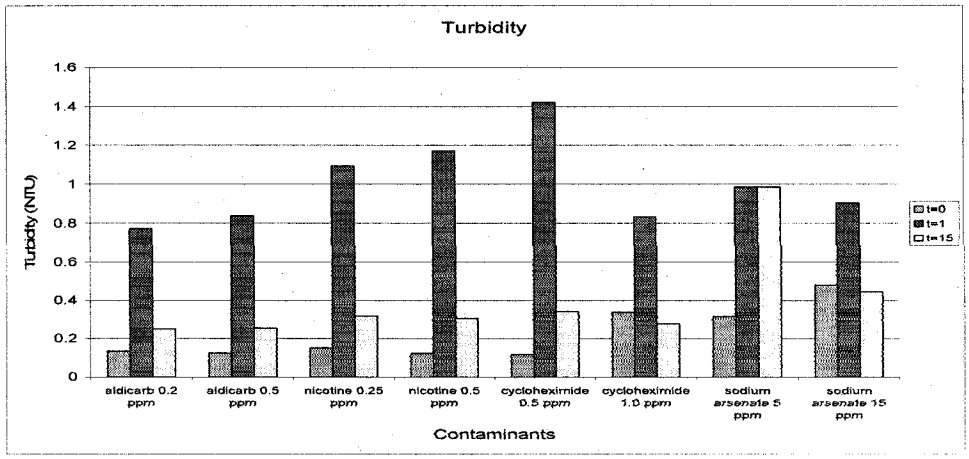



**Figure 5-7** Turbidity Response (On-line Turbidimeter) from Biofilm Exposure to Contaminants

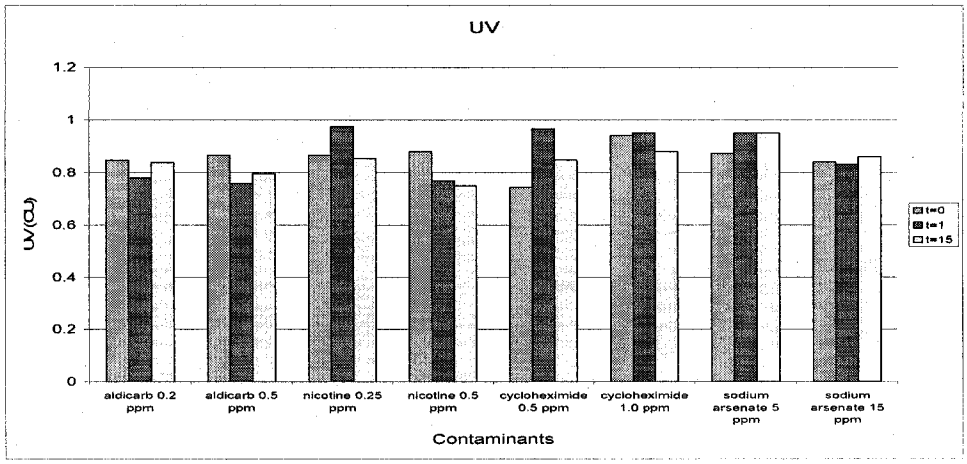



**Figure 5-8** UV Response from Biofilm Exposure to Contaminants

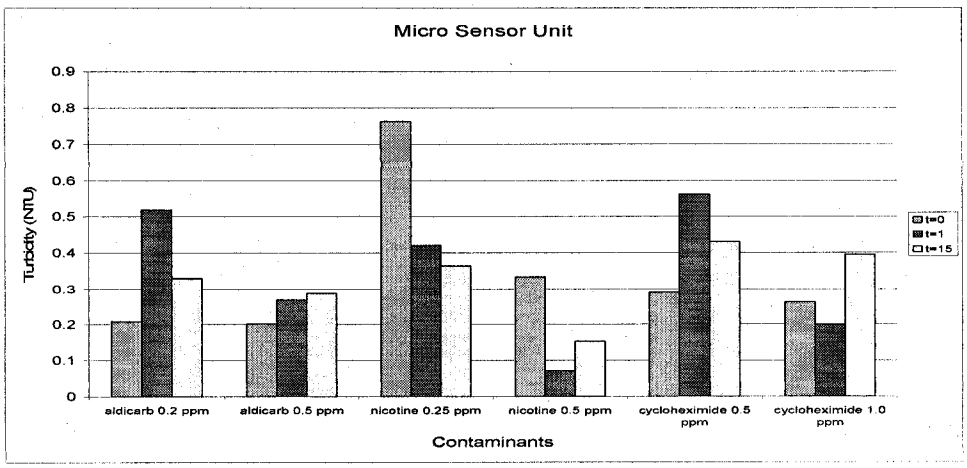



**Figure 5-9** Turbidity response (MSU) from Biofilm Exposure to Contaminants

Figures 5-10 through 5-14 each show the response from the on-line turbidimeter, the UV254 unit, and the micro sensor unit (MSU), after the contaminants were added to pipes at different concentrations. Of the two turbidity sensors, the on-line turbidimeter showed less noise; it responded with a higher peak value at t = 1 and subsequent, lesser peaks. The MSU turbidity response shows one strong peak with other peaks not comparable to those of the turbidimeter. In most of the UV data, spikes after the initial peak varied, and response to contaminant was less marked than turbidity response. It is likely variation in all responses reflect the process of biofilm attachment and detachment.

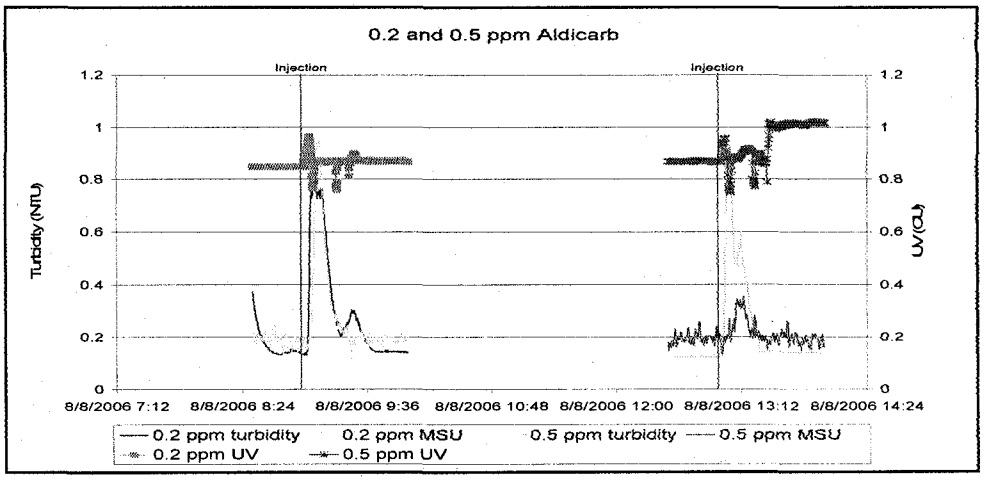



**Figure 5-10** Turbidity and UV254 Absorption Response from Biofilm Exposure to Aldicarb

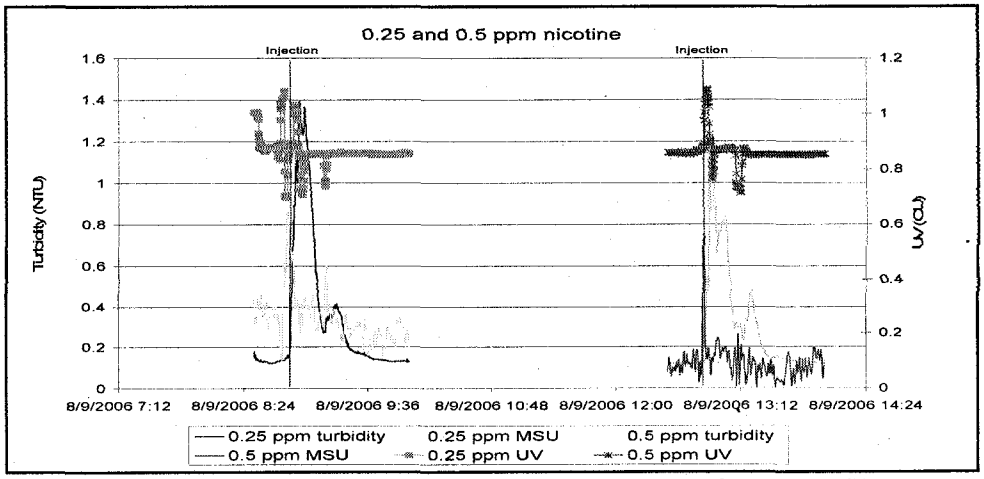



**Figure 5-11** Turbidity and UV254 Absorption Response from Biofilm Exposure to Nicotine

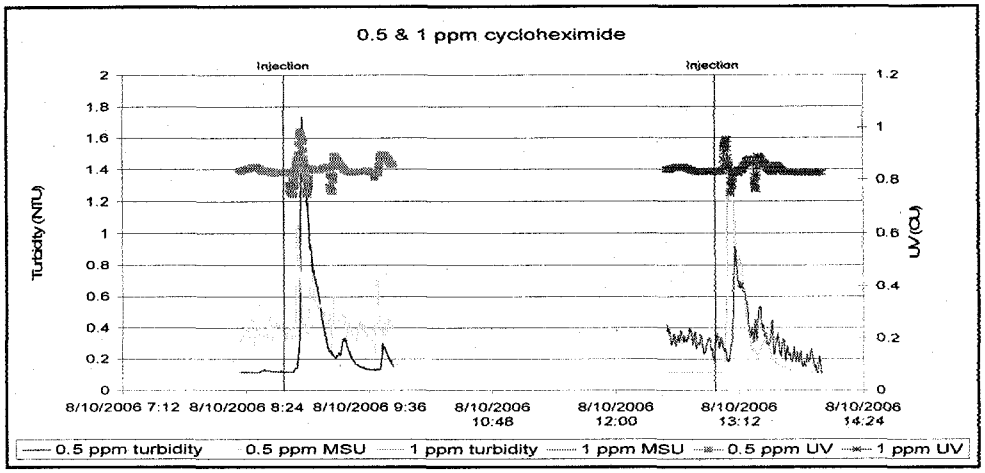



**Figure 5-12** Turbidity and UV254 Absorption Response from Biofilm Exposure to Cycloheximide

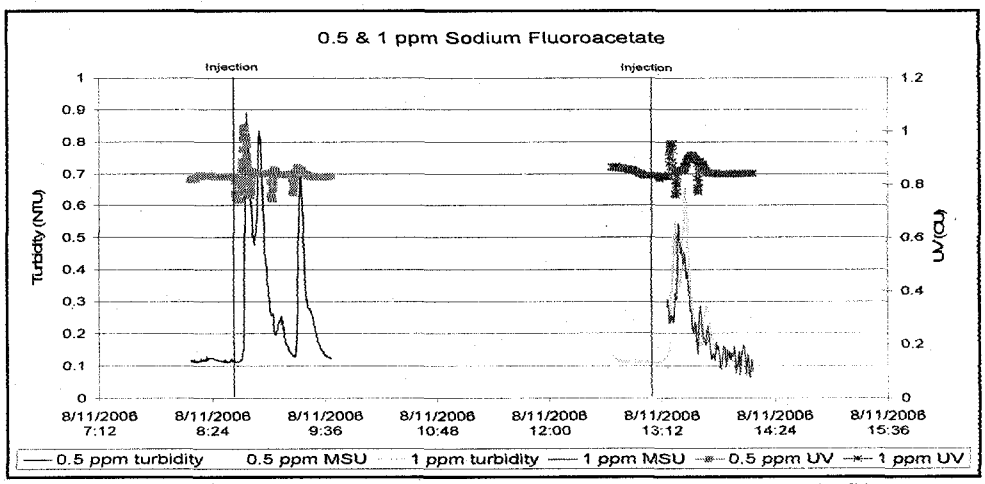



**Figure 5-13** Turbidity and UV254 Absorption Response from Biofilm Exposure to Sodium Fluoroacetate

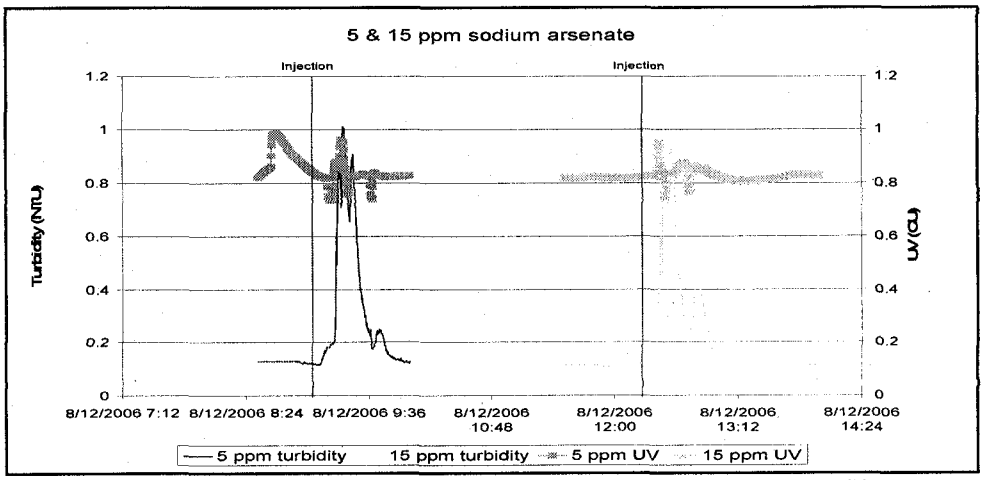



**Figure 5-14** Turbidity and UV254 Absorption Response from Biofilm Exposure to Sodium Arsenate

Figures 5-15 and 5-16 display the log-removal of live and dead cells in the current study after exposure to the contaminants. The expected trend would be for an increased log removal of cells as the exposure time and contaminant concentration increases. In cases where this does not happen, consideration should be given to the variance in biomass on the individual coupons, remembering that one coupon was pulled at t = 0. Figure 5-15 clearly indicates a direct relationship between the concentration of the contaminant and cell removal for nicotine and aldicarb. Cycloheximide and arsenate do not exhibit a similar relationship between contaminant concentration and log removal rates, likely due to variance in cell counts per coupon. Again, in most cases, the coupons were shown to be homogeneous, but when they weren't, it impacted the results. Dead cell log removal results do not reflect a relationship between the concentration of the contaminant and cell removal.

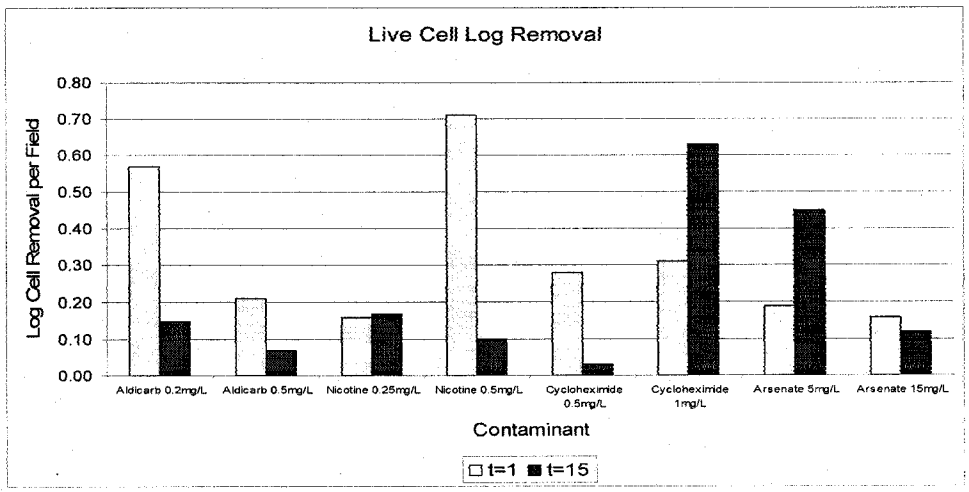



**Figure 5-15** Toxicity-Induced Cell Death for Each Contaminant Concentration

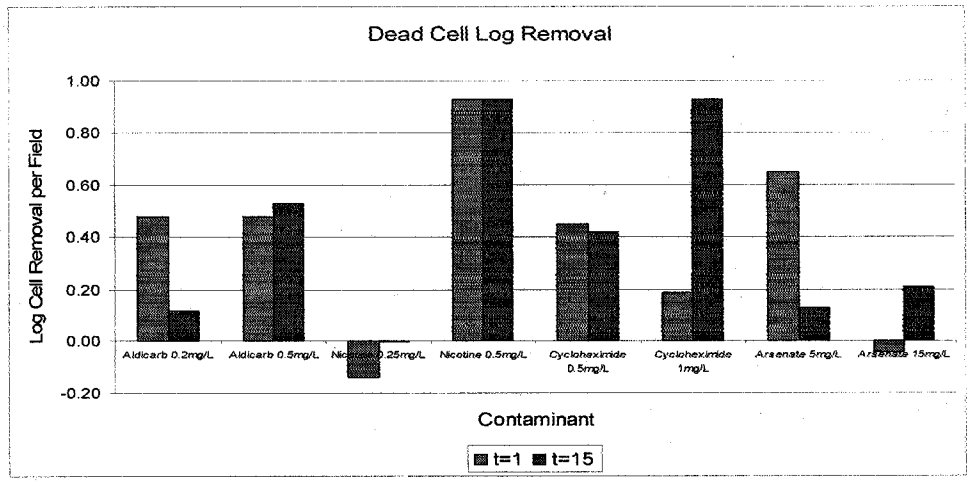



**Figure 5-16** Toxicity-Induced Cell Death for Each Contaminant Concentration

Comparing the documented batch reactor test results and those from the current bench-scale distribution system test, turbidity response to aldicarb was similar; turbidity response to sodium arsenate was not. However, log-removal data were similar, except for those with sodium arsenate at 5ppm.

## 5.4 Conclusion

In this study, the impact of chemical contamination on biofilm sloughing and the resulting change in measured turbidity and UV absorption with different contaminants, concentrations, and residual times was made. The interaction between toxic industrial chemicals and biofilm in the distribution system resulted in cell death and the sloughing off of biomass. As was demonstrated in the cell count experiments, there was a correlation between introduction of a chemical contaminant and the log-removal of cells from inline PVC coupons. It was further demonstrated that the sloughed-off biomass contributed to a measurable change in turbidity and UV254 absorption, with a greater response shown in turbidity for all contamination events, including those at lower concentrations. Increasing turbidity reduced the limit of detection of chemical contaminants by increasing the contaminant-instrument response. The results of this study emphasize the value of on-line turbidity monitoring in the water distribution system. Results further emphasize that biofilm in the distribution system might be a key tool in using on-line turbidity monitoring to detect the presence of toxic industrial chemicals. This relationship can help provide the early warning needed to protect public health in the event of distribution system chemical contamination.

## 5.5 References

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# Chapter 6
## Application and Modeling of Sensing for Real-time Monitoring of the Drinking Water System on the Colorado State University Campus

The water distribution system is the most vulnerable place for contamination, corrosion and biofilm buildup due to stagnation since it is openly accessible because of the miles of pipeline and connections. In order to have a low threat detection timeframe, multiple instruments measuring water quality real-time throughout the distribution system need to be installed. The instruments that are presently available are relatively expensive to purchase ($5-10K a piece) and install (up to $50K per detection point) and therefore providing adequate coverage of a typical distribution system is usually prohibitively expensive.

One of the primary objectives of this project was to work with the sponsor, ST-Infonox, to develop and test a cost-effective detection instrument that could easily be installed throughout a water distribution system. Rather than beginning with instruments developed for regulatory compliance measurements in a water plant or laboratory, the project team developed sensors with the intention of less resolution and accuracy in exchange for lower cost. The Micro Sensor Unit (MSU) that was developed and the testing and modeling completed to demonstrate its effectiveness is discussed in this chapter.

The real-time data collected by the MSU network can be used in conjunction with hydraulic models to predict the behavior and spread of substances throughout the water system. The MSU network that we have developed with this project provides real-time surveillance and helps pin-point exact locations of contamination through data collection and modeling.

$H_2O$ MAP, software that can model the hydraulic and chemical characteristics of a distribution system, has been used to study the CSU facility. Using input data from the actual CSU system, we calibrate the model based on flow rates and pipe characteristics. We simulate several intentional contamination scenarios at different points around campus and determine how effective different configurations of the MSU network are at detecting the event. The hydraulic model will also be used to determine the optimum location and number of MSUs. Finally, the modeling software will be used to predict transport of a contaminant out of the system so that mitigation procedures can be developed.

## 6.1. Introduction

This study utilized virtual real-time monitoring of bench scale and Colorado State University campus water distribution systems. Detection of intended and unintended water quality changes due to contamination, pipe breaks, and cross-connections in the system can prevent waterborne illness and outbreaks. Although high resolution instruments are currently available, the cost of these units makes it prohibitive to provide monitoring at the number of points required. The approach studied in this project was to develop and deploy the instruments which is low resolution and low cost at multiple points in a distribution system.

Two main groups (fixed and movable) of water quality instruments were used to run bench scale water distribution system experiments. The fixed water quality installation group included four Hach Company instruments, pH, conductivity, turbidity, and chlorine residual sensors and an Optek UV 254 sensor. The Micro Sensor Unit, which includes pH, turbidity, chlorine and temperature is more mobile and could potentially be moved to different sites. The installation of non-permanent, mobile sensors needs pipe connections to the main pipes and a power supply that is simple and easy to install and maintain.

There are several water distribution design software packages including $H_2O$ Map and Infowater which have been developed by the MWHSoft Company. Although the cost of an MSU is less than corresponding fixed water quality instruments, it is not possible to install these units everywhere we might want to. Therefore, $H_2O$ Map modeling was used to determine MSU installation locations on the Colorado State University campus to optimize contaminant detection.

### 6.1.1. SCADA System

SCADA (Supervisory Control and Data Acquisition) refers to a central system that monitors and controls a complete site or a system spread out over a long distance or a large-scale, distributed measurement system. It is typical to use SCADA technology to monitor/control chemical, physical or transport processes, in municipal water supply systems. SCADA systems include the means for connecting instruments to other system components, including input/output signal hardware, controllers, Human Machine Interface (HMI), networks, communication, Remote Terminal Unit (RTU) or a Programmable Logic Controller (PLC),and software as demonstrated in Figure 6-1.

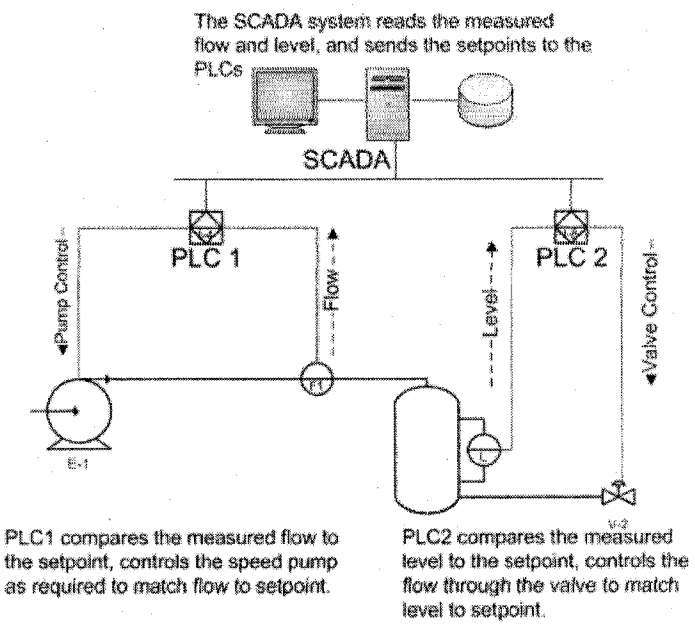



**Figure 6-1** Diagram of SCADA System [5]

Monitoring instruments are connected to remote telemetry units or programmable logic controllers to convert instrument outputs to appropriate units, compare the instrument responses to programmed criteria, generate alarms if required, and send control signals to other equipment. The host computer polls the PLCs and RTUs for data and in some systems, analyzes this data and provides specified information to system operators.

A HMI is the device which presents process data to a human operator, and through which the human operator controls the process. PLC units provide automated, pre-programmed control over a process. The RTU connects to physical equipment, and reads status data such as the open/closed status from a switch or a valve, and reads measurements such as pressure, flow, voltage or current.

### 6.1.2. Micro Sensor Unit (MSU)

The Micro Sensor Unit that was developed for this project includes sensors to measure four water quality parameters including pH, chlorine, turbidity, and temperature (Figure 6-2). It has been designed to be plug and play to ease installation. Tap or test water flows through the four sensors, and the MSU requires a drain for discharging the water. The MSU can be easily opened for cleaning or sensor replacement and can be installed in a remote location with no local internet access.

Four water quality parameters were selected – pH, turbidity, free chlorine and temperature – since they are widely measured in water treatment facilities, and are familiar to water plant operators and management staff. While providing an excellent foundation for detecting contamination events, these parameters also allow detection of corrosion, biofilm buildup, and general water quality upsets in the distribution system.

The sensitivity and accuracy of the pH, chlorine, turbidity, and temperature sensors within the MSU compares well against industry standard instruments. The detection capability is sufficient and accurate to detect changes for purposes of contamination, corrosion and stagnation monitoring. The Micro Sensor Units use detection micro sensors which are reliable, low cost and easily upgraded or replaced as sensors are added to measure other parameters. Development of the MSU occurred at the CSU Environmental labs during 2005 and 2006 in collaboration with ST-Infonox.

For integration into the Micro Sensor Network, four secure communication options are available depending on usage and location requirements. Short range Zigbee, short range 802.11b, Medium range spread spectrum and long range cellular (GSM).

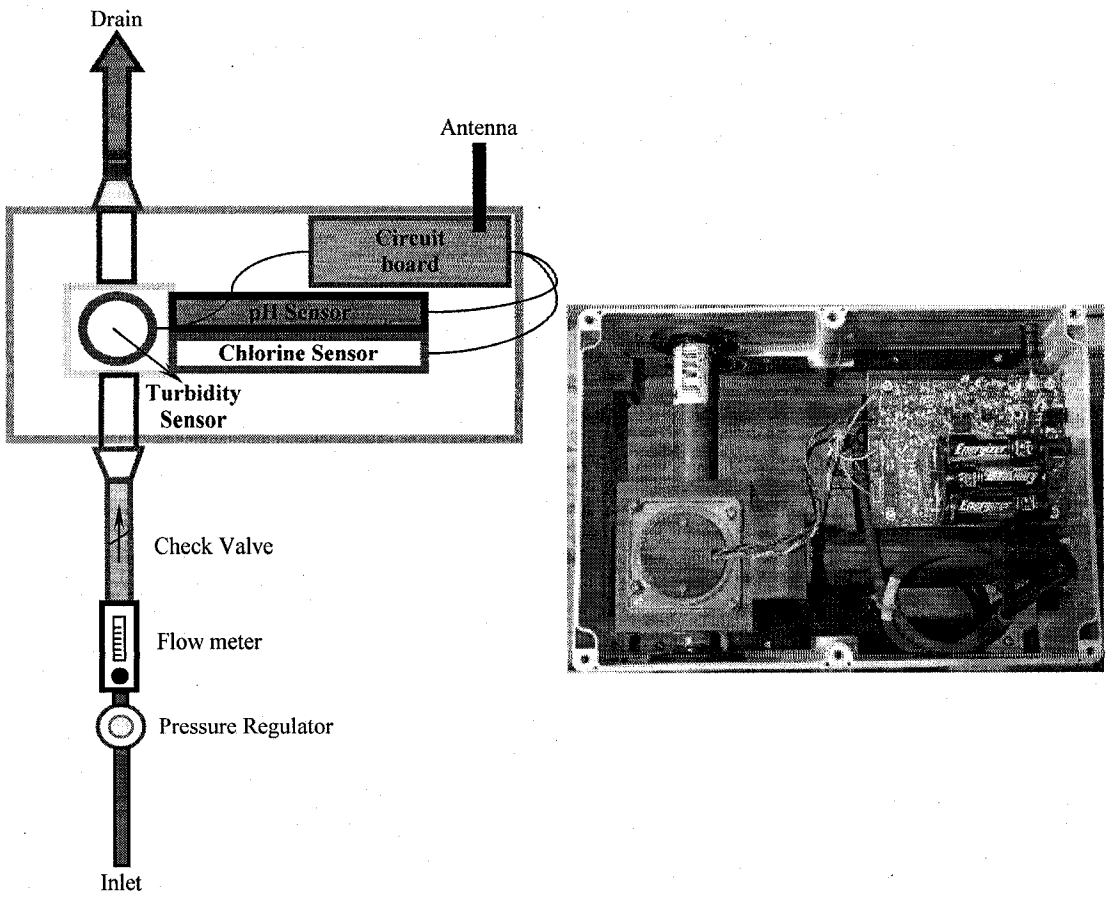



**Figure 6-2** Micro Sensor Unit Architecture and Real Picture

For this project, the research team chose to send the output from each MSU over a wireless (Zigbee or GSM Cellular) or wired (Ethernet) communication channel to the SCOPE$H_2O$ server located in the Environmental Engineering Lab, where the data is stored.

### 6.1.3. SCOPE

SCOPE-$H_2O$™ is a complete solution for Real-Time Water Distribution System Monitoring that has been developed and marketed by ST-Infonox, the company that collaborated on the development of the MSU prototype. SCOPE-$H_2O$™ monitors the water throughout the city distribution system using MSU networks. Multiple MSUs are spatially distributed throughout the water distribution system to detect contamination, corrosion build-up and stagnation points, allowing for early pre-emption by taking corrective action. The SCOPE$H_2O$ platform used in this project has several benefits, including:

- Sensor network approach yields coverage of an entire city, not just single points
- Cost effective due to relatively inexpensive sensors which are optimized for detecting contamination events

The overall goals and results of the SCOPE-MSU System are shown in Table 6-1. There were 5 different goals and each goal was completed. Several chemicals which are recommended by EPA were used for this test and MSU detected these chemicals. Multiple MSUs were installed across the campus and data communications and collection were verified. Using SCOPE, real-time data were collected and imported into Excel for archiving and analysis.

**Table 6-1** SCOPE $H_2O$ System Goals

| Goal | Result |
|---|---|
| Ensure detection sensors properly detect chemical contaminants, bio-film buildup, corrosion, etc. | Demonstrated detection of EPA contaminants, other chemicals, pipe bio-film buildup, corrosion agents. |
| Demonstrate straightforward installation and communication scenarios. | Multiple installation scenarios demonstrated on CSU campus, labs, and local businesses. Zigbee and Ethernet communication solutions tested and verified. |
| View real-time and archived data using SCOPE dashboards and reports. Export data to other applications. | Verified proper operation of SCOPE monitoring dashboards. Reports generated, data imported into Excel. |
| Demonstrate complete system operation including detection, interdiction, and resolution of events. | Complete system demonstrated over campus wide setting. System used exclusively for contaminant and bio-film buildup tests. |
| Show the system is reliable and requires minimal maintenance. | Minimal maintenance required for initial test units. Almost no data dropouts encountered during 3 month test. Limited recalibrations required. |

In Figure 6-3, the flow chart of the use of a SCOPE-MSU system is shown. MSU that were installed multiple locations (Environmental Lab, Engineering Research Center, Colorado State University Main campus, and Commercial sites) were used to test this system In addition, the MSUs were used to do chemical injection tests, biofilm tests and to provide data for modeling.

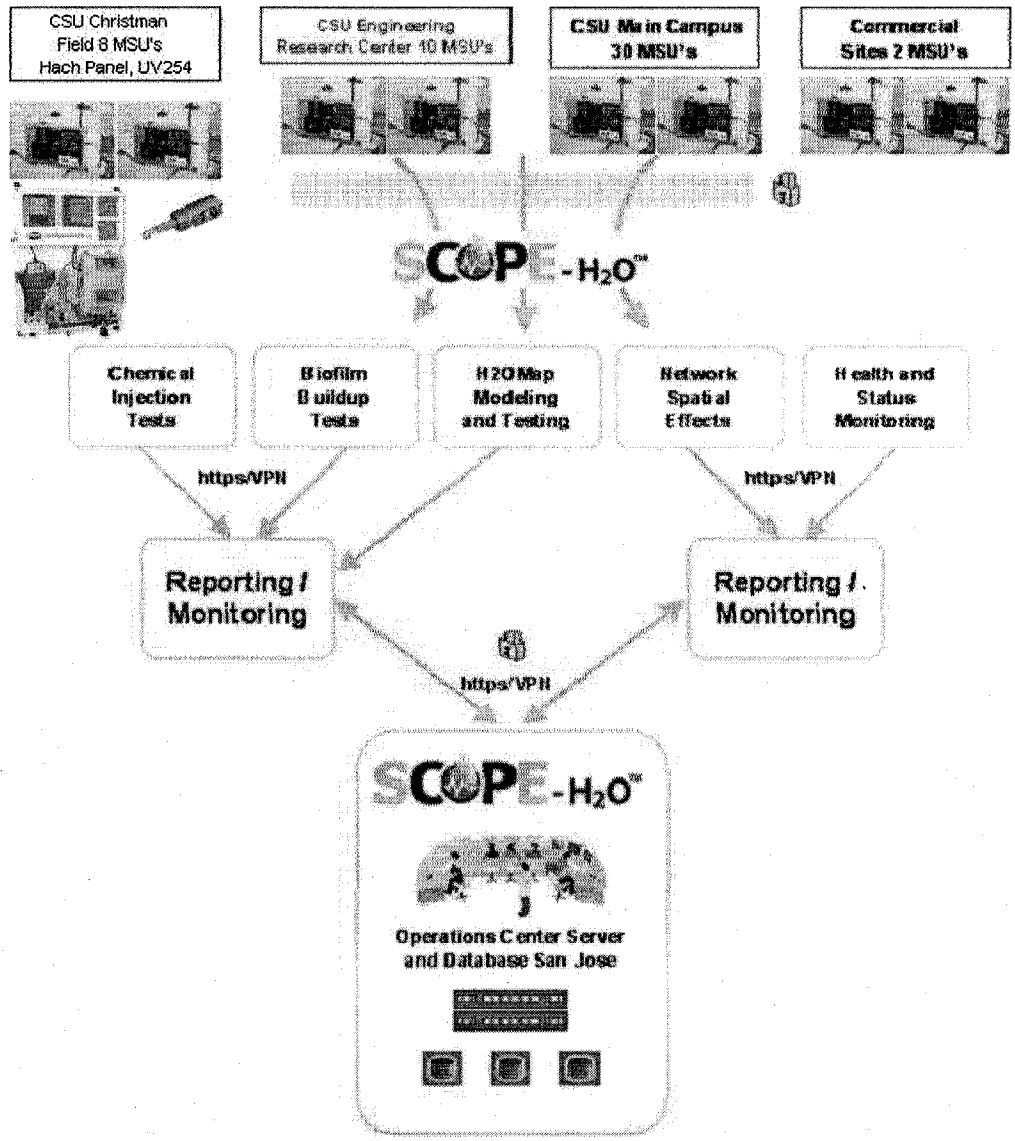



**Figure 6-3** Flow Chart of the use of a SCOPE-MSU system.

## 6.2. Methods and Materials

### 6.2.1. MSU Installation at Colorado State University

As shown in the Figure 6-4, installation of the Micro Sensor Unit (MSU) is straightforward. Water from the distribution system enters into a pressure regulator, flow meter, and check valve, and then passes into the MSU. All measurements are performed in the sample chamber. Water exits through the top of the MSU, where it is then sent to a drain. No reagents are added to the water; however, the discharge is typically put into the sanitary sewer. Typical flow rate is 4-6 GPH.

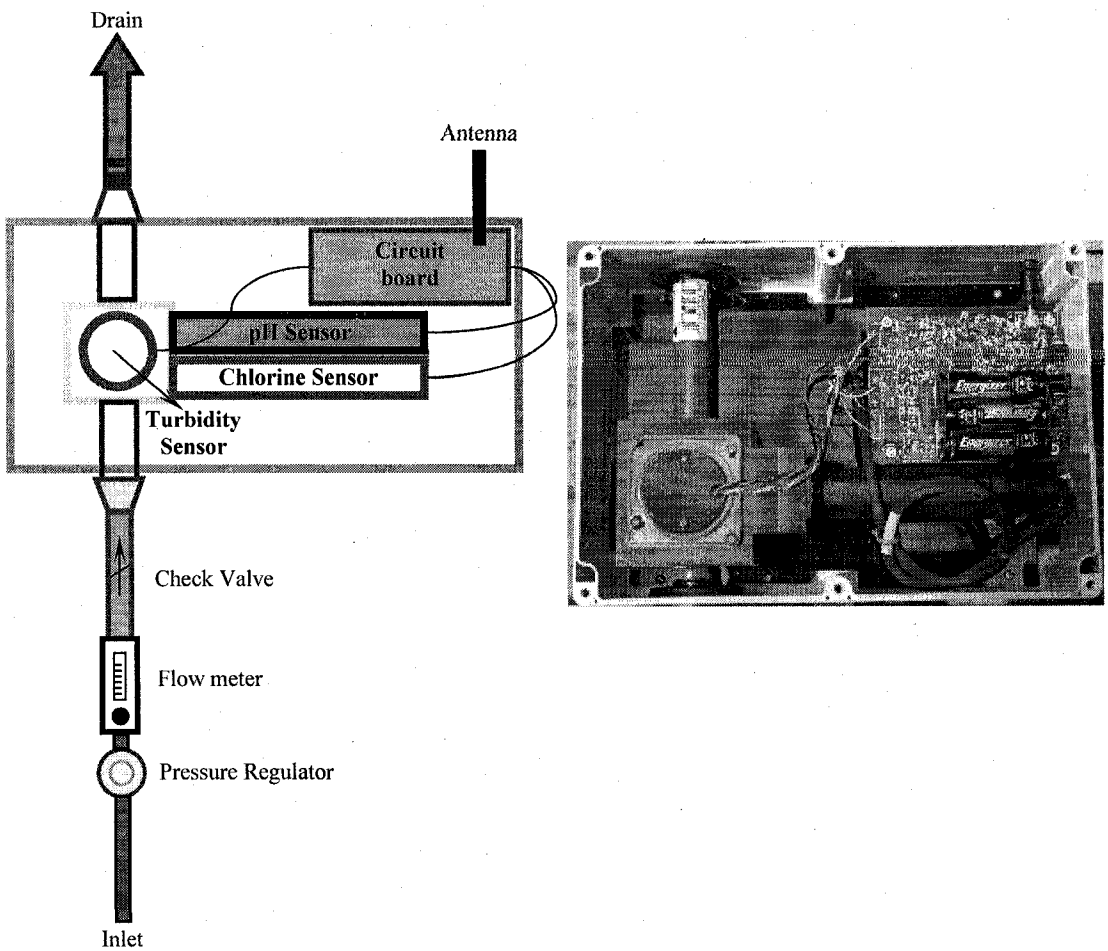



**Figure 6-4** Micro Sensor Unit Architecture and Real Picture

Five MSUs were installed on the CSU main campus and information (location's name and coordinate with communication) of each location and area are shown in Table 6-2 and Figure 6-5.

**Table 6-2** Five MSU Located at CSU Campus

| Description | Deployed | Unit ID | Communications | N | W |
|---|---|---|---|---|---|
| Facilities building | 12/7/2006 | 31A | GSM phone (970-412-3296) | 40.57142 | 105.07950 |
| Rockwell Hall | | 31B | GSM phone (970-412-3297) | 40.57753 | 105.08391 |
| Moby | 1/20/2007 | 31F | GSM phone (970-581-8865) | 40.57522 | 105.09334 |
| Visual arts | | 31C | GSM phone (970-581-9025) | 40.57043 | 105.08593 |
| Guggenheim | 1/25/2007 | 30F | GSM phone (970-581-9031) | 40.5777 | 105.08015 |

**Figure 6-5** Five Locations of MSU at CSU Campus

Facilities Service Center

Rockwell Hall

Moby Arena

Visual Art Building

Guggenheim Hall

### 6.2.2. $H_2O$ Map

There are four major capabilities for the modeling and analysis of water distribution systems by $H_2O$Map (MWH soft, Inc., Pasadena, CA). $H_2O$Map can construct an accurate representation of the distribution system attributes required for analysis. It may perform several different types of hydraulic and water quality network simulations. It offers many powerful GIS and mapping functions and it allows information to be easily exchanged with other applications such as CAD, spreadsheets, and relational databases. It has many tools to analyze model results such as annotating/labeling, color-coding, graphing, contouring, profiling, reporting, and animation.

Modeling water quality in water distribution systems has become a widely accepted tool in support of water supply planning, operations and research (John Frazey, 2004). Models can provide a picture of how water moves throughout the distribution system and one of the emerging abilities of models is to help utilities understand how the system will respond to either accidental or intentional contamination. Specifically, as applied to water system security, models have been used to examine three different time frames. First, they have been used as planning tools to assess vulnerabilities of the systems for various events. Second, they are used as a real-time tool during actual events for assistance in formulating responses. Third, they have been used for investigating events that occurred in the past.

**Water Quality Simulations**

There are three water simulations that these models can complete: water age, source tracing, and chemical constituent concentration spatial and temporal profiles.

The water age component calculates the age of the water in the network, computed at any node. The models compute this characteristic based on EPANET calculations, which is performed under constant hydraulic conditions and is a simple, non-specific measure of the overall quality of delivered water. This analysis tracks the percent of water over time that reaches any node in the network from an original specified node. The specified node can be any node in the network. The information required for age analysis is pipe velocity and flow rate; therefore, no reaction coefficients are required (Haestad Methods, 2002).

The trace function determines the fraction of water that originates from a specified node over time, again with the calculations based on EPANET. EPANET treats the source node as a constant source of non-reacting constituent, entering the network at the node with a concentration of 100 (Rossman, 2000). The analysis can be useful for analyzing systems with two or more raw water sources, thus showing how the water blended over time (Rossman, 2000). It can only be performed using the EPS method with input information of pipe velocity and flow rate (Haestad Methods, 2002).

The final water quality analysis is the chemical constituent. A constituent is defined as any substance for which the growth or decay can be adequately described through bulk and wall reaction coefficients (Haestad Methods, 2002). This type of analysis determines the concentration of the constituent at all nodes and links in the system. The constituent can be anything from chlorine to fluoride to an unwanted contaminant. This analysis determines the concentration of the constituent at all nodes and links in the system (Haestad Method, 2002). The source of the constituent can be

from the main treatment works, well head or satellite facility, or unwanted contaminant intrusion and either conservative or reactive species can be modeled.

This analysis can only be performed using the EPS (Expanding Period Simulation) the following must be input into the model for chemical constituent calculations:

- Initial Constituent: the initial concentration of the constituent at the beginning of the analysis.
- Bulk Reaction: reaction rate used to model reactions of the constituent within the bulk flow.
- Wall Reaction: reaction rate constant for the material reacting along the pipe wall.

The constituent analysis is based on the principles of conservation of mass and reaction kinetics. There are three processes used to conduct this calculation (MWH Soft, Inc., 2002):

- Advection in pipes: This is based on that fact that the constituent will travel down the pipe with the same average velocity as the fluid carrying it. While traveling, the constituent will react, either growing or decaying. Longitudinal dispersion is usually not an important transport mechanism under most operating conditions meaning there is no intermixing of mass between adjacent parcels of water traveling down a pipe.
- Mixing at Junctions: The mixing is assumed to be complete and instantaneous.
- Mixing at Tanks: There are several different types of mixing in tanks. These different types of mixing are discussed under tank mixing.

**Mode of contaminant entry**

Another similarity between these distribution models is the mode of entry for the contaminant. The models allow any node in the system to serve as the source for a chemical constituent. Each modeling program allows several different methods to introduce the contaminant into the system. These are explained below (Haestad Methods, 2002; MWH Soft, Inc., 2002; Rossman, 2000).

- Concentration: This method fixes the concentration of any external inflow entering the system at a node. An example would be a reservoir or a negative demand located at a junction.
- Flow Paced Booster: This method adds a fixed concentration to the flow resulting from the mixing of all inflow to the node from other points in the network.
- Setpoint booster: This fixes the concentration of any flow leaving the node. This can be used as long as the concentration resulting from all inflow to the node is below the setpoint.
- Mass Booster: This is used to add a fixed mass flow to the flow entering the node from other points in the network.

**Chemistry modeling**

The water models use the EPANET calculation methods for modeling chemical reactions. The EPANET method can model bulk and wall reactions, in regards to decay or growth. The bulk reactions used by these programs include: simple first-order decay, first-order saturation growth, two-component second order decay, Michealis-Menton Decay kinetics, or zero-order growth (Rossman, 2000).

**Tank mixing**

Tank mixing is another item that impacts the contaminant character with in the system. Again, the models complete this calculation based on EPANET methods, which includes complete mixing, two-compartment mixing, first in/first out plug flow, and last in/last out plug flow. These are described more in detail below.

- Completely mixed: This assumes that all water entering the tank is completely and instantaneously mixed with the water already in the tank. This is a reasonable assumption for many tanks operating under fill-and-draw conditions providing sufficient momentum flux imparted to inflow (Rossman, 2000).
- Two-compartment mixing: this assumes that the tank storage is divided into two completely mixed compartments. Inflow and outflow are assumed to take place in the first compartment. The second compartment receives over-flow from the first, and this overflow is completely mixed. The inlet and outlets of the tanks are in the first compartment. As new water enters, it completely mixes with the first compartment and overflow is sent to the second compartment. When water leaves the first compartment, it receives an equivalent amount of water from the second compartment. Based on this information, the second compartment can have dead zones (Rossman, 2000).
- First in/first out plug flow model: this model assumes there is no mixing of water during the time it is in the tank. Water parcels are effectively stacked on one another, moving through the tank in a segregated fashion where the first parcel to enter is the first parcel to leave. This is most appropriate for baffled tanks that operate with simultaneous inflow and out flow (Rossman, 2000).

- Last in/last out plug flow model: this model assumes that no water mixing occurs in the tank. Water parcels still stack up one on top of another and the last parcel to enter is the first to leave from the bottom of the tank. This is most appropriate for tall, narrow standpipes that have an inlet/outlet pipe at the bottom and low momentum inflow (Rossman, 2000).

Out of these tank mixing options, completely mixed option was used for this modeling. I used first-order decay for this modeling out of couple other reactions.

### 6.2.3 Contaminant explanation and source from EPA list

For testing of the MSU efficacy, a list of potential intentional contaminants needed to be generated. Key properties of credible threat contaminants are:

- high toxicity
- high water solubility
- chemical and physical stability
- a lack of taste, color and odor
- a low chance of detection with normal analytical methods

According to Khan (2000) chemical contaminants also possess these criteria:

- already known to be weaponized
- available to potential terrorists
- likely to cause major morbidity or mortality
- potential of causing public panic and social disruption
- requiring special action for public health preparedness

The National Research Council (2002) addresses morbidity and mortality, or toxicity, and focuses on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents and are persistent in water. The US Army Center for Health Promotion and Preventive Medicine listed sodium fluoroacetate as priority potential chemical threat agents (Burrows 1997). The following specific chemical compounds were used in this study to test the effectiveness of the MSU to detect intentional contamination:

**Aldicarb**

Aldicarb is directly toxic through oral, dermal, and inhalation routes. It is toxic through secondary poisoning – when plants systemically exposed are consumed or when exposed insects, rodents, and birds are consumed by predators and scavengers. Aldicarb is highly soluble in water, soluble in acetone, zylene, ethyl, ether, toluene, and other organic solvents, and is highly mobile in soil. Levels of aldicarb in drinking water exceeding the health advisory level of 10 ppb established by the Office of Drinking Water at EPA have been recorded in several states in the U.S.

**Dichlorvos** [10]

The other chemical name of Dichlorvos ($C_4H_7C_{12}O_4P$) is 2,2-dichlorovinyl dimethyl phosphate and it is a colorless to amber liquid with a mild chemical odor. The water solubility is 10,000 mg/L. Dichlorvos is an organophosphate compound used to control household, public health, and stored product insects. It is highly toxic, because it may cause cancer and there is only a small margin of safety for other effects. Dichlorvos is used to treat a variety of parasitic worm infections in dogs, livestock, and humans.

**Nicotine**

Nicotine is usually obtained from *Nicotiana tabacum*. Nicotine is one of the more than 4,000 chemicals found in the smoke from tobacco products such as cigarettes, cigars, and pipes. Nicotine is a naturally occurring colorless liquid that turns brown and acquires the odor of tobacco when exposed to air. The immediate effects of nicotine include increased blood pressure and heart rate, thickening of blood, narrowing of arteries, decrease in skin temperature, increase in respiration, and stimulation of the central nervous system, vomiting, and diarrhea.

**Cycloheximide**

Actidione (Cycloheximide) is an antibiotic that acts as an inhibitor of protein synthesis in eukaryotes but not prokaryotes. Cycloheximide is an odorless, white, crystalline powder used in hospital and research laboratories as an antibiotic, a protein synthesis inhibitor, or a plant growth regulator. Cycloheximide also has broader agricultural use as a fungicide, but such use is being discontinued due to the recent findings of birth defects at low doses in animals. Cycloheximide can irritate the skin and also may cause cancer.

**Sodium Fluoroacetate**

Sodium fluoroacetate, also commonly known as compound 1080, sodium monofluororacetate, fratol, furatol, ratbane, and yasoknock, is a rodenticide. Fluoroacetic acid differs from the fluoroacetate ion that makes up sodium fluoroacetate only in the addition of a hydrogen atom, $C_2H_3FO_2$ or as a more protonated form. Sodium fluoroacetate is a deadly human poison by ingestion. Fluoroacetate poisoning results in a lethal accumulation of citric acid, which in turn causes violent convulsions and death from cardiac failure or respiratory arrest.

**Glyphosate** [12]

The other chemical name of Glyphosate ($C_3H_8NO_5P$) is N-(phosphonomethyl) glycine and it is a colorless crystal at room temperature. The water solubility is 12,000 mg/L. It is a broad-spectrum, nonselective systemic herbicide used for control of annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. It is an acid and its salts are moderately toxic compounds in EPA toxicity class II. It is generally distributed as water-soluble concentrates and powders.

**Arsenic Trioxide** [9]

Arsenic trioxide is one of the arsenites found in nature and is produced mainly from by-products of copper smelting. Arsenic trioxide ($As_2O_3$) is a white or transparent solid in the form of glassy, shapeless lumps or a crystalline powder that resembles sugar. It has no odor or taste. The effect of arsenic trioxide may cause a burning sensation to the nose, mouth, and eyes and cause coughing, shortness of breath, headache, sore throat, and dizziness. The solubility is low in water. OSHA PEL (permissible exposure limit) is 10 $\mu g/m^3$ and NIOSH IDLH (immediately dangerous to life or health) is 5 mg $As/m^3$.

**Dicamba** [11]

The other chemical name of Dicamba ($C_8H_6C_{l2}O_3$) is 3,6-dichloro-O-anisic acid and it is an odorless, white crystalline solid. The technical acid is a pale buff crystalline solid. The water solubility is 6500 mg/L. It is a benzoic acid herbicide. It is used in pastures, range land, and non-crop areas such as fence-rows and roadways to control weeds with combination with a phenoxyalkanoic acid or other herbicide. It is has classified this toxicity class III (slightly toxic) by EPA because of its irritating, corrosive effect on skin and eyes.

**Potassium Ferricyanide** [13]

The other chemical name of Potassium Ferricyanide ($K_3Fe(CN)_6$) is Potassium ferricynate; tripotassium hexacyanoferrate; Ferrate (3-), hexacyano, tripotassium

Bright red, crystalline powder. It is odorless and Slowly soluble in 2.5 parts cold water. It is also stable. Very little information on the toxicity of potassium ferricyanide was found in the available literature. Exposure of the general population to potassium

ferricyanide occurs primarily through its use in photographic processing, particularly in home and school darkrooms.

### 6.3. Results from Chemical Injection Testing of MSUs

Chemical injection testing was conducted with the ten chemicals described above. The objective of the testing was to determine the response of the MSU sensors to varying concentrations of the potential chemical contaminants. Out of the ten chemicals, example results of the nicotine contaminant injection are shown in Figure 6-6. Two different group instruments were used and the comparison between two group instrument results is discussed.

A liter of nicotine solution (5 ppm) was injected twice for this test and the vertical red line indicates the time of the chemical injection (Figure 6-6). The response of the chlorine MSU sensor is compared to the Hach chlorine unit and the Optek UV absorbance instrument. Through Figure 6-7 to 6-9, the results of nicotine injection are shown about conductivity, pH, and turbidity respectively. The comparison between MSU and 1720D results are shown in Figure 6-9.

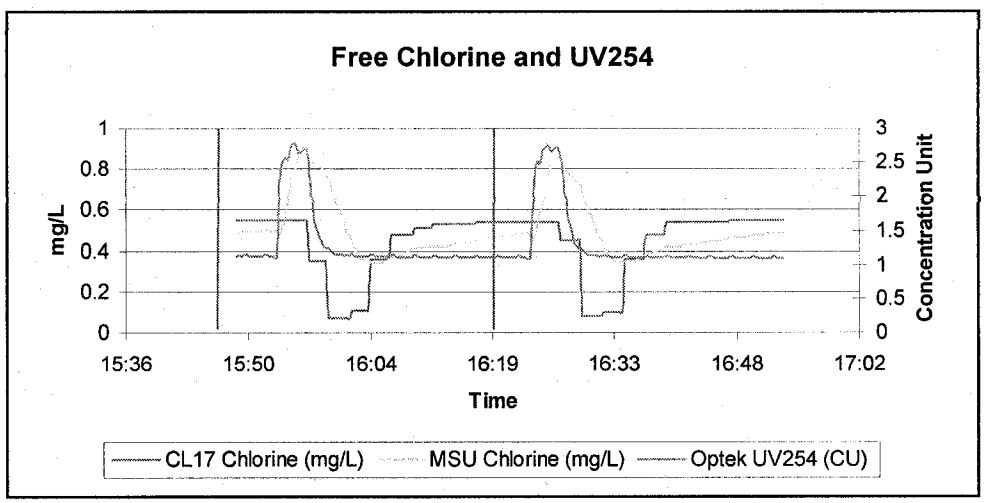



**Figure 6-6** CL17, UV 254, and MSU Chlorine Responses to Nicotine Inputs

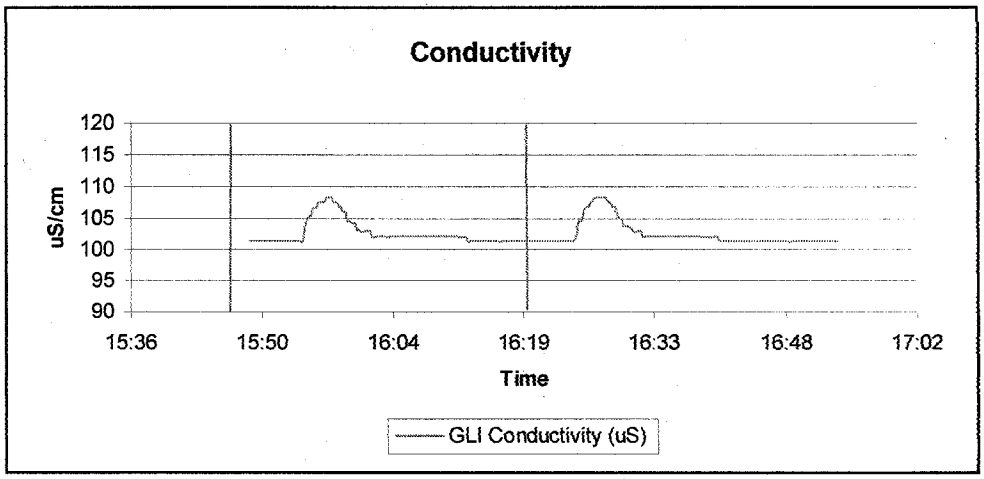



**Figure 6-7** Conductivity Result of Nicotine

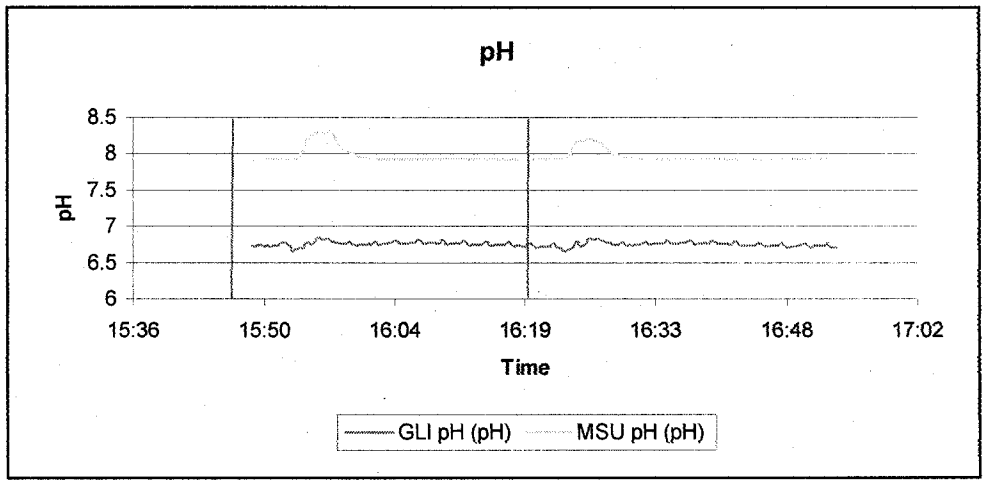



**Figure 6-8** pH Results of Nicotine

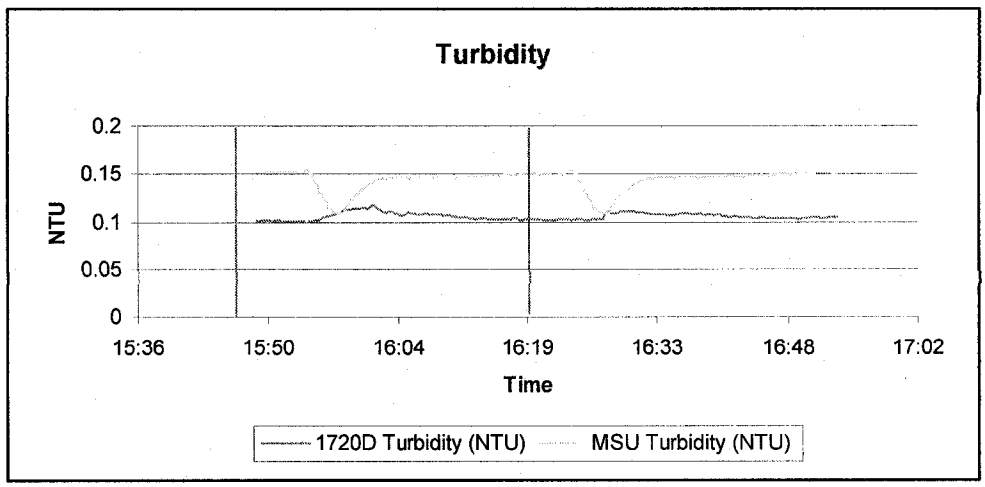



**Figure 6-9** Turbidity Results of Nicotine

The Nicotine injection graphs yield the following information:

- The UV254 instrument showed an almost identical response time to the MSU free chlorine, pH, and turbidity sensors. All four were < 2 minutes from the start of the injection.
- The cycle time of the Hach chlorine unit is approximately 2.5 minutes, causing the sharp steps in the reading. Response time of this unit was approximately 5 minutes from the start of the injection. MSU chlorine showed an initial peak, then downward trend which was not seen on the Hach CL17. The CL17 uses a DPD based colorimetric test which may have an interference with this chemical.
- Conductivity also showed an excellent response with a response time of approximately 2 minutes from the start of the injection.
- The pH response of the MSU was excellent; however the GLI unit did not show similar results. Any response with the GLI pH sensor was not greater than the background noise and thus could not be used as an event trigger.
- The delay of the Hach 1720D turbidity unit is primarily due to the large volume of water (~ 1.0 liter) inside the instrument body. Response time from the start of the injection is approximately 5 minutes for this unit. A comparison of these two instruments indicates that the response of the MSU was significantly larger than the 1720D probably due to the reduced dilution with the small detection cell.

The chemical injections were done twice for each chemical, in sequence over a period of two days. The first set is shown in Figure 6-10.

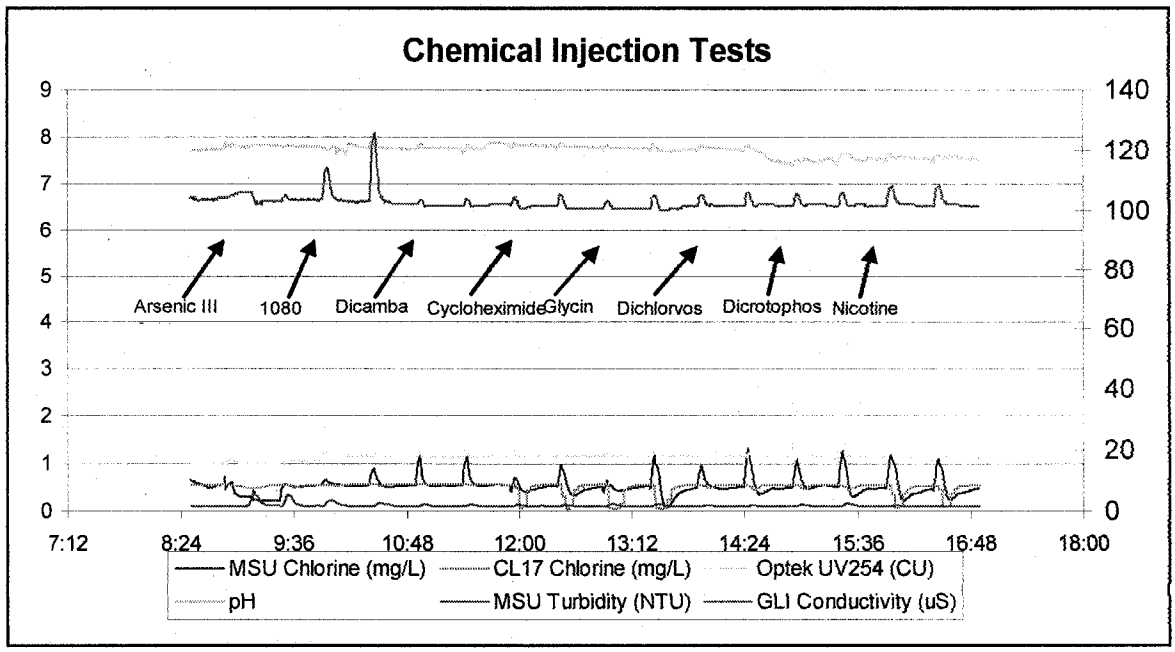



**Figure 6-10** Chemical Injection Test

The results of the chemical injections are shown in Table 6-3 where the responses are indicated by:

- \+ Positive response
- \- Negative response
- n/c No change

Sodium Fluoroacetate did not have a positive response except for conductivity. We expected that this contaminant would show a positive response with UV or chlorine residual but it did not, maybe since it is a relatively small, ionic organic compound that does not act as an electron donor. Both turbidity instruments and UV 254 had positive response for most chemicals and the Hach chlorine analyzer (CL17) had a negative response for most chemicals. The MSU suite of sensors (turbidity, chlorine and pH) was effective in detecting nine of the ten compounds studied. The addition of conductivity into the MSU instrument will be considered in the future.

**Table 6-3** Chemical Injection Results

| | Aldicarb | Arsenic trioxide | Dicro tophos | Dichlor Vos | Dicamba | Glypho sate | Cyclohexi mide | Nicotine | Potassium Ferricyanide | Sodium Fluoroacetate |
|---|---|---|---|---|---|---|---|---|---|---|
| MSU Turbidity | + | + | + | + | + | + | + | - | + | Nc |
| Hach Turbidity | + | + | + | + | + | + | + | + | + | Nc |
| MSU Chlorine | - | - | + | + | + | + | + | - | + | Nc |
| Hach Chlorine | - | - | - | - | Nc | - | - | - | + | Nc |
| MSU pH | - | - | + | + | Nc | + | + | + | - | Nc |
| Hach pH | - | - | + | + | Nc | + | + | + | - | Nc |
| Hach Conductivity | - | - | + | + | + | + | + | + | + | + |
| Optek UV254 | + | + | + | Nc | + | + | + | + | + | Nc |

### 6.3.1. $H_2O$ Map Modeling Results

An $H_2O$ Map hydraulic model was created for the main CSU campus to study contaminant spread under different scenarios. Initially, the system was drawn based on a campus map with inputs from the CSU facilities department (Figure 6-11). The main "water plant" (input to the system) was positioned on the north edge of the campus system as shown below. Although there is not a dedicated water plant supplying drinking water to CSU, this modeling approach was used to incorporate the entry into the system of water from the City of Fort Collins. In Figure 6-11, the red dots represent possible places that MSUs can be installed and the red line represents existing water pipelines.

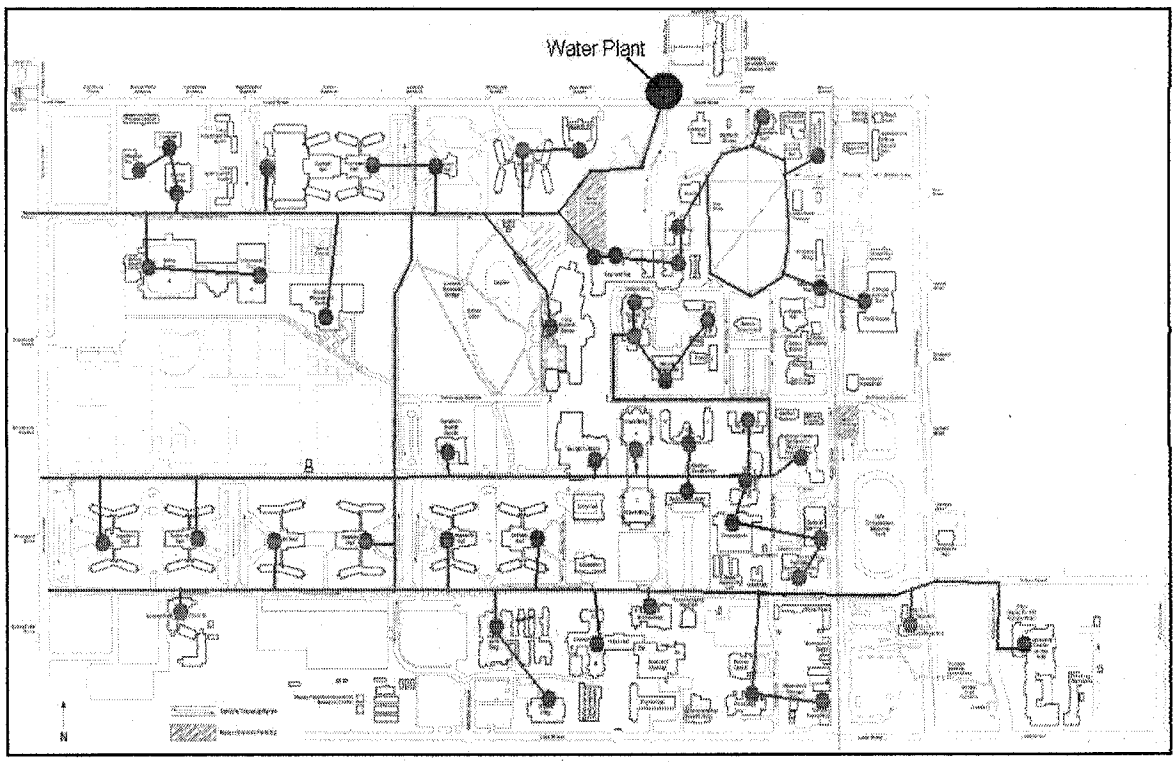



**Figure 6-11** $H_2O$ Map Hydraulic Model

Pipelines and nodes were input using $H_2O$ Map (Figure 6-12) and the system was drawn to incorporate much of the main CSU campus and the buildings.

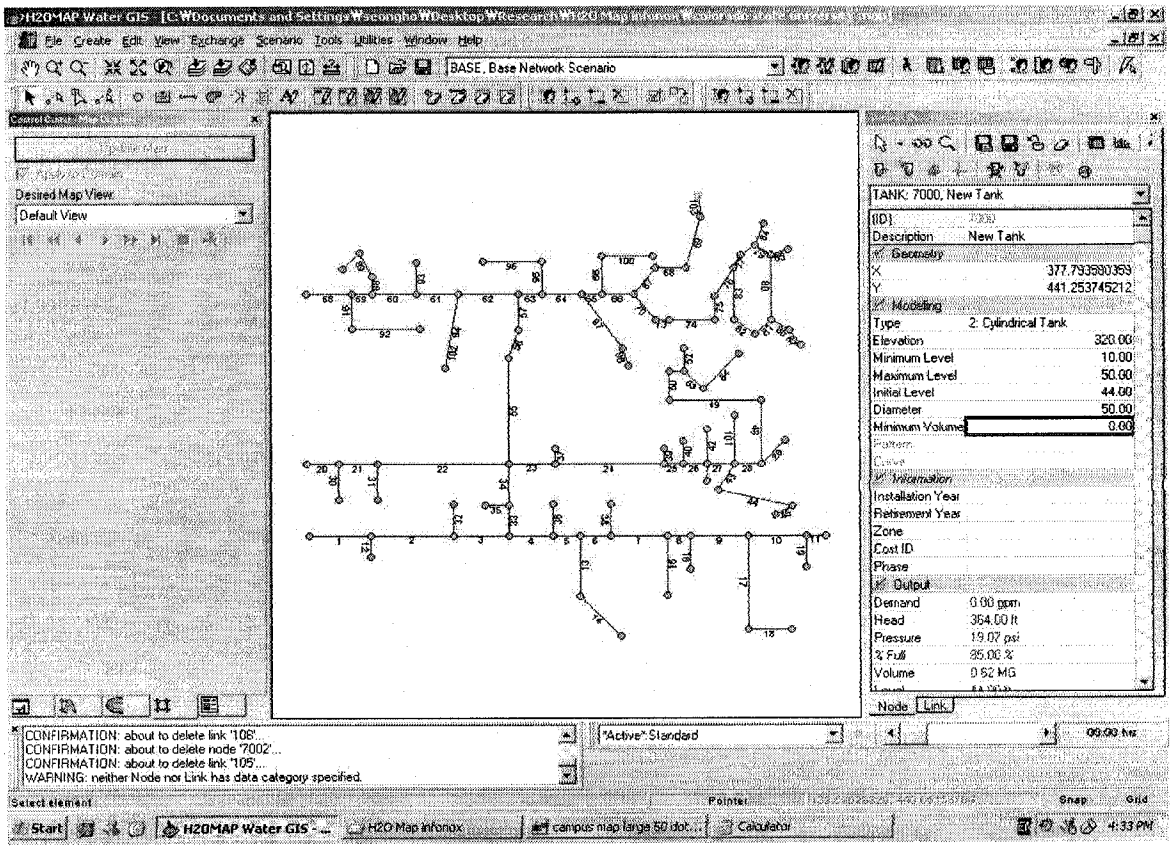
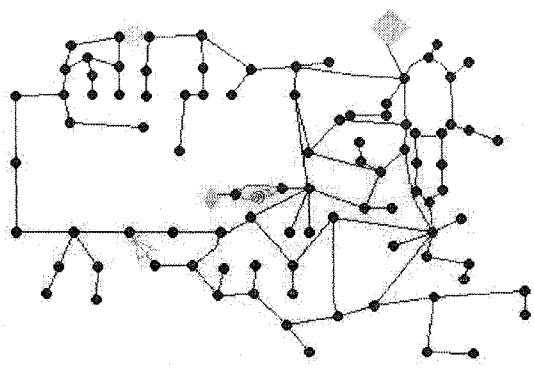
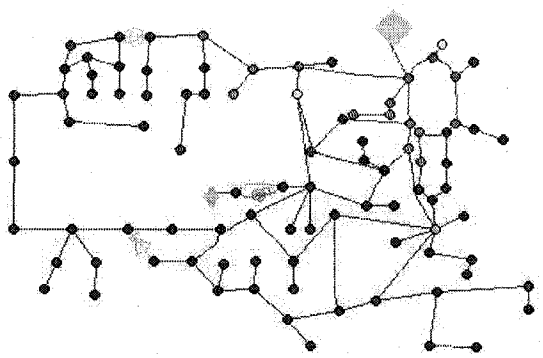



**Figure 6-12** $H_2O$ Map Hydraulic Model

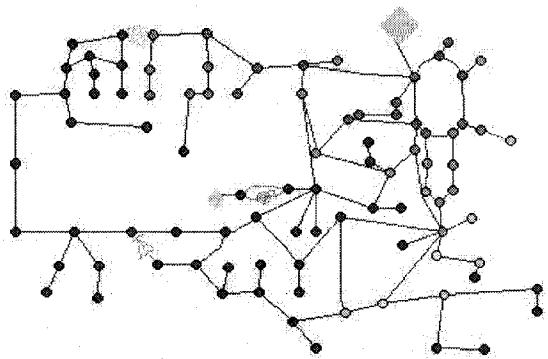
$H_2O$ map also provides a graphical representation of the injection run using a color mapper display. Each level of contaminant is set to display as a different color, and the system creates an animation over a given time period. Several snapshots from the campus model are shown in Figure 6-13. With these results, we can predict which nodes or locations will be contaminated with time and where we can install MSUs to detect contamination occurrences. Different colors represent different concentrations of contaminants.



CSU $H_2O$ Map Simulation – Step 1



CSU $H_2O$ Map Simulation – Step 5



CSU $H_2O$ Map Simulation – Step 10

**Figure 6-13** $H_2O$ Map Simulation Snap Shots

### 6.3.2. Probability results of $H_2O$ Map

The system was expanded to cover a 5 square mile area (500 total nodes) to more closely model a downtown area or shopping complex such as Fort Collin's Old Town or Loveland's Centerra. Twenty-five injection simulations were run using the $H_2O$ Map model. The data was compiled in Excel, where the time to detect the contaminant at each location was computed. This data was used to create a series of probability curves which show the ability to detect an event given the number of MSU's placed around the city, and the time to detect the event. For example, with 9 MSU's, there is an 80% probability of detecting an event in 3 hours.

Figure 6-14 shows the results of this probability of detection simulation. Out of 500 nodes, chemicals were injected at 25 different nodes (5 nodes from each square mile area) and 11 nodes were selected randomly for testing the probability of detection. With the data, we computed the probability of detection with one randomly installed MSU, two MSU's, three MSU's, etc. This procedure was repeated five times with different time periods and the results plotted.

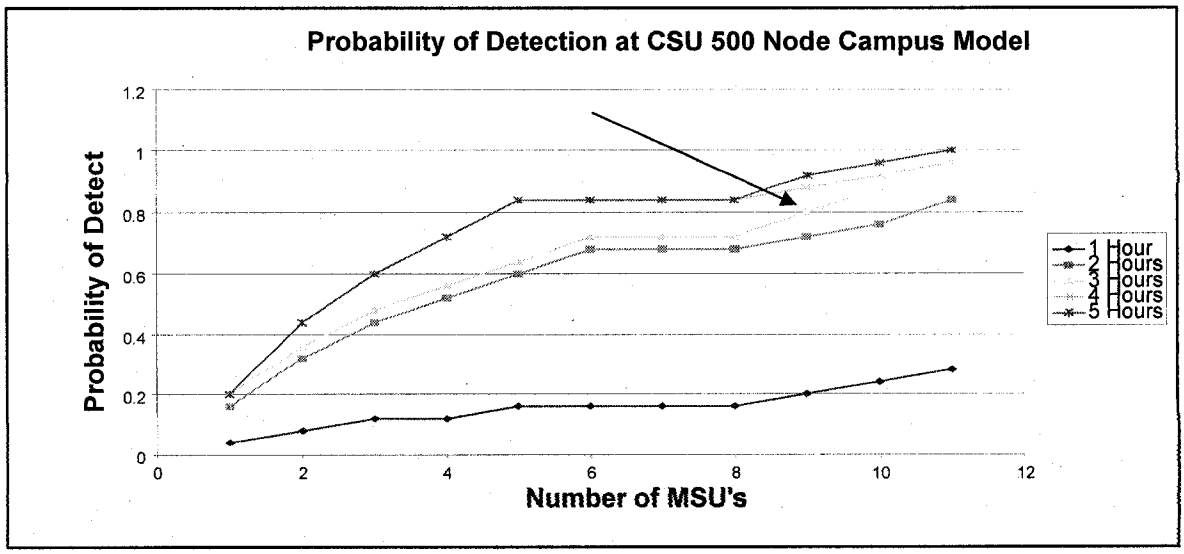



**Figure 6-14** Probability of Detection at CSU Main Campus. Arrow indicates reasonable design criteria.

### 6.3.3. Integrating SCOPE $H_2O$ for Campus Monitoring

The SCOPE$H_2O$ hierarchy for the campus test is shown below. MSU's are grouped by location, starting at the city level. Multiple levels can be created for logical groupings of sensors. Full password control and authentication is maintained across the hierarchy, allowing multiple users to login and see only the portion of the system necessary for them.

Figure 6-15 shows an example of SCOPE $H_2O$ data spread sheet for all MSUs installed on the CSU campus. We can see data collected every 10 seconds for 24 hours for each of the MSU instruments. We can click different MSUs at left side to show different MSU data. The data can be shown as a report or graph.

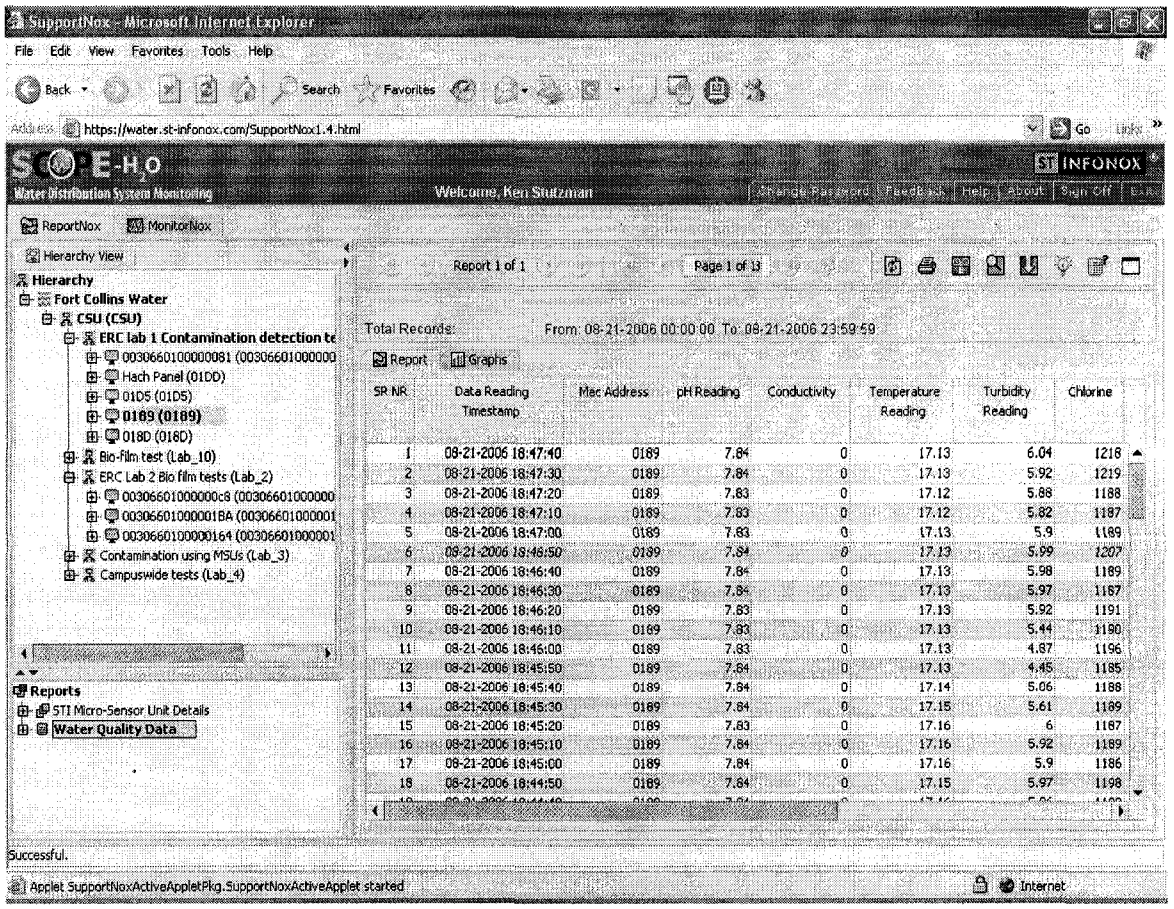



**Figure 6-15** Sample of SCOPE's Results

Each MSU is displayed on the SCOPE$H_2O$ main page once it is activated. A time stamped entry is placed in the database when each reading is received. Later, the data can be filtered according to time/date, and displayed as a table, graph, or easily exported to other applications.

The status dashboard for each MSU is shown below. A green box indicates the MSU is online and is operating normally. Additional health and status information such as microprocessor temperature, microprocessor voltage, RF radio strength, and laser intensity, are continuously monitored and activate user defined actions such as a page or email. Through the status dashboard, we can predict which MSUs need maintenance or maybe taken off-line.

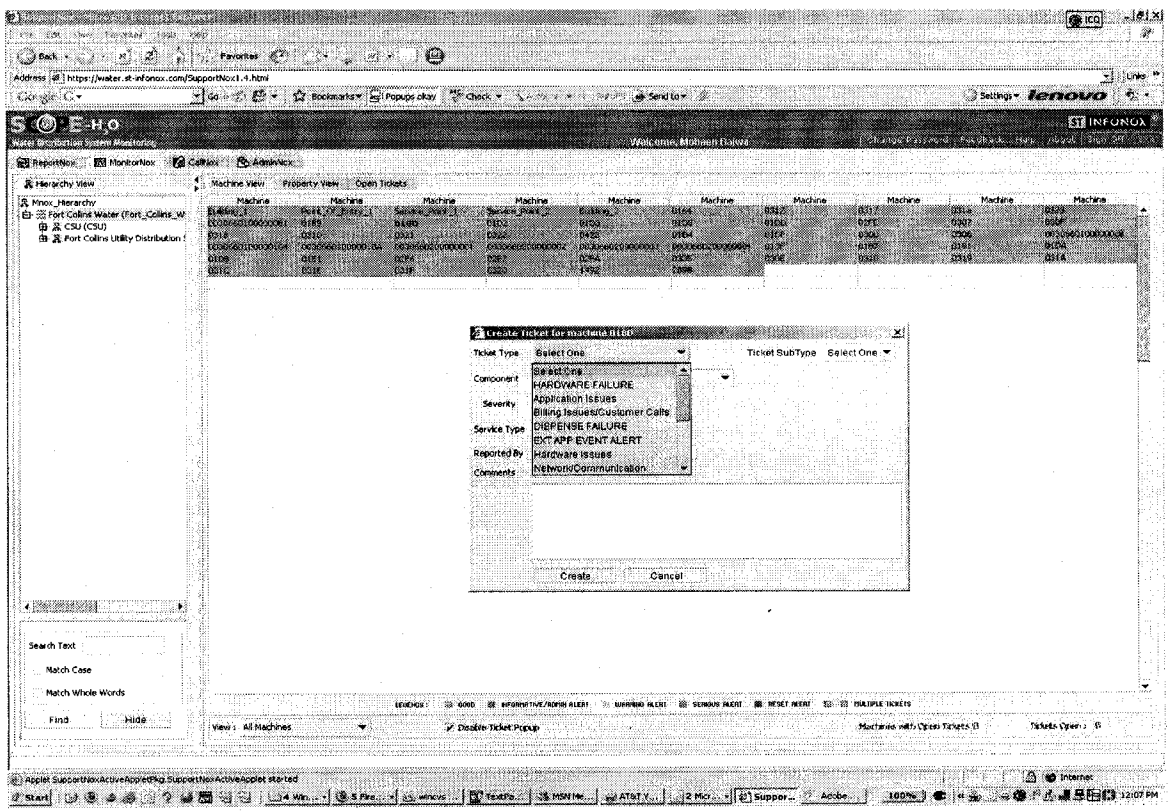



**Figure 6-16** View of Micro Sensor Data

### 6.4. Conclusion

Highlights of the testing include:

- Clear responses are seen from all EPA contaminant injection chemicals. These responses match up well with the Hach reference instruments.
- Response time of the MSU chlorine, turbidity and pH channels is approximately 2 minutes from the start of an injection event — equal or faster to the reference instruments.
- Detection of biofilm sloughing events using turbidity after an injection event shows good results with both the MSU's and reference instruments.

Improvements opportunities to the system for the next generation include:

- Temperature compensation for MSU free chlorine probe
- Implementing map display / real-time user dashboards in SCOPE
- Setting operator defined rules in a real world operation
- Show clear benefits / value proposition of the three operations concepts presented
- Demonstrate rapid deployment at new sites
- Roll out into Water Sentinel Pilot fall 2007

The beta system has demonstrated it is reliable, cost effective, and requires limited maintenance over the initial 6 month test period.

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# Chapter 7
## Conclusion

The threat of chemical contamination to drinking water is well established and requires an urgent effort to protect our drinking water systems from malevolent acts of sabotage. As it presently stands, the technology to detect these contaminants is lacking. Early detection of these contaminants via on-line or real-time monitoring has been identified as a feasible way to provide early warning to protect public health.

Due to increased concern of terrorism, the early detection of chemical contaminants in drinking water distribution systems has become an issue of great interest. This study examined the detection of chemical contaminants in a bench-scale drinking water distribution system using common water quality parameters as surrogate indicators. It is important establishing baseline water quality to provide a significant amount of data that represents "normal" condition to compare suspected contamination events to. From baseline data, 3 sigma values of all instruments were measured and used to determine detection limits with 7 different potential chemical agents.

To measure organic chemical compounds in water, two specific water quality instruments were used: UV 254 and TOC analyzers. Overall, the UV254 instrument performed very well, sometimes even detecting events missed by the TOC analyzer. Measuring UV254 and correlating it with TOC is much simpler than measuring TOC directly, and the correlation for these chemcials has been shown to be practicably accurate. The first hypothesis that Ultra Violet (UV) 254 monitoring of distribution system water is a cost-effective sensitive alternative to on-line Total Organic Carbon (TOC) analysis can be accepted based on our results.

Of the six on-line monitoring instruments used, the UV analyzer and the TOC analyzers provided responses that correlated well to the organic compound contaminants present. TOC also showed response to the presence of inorganic sodium cyanide. The chlorine residual analyzer provided the best surrogate detection of the inorganic compound introduced to this distribution system. The on-line turbidimeter did not respond directly to the presence of chemical contaminants in this study, a result that would be expected since the contaminants are dissolved compounds and the light scattering technique is designed to detect solids. The second hypothesis, that routine bulk water quality parameter monitoring is effective for detecting chemical contaminants in a drinking water distribution system can be accepted with exception of direct turbidity measurement.

Indirect detection of the contaminants was studied by considering the biofilm viability with and without toxic conditions. With different contaminants, concentrations, and residual times, the impact of chemical contamination on biofilm sloughing contributed to a measurable change in turbidity and UV254 absorption with a greater response shown in turbidity for all contamination events, including those at lower concentrations. The third hypothesis that biofilm in the distribution system can provide a measurable secondary response to a chemical contamination event can be accepted based on our results. The interaction between toxic industrial chemicals and biofilm in the distribution system resulted in cell death and the sloughing off of biomass. There was a correlation between introduction of a chemical contaminant and the log-removal of cells from inline PVC coupons. Results further emphasize that biofilm in the distribution system might be a key tool in using on-line turbidity monitoring to detect the presence of

toxic chemicals. This relationship can help provide the early warning needed to protect public health in the event of distribution system chemical contamination.

Testing of low-cost, low-resolution MSUs has demonstrated the instruments as reliable requiring limited maintenance over the initial 6 month test period leading to the acceptance of the fourth hypothesis. The MSU instrument had clear responses with all EPA listed contaminant injection chemicals. These responses match up well with the Hach reference instruments such as chlorine residual, turbidity, and pH. Response time of the MSU chlorine, turbidity and pH channels is approximately 2 minutes from the start of an injection event which is equal or faster than the reference instruments. Both the MSU's and reference instruments were effective at detecting biofilm sloughing events using turbidity instrument.

Water distribution system modeling software, $H_2O$ Map, was effective for predicting contaminant transport in the Colorado State University main campus system. Modeling was used to optimize MSU sensor placement and determine the probability of contaminant detection with different scenarios, validating the acceptance of the fifth hypothesis.

# Chapter 8
## Recommendations for Further Research

Through the study, several recommendations are presented for further research.

1. It would be more effective and practical to use a higher absorbance wavelength (e.g. 400 nm or blue-ray) for detecting contaminants due to the lower cost.

2. One of the issues that should be considered in a future study is the bench scale distribution test with TOC and UV254 analyzers for more than one peak. Our assumption for this situation is that all injected contaminants were not diffused equally, and a residual in the loop caused the second peak.

3. In this research, a constant flow rate was used. For future research, the relationship between UV254 and flow rate should be further investigated.

4. Biofilm growth on the optical surfaces of the UV254 analyzer should be studied to ensure sensor fouling is not an issue with the instrument.

5. The on-line turbidimeter did not respond well to the presence of chemical contaminants in this study; however, future research will examine the use of turbidity to monitor the distribution system for the presence of biofilm.

6. For testing one chemical which is sodium fluoroacetate, conductivity is the only instrument to show positive response. An additional sensor for the MSU should be explored.

7. Instrument improvements to the system for the next generation include temperature compensation for the MSU free chlorine probe, implementing map display/real-time user dashboards in SCOPE, setting operator defined rules in a real world operation.

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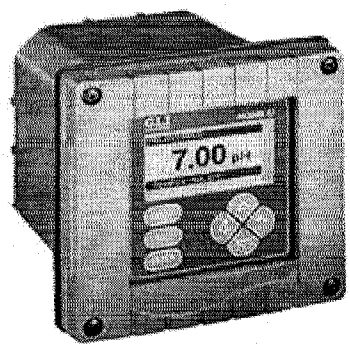
# Appendix A Equipment Overview & Specifications

Appendix A provides a summary of information on selected instruments that are used to monitor contaminants in water and this project. This appendix includes 6 different instrument's review and specification.

**1. P53 pH and ORP Analyzer**: This is a full-featured, easy-to-use analyzer. This versatile analyzer can be used with any GLI Differential Technique pH or ORP sensor, or any conventional combination electrode. The large display, simple keypad, and logical menu structure make the P53 easy to use. Menu screens, containing up to six text lines, guide you through setup, calibration, operation, and test/maintenance functions. The display shows measured pH (or ORP), the process temperature, and both analog outputs. Display screen annunciators indicate relay "on/off" status. Each of the two isolated analog outputs can be set to 0-20 mA or 4-20 mA, and assigned to represent the measured pH (or ORP). The P53 is housed in a 1/2 DIN, epoxy-coated, metal NEMA 4X case. Its hinged front panel provides easy wiring access. The analyzer exceeds U.S. and meets European standards for EMI and RFI,and has multiple language capabilities.




A. Features/Benefits

- Large Backlit LCD Readout.
  The large display shows measured pH (or ORP) in 1/2-inch (13 mm) high numerals. The P53 can also display the process temperature, and both analog outputs. Display screen annunciators indicate relay "on/off" status.
- Universal-mount 1/2 DIN Case.
  The P53 is housed in a 1/2 DIN, epoxy-coated, metal NEMA 4X case. Its hinged front panel provides easy wiring access. The supplied bracket and stainless steel hardware enable panel, surface, and pipe mounting.
- Electromagnetic Conformance.
  The analyzer exceeds U.S. and meets European standards for EMI and RFI.
- Simple Interactive Diagnostics.
  Built-in diagnostics continuously tests analyzer and sensor operation.
- Multiple Language Capability.
  All screens can be selected for display in English, French, German or Spanish. (Other available languages can be substituted.)
- "Menu-guided" Operation.
  The large display, simple keypad, and logical menu structure make the P53 easy to use. Menu screens, containing up to six text lines, guide you through setup, calibration, operation, and test/maintenance functions.
- Passcode-protected Access.
  For security, use the P53's passcode capability to restrict access to configuration settings and calibration to authorized personnel only.
- GLI Differential Sensor or Conventional Combination Electrode Compatibility.
  The Model P53 can be used with any GLI Differential Technique pH or ORP sensor, or any conventional combination electrode. The P53 accepts Pt 1000 RTD, Pt 100 RTD, or NTC 300 ohm thermistor temperature compensators.
- Two 0/4-20 mA Analog Outputs.
  Each of the two isolated analog outputs can be set to 0-20 mA or 4-20 mA, and assigned to represent the measured pH (or ORP) or temperature. During

calibration, both outputs can be held at their present values, transferred to preset values, or remain active to respond to the measured value.

B. Operational

- Display:

| Measurement | Selectable ranges |
|---|---|
| pH | -2.0 to 14.0 pH or -2.00 to 14.00 pH |
| ORP | -2100 to +2100 mV |
| Temperature | -20.0 to +200.0 °C or -4.0 to +392.0 °F |
| Analog Outputs | 0.00 to 20.00 mA or 4.00 to 20.00 mA |

- Ambient Conditions:
  a. Operation: -4 to +140 °F (-20 to +60 °C); 0-95% relative humidity, non-condensing
  b. Storage: -22 to +158 °F (-30 to +70 °C); 0-95% relative humidity, non-condensing
- Function Modes:
  a. Control: Settings for high/low phasing, set-point, dead-band, overfeed timer, off delay, and on delay
  b. Alarm: Settings for low alarm point, low alarm point dead-band, high alarm point, high alarm point dead-band, off delay, and on delay
  c. Status: Not configurable; relay only activates when a sensor or analyzer "fail" diagnostic WARNING condition exists
  d. Timer: Relay is activated by user-entered interval and time duration values to control GLI cleaning system
  e. Relay annunciators indicate respective relay on/off status
- Sensor-to-Analyzer Distance:
  a. GLI Differential (Technique Sensor): 3000ft. (914m) maximum
  b. Conventional Combination (Electrode with preamp): 985ft. (300m) maximum
  c. Conventional Combination (Electrode without preamp): 100 ft. 30m) maximum with electrode cable capacitance of less than 30pF/foot
- Power Requirement: 90-130 VAC, 50/60 Hz/ (10 VA max.) or 180-260 VAC, 50/60 Hz/ (10 VA max.)
- Analog Outputs: Two isolated 0/4-20 mA outputs; each with 0.004 mA (12 bit) resolution and capability to drive up to 600 ohm loads

C. Analyzer Performance

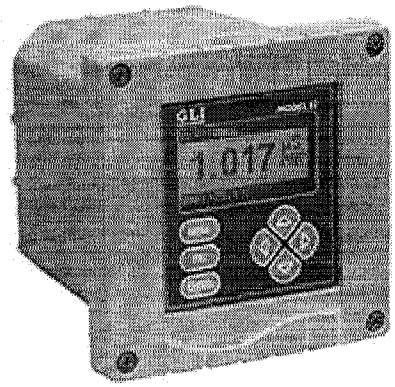
- Display:

| | |
|---|---|
| Accuracy | 0.1 % of span |
| Stability | 0.05 % span per 24 hours, non-cumulative |
| Repeatability | 0.1 % of span or better |
| Temperature Drift | Zero and Span; less than 0.03% of span/°C |

D. Mechanical

- Net Weight: 3.5 lbs. (1.6 kg) approximately

**2. Model C53 Conductivity Analyzer**: It is compact and full-featured yet easy-to-use, offering benefits usually found only in larger, more expensive analyzers. The Model C53 has two sensor inputs that can be independently configured to measure conductivity, resistivity or total dissolved solids. One appealing C53 feature is the "Dry Calibration" method which provides ultimate accuracy across the conductivity ranges of ultra-pure water to 200,000 microSiemens/cm. The analyzer has a large backlit graphic LCD to display the two measured conductivity points, process temperature, two analog outputs and four alarms. Menu screens contain up to six full lines of text to logically guide the user through setup, calibration and operation. Its powerful firmware enables multi-language operation.




A. Operational

- Display:

| Measurement | Selectable Ranges |
|---|---|
| Conductivity | uS/cm: 0-2.000, 0-20.00, 0-200.0 or 0-2000<br>mS/cm: 0-2.000, 0-20.00, 0-200.0 or 0-2000 |
| Resistivity | 0-19.99 MΩ • cm or0-19.99kΩ • cm |
| TDS | 0-9999ppm or 0-9999ppb |
| Temperature | -4.0 to +392.0 °F pr -20.0 to +200.0°C |
| Analog Outputs | 0.00 to 20.00 mA or 4.00 to 20.00 mA |

- Ambient Conditions:
  a. Operation: -4 to +140 °F (-20 to +60 °C); 0-95% relative humidity, non-condensing
  b. Storage: -22 to +158 °F (-30 to +70 °C); 0-95% relative humidity, non-condensing
- Function Modes:
  a. Control: Settings for high/low phasing, set-point, dead-band, overfeed timer, off delay, and on delay
  b. Alarm: Settings for low alarm point, low alarm point dead-band, high alarm point, high alarm point dead-band, off delay, and on delay
  c. Timer: Relay is activated by user-entered interval and time duration values
  d. Status: Not configurable; relay only activates when a sensor or analyzer "fail" diagnostic WARNING condition exists
  e. Relay annunciators indicate respective relay on/off status
- Sensor-to-Analyzer Distance: 300 ft. (91m) maximum
- Power Requirement: 90-130 VAC, 50/60 Hz/ (10 VA max.) or 180-260 VAC, 50/60 Hz/ (10 VA max.)
- Analog Outputs: Two isolated 0/4-20 mA outputs; each with 0.004 mA (12 bit) resolution and capability to drive up to 600 ohm loads

B. Analyzer Performance

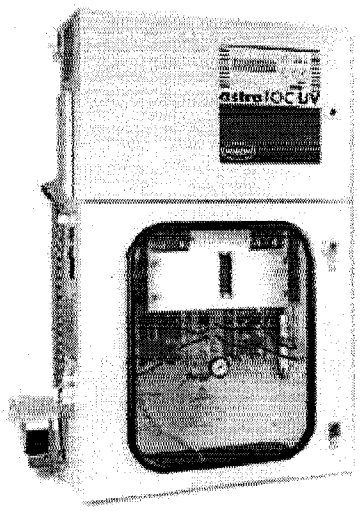
- Display:

| | |
|---|---|
| Accuracy | 0.1 % of span |
| Stability | 0.05 % span per 24 hours, non-cumulative |
| Repeatability | 0.1 % of span or better |
| Temperature Drift | Zero and Span; less than 0.03% of span/°C |

C. Mechanical

- Net Weight: 3.5 lbs. (1.6 kg) approximately

**3. astroTOC UV Process TOC Analyzer**: It was developed primarily for Petrochemical/Chemical applications such as unit outfall, cooling water, and process condensate, though it is also well-adapted to other applications in industrial process water and wastewater. It offers a quick response time of T90 in < 8 minutes (includes TIC sparging). The astroTOC UV Process TOC Analyzer is a rugged, low-maintenance analyzer designed to withstand severe industrial conditions. A dual range NDIR detector and a multi-staged UV lamp reactor enable the analysis of high salts, high suspended solids, and hard-to oxidize samples.



A. Operation

- Analysis method: UV persulfate oxidation with acid sparging for TIC removal followed by CO2 NDIR detector measurement
- Measurement range: TOC from 0-5 up to 0-20,000mg/L
- Response time: T90≤8 minutes; T20≤3 minutes
- Accuracy/Repeatability/Linearity: ±2% of full scale nondiluted range, ±4% of full scale diluted range
- Method detection limit per EPA Appendix B to Part 136: ≤0.015 mg/L at range 0-5 mg/L at 25 °C (77 °F)
- Signal drift (60 days) : < 2% with auto-clean and auto-calibration

B. Environmental Condition

- Indoor use:
  a. Temperature 5-40 °C (41-104 °F)
  b. Maximum relative humidity 80 % for temperatures up to 31 °C decreasing linearly to 50 % relative humidity at 40 °C
  c. Mains supply voltage fluctuations not to exceed ±10% of the nominal voltage
  d. Transient overvoltages according to installation categories (over voltage categories) II per IEC 664
  e. Pollution Degree 2 in accordance with IEC 664

- Enclosure:
    a. Cold rolled epoxy powder-coated steel; optional stainless steel
    b. Weight: 54kg (120 lb) for epoxy-coated steel cabinet

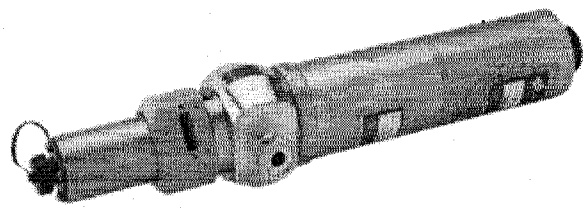
C. Samples: Single stream fast loop inlet
- Inlet pressure: 0.15-6 bar (2-87 psig)
- Outlet pressure: Ambient
- Inlet temperature: 2-70 °C (36-158 °F) Optional Passive Cooler to extend the range to 100 °C (212 °F)
- Flow rate: 25-200 mL/min

D. Power requirement: Switch selectable 115 or 230 V ac ±10 %, 50/60 Hz
- Wire size information: Rigid solid: 0.2-40mm2; flexible stranded: 0.2-2.5 mm2; AWG: 24-12
- Maximum power consumption: 300 VA
- Installation category: II
- Fuses: ac mains fused for single phase only.

E. Carrier gas requirements: Clean, CO2 free air at 2.8 bar (40 psig) minimum to 6.5 bar (90 psig) maximum
- Carrier gas usage: Approximately 380 cc/min. at atmospheric pressure

**4. AF45 Single Wavelength UV Absorption Sensor**:

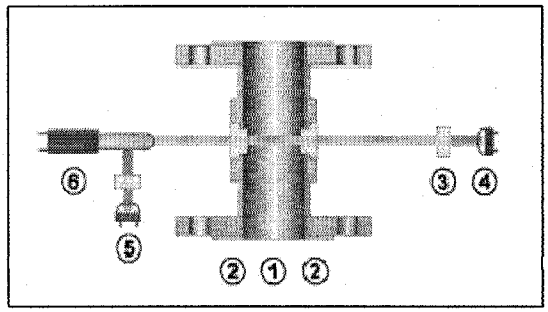
The model AF45 is a single channel Ultraviolet (UV) absorption sensor with a lamp compensation reference channel. The sensor is designed for inline operation and provides extremely accurate concentration measurements with great repeatability, linearity and resolution. The AF45 can be used for HPLC control, detection of aromatic compounds, organic load, protein concentration and other demanding applications.



The AF45 sensor uses light in the UV range at wavelengths of either 254, 280, 290, 300 or 313 nm. A precisely defined, constant light beam penetrates the process medium. The attenuation of the light intensity, caused by absorption and/or scattering by dissolved and undissolved substances, is detected by a sealed silicon photo diode the light intensity of the low-pressure mercury lamp itself is measured by a second hermetically-sealed silicon photo diode and compensates for any lamp intensity variations. This assures the highest level of precision and long-term performance.

A. Procedures
- Light from a Mercury Vapor UV lamp (6) passes through a sapphire window (2), and then through the process stream (1). The resulting light passes through a UV filter (3) and is detected by a photodiode (4).

- The narrow-band pass UV filter blocks all wavelengths except the specified UV wavelength. The photocurrents induced are directly proportional to the remaining light intensity at this wavelength.
- Light from the Mercury Vapor Lamp UV (6) also passes through a lamp reference filter (5) and lamp reference photodiode (5) installed within the lamp assembly. This compensates for any variations or intensity fluctuations of the UV lamp.
- The resulting photocurrents are precisely amplified, converted, and analyzed by the converter. The converter provides real time measurements and can send outputs to the process control system.

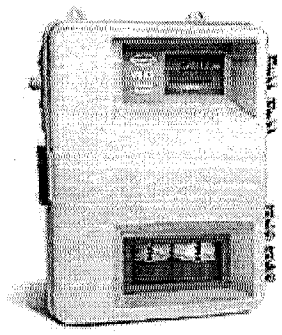



| | |
|---|---|
| 1. | Sensor Body |
| 2. | Sapphire Windows |
| 3. | UV Filter |
| 4. | Measurement Photo Diode |
| 5. | Lamp Reference Photo Diode |
| 6. | Mercury Vapor Lamp |

B. Specification

- Sensor body material: 316 Ti stainless steel, 316 L stainless steel, TFMC, Kynar, PEEK, Monel, Hastelloy C, Inconel, Tantalum, Titanium, and others.
- Line size: ¼" to 12"
- Optical windows: Sapphire for superior light transfer and process fluid resilience
- Optical path length: 1 mm to 500 mm
- Operating pressure: 0.15 psi (10 mbar) to 7,250 psi (500 bar) maximum 500 bar, depending on process connection/ material/ design
- Operating temperature: 0 °C (32 °F) to +70 °C (158 °F) continuous.
  0 °C (32 °F) to +135 °C (275 °F) periodic (max.15 min. per day).
- Ambient temperature: -20 °C (-4 °F) to +70 °C (158 °F) during transport.
  0 °C (32 °F) to +40 °C (104 °F) during operation.
- Light source: hybrid low pressure mercury lamp with phosphor coating lamp: 900 V AC start voltage, typically 200 V AC, 20 mA; 17,000 to 25,000 hours life (2 to 3 years).
- Wavelengths: Ultra-violett (UV): 254, 280, 290, 300 and 313 nm
- Detectors: two silicon photo diodes for measurement and reference channels hermetically sealed.
- Calibration: Factory calibration in CU (Concentration Units).
- Measuring range: any measuring range between 0-3 CU.
- Resolution: < ± 1% of respective measuring range.
- Repeatability: < ± 1% of respective measuring range.
- Linearity: specific to application.
- Protection: 316 Ti stainless steel lamp and detector enclosures, fixed optical bench.

**5. CL17 Chlorine Analyzer**: It is accurate and reliable in the most demanding process environments such as drinking water, wastewater, chemical/industrial feed or process water, food and beverage applications, reverse osmosis filtration systems, and heating and cooling systems.



A. Features and Benefits:

- Fast, automatic operation - CL17 samples every 2.5 minutes, using less than 475 mL each of indicator and buffer over a 30-day period.
- Colorimetric analysis - DPD (N, N-diethyl-p-phenylenediamine) colorimetry is simple and accurate, providing a reliable method for measuring free or total residual chlorine.
- Alarms and outputs - The CL17 provides a programmable 4-20 mA recorder output and two user-selectable alarms with SPDT relays that signal out-of-limit test results or system problems.
- Big LCD display, intelligent menus, and flexible programming - Set-up, maintenance and recorder/alarm programming are simple. They are all easily programmed with step-by-step menus and a simple keypad interface.

B. Sample requirements

- Sample flow rate to sample conditioning: 200 to 500 mL/min
- Inlet pressure to instrument: 1 to 5 psig; 1.5 psig is optimum. Exceeding 5 psig can cause sample tubing failure.
- Inlet pressure to sample conditioning: 1.5 to 75 psig (with sample tube level with the bottom of the instrument)
- Sample temperature range: 5 to 40 °C (41 to 104 °F)

C. Reagent/Standard Requirements

- Maximum reagent sage: one-half liter per month
- Reagent containers: High-density polyethylene (2) ½-liter bottles.
- Reagent containment: reagent bottles are contained inside the analyzer enclosure and are vented externally.

D. Electrical

- Power requirements: 100-115/230 V ac; 95 VA, 50/60 Hz, 2.5 Amp fuse
- Power connection: connection made by three wire barrier terminal block through a 1/2-inch conduit hole in the case.
- Recorder output: one isolated recorder output, 4-20 mA. Recommended load impedance 3.6 to 500 ohms.
- Recorder output connections: connection made by a removable three wire plug through a 1/2-inch conduit hole in the case.

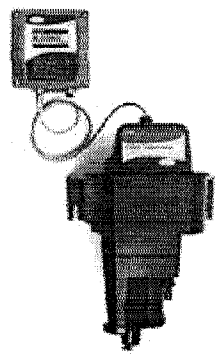
E. Performance

- Operating range: 0-5 mg/L free or residual chlorine
- Accuracy: ±5% or ±0.035 ppm whichever is greater
- Precision: ±5% or ±0.005 ppm whichever is greater
- Detection limit: 0.035 ppm
- Cycle time: 2.5 min
- Calibration: uses default calibration curve
- Recorder: One 4-20 mA/0-20 mA

F. Environmental

- Storage temperature range: -40 to 60 °C (-40 to 140 °F)
- Operating temperature range: 5 to 40 °C (41 to 104 °F)
- Humidity: 90% at 40 °C (90% at 104 °F)

**6. 1720D low range process Turbidimeter**: The 1720D Low Range Process Turbidimeter provide the sensitivity, stability and flexibility necessary to continuously track the low levels of turbidity found in high-quality filtered water. The 1720D is easy to calibrate and operate, and requires very little maintenance.



A. Key Instrument Features/Benefits

- Easy to Install- plug and play sensors
- No need for backup systems- built-in data logger
- Reduced Instrumentation- new controller accepts up to two sensors
- Eliminates false high readings at low levels- built-in bubble removal system
- Suitable for regulatory reporting- instrument design compliant with USEPA Method 180.1

B. Specification

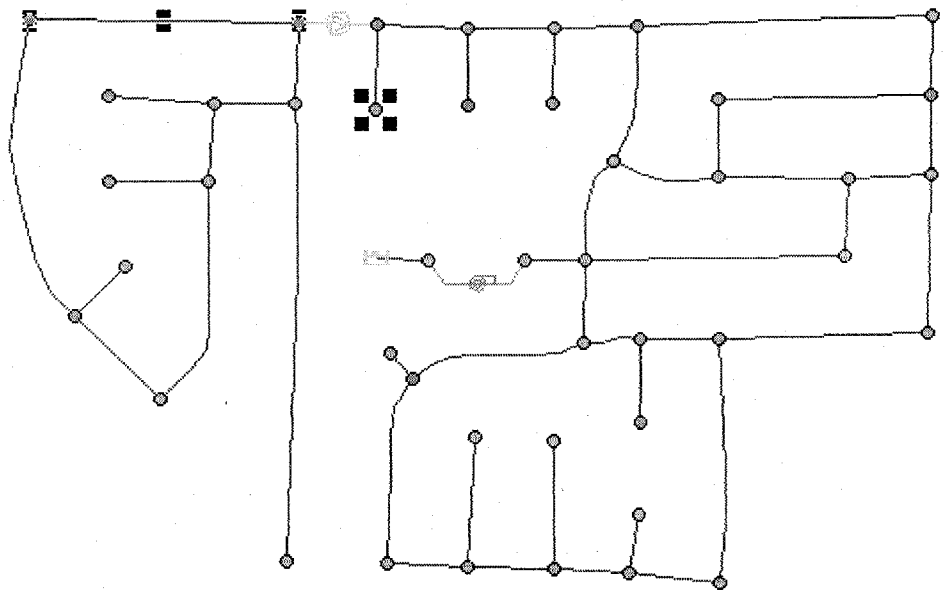
- Range: 0-100 nephelometric turbidity units (NTU)
- Accuracy: ±2% of reading or ±0.02 NTU (whichever is greater) from 0-40 NTU; ±5% of reading from 40 -100 NTU
- Resolution: 0.001 NTU
- Repeatability: better than ±1.0% or ±0.002 NTU, whichever is greater
- Sample flow required: 250-750 mL/min (4.0to11.9 gal/hour)
- Storage temperature: -20 to 60 °C
- Operating temperature: 0 to 40 °C
- Operating humidity: 5 to 95% non-condensing
- Sample temperature range: 0 to 50 °C
- Power requirements: 95-240 VAC, 50/60 Hz, Auto selecting; 40VA
- Date communications distance: maximum of 400 meters between devices with a 500 meter maximum per segment; distances in excess of 500 meters require a repeater. Up to 3 repeaters can be used for a total network length of 2000 meters.

## Appendix B A Procedure Sample of $H_2O$ Map

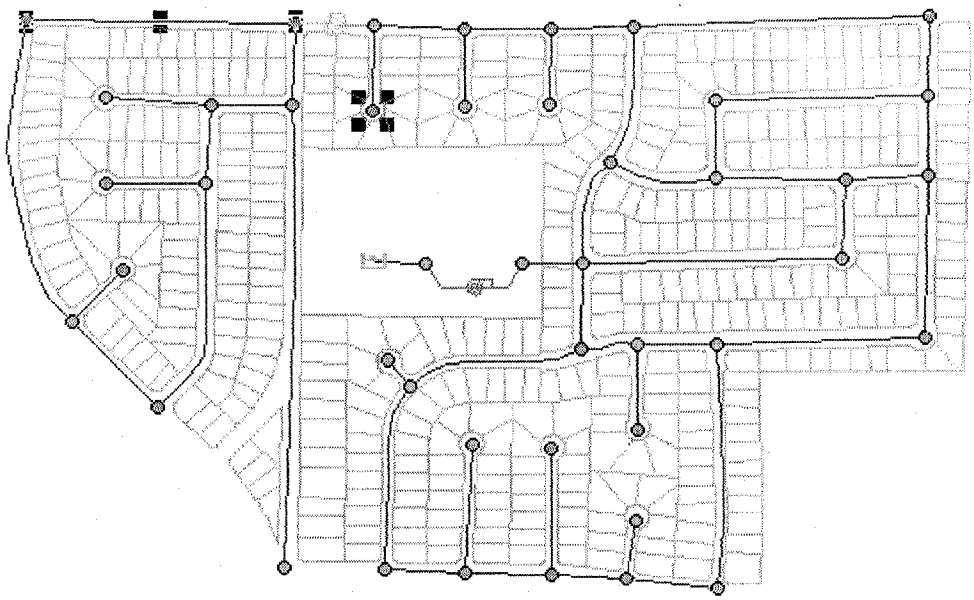
Appendix B provides a sample of the $H_2O$ Map modeling.

1. OPEN THE YOURTOWN PROJECT

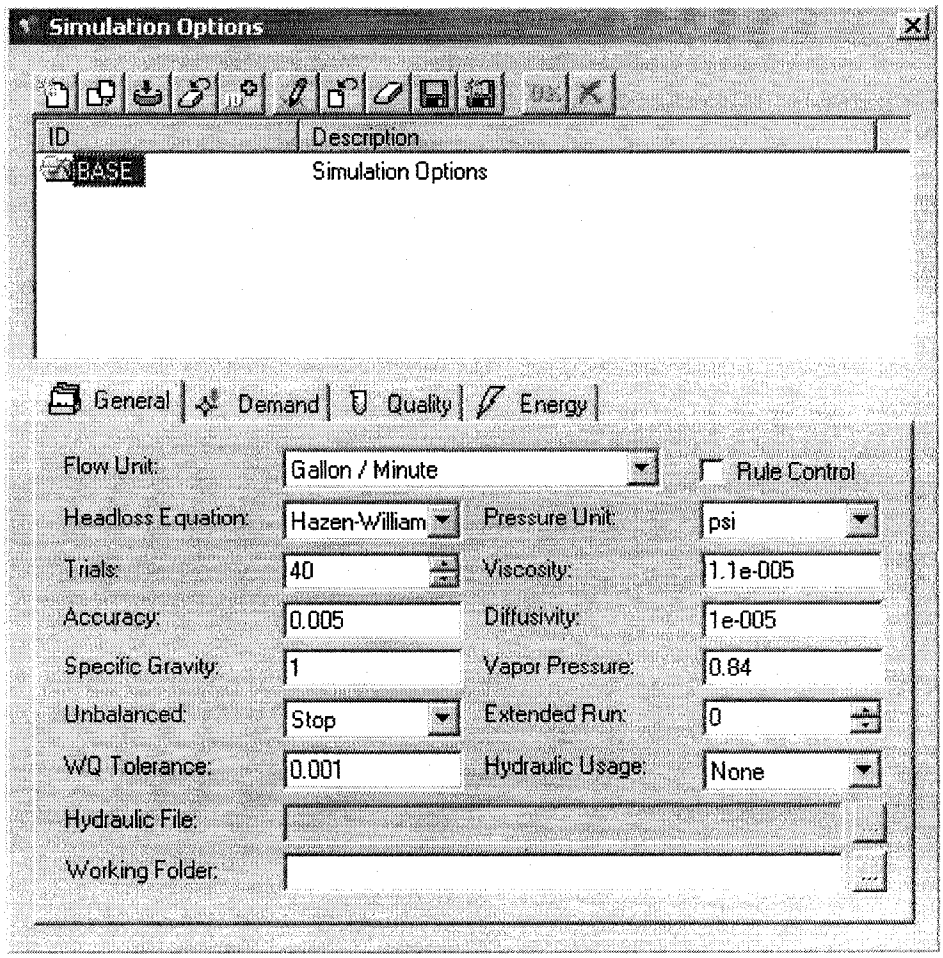
- Open from the file menu and navigate to your-town project and choose this file.



- Choose the MAP LEGEND tap from the control panel and choose the add layer button to select "townlot.shp" file.



2. DEFINE BASIC OPTIONS FOR THE NEW PROJECT

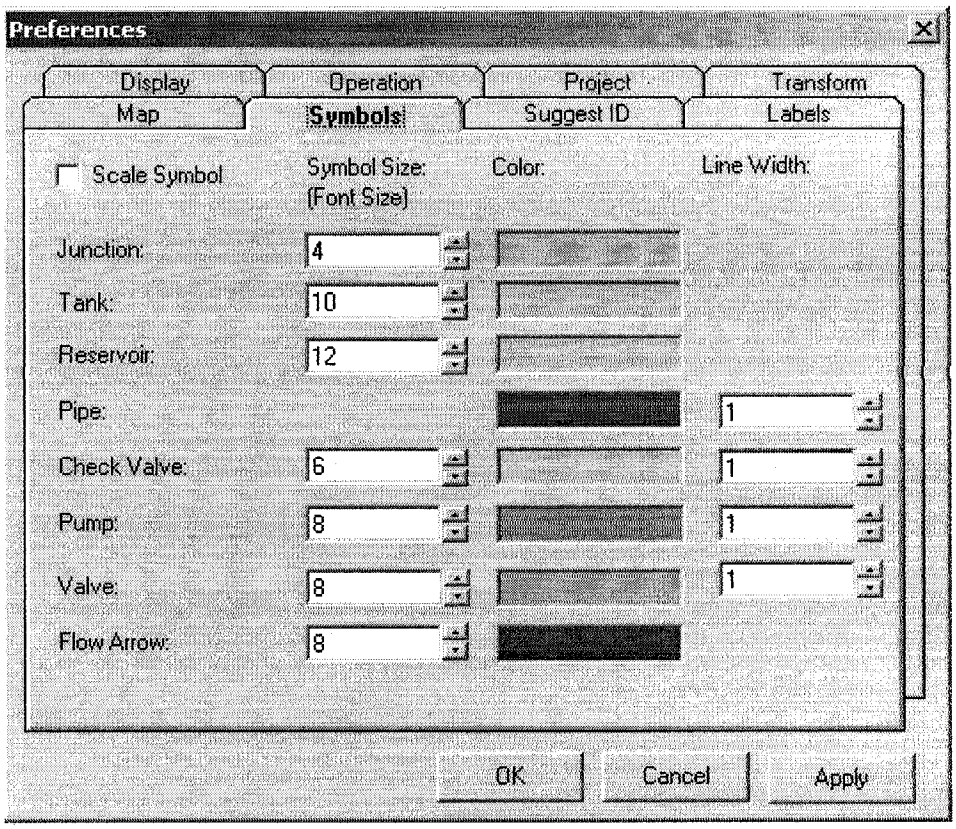



- Select the simulation options→base simulation options at the Operation Data Tab from the Control Center.
- Choose Flow Unit.
- Choose Pressure Unit.
- Choose Head-loss Equation.
- Then click OK button.

3. CREATE NETWORK COMPONTENTS

1) Set Symbol Sizes for new Components

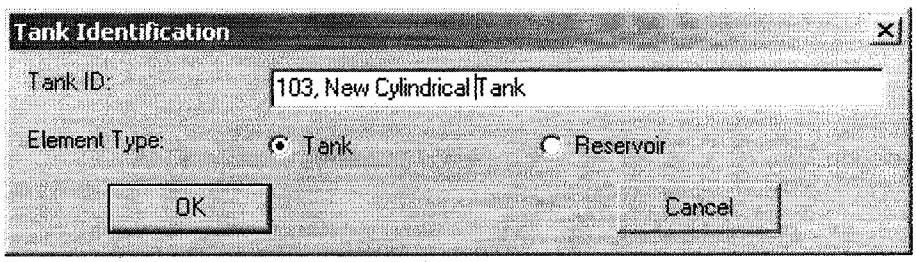
- Select the Preferences command from the Tools menu, and then select the Symbols tab.



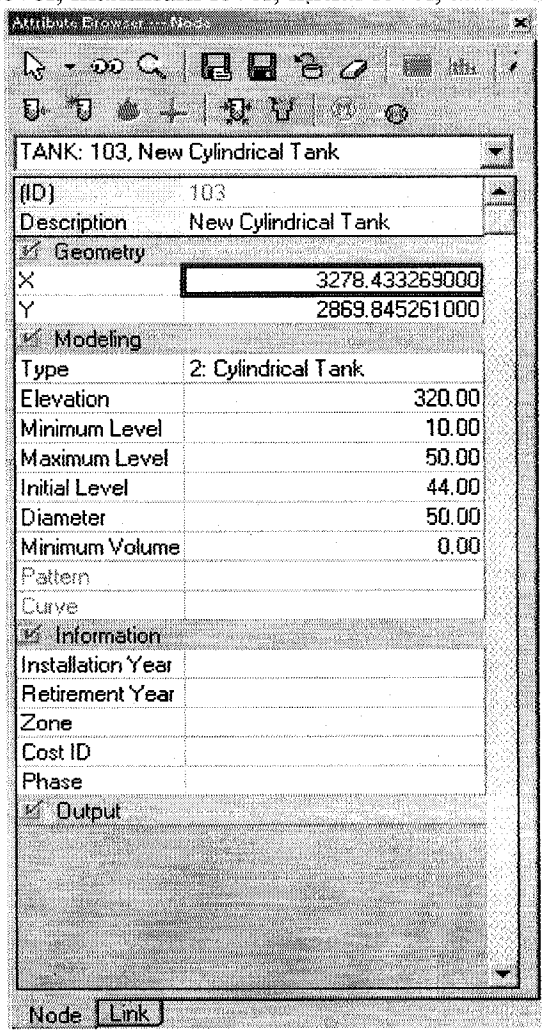

- It can also be chosen a different color for each component or symbol size

2) Adding Tanks

- Select the Add/Insert Tank command from the Create menu, and then move the cursor to the desired location and press the left mouse button.
- At the Identification box, enter the tank ID with a comma to separate the ID from the description, and then choose the tank type.



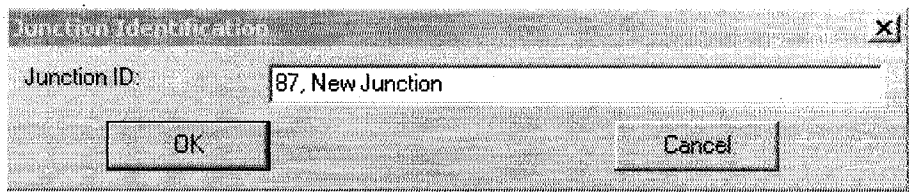

- In the Attribute Browser-Node window, enter value of bottom elevation, minimum level, maximum level, initial level, and diameter field.



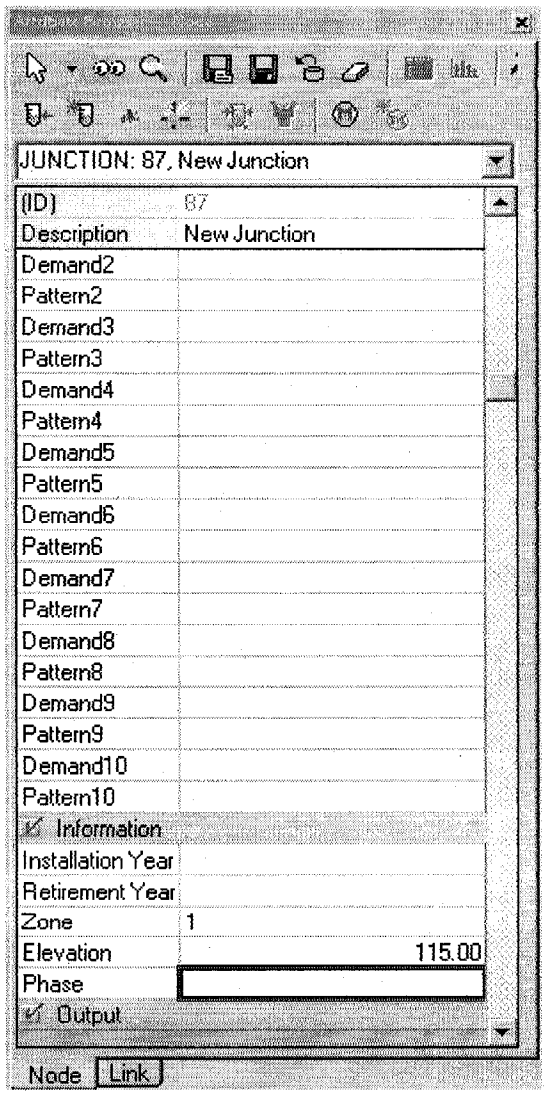

- Click save button.

3) Adding Junction Nodes

- Select the Add/Insert Junction command from the Create menu, and then move the cursor to the desired location and press the left mouse button.
- At the Identification box, enter the junction ID with a comma to separate the ID from the description.



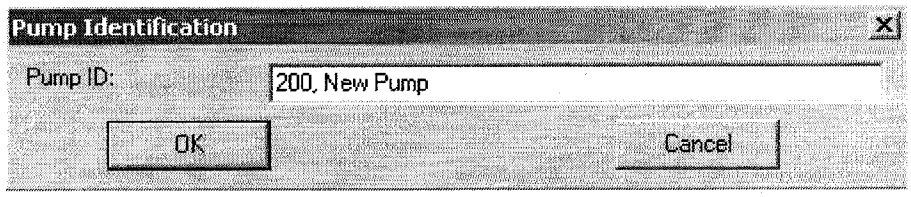

- In the Attribute Browser-Node window, enter value of elevation, and zone field.



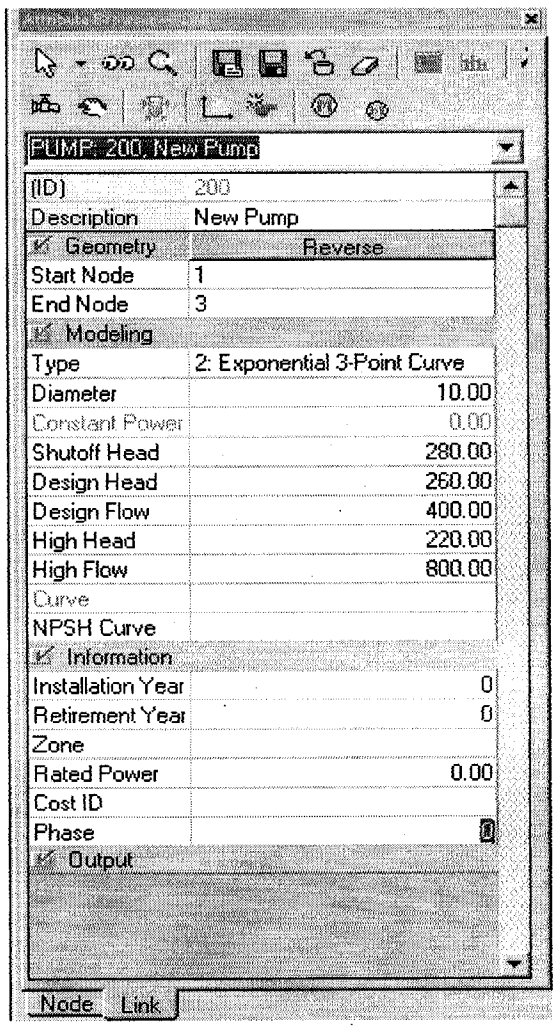

- Click save button.

4) Adding Pumps

- Select the Add Pump command from the Create menu, and then move the cursor to the desired location. Using mouse, left click on the upstream junction node then left click to define the two pump vertices, and then double-click on the downstream junction node.
- At the Identification box, enter the New pump ID with a comma to separate the ID from the description.



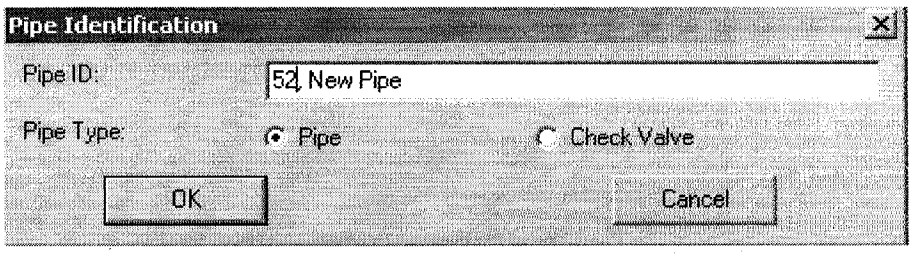

- In the Attribute Browser-Node window, enter value of type, diameter, shutoff head, design head, design flow, high head, and high flow field.



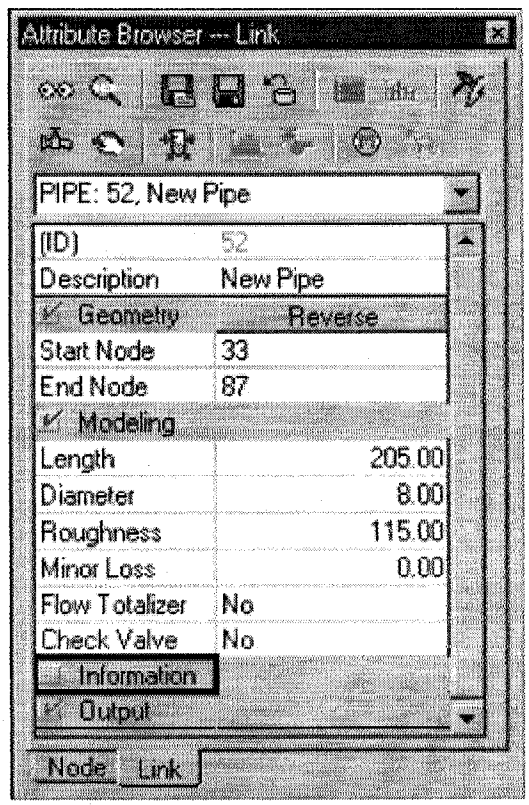

- Click save button.

5) Adding Pipes

- Select the Add Pipe command from the Create menu, and then move the cursor to the desired location. Using mouse, left click on the one junction node and then double-click on the other junction node to complete the straight line.
- At the Identification box, enter the pipe ID with a comma to separate the ID from the description.



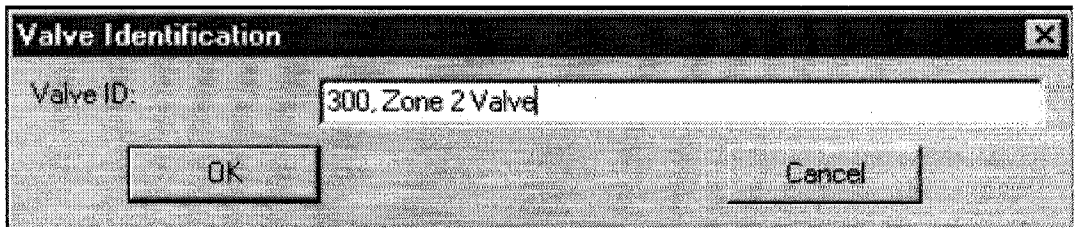

- In the Attribute Browser-Node window, enter value of length, diameter, and roughness field.



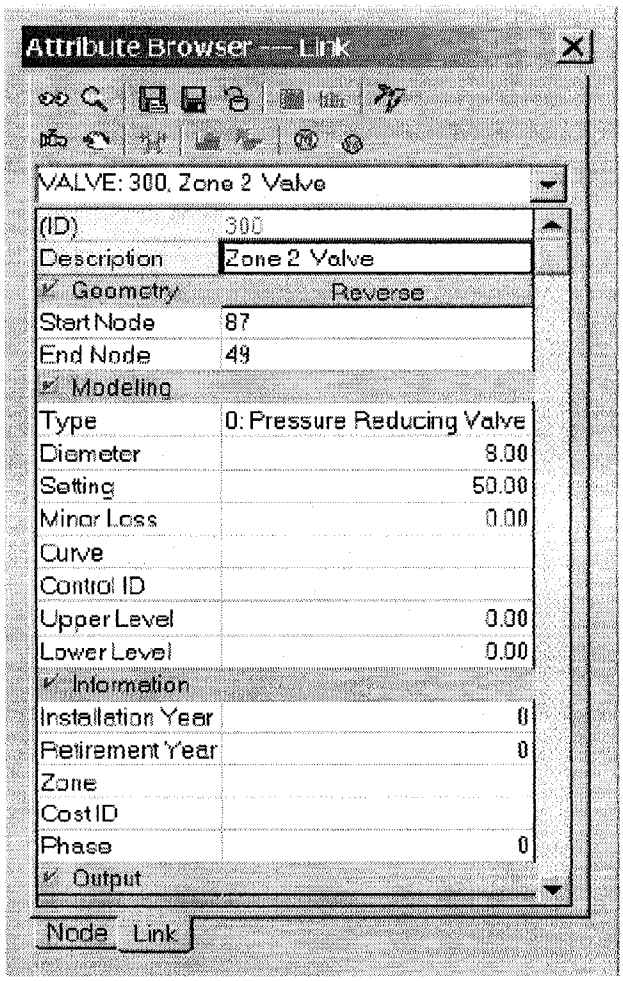

- Click save button.

6) Adding Valves

- Select the Add Valve command from the Create menu, and then move the cursor to the desired location. Using mouse, left click on the one junction node and then double-click on the other junction node to complete the straight line.
- At the Identification box, enter the pipe ID with a comma to separate the ID from the description.




- In the Attribute Browser-Node window, enter value of type, diameter, and pressure setting field.




- Click save button.

4. MODIFY THE NETWORK CONFIGURATION

1) Turning off "Auto Length Calculation"
   - Select the Preferences command from the Tools menu.
   - Choose the Operations tab and disable the Auto Length Calculation by clicking on the check-box.
   - Click OK button.

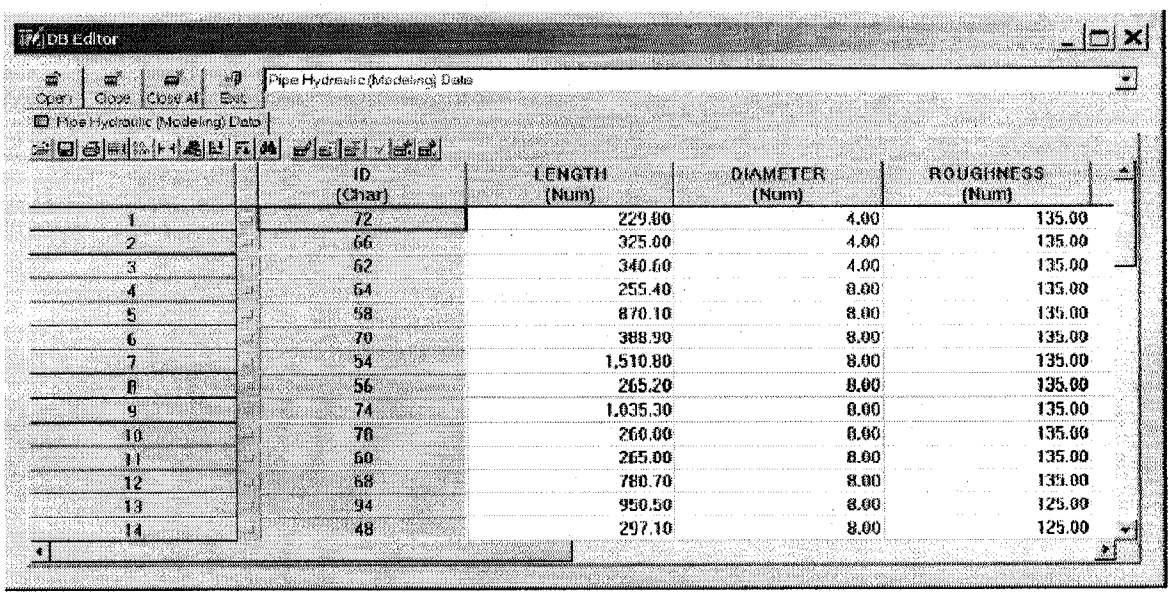
2) Modifying Link Shape
   - Place the cursor on the desired pipe and then select the Redraw Link command from the Edit menu.
   - Using mouse, left click on the start node and then left click to define intermediate vertices. Finally, double-click on the end node to terminate the redrawing process.

3) Moving Nodes
   - Place the cursor on the desired node to be moved and then press the left mouse button.
   - Drag the node to the desired location and release the left mouse button to indicate the new location.

## 5. MODIFY COMPONENT ATTRIBUTES

1) Modify Elements One at A Time
   - Place the cursor on desired place and then press the left mouse button.
   - In the Modeling section of the Attribute Browser-Link window, change the values which need to be changed.
   - Click save button.

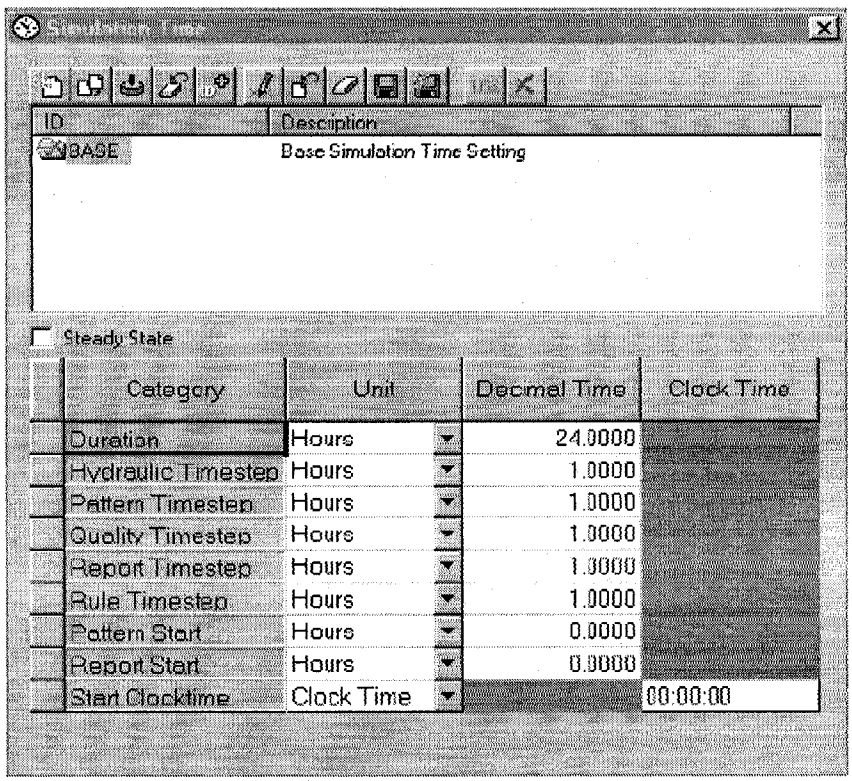
2) Group Editing with the DB Editor
   - Click the DB editor button.
   - Choose the any element data section at DB editor table, then select entire table in the display scope area, and click OK button.
   - To adjust the contents of an entire field, click once on the column header with the mouse.
   - To adjust all any coefficients by changing the current coefficients, choose the block editing button while that column remains highlighted. When the block editing dialog box appears on the screen, choose one of the operations such as add, subtract, multiple, and so on and enter a value, then click OK.
   - Select save button and then choose the close button.
   - Close the DB editor by selecting the exit button.
   - Click save button from the file menu.




| | ID (Char) | LENGTH (Num) | DIAMETER (Num) | ROUGHNESS (Num) |
|---|---|---|---|---|
| 1 | 72 | 229.80 | 4.00 | 135.00 |
| 2 | 66 | 325.00 | 4.00 | 135.00 |
| 3 | 62 | 340.60 | 4.00 | 135.00 |
| 4 | 64 | 255.40 | 8.00 | 135.00 |
| 5 | 58 | 870.10 | 8.00 | 135.00 |
| 6 | 70 | 388.90 | 8.00 | 135.00 |
| 7 | 54 | 1,510.80 | 8.00 | 135.00 |
| 8 | 56 | 265.20 | 8.00 | 135.00 |
| 9 | 74 | 1,035.30 | 8.00 | 135.00 |
| 10 | 76 | 260.00 | 8.00 | 135.00 |
| 11 | 60 | 265.00 | 8.00 | 135.00 |
| 12 | 68 | 780.70 | 8.00 | 135.00 |
| 13 | 94 | 950.50 | 8.00 | 125.00 |
| 14 | 48 | 297.10 | 8.00 | 125.00 |

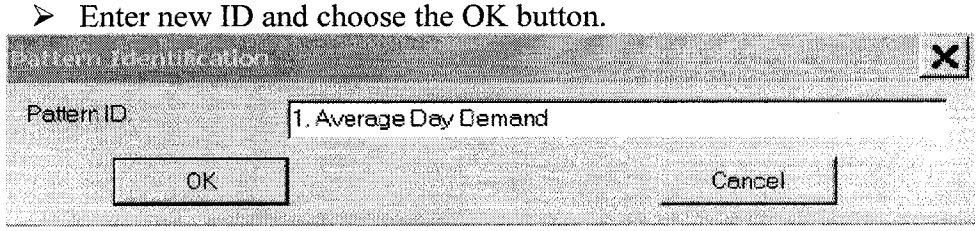
## 6. BUILD THE HYDRAULIC MODEL

1) Set Duration of the Simulation
   - Select Operation Data tap from the Control Center → Simulation Time → Base, Base Simulation Time Setting.
   - Double click and enter value on the Decimal Time field to the right of Duration Category. Choose the Hour Unit.
   - Double click and enter value on the Decimal Time field to the right of Hydraulic Time-step Category. Choose the Hour Unit.
   - Double click and enter value on the Decimal Time field to the right of Pattern Time-step Category. Choose the Hour Unit.

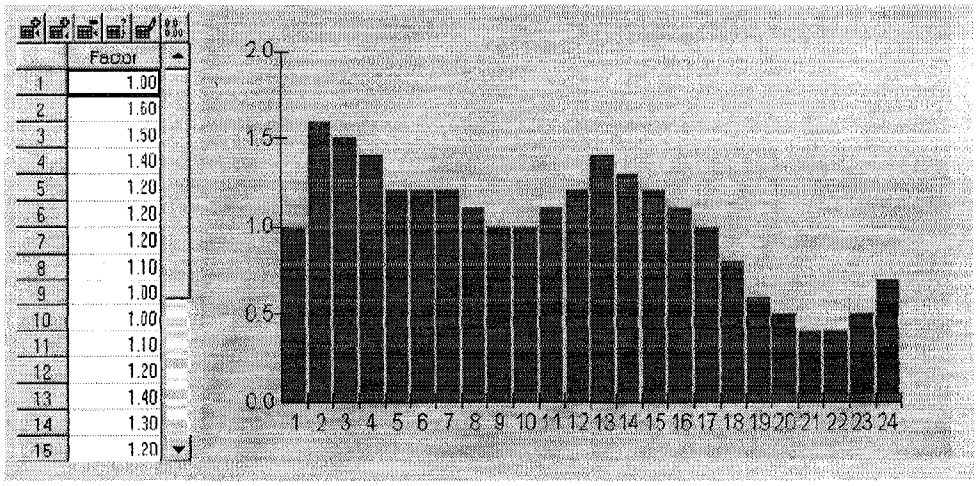



   - Click OK button.

2) Build a pattern to Define Variable Demands
   - Select the Operation Data tap from the Control Center, select Pattern and click on the new button.
   - Enter new ID and choose the OK button.



- Enter the 24 pattern multiplies.
- To define the twenty-four multipliers for pattern 1, perform the following:
  - Choose the Set Rows button, enter the value, and choose OK.
  - Enter the pattern factors and press the Tap key to apply the change. The graph will be automatically updated on the dialog box.
  - Click save button.

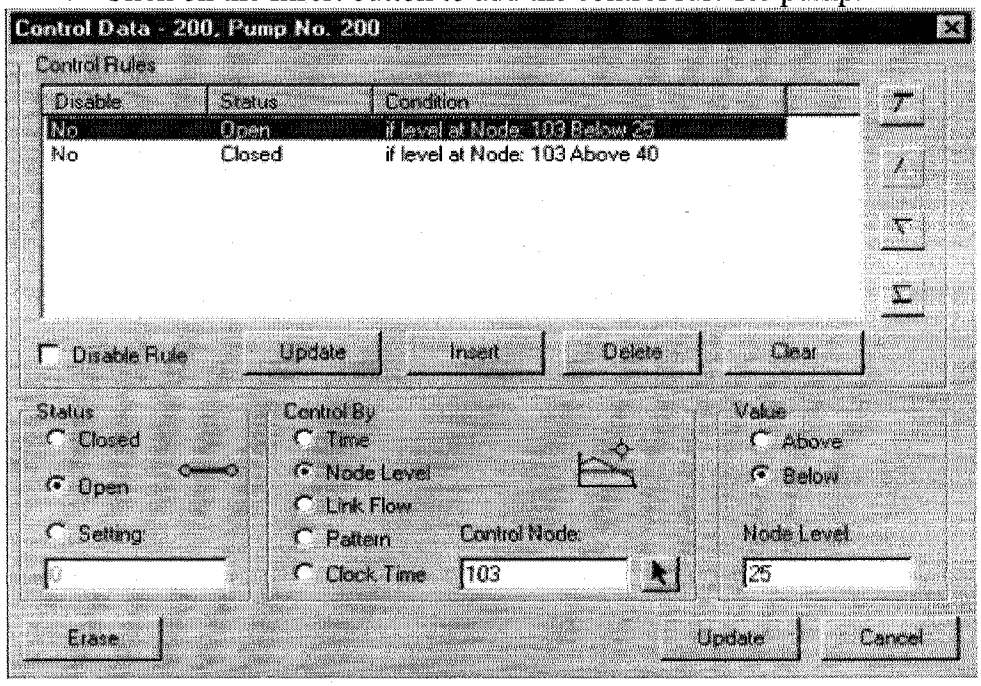



- Assign Click OK button.

3) Assign a Pattern to Junction Nodes
   - To assign the demand multipliers to the junction nodes, click once the DB editor button.
   - Choose the Junction Demand table in the Element Hydraulic Data section, select Entire Table in the Display Scope area, and Click OK button.
   - To adjust the contents of an entire field, click on the column header.
   - Now allocate pattern ID to each junction node. Choose the Block Editing button while the field remains highlighted. Enter the value of the pattern in the Replace with field.
   - Select the save button and then click the close button.
   - Click exit button to close DB editor window.

4) Set Operational Controls
   - Click select button, place the cursor on pump and then press the left mouse button.
   - To define the control rules to turn pump on and off, choose the control button of the Attribute Browser-Link window.
   - To define the control setting, perform the following:
     - Choose the Node Level method in the Control by area and enter the number in the Control Node entry field.
     - Select below or above in the Value area on the dialog box and enter a value in the Node Level entry field.
     - Choose the Open or Closed option in the Status area.

- Click on the Insert button to add the control rule for pump.




- Click on the Update button to close the Control Data dialog box.
- Click Save button of the Attribute Browser-Link window.

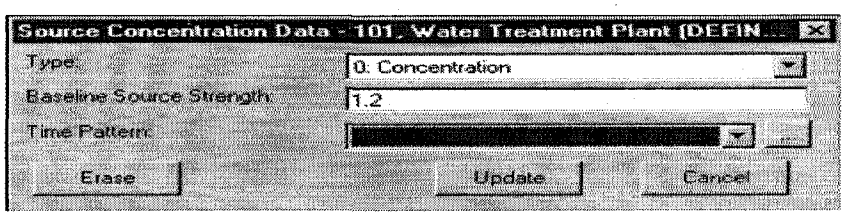
## 7. BUILD THE WATER QUALITY MODEL

1) Specify the Type of Water Quality Analysis and Reaction Rate Coefficients
   - Select Operation Data tap from the Control Center → Simulation Options → Base, Simulation Options.
   - Choose the Quality tab and then choose Chemical to indicate a chemical growth/decay analysis.
   - Enter chemical name in the chemical name entry filed and choose the unit in the mass Unit drop-down list.
   - Enter the value in the Global Bulk and Wall entry field. + indicates growth and – indicates decay.
   - Click OK button.

2) Specify the Initial Water Quality
   - Specify the initial water quality distribution throughout the network at the beginning of the simulation.
   - To do this it will be created a domain and use Group Edit on Domain function to edit water quality for a selected group of network components.

3) Domain and Group Editing
   - Click the "Domain Manager" button.
   - To add all junction nodes to the domain, choose Network in the Element Source area, select All Junctions from the list and then press the Add button.
   - To add other element to the domain, choose the Map Selection in the Element Source area and press the Add button. Click the left mouse button, then click the right mouse button and press enter to confirm the selection.
   - Click Group Edit on Domain icon.
   - Choose the Initial Quality tab on the Group Editing dialog box.
     - Enter the value in the Initial Water Quality entry field.
     - Choose the Apply button.
     - Press OK button and then close button.
   - Click the Reset button to clear the domain and then click the close button.

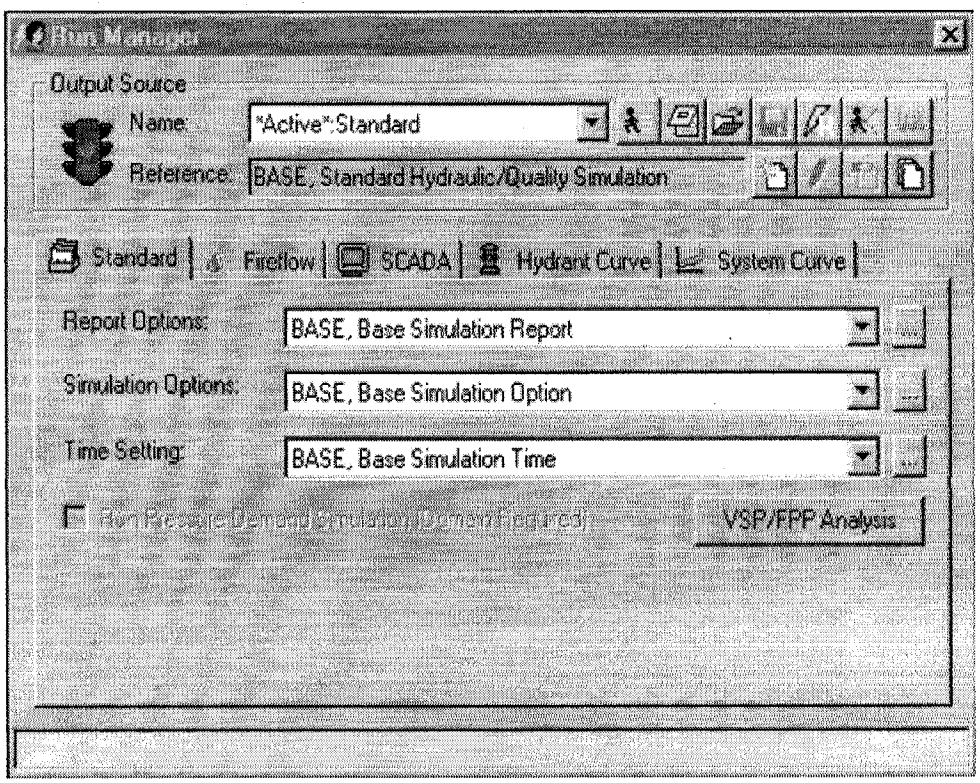
4) Specify the Source of Chlorine Injection
   - Click the select button and place the cursor the source.
   - In the Attribute Browser-Node window, choose the Water Quality Source button and select the type. Moreover, enter the value in the Baseline Strength entry field.




   - Click OK button and Save button.

8. RUN THE SIMULATION

1) Click the Run Manager button.



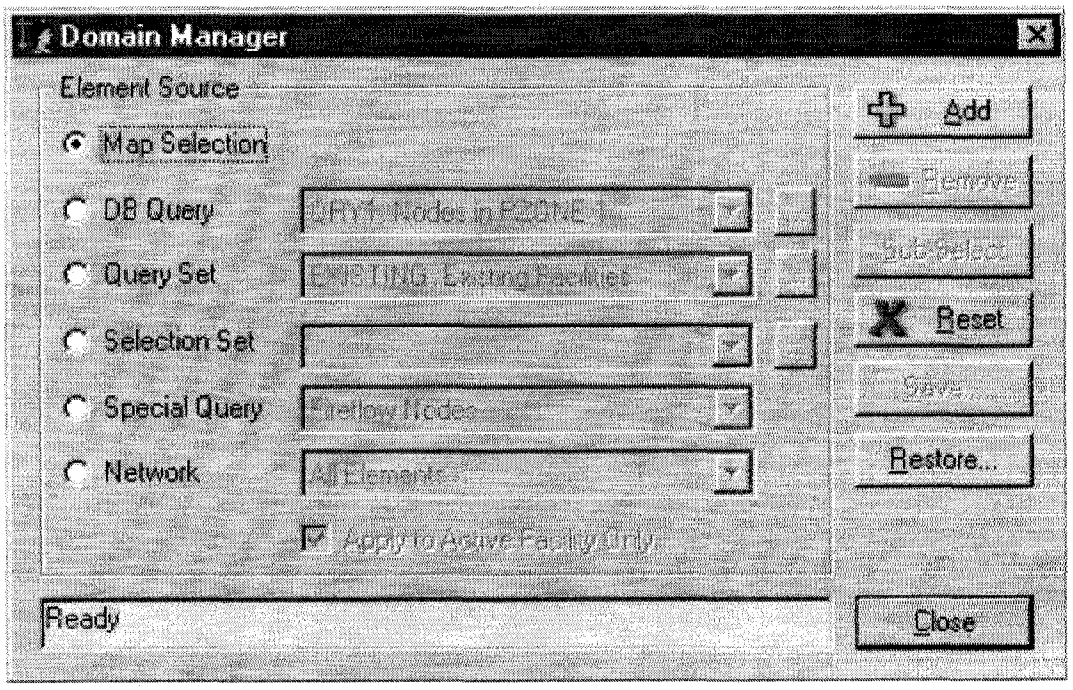

2) Choose the Standard tap. Before running the simulation, it is possible to pick the simulation options, time and duration options, and reporting options to be associated with the next simulation run.
3) Click the Run button. If the run is successful, then the status stoplight should show green. Click OK button to close the Run Manager dialog box.

9. REVIEW MODEL RESULTS

1) Review Results with the Attribute Browser
   - Click select button and then click on the desired node or link. Results are shown in the Output section of the Attribute Browser window.
   - To review how the model results change throughout the simulation, move the slider bar to the desired simulation time-step of the Active Output toolbox.

2) Customize the Map Display
   - Map Display tap from Control Center to customize the map display. It will only control components included in the current network domain.

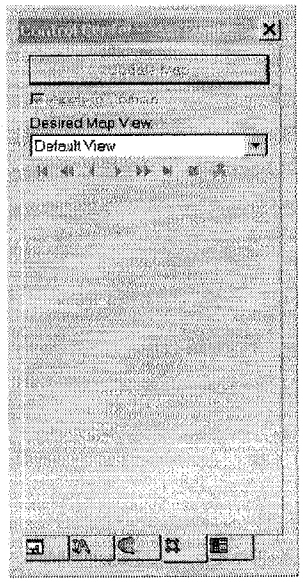
3) Create a Domain
   - Click the "Domain Manager" button.




   - Click the map Selection in the Element Source area and then click on the Add button.
   - Place the cursor anywhere in the network then press the left mouse button and drag the cursor to the desired selection window. Click on the right mouse button and choose enter to confirm the selection window.
   - All the network components that fall entirely within the selection window should now appear highlighted and are now included in the domain. Close the dialog box.

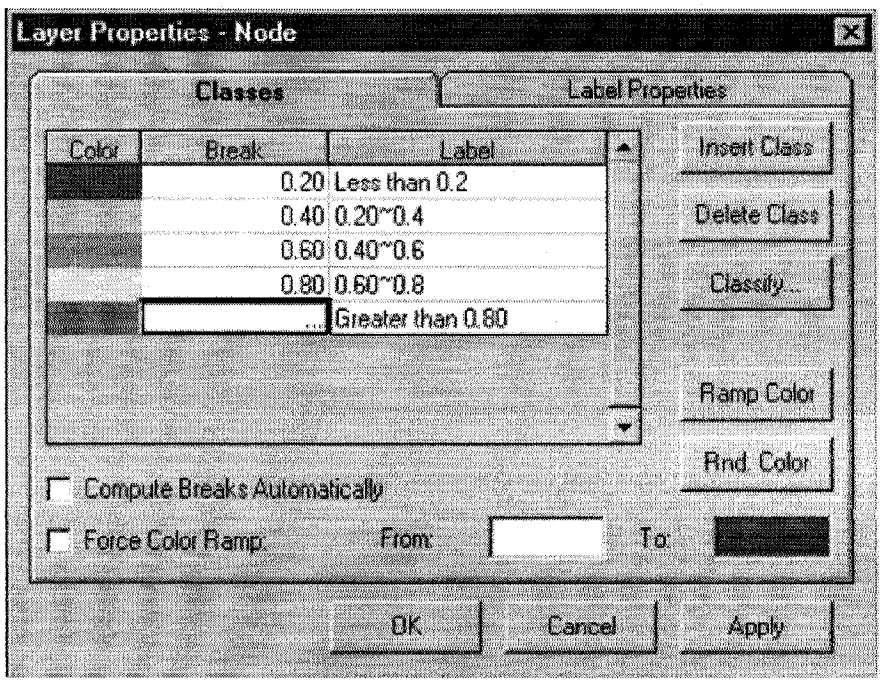
4) Specify Map Customization Options

- Choose the Map Display tab from the Control Center as shown below.




- Choose Output Data View as the Desired Map View.
- Select Junction as the Element Type from the Node tab and then select chemical as the Data Category that will be displayed.
- Choose simulation time-step in the Active output.
- Click on the Display Settings button to open the Layer Properties-Node window.

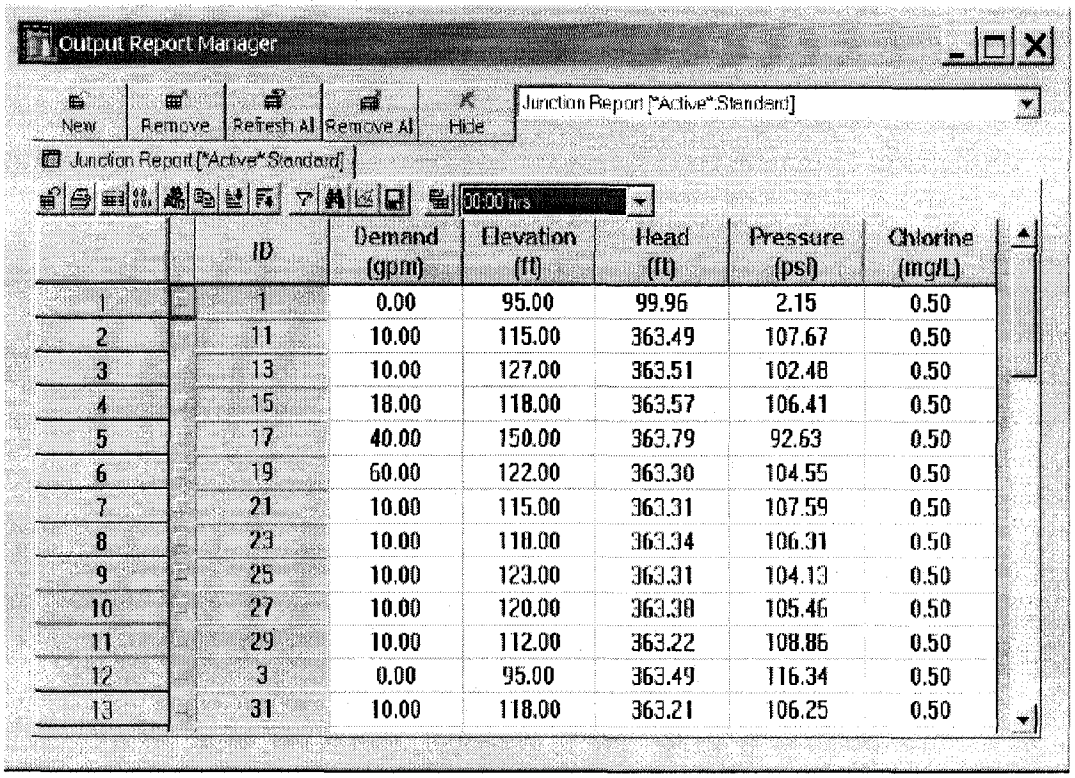
➢ Perform the following to define five classification range breaks in the Classes tap of the Layer Properties-node window as shown below.




- Enter the value in the Break field as the first break value and assign a specific color to highlight all junctions with a chemical concentration less than this value. Double-click on the corresponding color box in the Color section, choose the desired color and then click on the OK button.
- Repeat the above steps using the range breaks shown in the figure above.
- Choose the Label Properties tab and check the Show Text/Label check-box to see the labeling nodes with their chemical concentration values. Click on the Apply button and the OK button to close the window.
- Click on the Update map button of the map Display tab from the Control Center and the nodes in the current domain will be redrawn to reflect your choices.

## 10. BROWSE MODEL RESULTS

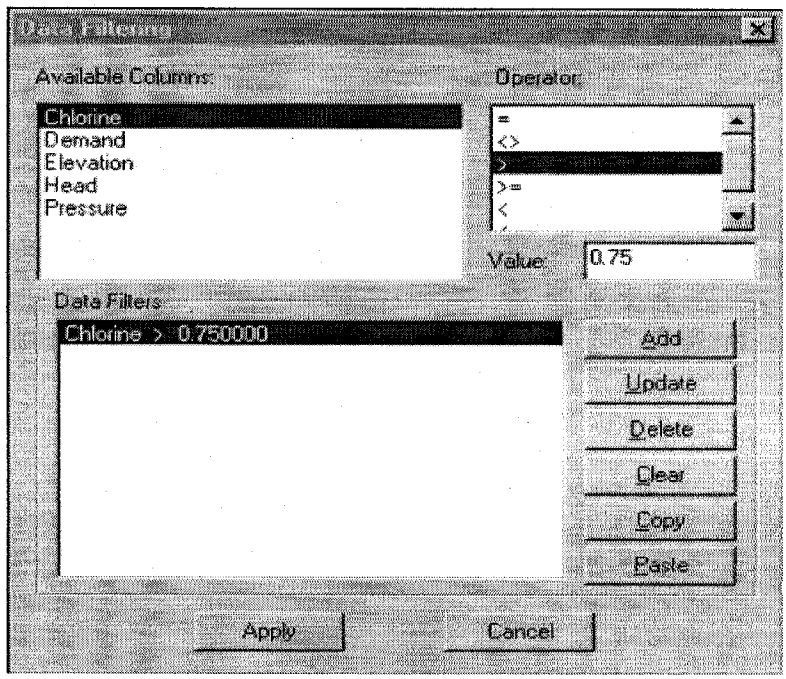
1) Open the Output Report Manager
   - ➢ Click the Output Report/Graph button.
   - ➢ On the Output Report Manager choose the new button. Select Active Standard from the All Output Sources area. Choose Junction Report from the Report tab, and then click the Open button. The Output Report Manager window should appear as shown below.



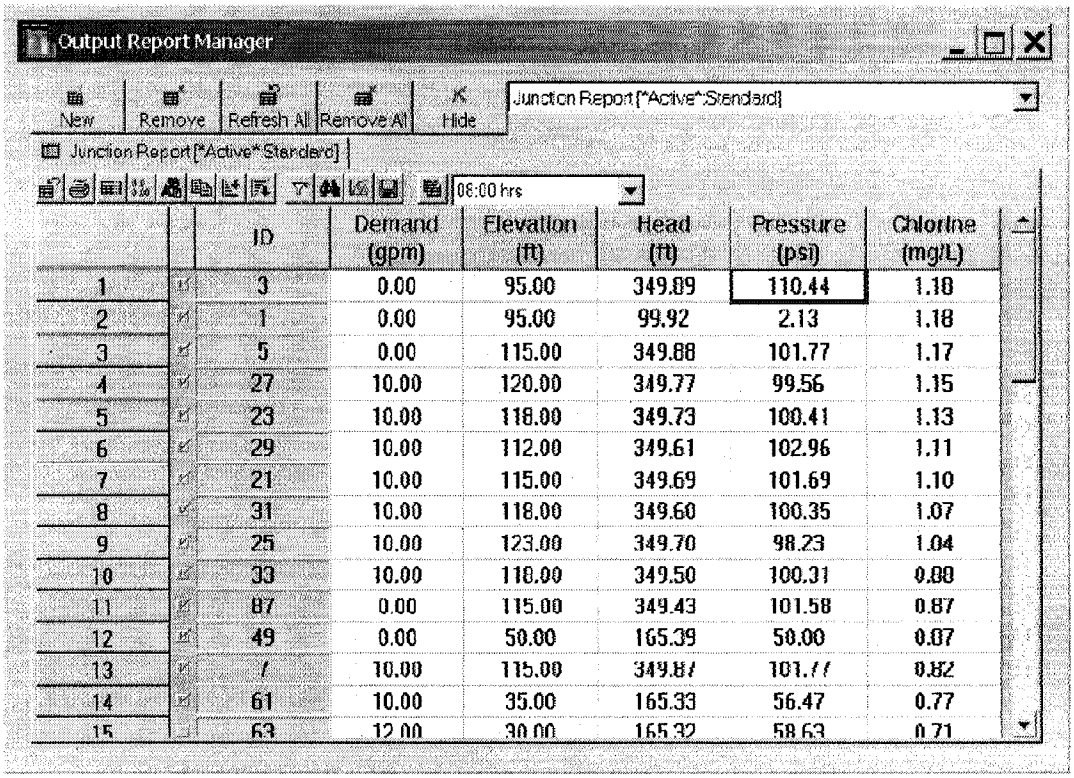

| | ID | Demand (gpm) | Elevation (ft) | Head (ft) | Pressure (psi) | Chlorine (mg/L) |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.00 | 95.00 | 99.96 | 2.15 | 0.50 |
| 2 | 11 | 10.00 | 115.00 | 363.49 | 107.67 | 0.50 |
| 3 | 13 | 10.00 | 127.00 | 363.51 | 102.48 | 0.50 |
| 4 | 15 | 18.00 | 118.00 | 363.57 | 106.41 | 0.50 |
| 5 | 17 | 40.00 | 150.00 | 363.79 | 92.63 | 0.50 |
| 6 | 19 | 60.00 | 122.00 | 363.30 | 104.55 | 0.50 |
| 7 | 21 | 10.00 | 115.00 | 363.31 | 107.59 | 0.50 |
| 8 | 23 | 10.00 | 118.00 | 363.34 | 106.31 | 0.50 |
| 9 | 25 | 10.00 | 123.00 | 363.31 | 104.13 | 0.50 |
| 10 | 27 | 10.00 | 120.00 | 363.38 | 105.46 | 0.50 |
| 11 | 29 | 10.00 | 112.00 | 363.22 | 108.86 | 0.50 |
| 12 | 3 | 0.00 | 95.00 | 363.49 | 116.34 | 0.50 |
| 13 | 31 | 10.00 | 118.00 | 363.21 | 106.25 | 0.50 |

   - ➢ The results are displayed for the first extended period simulation time-step. Pick the desired time from the drop-down list and the Output Report Manager will display junction node model results for the selected time period.

2) Sorting and Filtering Records
   - ➢ Select the time-step from the drop-down list and then choose the Filtering button.
     - Click on Chemical in the Available Columns area.
     - Click on any symbol in the Operator area.
     - Type the value in the value entry field.
     - Click on the Add button. The query should appear in the Data Filters list.
     - Click on the Apply button.



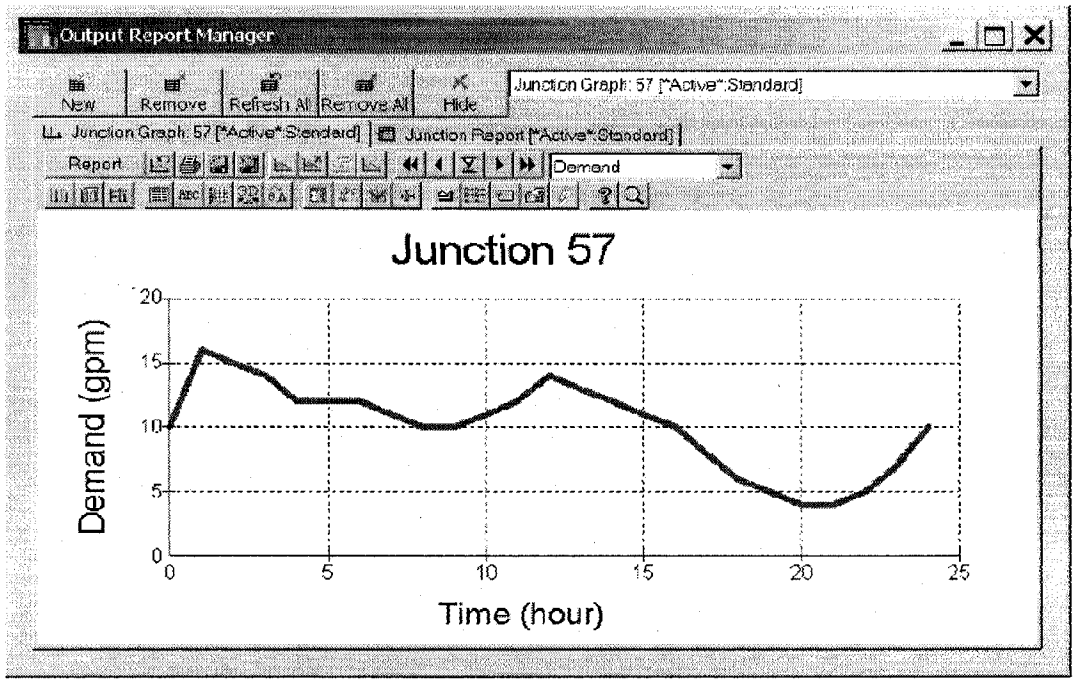

- Click on the chemical field header in the Output Report manager.
- Choose the Sort Descending button. The junction Report table is now sorted from the highest to lowest.




| | ID | Demand (gpm) | Elevation (ft) | Head (ft) | Pressure (psi) | Chlorine (mg/L) |
|---|---|---|---|---|---|---|
| 1 | 3 | 0.00 | 95.00 | 349.89 | 110.44 | 1.18 |
| 2 | 1 | 0.00 | 95.00 | 99.92 | 2.13 | 1.18 |
| 3 | 5 | 0.00 | 115.00 | 349.88 | 101.77 | 1.17 |
| 4 | 27 | 10.00 | 120.00 | 349.77 | 99.56 | 1.15 |
| 5 | 23 | 10.00 | 118.00 | 349.73 | 100.41 | 1.13 |
| 6 | 29 | 10.00 | 112.00 | 349.61 | 102.96 | 1.11 |
| 7 | 21 | 10.00 | 115.00 | 349.69 | 101.69 | 1.10 |
| 8 | 31 | 10.00 | 118.00 | 349.60 | 100.35 | 1.07 |
| 9 | 25 | 10.00 | 123.00 | 349.70 | 98.23 | 1.04 |
| 10 | 33 | 10.00 | 118.00 | 349.50 | 100.31 | 0.88 |
| 11 | 87 | 0.00 | 115.00 | 349.43 | 101.58 | 0.87 |
| 12 | 49 | 0.00 | 50.00 | 165.39 | 50.00 | 0.87 |
| 13 | 7 | 10.00 | 115.00 | 349.87 | 101.77 | 0.82 |
| 14 | 61 | 10.00 | 35.00 | 165.33 | 56.47 | 0.77 |
| 15 | 63 | 12.00 | 30.00 | 165.32 | 58.63 | 0.71 |

## 11. CREATE GRAPHS

1) Opening a Graph
   - ➢ While step 10 above is displaying the Junction Report, choose the new button. When the Output Report & Graph dialog box appears on the screen, select Active Standard in the All Output Sources area. Choose Junction Graph in the Graph tab, and then click on the Open button.
   - ➢ Move and place the cursor on the desired junction node and press the left mouse button.




   - ➢ To change to a chemical graph, choose the desired variable from the drop-down list above the graph.

## Appendix C Biofilm Data and Pictures

Figures C-1 through C-4 display the lab equipment that was used to obtain the biofilm data. Figure C-1 shows the bench-scale test pipe.

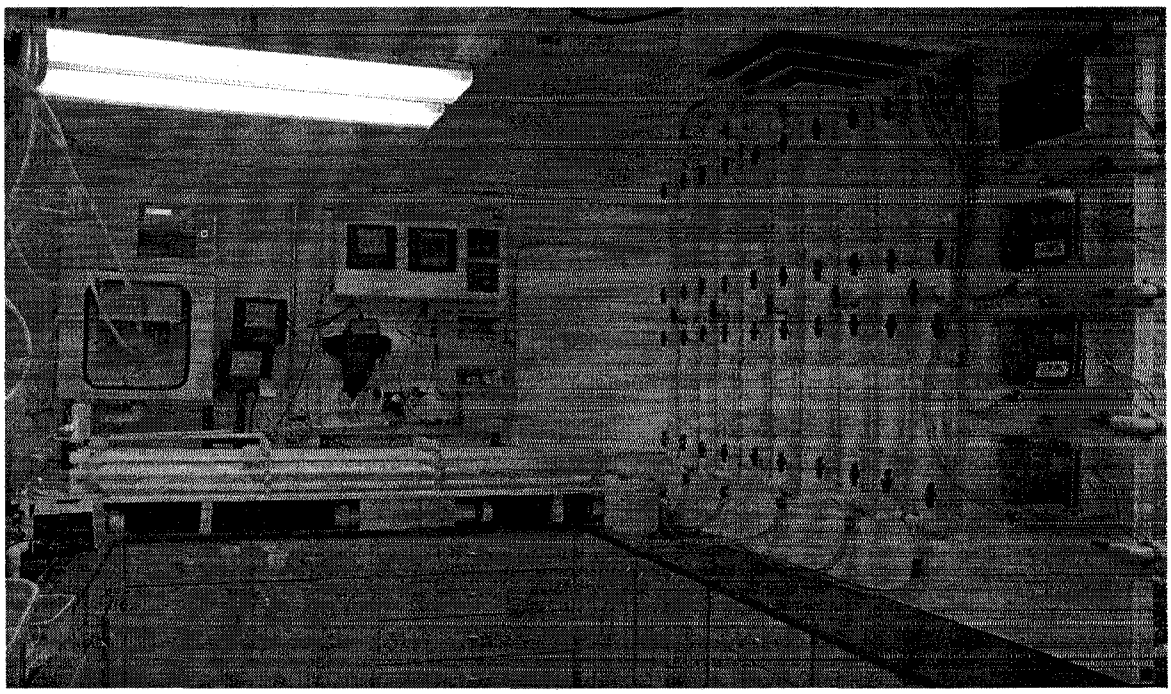


Figure C-1 Biofilm bench-scale test picture

Figure C-2 shows the PVC coupon that was used in the bench-scale test pipe. Three of these coupons were put inside of pipes. The coupon measures $5^{7/8"} * 5/8"$ for a surface area of 3.67 $in^2$.

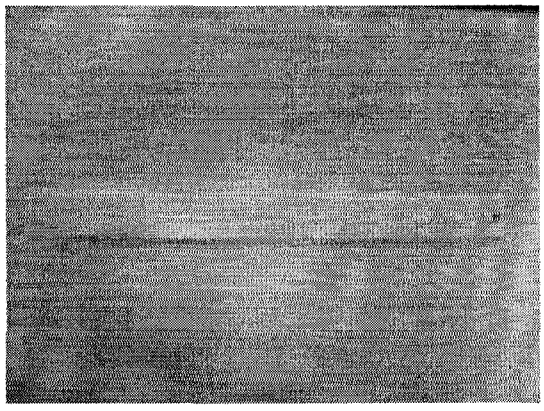


Figure C-2 PVC coupon

Figure C-3 displays the scraping tool that was used to remove the biofilm from the PVC coupons. This work was done by Dr. Pruden's student Matt Hewitt. The PVC coupons are apparent in the 200 mL test tubes in his hand. The coupons were scraped into solution in the test tube.

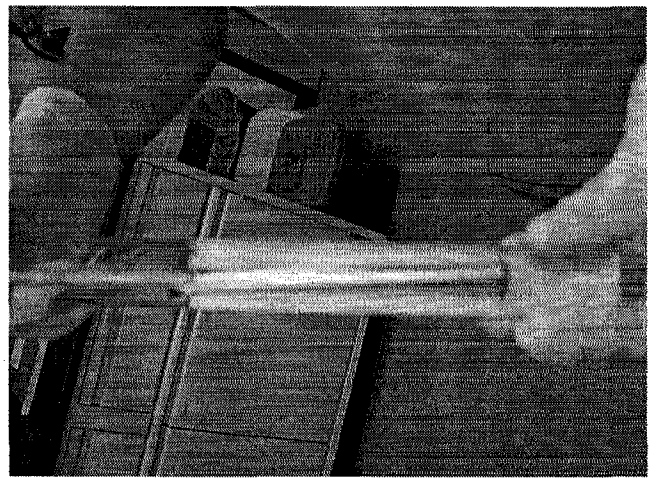


Figure C-3 Coupon scraper

Figure C-4 shows that the solution which has biofilm from PVC coupon was transferred into a 60ml Luer-Lock syringe and injected solutions into filter holder.

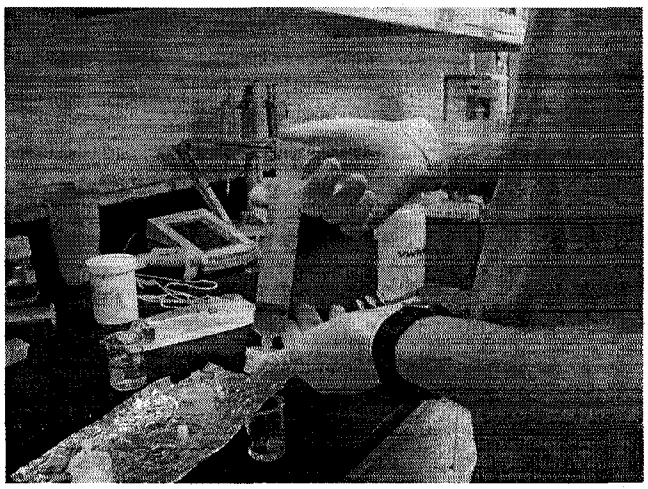


Figure C-4 Injection solution into filter holder

## APPENDIX D Beaker Test Data

Table D-1 notes the changes in water quality parameters when the specified contaminant at the designed concentration was added to local tap water. These tests utilized bench top analytical equipment (versus on-line monitors).

Table D-1 Beaker test experimental results

| Contaminant | Concentration (mg/L) | Δ pH | Δ Cond (uS/cm) | Δ Chl Res (mg/L) | Δ TOC (mg/L) |
|---|---|---|---|---|---|
| Sodium Arsenate | 0 | 0 | 0 | 0 | 0 |
| | 6 | 0 | 0 | -0.02 | 0 |
| | 12 | 0 | 4 | -0.04 | 0 |
| | 20 | 0 | 11 | -0.01 | 0 |
| | 40 | 0.02 | 21 | -0.01 | 0 |
| | 100 | 0 | 67 | -0.41 | 0 |
| Sodium Cyanide | 0 | 0 | 0 | 0 | 0 |
| | 1 | 0.44 | 0 | -0.47 | 0.13 |
| | 4 | 0.96 | 4 | -0.37 | 0.6 |
| | 6 | 1.05 | 8 | -0.37 | 1.01 |
| | 8 | 1.08 | 15 | -0.36 | 1.21 |
| | 12 | 1.21 | 26 | -0.36 | 1.86 |
| | 24 | 1.53 | 50 | -0.36 | 3.65 |
| Sodium Fluoroacetate | 0 | 0 | 0 | 0 | 0 |
| | 1 | -0.20 | 12 | 0 | 0.29 |
| | 4 | -0.32 | 16 | 0 | 0.89 |
| | 10 | -0.37 | 22 | 0 | 2.75 |
| | 20 | -0.44 | 28 | 0 | 5.18 |
| | 40 | -0.44 | 52 | 0 | 8.71 |
| Aldicarb | 0 | 0 | 0 | 0 | 0 |
| | 1 | 0 | 0 | -0.52 | 0.56 |
| | 2 | 0 | 0 | -0.55 | 1.12 |
| | 5 | 0 | 1 | -0.41 | 2.1 |
| | 10 | 0 | 4 | -0.43 | 4.07 |
| | 20 | 0 | 6 | -0.43 | 8.97 |
| | 40 | 0 | 7 | -0.42 | 8.97 |
| Cycloheximide | 0 | 0 | 0 | 0 | 0 |
| | 1 | -0.06 | 1 | -0.22 | 0.45 |
| | 2 | 0.08 | 0 | -0.4 | 1.11 |
| | 4 | -0.04 | -1 | -0.47 | 1.63 |
| | 6 | -0.17 | -38 | -0.48 | 1.64 |
| | 8 | -0.77 | -104 | -0.48 | 1.63 |
| Nicotine | 0 | 0 | 0 | 0 | 0 |
| | 1 | 0.12 | 2 | -0.27 | 0.7 |
| | 4 | 0.12 | 2 | -0.31 | 2.86 |
| | 10 | 0.36 | 5 | -0.31 | 6.83 |
| | 20 | 0.58 | 2 | -0.31 | 8.75 |
| Dicrotophos | 0 | 0 | 0 | 0 | 0 |
| | 1 | 0.18 | -1 | 0.04 | 0.48 |
| | 2 | 0.13 | -1 | -0.03 | 0.76 |
| | 5 | 0.05 | -1 | -0.11 | 1.85 |
| | 10 | -0.02 | 2 | -0.02 | 3.25 |
| | 20 | 0 | 2 | -0.07 | 6.04 |