

11-8-2005

Comparison of the Use of Single and Multiple Oxidants on the Generation of Particulate Matter in Water Distribution Systems Derived from Groundwater Sources Containing Hydrogen Sulfide and Dissolved Organics

Rochelle J. Minnis
University of South Florida

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Comparison of the Use of Single and Multiple Oxidants on the Generation of Particulate
Matter in Water Distribution Systems Derived from Groundwater Sources Containing
Hydrogen Sulfide and Dissolved Organics

by

Rochelle J. Minnis

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Major Professor: Audrey D. Levine, Ph.D.
Carlos A. Smith, Ph.D.
Carl Biver, Ph.D.

Date of Approval:
November 8, 2005

Keywords: turbidity, uv irradiation, chlorine, chloramine, particle count

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Dedication

I would like to dedicate this thesis to my family, especially my father, Mr. Randolph J. Minnis, my mother, Mrs. Julieth N. Minnis, and my sister Roya J. Ndimba. Without their support, encouragement and faith in my abilities, this thesis would not have been written.

Acknowledgements

Primarily, I would like to thank my major professor, Dr. Audrey D. Levine for her support and guidance over the past two years. She introduced me to the world of environmental engineering and that is a gift beyond measure. Her wealth of knowledge about environmental issues is outstanding and her dedication to her students is commendable. Her belief in my abilities allowed me to continue on this journey in spite of my own lagging confidence and many tearful days.

I would also like to thank Dr. Carlos A. Smith, and Dr. Carl Biver, for their guidance and encouragement while I pursued both my BSc. in Chemical Engineering and MSc. in Environmental Engineering.

Special thanks go out to Salah Albusami and Camilo Romero who were with me in the field every day, in good weather and bad. Without you guys, there would be no data for this thesis. I want to thank the staff in the USF Environmental Engineering lab for their help with the laboratory tests and David Edwards from the USF Center for Ocean Technology/MEMS Lab for his help with the SEM and EDS analyses.

I want to thank the staff of Aloha Utilities especially Mike McDonald, Charlie Painter, and Jack Burke for the construction of pilot plant and help with start-up and operation.

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**Comparison of the Use of Single and Multiple Oxidants on the Generation of
Particulate Matter in Water Distribution Systems Derived from Groundwater
Sources Containing Hydrogen Sulfide and Dissolved Organics**

Rochelle J. Minnis

ABSTRACT

Due to increasingly stringent regulations, concerns about disinfection byproduct formation, and the need for improved control of distribution system water quality, there has been a shift towards the use of alternative disinfectants and oxidants in the production of drinking water. Technologies that modify water chemistry, such as hydrogen peroxide, UV irradiation, chlorine and/or chloramines may result in the generation of mineral and organic precipitates. Turbidity provides an indirect measure of the presence of particles by evaluating the light scattering properties of water. Turbidity levels are currently not monitored or regulated in treated groundwater.

An important water quality parameter that influences groundwater quality is hydrogen sulfide. The control of sulfides in groundwater is of importance because its presence can cause odor and taste complaints, corrosion of pipes and other plumbing

fixtures, and black-water problems in distribution systems (Levine et. al, 2004). In addition, sulfides can impose a significant oxidant demand and possibly interfere with disinfection treatments.

Characteristics of particles from untreated and treated groundwater were tested as part of a field study to evaluate alternative wellhead treatment approaches for controlling hydrogen sulfide. A 1 gallon per minute (gpm) pilot-plant was used to test several groundwater treatment scenarios. The chemicals tested included chlorine, monochloramine, and hydrogen peroxide either alone or in tandem. Photochemical oxidation was evaluated using UV and advanced oxidation was evaluated using hydrogen peroxide coupled with UV. Testing was conducted either on water pumped directly from the well at ambient (7.0-7.5), or pretreated with caustic soda to evaluate the impact of elevated pH (8.2) conditions. The formation of particles was quantified using turbidity, solids (total, dissolved and suspended), and particle counts before and after oxidation. The particulate matter was characterized using a particle size analyzer in conjunction with scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS).

Treatment systems that rely on in-line treatment lack mechanisms for particle removal, therefore particles generated through treatment are introduced into the distribution system. It is evident from this project that treatment systems should be optimized to prevent particle formation.

Introduction

The presence of particulate matter in water systems is of importance because particles in water may be comprised of microorganisms (EPA Guidance Manual, 1999) or inert organic or inorganic constituents. The presence of particles may act to shield pathogens (viruses, bacteria, and protozoa) from the action of disinfectants (chlorine, ozone, UV irradiation). Particulate matter can also provide surface area for accumulation of microbial substrates and biofilms (EPA Guidance Manual, 1999).

There has been a shift in the drinking water industry towards the use of alternative treatments because of the need for improved control of distribution system water quality. The use of these alternative treatments can modify water chemistry and may impact the concentration of particulate matter in treated water. The impact that these treatments have on particle type and concentration needs to be addressed to develop proper engineering control strategies.

One of the major water quality factors that controls the solubility of particles in water is pH. pH also impacts the degree of sulfur ionization which influences the effectiveness of

removal pathways and the end products of oxidation reactions. At pH levels below 7.5, sulfur formation is favored whereas above 7.5, sulfate is the preferred product. Many water treatment plants adjust the pH and alkalinity of water in order to meet specific corrosion indices such as the Langelier index. Therefore, the impact that disinfectants and oxidants have on particle characteristics at different pH levels needs to be understood.

Objectives

This research project was conducted to evaluate the degree to which particulate matter is generated as a byproduct of groundwater treatment for the control of hydrogen sulfide. The specific objectives are:

1. Evaluate the impact of disinfection on the formation or dissolution of mineral and organic particles at ambient and elevated pH levels.
2. Compare alternative oxidation technologies for the control of hydrogen sulfide in groundwater at ambient and elevated pH levels.

Background

Background information on ground water quality is provided in this section. Two parameters that affect water quality are discussed: hydrogen sulfide and the presence of particles. Methods for sulfide removal appropriate for small water systems are summarized.

Groundwater Quality in Florida

More than 90 percent of Floridians rely on groundwater as their source for drinking water. In 2000, the United States Environmental Protection Agency (USEPA) proposed the Groundwater Rule (GWR) to regulate all groundwater sources that supply drinking water. This regulation is intended to protect public health by reducing the potential for exposure to microbial contaminants in drinking water (USEPA, 2005). The major components of the GWR are outlined in Table 1 (USEPA, 2000). The emphasis of the requirements is in monitoring for fecal contamination and designing disinfection systems to provide the capability of 4-log inactivation or removal of viruses (USEPA, 2000).

Table 1: Summary of the five major requirements proposed by the GWR

Component	Explanation	Frequency
Periodic Sanitary Surveys of Groundwater Systems	The Sanitary survey evaluates and documents the strengths and weaknesses of the water system's sources, treatment, storage, distribution, network, operation and maintenance, and overall management.	Once every three years for community water systems and at least once every five years for non-community water systems
Hydrogeological Assessments of wells	Identifies groundwater wells that are sensitive to fecal contamination. The GWR identifies three aquifer types that are sensitive: Karst, fractured bedrock, and gravel aquifers.	One test for each groundwater system that does not provide treatment to 4-log inactivation or removal of viruses is required and should be conducted before three years or five years elapse after publication of the Final Rule in the Federal Register for community water systems and non community water systems respectively.
Source Water Monitoring	Identifies the systems with source water contamination and systems with high sensitivity to possible fecal contamination by testing for total coliforms.	EPA requests comment on monitoring frequency
Corrective Treatment	Systems must eliminate the source of contamination, correct the significant deficiency, provide an alternative source water, or provide a treatment to achieve a 99.99 percent (4-log) inactivation or removal of viruses.	Must apply an appropriate treatment technique within 90 days of detection of the significant deficiency or source water contamination. If unable to do so, they must have a State-approved plan and schedule for doing so.
Compliance Monitoring	Ensures that disinfection treatment is reliably operated where it is used.	EPA requests comment on monitoring frequency.

Until the GWR is implemented, groundwater disinfection is governed by monitoring for indicator bacteria in the distribution system and must meet appropriate regulations under the Safe Drinking Water Act (SDWA) for primary and secondary contaminants. A summary of other regulatory requirements is outlined in Table 2 (USEPA, 2000). Hydrogen sulfide and the presence of particulates in water are not directly addressed in any of the current regulations.

Table 2: Comparison of regulations pertain to particles and disinfection rules in groundwater and surface water treatment

Regulations	Existing or Future Date Anticipated for Final Rule	Description	Monitored at Treatment Plant or Distribution System
Total Coliform Rule (TCR)	Existing (1989), but under revision.	TCR monitors for the presence of total and fecal coliform. Presence indicates that other harmful bacteria may be present. The total number and location of samples is based on the population served.	Distribution System
Lead & Copper Rule (LCR)	Revised in 2000	LCR sets maximum contaminant levels (MCLs) for lead (0.015mg/L) and copper (1.3 mg/L) based on the 90 th percentile level of tap water samples.	Distribution System
Long Term 2 Enhanced Surface Water Treatment Rule	July 2005	Requires monitoring for large systems (>10,000 people) of <i>Cryptosporidium</i> for two years to characterize water quality. Then depending on the concentration, methods of removal in addition to conventional treatment and filtering will have to be implemented. Small systems (< 10,000 people), monitor <i>E.Coli</i> .	Treatment Plant
stage 2 disinfectants/di sinfection byproducts rule	July 2005	Regulates the disinfectant concentration and disinfection byproduct amounts in treated water. Large and medium systems must comply with 0.0080/0.060mg/L TTHM/HAA5 LRAA six years after promulgation and after ten years for small systems	Distribution System

^{a,b}Only applies to groundwater sources that are under the direct influence of surface water

Sulfide Chemistry

Sulfur exists in nine oxidation states in water and can transition from one state to another depending on localized chemical and biological reactions. Sulfides in water are undesirable because of their “rotten egg” odor and their corrosivity properties (Dohnalek, 1983). The term “total sulfides” refer to dissolved hydrogen sulfide (H_2S), ionized sulfide (HS^- and S^{2-}), and acid-soluble metallic sulfides, and polysulfides. The equilibrium equations for the three sulfide species are outlined in equations 1 and 2 and illustrated in Figure 1 with respect to pH. Various values have been reported for the second equilibrium constant at 25°C. A summary of values is given in Table 3.

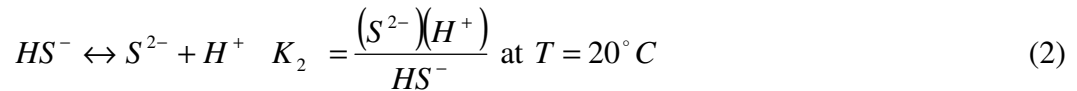
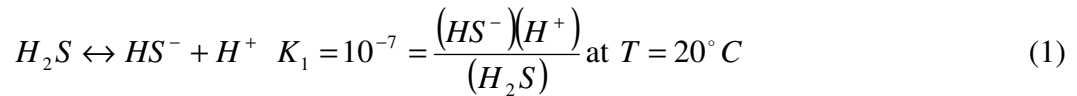


Table 3: Values of K_2 obtained from various sources

Source	Benjamin, 2002	Garrels, et.al, 1965	Sillen, et. al 1964	Knox, 1906	Maronny, 1959
Value	$10^{-12.92}$	10^{-14}	$10^{-17.1}$	$10^{-14.92}$	$10^{-13.78}$

The speciation of reduced sulfur in water is controlled mainly by pH as shown in Figure 1. The form of reduced sulfur in water dictates the effectiveness of the type of treatment used. The non-ionized form of reduced sulfur (hydrogen sulfide) is very volatile and is mostly present at the pH levels below six. Thus, the use of aeration can be

more effective for stripping the volatile form of hydrogen sulfide from water. The pH levels of most water sources range from approximately 6.5 to 8.5. Above a pH of 8 bisulfide (HS^-) is the prevalent form of reduced sulfur. Polysulfides (S_n^{2-}) are prevalent above the second equilibrium constant (see Table 3).

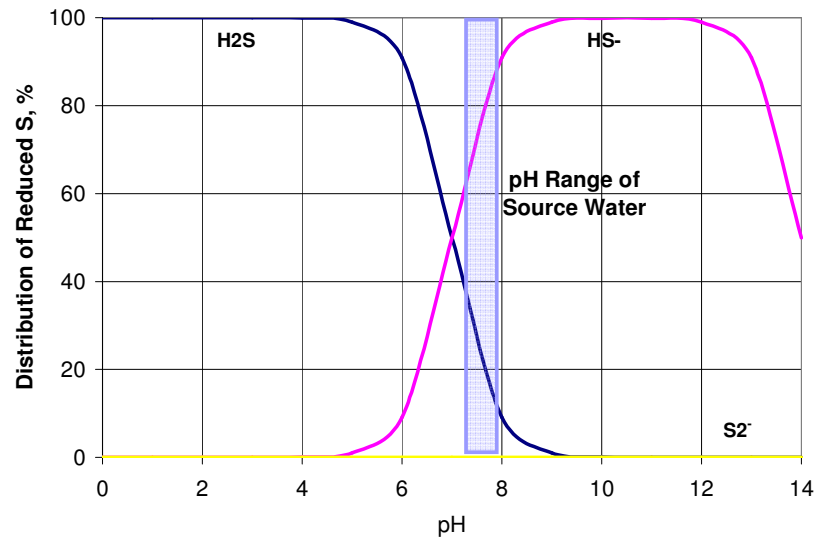


Figure 1: Theoretical distribution of sulfide species in water as a function of pH

Sulfide Control in Groundwater

Methods for sulfide control in groundwater include aeration, oxidation (biological or chemical), and anion exchange. The following section discusses the use of oxidation for sulfide control.

The addition of oxidants such as chlorine, hydrogen peroxide or ozone to groundwater serves to increase its oxidation potential because of reactions with reduced constituents in water. The extent of the change in oxidation potential is influenced by the reaction rates. By manipulating the pH and the dosages of chemical oxidants, the oxidation potential and end products of sulfur oxidation can be controlled. This is illustrated in Figure 2.

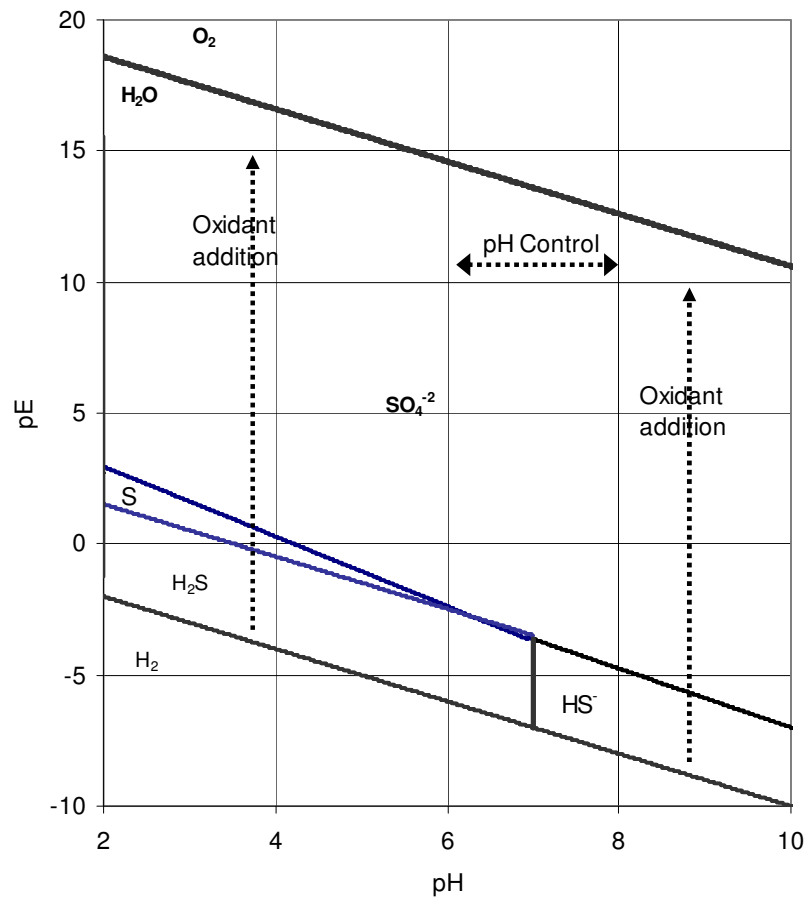


Figure 2: pE-pH equilibrium diagram for thermodynamically stable sulfur species

Chlorine Oxidation of Sulfide

Chlorine is widely used in water treatment as a disinfectant. Because chlorine is a strong oxidant, it can oxidize reduced forms of sulfide. Chlorine is added to water as gaseous chlorine (Cl₂), or liquid chlorine (sodium hypochlorite). Sodium hypochlorite disassociates in water according to reaction (4).



The OCl⁻ ion then reacts with H₂S or HS⁻ to form sulfur or sulfate according to reactions (5)-(8) (Lyn, 1992).



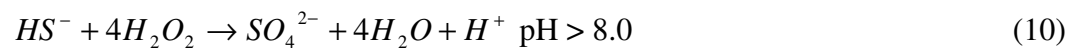
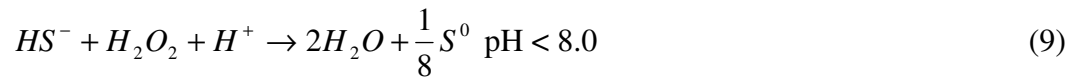
Reactions (5) and (6) are more likely to occur at pH levels below 7.5 while reactions (7) and (8) are more likely to occur above pH 7.5 (Cadena, 1988).

According to a study conducted by Lyn and Taylor on a water source in Pinellas County, Florida, one of the side effects of using chlorine for the oxidation of sulfide is that it always produces turbidity in the treated water. However, while elevated turbidity

levels were noted in their study, no particle analysis was ever done to verify that the turbidity was indeed caused by sulfur precipitation.

Hydrogen Peroxide Oxidation of Sulfide

Hydrogen peroxide is a powerful oxidant with an oxidation potential of -1.76V (Dohnalek, 1983). Only a few other oxidizers exceed the power of peroxide, such as elemental fluorine, ozone, peroxodisulfate (Dohnalek, 1988), and peroxide coupled with UV irradiation, ozone, or iron to yield hydroxyl radicals. Several benefits that are associated with using hydrogen peroxide include: it breaks down into oxygen and water, it does not contribute to disinfection-by-products, and it is neither toxic nor corrosive (Dohnalek, 1988). The reactions that can occur between hydrogen peroxide and sulfide are shown in equations (9) and (10) (Dohnalek, 1988). Limited data are available on the kinetics of these reactions in groundwater (Black, 1952, Hoffman, 1977, Levine, 2004).



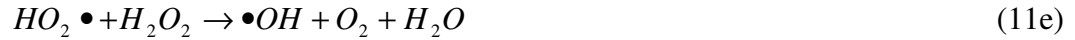
Ultraviolet (UV) Irradiation

UV irradiation can be an effective disinfectant. It is widely used in wastewater disinfection. UV can also reduce sulfides in groundwater through photolysis. Most UV lamps operate at a maximum energy output of 253.7 nm, which provides for inactivation of microorganisms in the water. Because of the lack of residual left in the water after UV irradiation, it is often used in conjunction with other oxidants such as hydrogen peroxide, ozone, or chlorine. These treatments are known as advanced oxidation processes. It can also be used as a primary disinfectant, followed by chlorine or chloramines as secondary disinfectants.

Hydrogen-Peroxide/UV Advanced Oxidation Process

Hydrogen peroxide in conjunction with UV irradiation is an advanced oxidation process that is widely used for oxidation of organic contaminants in groundwater. The UV reacts with hydrogen peroxide to form hydroxyl radicals which are more powerful than any other oxidant used for hydrogen sulfide oxidation. The oxidation potential of hydroxyl radicals is 2.8V (U.S. Peroxide, 2005). Glaze et. al. gave the following reactions as a proposed pathway that may be used for this process (equations 11a-11f).





This treatment has been proven effective in oxidizing organic compounds in both water and wastewater (Kang et al 1997, Crittenden et al 1999, Lopez, 2003) and has not been evaluated to a great extent for its treatment of inorganics.

Particles in Groundwater

Particles in groundwater are a concern because they may shelter microorganisms from inactivation by disinfectants, provide a sorbent site for pesticides, synthetic organic chemicals, and heavy metals (USEPA, 1999). They are also of concern because they prevent treated water from being aesthetically pleasing to consumers by giving the water a cloudy appearance. These particles can range in size from below one micron to over 20 microns (McCarthy, 1993). There are many causes for the presence of these particles in groundwater including water quality within the aquifer and chemical changes due to treatment. Common methods used for particle characterization include turbidity measurements, particle counting, and scanning electron microscopy. The following sections outline the types of particles in groundwater, their sources, and characterization methods.

Types of Particles Found in Groundwater

The organic particles in groundwater consist of microorganisms including viruses and bacteria, natural organic matter (NOM) or synthetic organics which (M^cCarthy, 1993) may give water an unpleasant color, taste, and/or odor. When treated by chlorine, NOM may react to form to disinfection-by-products, including trihalomethanes and haloacetic acids, which are regulated under the Safe Drinking Water Act. One approach to reduce the production of disinfection byproducts is to reduce the amount of chlorine that is used for treatment by using other oxidants or by adding ammonia to the water to form chloramines (AWWA, 1999). The inorganic particles may consist of mineral precipitates such as iron, calcium, and manganese, rock and mineral fragments, metal sulfides, elemental sulfur, silts and clays (M^cCarthy, 1993).

Causes of Particle Presence in Groundwater

There are several contributing factors to particle formation in groundwater as are listed in Table 4.

Table 4: Factors that influence particle formation

Factor	Impact
pH Changes	Increase in pH results in precipitation of minerals, while a decrease in pH results in dissolution of minerals
Redox Potential	Increases or decreases in redox potential affect the solubility of nutrients in water, especially minerals
Partial Pressure	Changes in partial pressures of gases such as causes a disruption in the equilibrium status of those systems and may result in precipitation or dissolution depending on which pathway reestablishes equilibrium conditions.

Typically, the mineral content of precipitates in groundwater depends on local geohydrology and includes iron and manganese oxides, calcium carbonates, or metal sulfides. These precipitates may also be formed by microbiological activity or anthropogenic influences (M^cCarthy, 1993).

Particles can also be generated through water treatment. The introduction of oxidants and disinfectants, such as chlorine and/or chloramines modifies water chemistry and may promote the precipitation of minerals and organic materials. Groundwater treatments such as forced-draft aeration (Duranceau et al. 2002) and softening have the potential to generate particles. Filtration and membrane technologies selectively remove particles.

Particle Characterization Methods

There are many methods used to characterize particles in groundwater. The methods used in this project are described in the following section. The methods are turbidity measurements, particle count with size distribution, and scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS).

Turbidity

Turbidity is a measurement of the relative clarity of water. It is not to be confused with color, however, the particles that cause turbidity may affect the color of the water and the color of the water may interfere with the measurement of turbidity. Turbidity is quantified using principles of nephelometry and operates by passing a beam of light at a wavelength of 450 nm through a sample of water. The intensity of the scattered light is measured by a photoelectric cell perpendicular to the light source. The current standard units of measurement are nephelometric turbidity units (NTUs) and are derived based on the light scattering signal from different concentrations of a colloidal formazin suspension. Turbidity is a primary drinking water contaminant under the Safe Drinking Water Act (SDWA). The maximum contaminant level (MCL) for turbidity in surface water is 0.3 NTU, but there is no limit currently set for groundwater. The primary downfall for turbidity measurement is that it gives no indication as to the amount of particles in a water source or the size of those particles. There is no direct correlation between particle size, light scattering, and particle mass. There are also inconsistencies in turbidity measurements due to variations in turbidimeter models, calibration techniques, and standard operating procedures.

Particle Count and Size Distribution

Particle count is an important measurement for the assessment of water quality and treatment efficiency (AWWARF, 1995). This measurement allows for total particle count as well as obtaining a size distribution. This measurement correlates to turbidity measurements except in cases of very low turbidity samples (AWWARF, 1995). In a study performed by Borrill and McKean, it was found that there was a correlation between particle count and turbidity in a high turbidity water with a R^2 value of 0.87, but a poor correlation between the two measurements for filtered water with a R^2 value of only 0.40 (AWWARF, 1995). Particle counting has mostly been associated with evaluating filter performance in water treatment plants (AWWARF, 1995).

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) allows for research into the structure and properties of particles that are too small to be seen with a normal microscope. This technology provides detailed 3-dimensional images of microscopic particles. The SEM works by bombarding a sample with a concentrated beam of high energy electrons which excites the sample and creates an image. Therefore, by studying the interaction of the disinfectants with the water and evaluating the particles produced, conclusions can be drawn about the impact that disinfection has on ground water quality.

Article 1: Potential for Colloidal Particle Formation Resulting from Groundwater

Disinfection

Abstract

Typically, groundwater treatment systems are targeted at removal of dissolved minerals (e.g. iron, manganese, calcium, magnesium) and/or dissolved gases (carbon dioxide, hydrogen sulfide) followed by disinfection. In other cases, disinfection may be the sole treatment step. The upcoming groundwater rule (GWR) will introduce more detailed requirements for disinfection and monitoring of water systems served by groundwater. In many groundwater treatment systems, disinfection consists of in-line introduction of disinfectant chemicals such as ozone, chlorine, or chlorine and ammonia. The effectiveness of disinfection is assessed through distribution system monitoring in accordance with the Total Coliform Rule (TCR). Limited information is available on secondary reactions that occur downstream of chemical addition. Water quality impacts associated with disinfection are evaluated in this paper with an emphasis on the potential for formation of colloidal particles due to oxidation, precipitation, or biological reactions. Pilot-scale disinfection of a groundwater source in west-central Florida was conducted using chlorine, chlorine-ammonia, UV, UV-chlorine, and UV-chlorine-ammonia at

ambient (7.0-7.5) and elevated (8.2-8.3) pH. Under ambient pH conditions, the use of UV as a primary disinfectant followed by chloramination produced the highest concentration of particulate material. However, under elevated pH conditions, higher particle concentrations were associated with the use of chlorine alone or in combination with ammonia. In general, submicron colloidal particles (< 0.2 microns) consisting of organic microspheres with trace amounts of iron and sulfur were generated downstream of chemical addition.

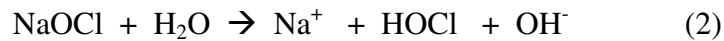
Key words—chlorine, UV irradiation, sulfur, groundwater rule,, 4-log inactivation

Introduction

The groundwater rule (GWR) will require all groundwater treatment systems to be capable of achieving 4-log inactivation or removal of viruses and the maintenance of a disinfectant residual throughout the distribution system (GWR, 2000). Design of disinfection systems requires that the product of the residual disinfectant concentration (C) and contact time (T), or CT value, is appropriate for 4-log virus inactivation based on the disinfectant chemical, pH, and temperature. The effectiveness of disinfection is assessed through monitoring of total coliforms and disinfectant residuals in the distribution system, in accordance with the Total Coliform Rule (TCR).

Chlorine is the most widely used disinfectant for groundwater systems (Sincero, 2003) and, in most cases, it is added in either gaseous (Cl_2) or liquid (NaOCl) form. The

addition of chlorine to water can result in a change in pH, depending on the form of chlorine, the dose, and the alkalinity. Gaseous chlorine can result in a pH decrease, whereas the use of sodium hypochlorite can increase the pH as shown in equations (1) and (2).



The extent of pH change due to the addition of either form of chlorine is controlled by the concentrations of alkalinity and dissolved carbon dioxide and the extent of treatment prior to chlorination. Groundwater typically contains dissolved carbon dioxide that can react with the hydroxide released during the addition of sodium hypochlorite, resulting in an increase in alkalinity. The pH affects the degree of ionization of hypochlorous acid as shown in equation (3)



Because the oxidation potential of hypochlorous acid and hypochlorite are different, 1.611 and 0.81, respectively (Lide, 1990), the pH impacts the net oxidation potential available for disinfection.

Over the past decade, chlorination practices have shifted due to concerns about water system security and the hazards of on-site storage of gaseous chlorine, many

utilities have switched from the use of gaseous chlorine to liquid chlorine. In addition, more stringent limits for disinfection byproducts (DBPs) have prompted utilities to convert from the traditional practice of maintaining a free chlorine residual to the use of a primary disinfectant followed by chloramination for maintenance of a residual in the distribution system. In addition to chlorine, primary disinfectants include ozone or UV. The addition of ammonia to form chloramines can also impact the pH.

Chlorine and other disinfection chemicals also react with reduced minerals and organics in water. The dose of disinfectant chemical needed to meet the CT requirements includes the dose required to satisfy oxidation reactions and the dose required to maintain a disinfectant residual between 0.2 and 5 mg/L. Constituents in groundwater that react with disinfection chemicals include hydrogen sulfide, reduced iron, and reduced manganese. A summary of the chlorine demand associated with these oxidation reactions is given in Table 5. The chlorination reactions can result in a net increase or decrease in pH, depending on the chemical dose and alkalinity. In addition, the solubility of the reaction products is impacted by pH.

Table 5: Chlorine oxidation of iron, manganese, and hydrogen sulfide

Oxidation Reaction	Chlorine requirement, mg/mg
$\text{Fe}^{+2} + \text{HOCl} \rightarrow \text{Fe}^{+3} + \text{Cl}^- + \text{OH}^-$	0.94
$\text{Mn}^{+2} + \text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_{2(s)} + 2\text{Cl}^- + \text{H}^+$	1.27
$\text{H}_2\text{S} + 4\text{HOCl} \rightarrow \text{SO}_4^{-2} + \text{Cl}^- + 4\text{H}^+$	8.23
$\text{H}_2\text{S} + \text{HOCl} \rightarrow \text{S}^0 + \text{Cl}^- + \text{OH}^-$	2.06

It has been widely reported that particulate matter can interfere with disinfection effectiveness in drinking water systems by shielding pathogens from the action of disinfectants, and may provide surface area for the accumulation of microbial substrates and biofilms (USEPA, 1999). Thus the formation of particulates through oxidation reactions may impact disinfection effectiveness.

Typically, the concentration of particulate matter in water systems is assessed through monitoring of turbidity. In surface water treatment systems, turbidity is used as a measure of the effectiveness of filtration. The Surface Water Treatment Rule (SWTR) requires that treated water turbidity must be below 0.3 NTU in at least 95 percent of the samples measured per month and must never exceed 1 NTU (EPA Guidance Manual, 1999). However, limited information is available about turbidity levels in groundwater and the potential role of particulate matter in disinfection systems. The regulations that apply to groundwater treatment are outlined in Table 6.

Table 6: Comparison of regulations pertaining to particles and disinfection rules in groundwater and surface water treatment

Regulations	Existing or Future Implementation Date	Description	Monitored at Treatment Plant or Distribution System
Total Coliform Rule (TCR)	Existing (1989), but under revision.	TCR monitors for the presence of total and fecal coliform. Presence indicates that other harmful bacteria may be present. The total number and location of samples is based on the population served.	Distribution System
Lead & Copper Rule (LCR)	Revised in 2000	LCR sets maximum contaminant levels (MCLs) for lead (0.015mg/L) and copper (1.3 mg/L) based on the 90 th percentile level of tap water samples. Need to explain how samples are collected	Distribution System
Long Term 2 Enhanced Surface Water Treatment Rule	July 2005	Requires monthly monitoring for large systems (>10,000 people) of <i>Cryptosporidium</i> for two years to characterize water quality. Then depending on the concentration, methods of removal in addition to conventional treatment and filtering will have to be implemented. Small systems (< 10,000 people), monitor <i>E. Coli</i> .	Treatment Plant
stage 2 disinfectants/disinfection byproducts rule		Regulates the disinfectant concentration and disinfection byproduct amounts in treated water. Large and medium systems must comply with 0.0080/0.060mg/L TTHM/HAA5 LRAA six years after promulgation and after ten years for small systems.	Plant and distribution system

The purpose of this paper is to evaluate the potential for particulate material to form in groundwater as a result of disinfection. The objectives are:

1. Identify sources and characteristics of groundwater particles
2. Examine particle characteristics in a Floridan groundwater.
3. Evaluate the impact of disinfection treatment on particle characteristics at ambient and elevated pH levels.

Background

Sources of particles in groundwater include minerals, microorganisms, and organic material. Water treatment technologies, such as those used for oxidation, disinfection, and softening can act to modify the types and characteristics of groundwater particles by oxidation, precipitation reactions or by liquid-solid separation. Organic particles may consist of microorganisms such as viruses, bacteria, protozoa, and algae, natural organic matter (NOM), or synthetic organics due to localized contamination (need reference here). Inorganic particles in groundwater consist of mineral precipitates such as iron, calcium, and manganese, rock and mineral fragments, metal sulfides, elemental sulfur, silts, and/or clays (M^cCarthy, 1993). The dominant cations in water include calcium, magnesium, iron, and manganese. These constituents can precipitate with carbonates, sulfates, sulfides, phosphates, hydroxides, and fluorides. A summary of the solubility products for mineral precipitates that may form in groundwater is given in

Table 7 (Lide, 1990). In general, higher values of solubility products reflect a higher degree of solubility.

Table 7: Potential forms of mineral precipitates in groundwater and their corresponding solubility products at 25°C

Anions	Cations				
	Calcium, Ca ²⁺	Ferrous Iron, Fe ²⁺	Ferric Iron, Fe ³⁺	Magnesium, Mg ²⁺	Manganese, Mn ²⁺
Carbonate, CO ₃ ²⁻	4.96*10 ⁻⁹	3.07*10 ⁻¹¹		6.82*10 ⁻⁶	2.24*10 ⁻¹¹
Fluoride, F ⁻	1.46*10 ⁻¹⁰	2.36*10 ⁻⁶		7.42*10 ⁻¹¹	
Hydroxide, OH ⁻	4.68*10 ⁻⁶	4.87*10 ⁻¹⁷	2.64*10 ⁻³⁹	5.61*10 ⁻¹²	2.06*10 ⁻¹³
Sulfate, SO ₄ ²⁻	7.10*10 ⁻⁵				
Sulfides, S ²⁻		1.59*10 ⁻¹⁹			4.65*10 ⁻¹⁴
Phosphates, PO ₄ ³⁻	2.07*10 ⁻³³	9.92*10 ⁻²⁹	9.92*10 ⁻²⁹	9.86*10 ⁻²⁵	

The major factors that contribute to the presence of particles in groundwater are pH, redox potential, and partial pressure fluctuations (McCarthy, 1993).

Particles may also be generated through water treatment. The introduction of oxidants and disinfectants, such as chlorine and/or chloramines can affect the chemistry

of water and may promote the precipitation of minerals and organic materials. Groundwater treatments such as forced-draft aeration (Duranceau et al. 2002) and softening have the potential to generate particles. Filtration and membrane technologies selectively remove particles. Most of the groundwater treatment plants that do not use aeration or softening do not have mechanisms in place for particle removal. The possible generation of other treatments such as disinfection producing particles that may need to be removed is rarely given consideration. As such, this paper was produced to show that there is a potential for particle generation from disinfection treatment.

Methods

This project consisted of bench-scale and pilot-scale testing of groundwater derived from wells in west-central Florida. The utility withdraws two million gallons per day (MGD) from the Floridan aquifer through eight wells distributed through their service area. Prior to 2005, water was treated at each well site using in-line addition of chlorine and a polyphosphate corrosion inhibitor, followed by a 10 minute reaction time in a hydropneumatic tank. Under typical operating conditions, the pumps at each treatment system do not operate continuously, but cycle on and off in response to pressure demands within the system. The ability to store treated water within the existing system is limited to hydropneumatic tanks at the well sites with a combined effective volume of 27,500 gallons and a 500,00 gallon ground storage tank that provides supplemental storage. The utility is in the process of modifying their treatment to

provide chlorine as a primary disinfectant, followed by the addition of ammonia to form chloramines for secondary disinfection.

The bench-scale tests were conducted to gain information about the optimum chlorine dose and pH levels, and changes in water quality. For the bench-scale tests 1 or 2 liter reactors were used. Samples were collected using a special sampling device that minimized exposure to air.

The impact of disinfection on particle concentrations and characteristics was evaluated. The disinfectants tested included chlorine, chloramine, UV, UV-chlorine, or UV-chloramine were evaluated using a 1 gpm (3.78 L/min) pilot plant unit. The treatments were tested at ambient pH and elevated pH. An elevated pH of 8.2-8.3 was used to simulate treatment plants that control corrosion using pH and alkalinity control. Talk Water was pumped from one of the wells into a 1 gallon per minute (3.78 L/min) pilot plant. The detention times for relevant segments of the pilot plant are summarized in Table 8. The schematic for the pilot plant is shown in Figure 3.

Table 8: Detention times of reactors

From	To	Detention Time (min)
Inlet	Outlet	22
pH Injection	UV Unit	2
UV Unit	Chlorine Injection	5
Chlorine Injection	Ammonia Injection	3
Ammonia Injection	Outlet	10

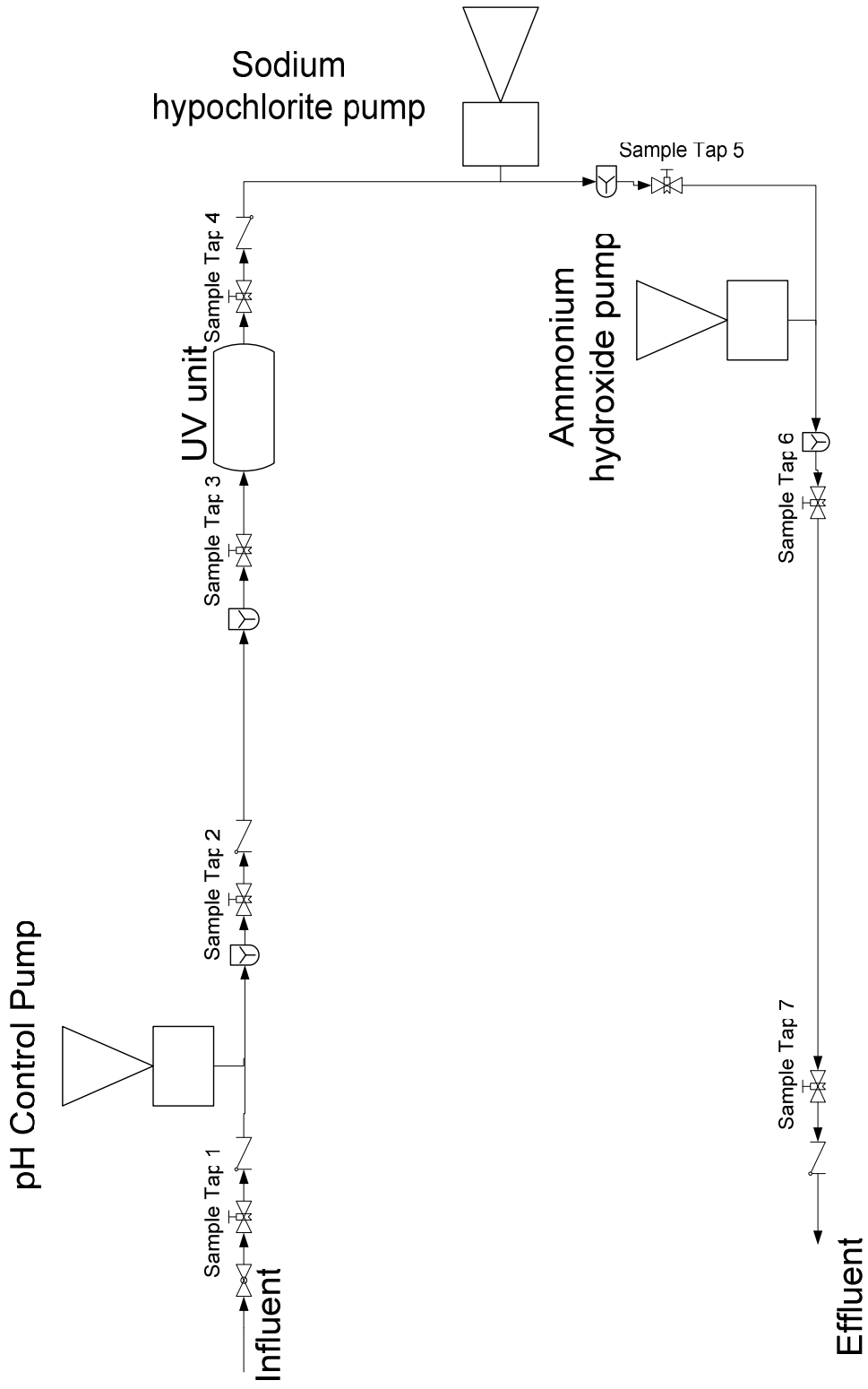


Figure 3: Schematic of pilot plant

A 10.5% sodium hypochlorite (liquid chlorine) solution was dosed to the system within the range of 21-25 mg/L. For chloramine experiments, a 25% ammonium hydroxide (ammonia) solution was dosed to the system within the range of 0.1 to 1 mg/L based on a 1:4 ratio of ammonia to chlorine residual. The UV intensity ranged from 10 to 20 mW·sec/cm².

Water quality tests were performed on the bench-scale and pilot-scale tests. The procedures for each test were based on Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998). A list of the tests conducted is outlined in Table 9. Field analyses were conducted at the well site and laboratory analyses were conducted in the USF environmental laboratory.

Table 9: Summary of analytical parameters tested

Test	Field or Lab	Standard Method, 20 th Edition-number	Instrument Used	Detection Limit/Sensitivity	Storage/Preservation
Alkalinity, mg/L CaCO ₃	Field	2320 B. Titration Method	Bromocresol green/methyl red Hach DR/2400	20 mg/L CaCO ₃	N/A
Color(true & apparent), mg/L PtCo	Field	2120 C Spectrometric Method	Portable Spectrophotometer	5 PtCo Units	N/A
Conductivity, μS/cm	Field	2510 B Laboratory Method	Hach sension 156 Portable Multiparameter Meter	20 μS/cm	N/A
ORP, mV	Field		ExStik pH and ORP Probe	±999mV	N/A
pH	Field	4500-H+ B. Electrometric Method	Hach sension 156 Portable Multiparameter Meter	0.01 pH units	N/A
Solids (total, suspended, and dissolved) (0.2μm filter used)	Lab	2540 A-D. Solids	N/A	10 mg/L	Store at 4°C and begin test within three days
Sulfate, mg/L SO ₄ ²⁻	Field	4500- SO ₄ ²⁻ E. Turbidimetric method	Hach DR/2400 Portable Spectrophotometer	2 mg/L as SO ₄ ²⁻	N/A
Sulfide, mg/L S ²⁻	Field	4500-S ²⁻ D Methylene blue method	Hach DR/2400 Portable Spectrophotometer	0.1 mg/L as S ²⁻	N/A

Table 9: continued					
Temperature, °C	Field	2550 B. Laboratory Method.	Hach sension 156 Portable Multiparameter Meter	0.01°C	N/A
TOC, mg/L	Lab	5310 C. Persulfate-UV Method	Seivers 800 Portable Total Organic Carbon Analyzer	0.05 mg/L	Acidified to pH=2 with sulfuric acid and analyze as soon as possible
Turbidity, NTU	Field	2130 B Nephelometric Turbidity	Hach model 2100 AN Laboratory Turbidimeter	0.01 NTU	

Sample aliquots were also stored and preserved for Scanning Electron Microscopy (SEM) / Electron Dispersive Spectroscopy (EDS) analysis. 5 mL of 10% glutaraldehyde was added to 20 mL of sample to yield an overall glutaraldehyde concentration of 2%. Following glutaraldehyde preservation, particulate matter was concentrated by filtration through a 47 mm nylon filter with a pore size of 0.1 μm . The filters were rinsed 3 times with deionized water to remove the salts and then dehydrated using a graded series of ethanol (30%, 50%, 70%, 95%, and 100%). Samples were submerged in each ethanol solution for a minimum of two sequential 10 minute periods. After the final soak, the ethanol was decanted off and the samples were dried overnight at 50°C.

In order to minimize field sample contamination, the samples were collected using a special sampling device that prevented exposure to the atmosphere for field tests. The samples were then analyzed immediately. The Erlenmeyer flasks used to hold the samples in the field were rinsed thoroughly with Nanopure™ water twice, then rinsed with sample three times. 10-50mL disposable serological pipettes were used and rinsed with Nanopure™ water after each use and discarded after each experiment. The samples that were transported to the lab were collected in black or foil-covered BOD bottles to prevent photoreactions. The bottles and stoppers were pre-cleaned by soaking in 1% nitric acid overnight, then rinsed with Nanopure™ water and allowed to air dry for 24 hours. The samples for SEM were preserved immediately to prevent bacterial growth.

Results and Discussion

The goal of this study was to identify the sources of particles in this groundwater source, and to characterize the particles found in both the raw and treated water. Therefore this section first discusses the source water quality and the sources of potential particle formation, followed by the characterization of particles formed from treatment using turbidity analysis, solids data analysis, particle count, and SEM analysis.

Source water characteristics are summarized in Table 10. Sulfide and TOC are the major contributors to oxidant demand in groundwater.

Table 10: Summary of untreated water quality data from a groundwater source in west-central Florida (2004-2005 monitoring data)

Parameter	Range	Average	Standard Deviation	n
pH	7.22 - 7.77	7.46	0.10	46
Temperature, °C	25 – 31	26	1.5	23
Conductivity $\mu\text{S}/\text{cm}$	479 – 661	529	36	41
Turbidity, NTU	0.1 - 5.1	0.7	1.1	44
Anions				
Alkalinity, mg/L CaCO_3	130-240	199	19	32
Sulfate, mg/L SO_4^{2-}	11 – 43	27	6	25
Sulfide, mg/L S^{2-}	0.8 - 3.4	2.3	0.5	47
Chloride, mg/L Cl^-	21 – 26	23	4	2
Cations				
Calcium, mg/L Ca^{2+}	80.8 - 116.3	92.3	16.4	6
Magnesium, mg/L Mg^{2+}	3.78 – 6.95	5.05	1.34	6
Ferrous Iron, mg/L Fe^{2+}	<0.01-0.47	0.10	0.12	21
TOC, mg/L C	2.6-3.5	3.1	0.31	9
True Color mg/L PtCo	3 - 12	7	3	6

Table 11: Affect of disinfection treatment on water quality parameters at pH 8.2

Parameter	Treatment					
	Raw Water	Chlorine Only	Chlorine-Ammonia	UV Only	UV-Chlorine	UV-Chlorine-Ammonia
Alkalinity, mg/L CaCO ₃	195	225	235	225	225	240
Sulfide, S ²⁻	2.49	0	0	1.12	0	0
Sulfate, SO ₄ ²⁻	36.6	37	36.1	36.9	37.2	37.8
Calcium, mg/L Ca ²⁺	59	54	51	61	57	57
Magnesium, mg/L Mg ²⁺	7.4	7.2	7.3	7.2	7.2	7.3
TOC, mg/L C	3.0	2.7	2.8	2.7	2.7	2.7
Chlorine Demand, mg/L Cl ₂		13.9	13.6		17.2	11.0

The sulfide in the water was oxidized to a combination of sulfur and sulfate. The dissolved calcium and magnesium decreased with treatment, which indicates mineral precipitation. There was also a decrease in soluble TOC, which is an indication of organic particle precipitation. Although the decrease was slight, the fact that only about 40 percent of the mass of the organic particles is comprised of carbon, the total mass of organics that precipitates out may be significant.

At ambient pH, the addition of the disinfectants causes the turbidity levels to increase as shown in figure 5. All treatments generated turbidity levels above 1 NTU at ambient pH. The turbidity increases in chlorine and chloramine were moderate with increases of approximately 4 and 2 NTUs respectively. However, when the experiments were conducted with UV, a significant spike in turbidity was seen. Combining UV with

chlorine or chloramine generates greater turbidity levels than UV only at ambient pH. However, when the pH is elevated, the reverse is seen, in that the turbidity generated due to UV disinfection was minimal whereas the turbidity generated by chlorine and chloramine treatments was the highest. The UV-chlorine and UV-chloramine produced turbidity levels between those treatments. All treatments with the exception of UV only at an elevated pH of 8.2 showed turbidity levels above 0.3 NTU, which is the standard for surface water which is outlined in the Surface Water Treatment Rule..

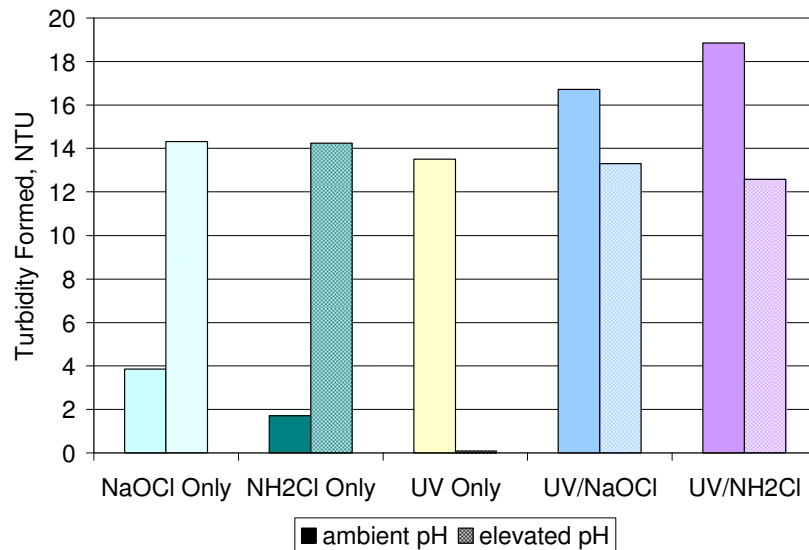


Figure 5: Turbidity formed as a result of disinfection treatment

The weight of the total solids was another variable that was affected by the addition of disinfectants to the water (Figure 6). The treatments that included chlorine showed roughly the same increase in mass of total solids of approximately 20% from that in raw water, but the UV treatment showed a slight decrease. However, taking into

account the errors associated with the test, it is justified to say that there was relatively no change in total solids associated with UV. Elevating the pH slightly decreased the mass of total solids produced by the chloramine only and UV-chloramine treatments, and had the reverse affect on chlorine and UV-chlorine. Adding disinfectants to the water had an interesting affect on suspended particles. For all treatments besides chloramine only and UV-chloramine, the change in suspended solids was negative. This is significant because it indicates that the particles generated through treatment are smaller than the filter pore size used to obtain the results which was 0.2 μ m. Therefore, if a water treatment plant wanted to filter this water to remove the particles, it would have to be a filter that would allow them to capture particles smaller that 0.2 μ m.

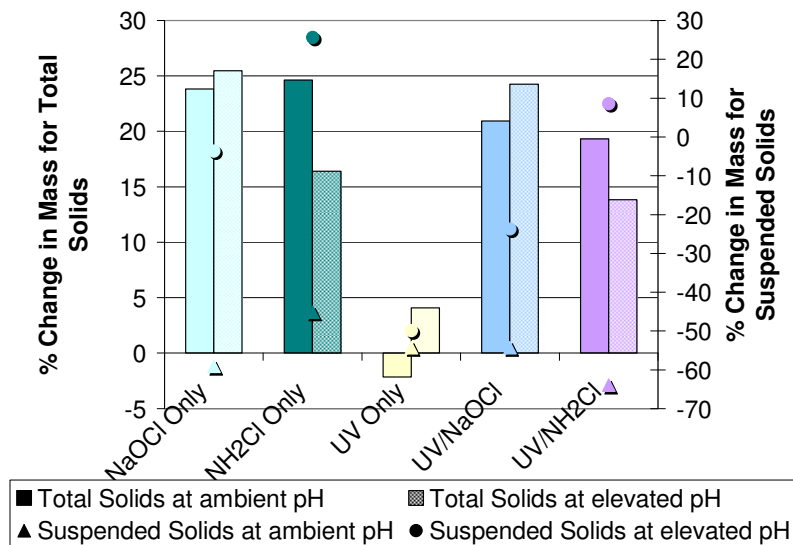


Figure 6: Comparison of % total and suspended solids from disinfection treatments

The total particle count was measured to see how treatment affects the number of particles and how the number of particles is affected by changes in pH. Table 12 outlines

the total particle count for the treatments and the impact that pH has on them. The average raw water particle count is 4636/mL with a standard deviation of 2979/mL. Disinfection addition greatly raised the total particle count at ambient pH. The greatest increase on particle count was seen by chloramine only and UV-chloramine treatments which parallels the results seen from the total solids data. Elevating pH causes a significant change in the particle count number for UV-Chlorine in that it decreased by 113%. This is in direct contrast with the total solids data which showed a mass increase of almost 20%. The remaining treatments also showed this inverse relationship between change in mass of total solids and change in particle count.

Table 12: Affect of pH on total particle count

Treatment	Count at Ambient pH, #/mL	Count at Raised pH, #/mL	Δ Particle Count (Ambient-Raised), #/mL	% Change in Particle Count, %
Chlorine Only	3.5E+04	4.9E+04	-1.4E+04	-40
Chloramine Only	5.3E+04	3.6E+04	1.6E+04	32
UV Only	1.5E+04	1.7E+04	-0.2E+04	-13
UV-Chlorine	1.6E+04	3.4E+4	-1.8+04	-113
UV-Chloramine	5.0E+04	3.6E+04	1.3E+04	26

The addition of disinfectants did not seem to impact the size distribution of the particles above 1 micron. However, it was established from the suspended solids data that the majority of particles that are generated by disinfection addition are less than 1 micron in size. This observation was further corroborated by the SEM analysis. The particles found in the analysis of the untreated groundwater ranged from 1 micron to over

15 microns as shown in Figure 7. The particles were mostly microorganisms, with trace amounts of inorganic matter such as iron and sulfur.

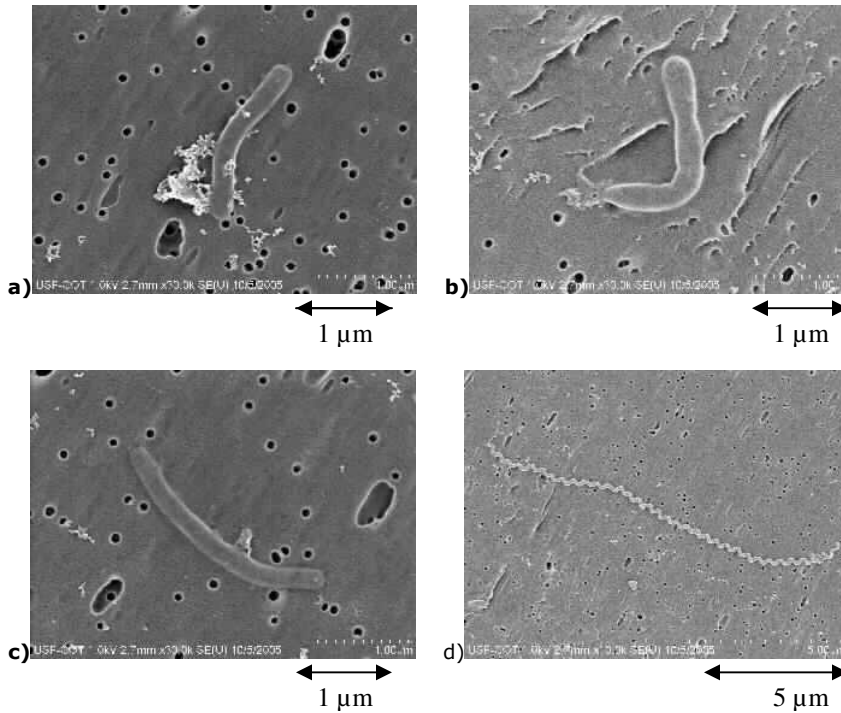


Figure 7: Scanning electron micrographs of particles in untreated groundwater. The approximate size of the particles are a) 2 microns b) 3 microns c) 3 microns and d) 15 microns

After the addition of disinfectants to the water, the size range of the particles changed. The majority of the particles were less than 1 micron as shown in figure 8. The EDS analysis still showed that the major elements within these particles were carbon and oxygen, meaning that they are organic in nature.

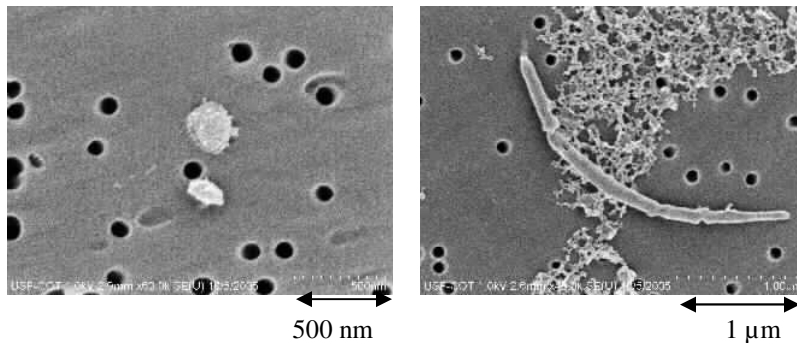


Figure 8: Scanning electron micrographs of particles in treated groundwater

The SEM micrographs also highlights one of the issues associated with particles in water. Figure 9 clearly shows microorganisms that are attached to particulate matter. The microorganisms shown are possibly using the particles as shields from disinfection, a food source, or as a substance to grow on.

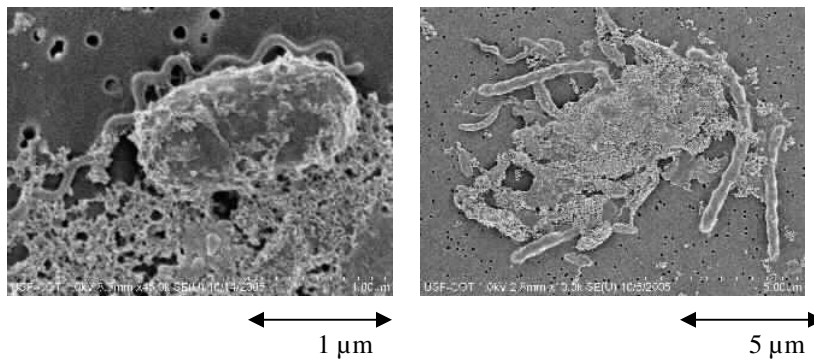


Figure 9: Scanning electron micrographs of microorganisms in groundwater that are attached to particulate matter

Conclusions

The experimental studies described in this paper suggest the following conclusions with respect to the particles found in untreated groundwater and the effect that disinfection using chlorine, chloramine, and/or UV has on them.

1. The sources of particles in treated groundwater include mineral precipitates of carbonates, calcium, and magnesium. From the SEM analysis, the particles were composed of mostly carbon and oxygen, suggesting that they are mostly organics.
2. The particles found in the untreated water ranged from 1 micron to over 15 microns, while the particles produced from treatment were smaller than 1 micron.
3. There is a need for a mechanism to be put into place that would remove the particles generated through treatment before the water is sent out to the distribution because of the high turbidity levels seen by all treatment except UV Only at elevated pH. These turbidity levels exceed the 0.3 NTU turbidity limit set by the Surface Water Treatment Rule.

Acknowledgements

This project was funded by Aloha Utilities as part of a larger project on treatment alternatives. Jack Burke, Mike McDonald, and Charlie Painter assisted in the construction of pilot plant, start-up and operation. Salah Albustami and Camilo Romero assisted with field and laboratory analyses. Dave Edwards conducted the SEM/EDS analyses.

Article 2: A Pilot Study Used to Evaluate In-Pipe Control of Hydrogen Sulfide for Well-head Treatment of Groundwater

Abstract

In many groundwater treatment systems, chlorine serves a dual role as an oxidant and as a disinfectant. The chlorine demand exerted by hydrogen sulfide ranges from 5 to 8 mg chlorine per mg hydrogen sulfide. In groundwater systems that contain dissolved organic carbon and hydrogen sulfide, the high chlorine dosages can lead to the formation of disinfection byproducts. One approach to reducing the chlorine demand is developing a pre-treatment system to oxidize the hydrogen sulfide prior to chlorination. This project was conducted to evaluate the use of alternative oxidants appropriate for well-head treatment of groundwater. Oxidants evaluated included hydrogen peroxide and photochemical oxidation using UV or hydrogen peroxide coupled with UV. While each oxidant was capable of reducing the hydrogen sulfide concentration, reaction rates and reaction products varied. To minimize the production of turbidity, it was necessary to optimize the pH within a fairly narrow window.

Introduction

The control of sulfides in groundwater is of importance because its presence can cause odor and taste complaints, corrosion of pipes and other plumbing fixtures, and black-water problems in distribution systems (Levine et. al, 2004). Currently, the Safe Drinking Water Act (SDWA) or any of its amendments do not specifically address hydrogen sulfide. However, sulfides are indirectly regulated through the secondary drinking water standard for taste and odor. The secondary contaminants and their limits in water are outlined in Table 13 (USEPA, 2005).

Table 13: Secondary drinking water standards set for compounds that contribute to odor and taste problems

Contaminant	Secondary Maximum Contaminant Level
Chloride	250 mg/L
Copper	1 mg/L
Foaming Agents	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
pH	6.5 - 8.5
Sulfate	250 mg/L
Threshold Odor Number (TON)	3 TON
Total Dissolved Solids	500 mg/L
Zinc	5 mg/L

In 2003, the Florida Department of Environmental Protection implemented a new rule pertaining to hydrogen sulfide removal under Chapter 62-555.35(5) (FDEP, 2005). This rule was implemented to control copper pipe corrosion and black water production which is caused by the interaction of sulfides with copper (FDEP, 2003). The rule calls for a minimum of one sample of raw water to be measured for total sulfides and action is recommended if the total sulfide level is above 0.3 mg/L. The treatment recommendations are outlined in Table 14. Some of the major drawbacks associated with this rule are the lack of guidelines for sampling for sulfide testing, lack of the number of samples needed to categorize the sulfide level, and lack of a monitoring frequency.

Table 14: Summary of FDEP treatment recommendations for control of total sulfide in new or altered wells (adapted from FDEP Chapter 62-555.315 (5))

Total Sulfide concentration in untreated water, mg/L	pH range			Treatment recommendations	Maximum removal efficiency
	<7.2	7.2	>7.2		
<0.3	X	X	X	Chlorination	>90%
0.3 to 0.6	X	X		Conventional aeration	~40-50%
			X	Conventional aeration with pH adjustment	
0.6 to 3	X	X		Forced draft aeration	~90%
			X	Forced draft aeration with pH adjustment	
>3.0	X	X	X	Packed tower aeration with pH adjustment	>90%

Typically, for small water treatment systems, hydrogen sulfide is controlled through in-pipe treatment using chlorination. Aeration is also used in many treatment

facilities, but that also requires disinfection downstream to comply with disinfection regulations. The objective of this study is to evaluate the efficacy of using alternative oxidants for in-pipe oxidation of hydrogen sulfide prior to chlorination. Hydrogen peroxide was used in this study because of past research on the effectiveness of its use to control hydrogen sulfide levels in wastewater (Cadena, 1988, Tomar, 1994, Hoffman, 1977) and groundwater (Dohnalek, 1983). This paper is based on a case study done in west-central Florida.

Background

This section covers sulfide chemistry in groundwater. Also discussed are treatment alternatives for its control with the emphasis on oxidation treatments.

Sulfide in Groundwater

Sulfur exists in a nine oxidation states in water and can transition from one state to the next depending on localized chemical and biological reactions. Sulfide is formed in water through the action of sulfur reducing bacteria decomposing organic matter (Dohnalek, 1983) or by the desulfuration of organic compounds. Sulfides in water are undesirable because of their “rotten egg” odor and their corrosivity properties (Dohnalek, 1983). Total sulfides refer to dissolved hydrogen sulfide (H_2S), ionized sulfide (HS^- and S^{2-}) and acid-soluble metallic sulfides, and polysulfides. The equilibrium equations for

the three sulfide species are outlined in equations 1 and 2 and illustrated in Figure 10 with respect to pH. Various values have been reported for the second equilibrium constant at 25°C. A summary of values is given in Table 15.

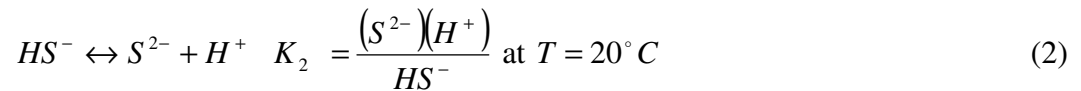
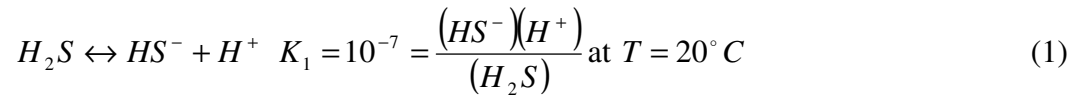


Table 15: Values of K_2 obtained from various sources

Source	Benjamin, 2002	Garrels, et.al, 1965	Sillen, et. al 1964	Knox, 1906	Maronny, 1959
Value	$10^{-12.92}$	10^{-14}	$10^{-17.1}$	$10^{-14.92}$	$10^{-13.78}$

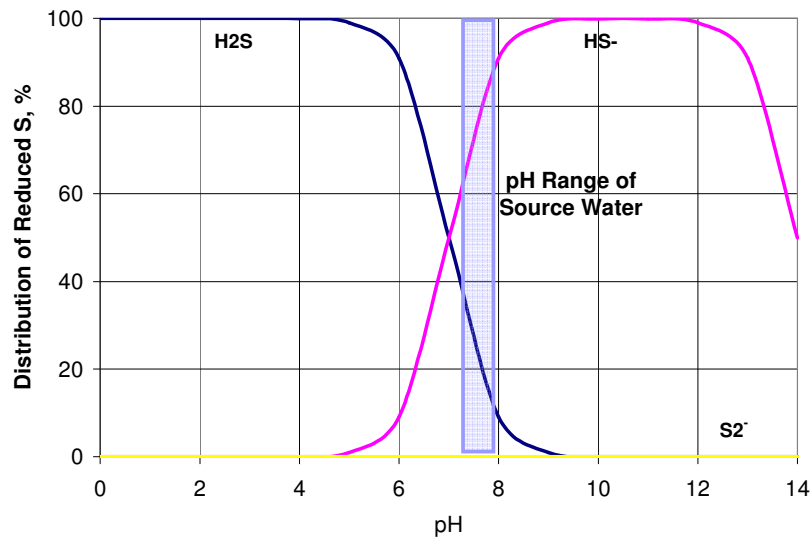


Figure 10: Illustration of sulfide equilibrium in terms of pH

Treatment Alternatives for the Control of Hydrogen Sulfide

In addition to the treatment methods outlined in Table 14, it is worthwhile to consider alternative approaches for control of hydrogen sulfide that might be appropriate for small water systems such as anion exchange. Oxidation treatments are discussed below.

Oxidation

The addition of oxidants such as chlorine, hydrogen peroxide or ozone to groundwater serves to increase its oxidation potential. By manipulating the pH and the extent of the increase of oxidation potential which is controlled by chemical oxidant addition, the end products of sulfur oxidation can be controlled. This is illustrated in Figure 11. Theoretically, at a pH below 7, the product formed from the oxidation of sulfide is either elemental sulfur or sulfate, depending on the oxidant's affect on the overall potential and at a pH above 7 only sulfate is formed, regardless of the oxidant used.

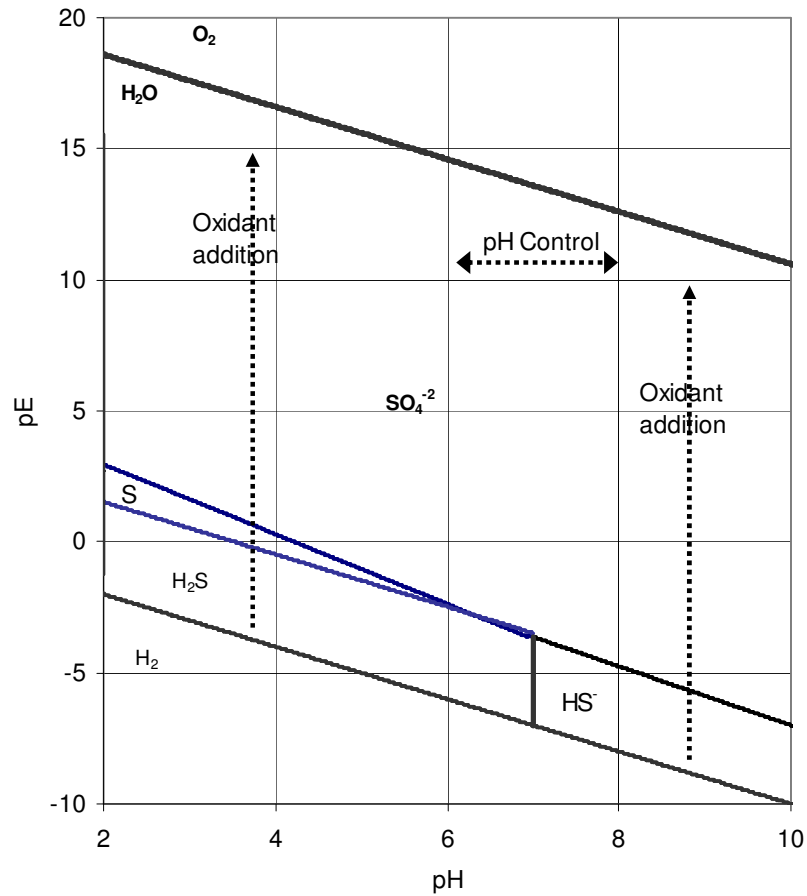
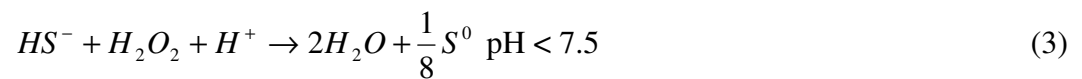
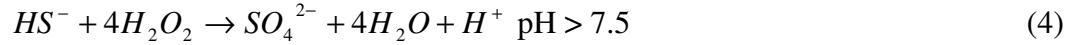


Figure 11: pE-pH equilibrium diagram for thermodynamically stable sulfur species (Thermodynamic constants from Stumm and Morgan 1999)

Hydrogen Peroxide Oxidation of Hydrogen Sulfide

Hydrogen peroxide is a powerful oxidant with an oxidation potential of -1.76V (Dohnalek, 1983). Cadena et. al states that sulfate is the major product of peroxide-sulfide oxidation over a pH of 7.5.





Only a few other oxidizers exceed the power of peroxide, such as elemental fluorine, ozone, and peroxodisulfate (Dohnalek, 1988), and advanced oxidation technologies that generate hydroxyl radicals. Several benefits that are associated with using hydrogen peroxide are that it breaks down into oxygen and water, it does not contribute to disinfection-by-products, and it is neither toxic nor corrosive (Dohnalek, 1988). The kinetics for hydrogen peroxide oxidation of sulfide depends on dose, pH and temperature.

Hydrogen-Peroxide/UV Advanced Oxidation Process

Hydrogen peroxide in conjunction with UV irradiation is an advanced oxidation process that is gaining ground as an alternative to traditional treatment methods such as chlorination. The UV reacts with hydrogen peroxide to form hydroxyl radicals which are more powerful than any other oxidant used for hydrogen sulfide oxidation. Glaze et. al. gave the following reactions as a proposed pathway that may be used for this process (equations 5a-5f).





This treatment has been proven effective in oxidizing organic compounds in both water and wastewater (Kang et al 1997, Crittenden et al 1999, Lopez, 2003) and has not been evaluated for the removal of hydrogen sulfide. Therefore, there is a need for research into this topic, as it may provide a new option for sulfide control in groundwater treatment.

Methods

All water samples used in this project were obtained from a utility in west-central Florida that produces two million gallons per day (MGD) from the Floridan aquifer. Treatment consists of in-pipe treatment at each of eight well sites using chlorination. Bench-scale and pilot-scale tests were used to evaluate the effectiveness of alternative treatment approaches for control of hydrogen sulfide in groundwater before chlorination. Information on the experimental design and methodologies used in this study is given below.

Experimental Design

Bench-scale tests were completed at several wells to evaluate the hydrogen peroxide reaction rates and obtain the correct chemical dose and pH level. Pilot-scale tests were completed to evaluate the effectiveness of the hydrogen peroxide on sulfide removal in a flow-through system prior to chlorination, and also to evaluate its effect on other water quality parameters. An outline of the oxidation tests conducted is given in Table 16.

Table 16: Summary of bench-scale and pilot-scale tests conducted

Technology	Testing Goals				
	pH Optimum	Chemical Dose Requirements	Sulfide removal/ conversion	Turbidity formation potential	Chlorine demand
Bench-scale Tests					
Hydrogen Peroxide	Yes	Yes	Yes	No	Yes
Hydrogen Peroxide-Chlorine	Yes	Yes	Yes	No	Yes
Pilot -Scale Tests					
Chlorine	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide-UV	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide-chlorine	Yes	Yes	Yes	Yes	Yes
Hydrogen peroxide-UV-chlorine	Yes	Yes	Yes	Yes	Yes

Analytical Tests

Analytical tests were performed on the bench-scale and pilot-scale tests. The procedures for each test were based on Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998). A list of the tests conducted is given in Table 17. Field analyses were conducted at the well site and laboratory analyses were conducted in the USF environmental laboratory.

Hydrogen Peroxide Determination

The method used for measuring hydrogen peroxide was derived from its reaction with titanium ions which forms a yellow colored complex. This complex absorbs most strongly at 410nm and can be measured spectrophotometrically to determine hydrogen peroxide concentrations in the ppm range. The reagent for making hydrogen peroxide determinations is an acidic solution of titanium prepared by adding 24 mL of titanium tetrachloride to 300 mL of 6M HCl. This reagent needs to be tightly capped and stored in a cool dark place. The interferences are strong alkaline samples, turbidity, reducing agents, and any substance that absorbs at 410 nm.

Table 17: Summary of analytical parameters tested

Test	Field or Lab	Standard Method, 20 th Edition-number	Instrument Used	Detection Limit/ Sensitivity	Storage/ Preservation
Alkalinity, mg/L	Field	2320 B. Titration Method	Bromocresol green/methyl red	20 mg/L CaCO ₃	N/A
CaCO ₃					
Color(true & apparent), mg/L	Field	2120 C Spectrometric Method	Hach DR/2400 Portable Spectrophotometer	5 PtCo Units	N/A
PtCo					
Conductivity, µS/cm	Field	2510 B Laboratory Method	Hach sension 156 Portable Multiparameter Meter	20 µS/cm	N/A
ORP, mV	Field	4500-H+ B. Electrometric Method	ExStik pH and ORP Probe	±999mV	N/A
pH	Field	4500-H+ B. Electrometric Method	Hach sension 156 Portable Multiparameter Meter	0.01 pH units	N/A
Sulfate, mg/L	Field	4500- SO ₄ ²⁻ E. Turbidimetric method	Hach DR/2400 Portable Spectrophotometer	2 mg/L as SO ₄ ²⁻	N/A
SO ₄ ²⁻					
Sulfide, mg/L	Field	4500-S ²⁻ D Methylene blue method	Hach DR/2400 Portable Spectrophotometer	0.1 mg/L as S ²⁻	N/A
Temperature, °C	Field	2550 B. Laboratory Method.	Hach sension 156 Portable Multiparameter Meter	0.01°C	N/A
TOC, mg/L	Lab	5310 C. Persulfate-UV Method	Seivers 800 Portable Total Organic Carbon Analyzer	0.05 mg/L	Acidified to pH=2 with sulfuric acid and analyze as soon as possible
TOC					
Turbidity, NTU	Field	2130 B Nephelometric Turbidity	Hach model 2100 AN Laboratory Turbidimeter	0.01 NTU	

Bench-Scale Tests

The bench-scale tests were conducted to gain information about the optimum hydrogen peroxide dose, optimum pH level, the reactions rates, and changes in water quality. For the bench-scale tests 1 or 2 liter batch reactors were used. Samples were collected using a special sampling device that minimized hydrogen sulfide loss. Water entered at the bottom of the device and overflowed at the top. The samples were collected from a tube located midway on the device. This allowed for minimum gaseous exchange.

A 3% hydrogen peroxide solution was dosed at concentrations of 1.5 to 18 mg/L. The sulfide levels were monitored at one minute intervals 10 minutes. This allowed for the evaluation of the reaction kinetics and allowed for the determination of the reactor dimensions and detention times for the pilot plant. These experiments were conducted at pH levels within the range of 7.5 to 8.5 to determine the optimum pH for this treatment. Based on these experiments conducted, it was determined that a 0.5mg hydrogen peroxide per mg sulfide was the optimum ratio and the optimum pH was 8.3.

Pilot Plant Design

From the results gathered from the bench-scale tests, a pilot-scale treatment unit was built. In-line chemical treatment of groundwater was tested in a flow-through pilot

plant consisting of approximately 40 meters of clear schedule 40 PVC pipe (2 inch ID) with approximately 8 meters of ¾ inch ID connectors joining each section of pipe. Chemical injection ports containing in-line mixers were placed at intervals through the plant to allow for injection of different test chemicals.

Tracer tests using either salt solutions or dyes were conducted to evaluate the hydraulic conditions and the detention times for each portion of the pilot plant. The sequence of chemical addition points, detention time of each segment of the pilot plant, and chemical dose ranges are summarized in Table 18.

Table 18: Detention times of reactors

From	To	Detention Time (min)	Chemical Dose Range, mg/L
Inlet	Outlet	20	N/A
pH Injection	Hydrogen Peroxide Injection	1	N/A
Hydrogen Peroxide Injection	UV Unit	1	1.15-1.35
UV Unit	Chlorine Injection	5	1.15-1.35
Chlorine Injection	Outlet	13	21-25

The hydrogen peroxide dose was approximately 1.25 mg/L. This dosage was based on the optimum ratio of 0.5 mg of hydrogen peroxide/mg sulfide that was derived from the bench-scale tests, using an average sulfide level of 2.5 mg/L based on historical sulfide data for the well. The hydrogen peroxide concentration was tested photometrically using a titanium chloride method. A 10.5% sodium hypochlorite (liquid chlorine) solution was dosed to the system within the range of 21-25 mg/L.

Results and Discussion

The source water characteristics are summarized in Table 19. From the table, it is seen that sulfide levels for the wells vary from 0.8 to 3.4 mg/L. However, over 90% of the sulfide measurements above 2 mg/L were from well 9. Therefore, the majority of the bench-scale and pilot testing was done at well 9.

Table 19: Summary of untreated water quality data from a groundwater source in west-central Florida (2004-2005 monitoring data)

Parameter	Range	Average	Standard Deviation	Number of samples
pH	7.22 - 7.77	7.46	0.10	46
Temperature, °C	25 – 31	26	1.5	23
Conductivity $\mu\text{S}/\text{cm}$	479 – 661	529	36	41
Turbidity, NTU	0.1 - 5.1	0.7	1.1	44
Anions				
Alkalinity, mg/L CaCO_3	130-240	199	19	32
Sulfate, mg/L SO_4^{2-}	11 – 43	27	6	25
Sulfide, mg/L S^{2-}	0.8 - 3.4	2.3	0.5	47
Chloride, mg/L Cl^-	21 – 26	23	4	2
Cations				
Calcium, mg/L Ca^{2+}	80.8 - 116.3	92.3	16.4	6
Magnesium, mg/L Mg^{2+}	3.78 – 6.95	5.05	1.34	6
Ferrous Iron, mg/L Fe^{2+}	<0.01-0.47	0.10	0.12	21
TOC, mg/L C	2.6-3.5	3.1	0.31	9
True Color mg/L PtCo	3 - 12	7	3	6

Bench-Scale Tests

From the bench scale tests using a hydrogen peroxide to hydrogen sulfide ratio of 0.5:1 at pH 8.2, it can be seen in figure 12 that approximately 70 to 85% of the sulfide was removed within the first six minutes of the reaction for three wells. After that, the reaction plateaued and little change in sulfide level was noted.

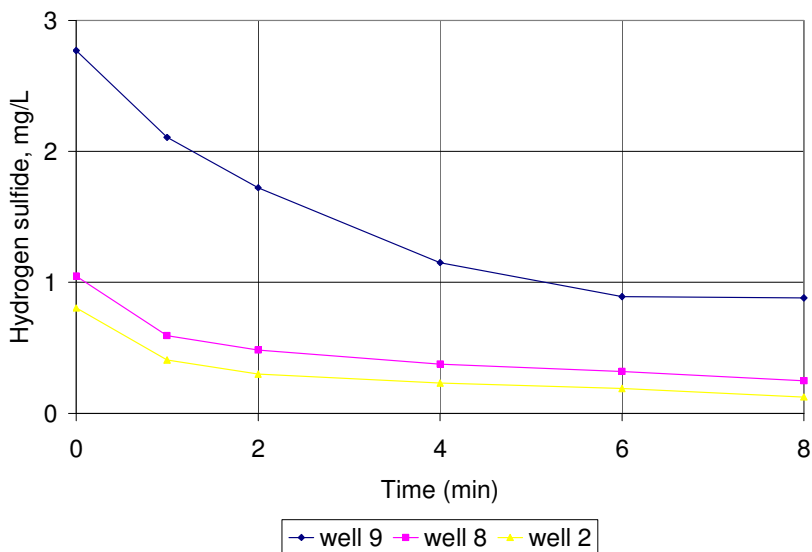


Figure 12: Hydrogen sulfide removal using a hydrogen peroxide to hydrogen sulfide ratio of 1:1

The initial rate of hydrogen sulfide removal could be modeled as a zero order reaction for the first two minutes. After two minutes, the rate of hydrogen sulfide removal was modeled as a pseudo first order reaction with a rate constant of 0.05 min^{-1} (Levine, 2004).

Pilot Scale Tests

The pilot scale tests were conducted to evaluate the effectiveness of using hydrogen peroxide as a pretreatment before chlorination. For these tests, two pH levels were used: ambient and elevated. The sulfide removal amount and percentages are shown in figure 13. The results validated the results from the bench scale tests in that better sulfide removal is achieved at a pH of 8.2.

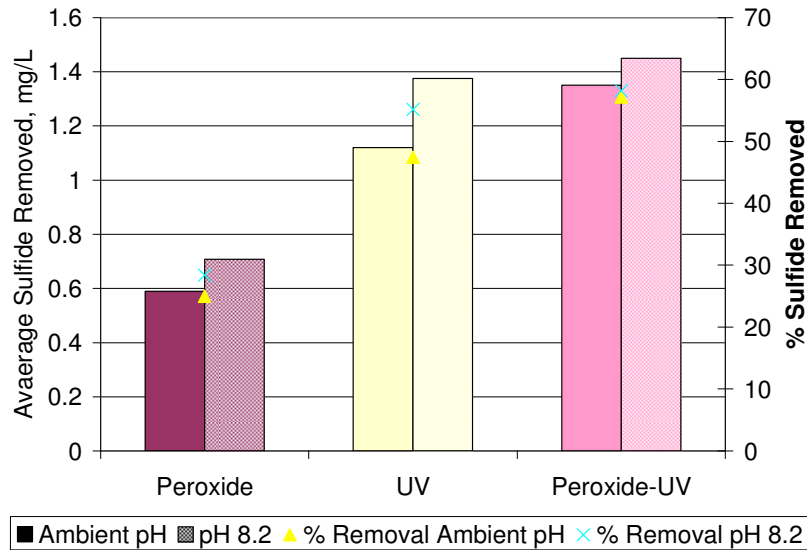
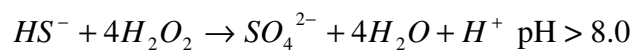


Figure 13: % Sulfide removal at ambient and elevated pH levels

Based on the stoichiometric equation for the reaction between hydrogen peroxide and hydrogen sulfide,



for each mole of sulfide consumed, a mole of sulfate is produced. Therefore, from a theoretical point of view, the change in the amount of sulfate can be evaluated.

For ambient pH, 0.59 mg of sulfide was consumed using hydrogen peroxide only.

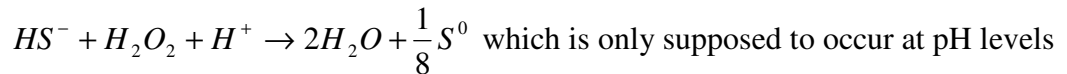
Therefore,

$$0.59\text{mgS}^{2-} \times \frac{1\text{mmolS}^{2-}}{32\text{mgS}^{2-}} \times \frac{\text{mmolHS}^-}{\text{mmolS}^{2-}} = \underline{\underline{0.018\text{mmolHS}^-}} \text{ was consumed.}$$

Therefore, 0.018mmol of sulfate or

$$0.018\text{mmolSO}_4^{2-} \times \frac{96\text{mgSO}_4^{2-}}{\text{mmolSO}_4^{2-}} = \underline{\underline{1.77\text{mgSO}_4^{2-}}}$$

should have been produced. The sulfate measurements were taken using a spectrophotometer with limited sensitivity. The test has an error associated with it of \pm 2mg/L. The measured sulfate formed was 0.5 mg/L. Therefore, the theoretical amount of sulfur that was produced can be calculated from the stoichiometric equation,



below 8. The amount of sulfide that produced the elemental sulfur is

$$1.77\text{mgSO}_4^{2-} - 0.5\text{mgSO}_4^{2-} = 1.27\text{mgSO}_4^{2-}$$

$$1.27\text{mgSO}_4^{2-} \times \frac{1\text{mmolSO}_4^{2-}}{96\text{mgSO}_4^{2-}} \times \frac{1\text{mmolHS}^-}{\text{mmolSO}_4^{2-}} = \underline{\underline{0.01323\text{mmolHS}^-}}$$

For every mole of sulfide consumed, 1/8mole of elemental sulfur is formed, therefore,

$$0.01323 \text{ mmolHS}^- \times \frac{1 \text{ mmolS}^0}{8 \text{ mmolHS}^-} \times \frac{32 \text{ mgS}^0}{\text{mmolS}^0} = \underline{\underline{0.053 \text{ mgS}^0}} \text{ or } 78.3 \text{ } \mu\text{g of elemental}$$

sulfur is produced per liter of water. The elemental sulfur predictions are outlined in Tables 20 and 21.

Table 20: Prediction of elemental sulfur produced at ambient pH

	Theoretical Sulfate Produced, mg/L SO_4^{2-}	Actual Sulfate Produced, mg/L SO_4^{2-}	Prediction of amount of elemental sulfur produced, mg/L
Peroxide only	1.77	0.5	0.053
UV Only	3.36	6	-0.110
Peroxide-UV	3.36	1.5	0.078

Table 21: Prediction of elemental sulfur produced at pH 8.2

	Theoretical Sulfate Produced, mg/L SO_4^{2-}	Actual Sulfate Produced, mg/L SO_4^{2-}	Prediction of amount of elemental sulfur produced, mg/L
Peroxide only	3.17	-0.5	0.153
UV Only	4.13	-1.5	0.234
Peroxide-UV	4.64	-2.7	0.306

When analyzing the solids data to see if this corresponded to a rise in suspended solids, it was found that there wasn't. However, the error associated with the suspended solids test is ± 10 mg/L. The same problem is seen with turbidity. With the production of elemental sulfur, an increase in turbidity is expected. However, the opposite is seen in Figure 6. For both pH levels, the turbidity levels decreased. Therefore, it leads to the conclusion that the amount of elemental sulfur produced is too small to create a signal for turbidity. This leads to the question of what is actually contributing to turbidity levels in

this water. When looking into this issue, it was determined that the majority of the particles were organic in nature (Minnis et. al, 2005).

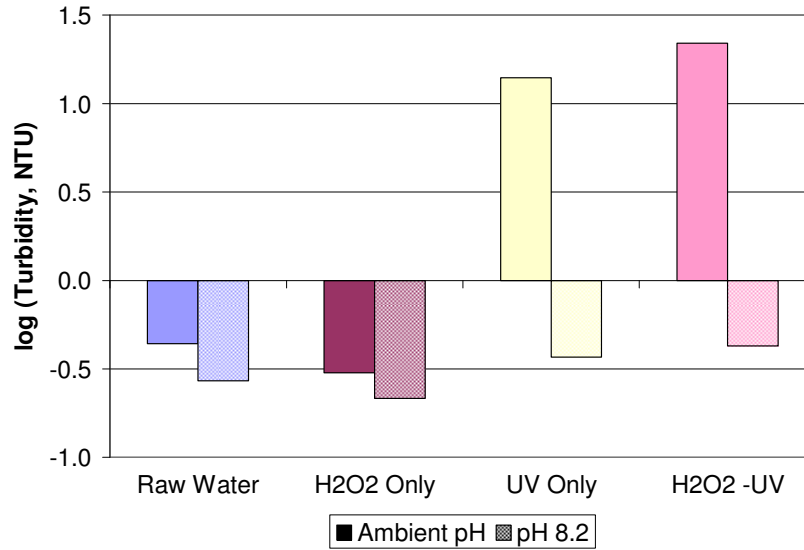
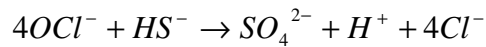


Figure 14: Average turbidity values for ambient pH and pH 8.2

When chlorine was added after the pretreatments, it oxidized the remaining sulfide in the water. The end product of sulfide oxidation by chlorine is sulfate above a pH of 7.5 (Cadena, 1988) according to the reaction



and forms elemental sulfur according to the reaction

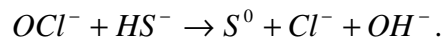


Figure 11 shows the potential pathways for these reactions. The elemental sulfur predictions are outlined in Tables 22 and 23.

Table 22: Prediction of elemental sulfur produced during chlorination after hydrogen peroxide addition

	Δ Sulfide, mg/L S^{2-}	Δ Sulfate, mg/L SO_4^{2-}	% Conversion (S^{2-} to SO_4^{2-})	Theoretical Sulfate Produced, mg/L SO_4^{2-} (100% conversion)	Prediction of amount of elemental sulfur produced, --
Ambient pH (1)	1.865	4	71%	5.6	0.533
Ambient pH (2)	1.675	3	90%	5.0	0.675
pH 8.2 (1)	1.51	4	89%	4.5	0.177
pH 8.2 (2)	1.36	3	73%	4.1	0.360

With the addition of chlorine, there was an increase in turbidity as shown in Figure 15. However, the sulfur generated was very small and cannot account for the turbidity signal. Another possibility source is that the combined effects of the two oxidants result in the production of turbidity from other sources.

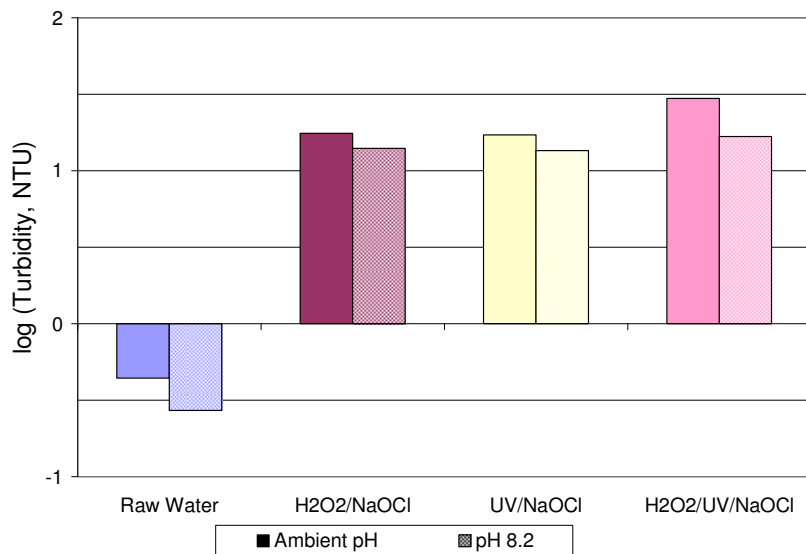


Figure 15: Average turbidity values after chlorine addition at ambient pH and pH 8.2

Conclusions & Recommendations

Hydrogen peroxide was effective in removing 40 to 45% of sulfide at a pH of 8.2 in a pilot flow through system using a hydrogen peroxide-sulfide ratio of 0.5:1. Hydrogen peroxide use as a pretreatment for hydrogen sulfide removal before chlorination is recommended only for those utilities that use filters because of the amount of turbidity generated. The hydrogen peroxide also had a positive effect on chlorine demand, reducing it by 8.4 and 1.4 % at ambient pH and pH 8.2 respectively.

Acknowledgements

Funding for this project was provided by Aloha Utilities, Inc. The assistance of Jack Burke, Mike McDonald, and Charlie Painter of Aloha Utilities is appreciated. Salah Albustami and Camilo Romero of USF assisted with field and laboratory analyses.

Conclusions

Several alternative oxidation treatments for the removal of hydrogen sulfide were tested to evaluate the impact on turbidity generation. The major conclusions from this project are:

1. Turbidity in groundwater is a variable parameter that depends on many factors including pH.
2. The sources of particles in treated groundwater include mineral precipitates of carbonates, calcium, and magnesium. From the SEM analysis, the particles were composed of mostly carbon and oxygen, suggesting that they are mostly organics.
3. The particles found in the untreated water ranged from 1 micron to over 15 microns, while the particles produced from treatment were smaller than 1 micron.
4. There is a need for a mechanism to be put into place that would remove the particles generated through treatment before the water is sent out to the

distribution because of the high turbidity levels seen by all treatment except UV
Only at elevated pH. These turbidity levels exceed the 0.3 NTU turbidity limit set
by the Surface Water Treatment Rule.

5. Using hydrogen peroxide only or coupled with UV as a pretreatment for hydrogen sulfide before chlorination is recommended only for water treatment plants that filter because of the turbidity levels generated.

Engineering Implications

Historically, groundwater sources were considered to be relatively safe and for the most part protected from contamination (EPA, 2005). However, societal development and encroachment on natural resources have resulted in increasing vulnerability of groundwater systems. To improve protection of public health, the EPA drafted a proposed groundwater rule that addresses increased disinfection and monitoring. One of the side effects of using disinfectants such as liquid chlorine, chloramine, and UV irradiation is the potential for generation of particulate matter.

Turbidity is not a water quality parameter that is currently monitored or regulated in groundwater. Turbidity in groundwater cannot be taken lightly as it can serve as a shield for pathogens from disinfectants, can provide substrate for microorganisms within the distribution system, and can serve as a home for organisms to grow on. Based on the research conducted in this project, it is evident that the particles present in untreated groundwater should be characterized and their response to disinfectants should be evaluated.

One of the important finds of this study was that the particles that were generated from disinfectant treatment tended to be in the sub-micron range. One of the implications of this is that if a utility wanted to remove these particles before the treated water is sent out into the distribution system, it could not be achieved by using conventional granular media filtration. Instead, other methods such as nanofiltration may have to be employed. Or, it may be more feasible to remove the substances that react with the disinfectants to prevent particle formation before disinfection.

This study was completed on a groundwater system in west-central Florida, therefore the conclusions and recommendations drawn may not be applicable to every groundwater system. But, to avoid potential problems associated with turbidity generation, a comprehensive study of the groundwater source and effects of alternative disinfectant treatment needs to be completed before implementation of alternative treatment systems. This will allow a utility to make the best choice in treatment for their groundwater source.

Recommendations for Further Research

Recommendations for further research on the effect of disinfection on particle characteristics, and control of hydrogen sulfide in groundwater are presented in this section.

1. Research the particle characteristics found in untreated and disinfected groundwater using different characterization methods. This would provide additional information about these particles.
2. Research other groundwater system particles and the effect that chlorine, chloramine, and UV irradiation have on the particle characteristics. Turbidity levels should be compared to the findings of this research to establish whether or not there are commonalities among the source waters that may be contributing to the turbidity generation.
3. Research on the reactions and reaction kinetics that are occurring when the disinfectants are applied to the water that cause the particles to form. The kinetic

studies may give insight into the mechanisms of the reactions. This may give engineers the opportunity to establish a way to make those reactions unfavorable thus circumventing the problem.

4. Research alternative disinfection treatments such as ozone and chlorine dioxide, to evaluate whether or not they have an effect on groundwater particles. This may provide an alternative treatment to chlorine, chloramine, or UV.
5. Evaluate pretreatment options before disinfection. These pretreatment options include nanofiltration and anion exchange to remove the substances that are present in the groundwater that are reacting with the disinfectant. This study should be done on a flow-through system, so that the evaluation more closely mimics a full-scale treatment plant.
6. Research the impact that rainfall has on particle characteristics in groundwater. This could give indications on how sensitive the groundwater source is to contamination from above ground sources.
7. Research the effect that storage has on sulfide reversion in groundwater that has been disinfected. This should be done at different temperatures and storage time lengths to evaluate what happens when water is stagnant in the distribution system. In addition, the reactivity of this water with metals such as copper and

iron should be evaluated. This would provide insight onto which conditions promote metal sulfide production and ways to correct it.

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Appendices

Appendix A: Pilot Plant Design and Operation

The pilot plant consisted of pipe reactors that simulated plug flow reactors, chemical injection ports, sample taps and a UV unit. Two inch diameter clear schedule 40 PVC pipes were used as the reactors and $\frac{3}{4}$ inch diameter clear schedule 40 PVC pipes were used as connectors. There were five chemical injection ports included for sodium hydroxide (pH control), hydrogen peroxide, sodium hypochlorite, ammonium hydroxide, and a corrosion inhibitor. The UV unit is located between the hydrogen peroxide injection port and the sodium hypochlorite injection port. A schematic of the pilot plant is shown in Figure 1. The flow rate was controlled by a flow meter that ranged from 0 to 2 gallons per minute. The injection pumps were low flow pump and tank systems. The flowrate varied from approximately 3 mL/min to approximately 17 mL/min.

Appendix A (continued)

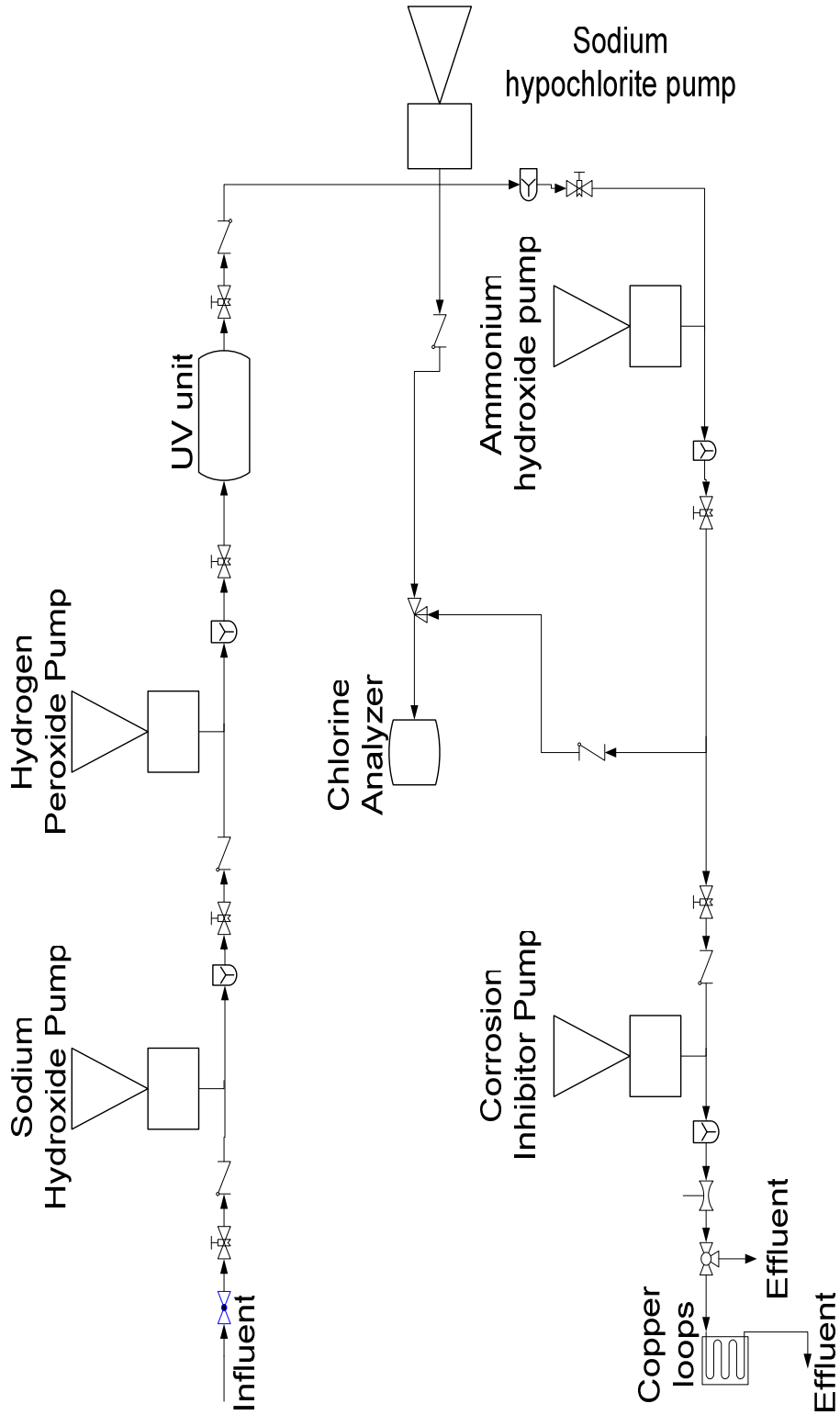


Figure A 1: Schematic of Pilot Plant Unit

Appendix A (continued)

The detention times for the reactors in the pilot plant are outlined in Table 1.

Table A 1: Detention times of reactors

From	To	Detention Time (min)
Inlet	Outlet	22
Inlet	pH Injection	~0
pH Injection	Hydrogen Peroxide Injection	1
Hydrogen Peroxide Injection	UV Unit	1
UV Unit	Chlorine Injection	5
Chlorine Injection	Ammonium Hydroxide Injection	3
Ammonium Hydroxide Injection	Outlet	10

The detention times were verified using a tracer tests. The first tracer test was completed using a saturated salt solution to verify the overall detention time of the pilot. The salt solution was injected at the pH injection port (residence time between inlet and pH injection port ~0) and conductivity measurements were taken in one minute intervals

Appendix A (continued)

for forty minutes. This is illustrated in Figure 1a. After the overall residence time was verified, tracer tests needed to be conducted on individual reactor times. Again, a saturated salt solution was injected at the pH injection port and conductivity measurements were taken in twenty second intervals. This is illustrated in Figure 1b.

Appendix A (continued)

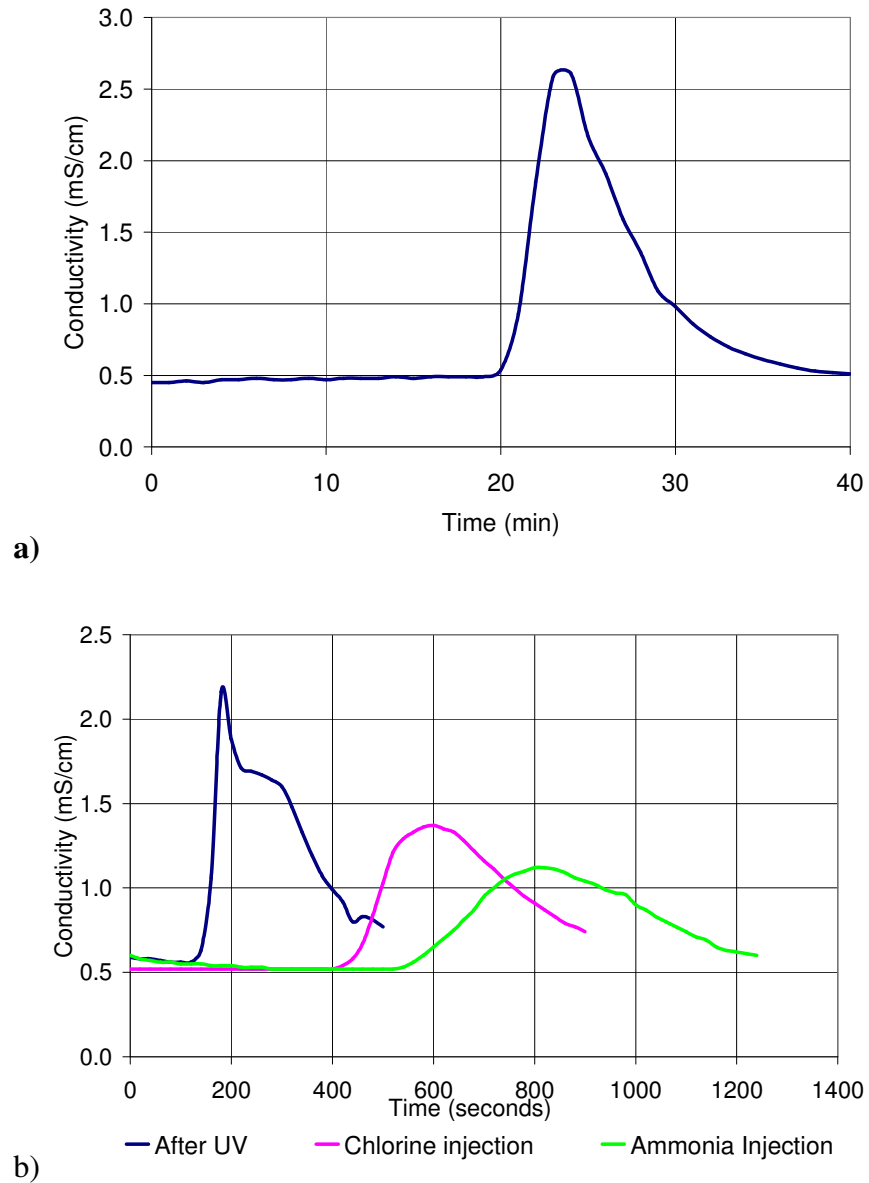


Figure A 2: Results from tracer tests for a) the entire pilot plant and b) the individual reactors

Before operation, the pilot plant is run at full speed to allow any impurities to flush through the system with the chemical pumps turned off. While the pilot plant is

Appendix A (continued)

flushing, the chemical concentrations in the tank were taken. Once the pilot has flushed, then the flow rate desired is set. For the experiments run, the preferred flow rate was 1 gallon per minute.

Before every run, the initial hydrogen sulfide concentration in the water was taken. This was the basis for the calculated dosages for the chemicals. The sodium hypochlorite (liquid chlorine) dose was based on a molar ratio of 5 moles of chlorine for every mole of sulfide. The residual chlorine was then measured. The pumps were then manually adjusted to obtain the desired chlorine residual. The ammonium chloride dose was based on a mole ratio of 1 mole of ammonia per 4 moles of chlorine. The hydrogen peroxide dose was based on a mass ratio of 0.5 mg of hydrogen peroxide per mg of sulfide. The chemical pumps were then set to dose the system correctly.

Appendix B: Procedure for Hydrogen Peroxide Measurement

The following section describes in detail the procedure used to measure hydrogen peroxide. The method was developed by Allen Hunter in the USF Environmental Engineering Laboratory.

Introduction

Titanium ions in aqueous solution form a yellow colored complex with hydrogen peroxide. This complex absorbs most strongly at 410nm and can be measured spectrophotometrically to determine hydrogen peroxide concentrations in the ppm range.

Required reagents and equipment

1. Titanium tetrachloride (TiCl_4)
2. 6M HCl
3. 125mL Erlenmeyer flask
4. Small glass funnel
5. Spectrophotometer
6. Storage container with tight fitting lid

Appendix B (continued)

Warning: Titanium Chloride is highly volatile liquid and hydrolyzes instantly upon contact with atmospheric moisture to form a dense white smoke of HCl and TiO₂.

Titanium chloride should not be opened outside of a properly functioning fume hood.

Chemical resistant gloves and goggles must be worn while working with pure TiCl₄.

Contact with liquid water is highly energetic and causes spattering.

Procedure for Preparing the Titanium Reagent

1. Place 30 mL of 6M HCl into a 125 or 250mL Erlenmeyer flask.
2. Set a clean and DRY, small (less than 30 grams) glass funnel, with a top diameter greater than that of the flask, into the mouth of the flask so that it rests lightly on top.
3. Make certain the stem of the funnel is at least 1 cm above the surface of the liquid in the flask - this prevents clogging of the funnel and reduces the risk the heat evolved in the reaction with the acidic solution from pushing the TiCl₄ back up the funnel.
4. Using a mechanical pipetter with a cotton vapor barrier tip, add 2.4mL TiCl₄ into the funnel. A white smoke will evolve from all surfaces with the

Appendix B (continued)

TiCl₄ on them. Eject the pipette tip into the mouth of the funnel and allow the apparatus to sit until the white smoke trapped in the Erlenmeyer flask has settled and a yellow solid residue (if present) can be seen on the tip of the funnel stem.

5. Rinse the outer surface of the pipette tip and the funnel into the flask with another 20.0 mL of HCl. If any yellow residue still remains, transfer the flask contents into a beaker and dip the funnel tip into the solution until all residue is dissolved. The reagent can now be safely handled outside the fume hood, safety precautions are now similar to those of 6-8M HCl.
6. Store the reagent tightly capped in a cool dark place.

Hydrogen peroxide determination

1. For a 10 mL volume, add 100μL of the titanium reagent for samples and standards 1-50ppm H₂O₂. Addition of excess reagent has no apparent effect other than dissolution of the sample. If the absorbance range and variance are outside of working conditions for the instrument, attempt choosing an absorbance cuvette with a different path length; Shorter for higher concentrations, and longer for lower concentrations.

Appendix B (continued)

2. Prepare a linear calibration curve using known concentrations of H_2O_2 .
Add equal portions of the titanium reagent to samples and standards.
Blank the spectrophotometer with a deionized water sample treated with the titanium reagent. Make sample measurements with respect to the calibration curve. Some instruments allow direct measurement after establishing an internal calibration curve using standards.

Interferences

1. Strongly alkaline samples may need to be partially neutralized before determination. Reagent E is strongly acidic, but a high pH can cause precipitation of the titanium ions and complexes.
2. Turbidity will interfere with any absorption method. Filtration of sample prior to reagent addition or other turbidity reduction method may be incorporated. Intermediate turbidity can be handled by blanking with a untreated sample – standard additions should be used to verify linearity of calibration under these conditions. If calibration deviates significantly from linear, reduce turbidity by another means before analysis.
3. Any substance with a strong absorbance at 410 nm will cause a positive interference and a loss of sensitivity.

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Appendix C (continued)

Bench Scale Tests

Table C 1: Peroxide sulfide ratio = 1:1 (well 9)

Time, min	Sulfide, mg S ²⁻ /L							
	pH 7.8	pH 7.9	pH 8.0	pH 8.1	pH 8.2	pH 8.3	pH 8.4	pH 8.5
0	3.0445	2.7240	3.8457	3.6854	2.5638	3.2047	2.7240	2.5638
1	3.0445	2.2433	3.6854	2.7240	2.4035	2.4035	2.5638	2.7240
2	1.2819	2.4035	2.2433	2.5638	2.4035	2.0831	2.5638	1.9228
3	1.6024	1.2819	1.9228	1.7626	1.7626	2.2433	2.2433	1.9228
4	2.0831	1.2819	1.9228	1.9228	2.0831	2.0831	3.0445	1.4421
5	1.4421	0.9614	2.0831	1.9228	1.7626	2.0831	1.9228	1.6024
6	0.6409	1.6024	2.0831	1.9228	1.4421		2.0831	1.4421
7	2.7240	0.8012	1.7626	2.2433	1.6024		1.6024	1.7626
8	0.9614	1.4421	1.6024	1.6024	1.1217		1.9228	1.6024

Table C 2: Peroxide sulfide ratio 2:1 (well 9)

Time, min	Sulfide, mg S ²⁻ /L					
	pH 7.8	pH 8.0	pH 8.2	pH 8.3	pH 8.4	pH 8.5
0	2.5638	2.8842	2.724	3.3650	2.8842	3.3650
1	2.4035	2.5638	2.5638	2.2433	2.7240	2.5638
2	1.4421	2.0831	2.724	2.2433	2.4035	2.0831
3	1.2819	1.6024	2.2433	2.2433	2.2433	1.7626

Appendix C (continued)

Table C 2: continued

4	0.9614	1.4421	2.0831	1.9228	1.9228	1.7626
5	0.8012	0.8012	1.9228	1.9228	1.7626	1.9228
6		1.1217	1.6024	1.9228	1.7626	1.9228
7			1.4421	1.9228	1.7626	1.9228
8			1.4421	1.2626	1.4421	1.6024
9			1.4421	1.4421	1.4421	1.6024
10			1.6024	1.6024	1.4421	1.4421

Table C 3: Peroxide sulfide ratio 3:1 (well 9)

Time, min	Sulfide, mg S ²⁻ /L			
	pH 8.0	pH 8.2	pH 8.4	pH 8.6
0	2.724	2.8842	2.7240	3.2047
1	2.0831	2.2433	2.8842	2.5638
2	1.6024	2.2433	2.5638	2.0831
3	1.6024	2.2433	2.2433	2.0831
4	1.4421	2.0831	1.9228	2.0831
5	1.2819	1.7626	1.9228	2.2433
6		1.6024	1.7626	2.2433
7		1.4421	1.7626	1.9228
8		1.4221	1.9228	1.9228
9		1.2819	1.9228	1.9228

Appendix C (continued)

Table C 4: Peroxide sulfide ratio 4:1 (well 9)

Time, min	Sulfide, mg S ²⁻ /L			
	pH 8.0	pH 8.2	pH 8.4	pH 8.6
0	2.8842	2.7240	2.8842	3.3650
1	2.2433	2.7240	2.2433	2.7240
2	2.0831	2.4035	2.2433	2.5638
3	1.9228	2.5638	2.5638	1.9228
4	1.7626	2.2433	2.5638	1.7626
5	1.4421	1.9228	1.9228	1.7626
6	1.1217	1.7626	1.9228	1.7626
7	1.2819	1.6024	1.7626	1.9228
8	0.9614	1.9228	1.9228	2.0831
9			1.7626	1.7626

Appendix C (continued)

Table C 5: Peroxide sulfide ratio 5:1 (well 9)

Time, min	Sulfide, mg S ²⁻ /L			
	pH 8.0	pH 8.2	pH 8.4	pH 8.6
0	2.5638	3.3650	2.8842	3.2047
1	2.724	2.7240	2.4035	2.8842
2	2.2433	2.7240	2.7240	2.7240
3	2.4035	2.2433	2.5638	2.2433
4	2.4035	2.2433	2.5638	2.0831
5	2.0831	1.9228	2.5638	2.2433
6	1.7626	2.0831		2.2433
7	1.6024	2.8842	1.9228	2.2433
8	1.7626	2.0831	1.7626	2.2433
9	1.6024	2.0831	1.9228	2.2433

Appendix C (continued)

Table C 6: Peroxide sulfide ratio 6:1 (well 9)

Time, min	mg S ²⁻ /L			
	pH 8.0	pH 8.2	pH 8.4	pH 8.6
0	3.2047	3.2047	2.8842	2.5638
1	2.4035	3.0445	2.4035	2.8842
2	2.5638	2.8842	2.2433	2.0831
3	2.2433	2.4035	2.2433	2.5638
4	2.0831	2.4035	2.0831	2.2433
5	1.9228	2.0831	2.0831	1.4421
6	1.4421	2.0831	1.7626	1.6024
7	1.6024	2.5638	1.9228	1.6024
8	1.4421	2.5638	1.6024	1.4421
9	1.2819	2.2433	1.4421	1.6024

Table C 7: Chlorine demand data for well 1 at ambient pH

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	7.14		0.00	0.00
0	90	10.58	7.16		0.00	0.00
5			7.17	0.28	4.00	6.58
10			7.17		4.00	6.58
15			7.18	0.37	3.70	6.88
20			7.19		3.70	6.88

Appendix C (continued)

Table C 8: Chlorine demand data for well 1 at pH 8.3

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl_2)	pH	Turbidity, NTU	Residual Cl_2 , mg/L Cl_2	Chlorine Demand, Cl_2
0	0.00	0.00	8.29		0.000	0.00
0	80.00	9.41	8.34		0.000	0.00
5			8.34	0.460	3.500	5.91
10			8.33		3.400	6.01
15			8.33	0.360	3.000	6.41
20			8.32		2.900	6.51

Table C 9: Chlorine demand data for well 2 at ambient pH

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl_2)	pH	Turbidity, NTU	Residual Cl_2 , mg/L Cl_2	Chlorine Demand, Cl_2
0	0	0.00	7.47	0.59	0.00	0.00
0	120	14.11	7.53		0.00	0.00
5			7.51		3.20	10.91
10			7.51	1.00	3.20	10.91
15			7.51	1.39	3.30	10.81
20			7.53	1.04	3.20	10.91

Appendix C (continued)

Table C 10: Chlorine demand data for well 2 at pH 8.3

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	8.30		0.00	0.00
0	120	14.11	8.37		0.00	0.00
5			8.37		6.50	7.61
10			8.38		5.90	8.21
15			8.37		5.60	8.51
20			8.37		5.60	8.51

Table C 11: Chlorine demand data for well 3 at ambient pH

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	7.53		0.00	0.00
0	140	16.46	7.64	0.52	0.00	0.00
5	0		7.64		4.30	12.16
10	0		7.58	0.75	4.00	12.46
15	0		7.58		3.80	12.66
20	0		7.58	1.04	3.70	12.76

Appendix C (continued)

Table C 12: Chlorine demand data for well 3 at pH 8.3

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0.00	0.00	8.32		0.000	0.00
0	140.00	16.46	8.43	1.030	0.000	0.00
5			8.43		4.800	11.66
10			8.39	1.880	4.400	12.06
15			8.38		4.100	12.36
20			8.38	2.270	4.000	12.46

Table C 13: Chlorine demand data for well 4 at pH 8.3

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	7.42			0.00
0	200	23.52	7.52			0.00
10			7.51	0.52	6.50	17.02
20			7.52	0.63	5.80	17.72

Table C 14: Chlorine demand data for well 6 at ambient pH

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	7.28	0.47	0.00	0.00
0	130	15.29	7.37		0.00	0.00
5			7.42	0.66	5.50	9.79
10			7.42	0.62	5.50	9.79
15			7.43		5.10	10.19
20			7.43		4.90	10.39

Appendix C (continued)

Table C 15: Chlorine demand data for well 6 at pH 8.3

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	8.30		0.00	0.00
0	120	14.11	8.38		0.00	0.00
5			8.35	0.34	6.70	7.41
10					6.80	7.31
15				0.65	5.70	8.41
20					5.80	8.31

Table C 16: Chlorine demand data for well 7 at ambient pH

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	7.37	2.86	0.00	0.00
0	60	7.06	7.40		0.00	0.00
5			7.44		3.50	3.56
10			7.43	2.48	4.00	3.06
15			7.44		3.10	3.96
20			7.44		3.00	4.06

Appendix C (continued)

Table C 17: Chlorine Demand data for well 7 at pH 8.3

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0.00	0.00	8.30	2.680	0.000	0.00
3	70.00	8.23	8.34		0.000	0.00
9			8.33		5.400	2.83
14			8.33	2.270	4.500	3.73
19			8.32		4.100	4.13
28			8.32		4.000	4.23

Table C 18: Chlorine demand data for well 8 at ambient pH

Time (min)	NaOCl (μ L)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	300.00	17.64	7.40			0.00
2			7.45			0.00
5			7.45		4.30	13.34
10			7.45	2.08	4.1	13.54
15			7.46		3.5	14.14
20			7.46		3.2	14.44

Appendix C (continued)

Table C 19: Chlorine demand data for well 8 at pH 8.3

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	8.32		0.00	0.00
3	320	18.82	8.40	1.34	0.00	0.00
5			8.40		5.20	13.62
10			8.38		5.40	13.42
15			8.38		5.40	13.42
20			8.38		5.40	13.42

Table C 20: Chlorine demand data for well 9 at ambient pH

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0.00	0.00	7.42		0.00	0.00
0	280.00	32.93	7.53	1.36	0.00	0.00
5			7.49		5.50	27.43
10			7.48	4.17	5.20	27.73
15			7.46		4.80	28.13
20			7.45	8.70	4.10	28.83

Table C 21: Chlorine demand data for well 9 at pH 8.3

Time (min)	NaOCl (μL)	NaOCl (mg/L Cl ₂)	pH	Turbidity, NTU	Residual Cl ₂ , mg/L Cl ₂	Chlorine Demand, Cl ₂
0	0	0.00	8.29		0.00	0.00
0	260	30.58	8.54		0.00	0.00
5			8.45		6.50	24.08
10			8.44	2.30	5.60	24.98
15			8.41		5.00	25.58
20			8.41	7.84	4.50	26.08

Appendix C (continued)

Table C 22: Combined peroxide, chlorine and ammonia runs at well 2 10/20/2004

Initial Conditions:						
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)
25.8	402	61	7.57	0.222	0.41	0.88

Set Parameters:

pH	Volume (L)	Peroxide ratio
8.3	2	0.5:1

Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Residual Chloramine (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
26.4	0	--	8.30	0	0	0	--	0	0	0
26.6	0	0.804	8.30	29.5	0	0	--	0	0	0
26.7	1	0.407	8.29	0	0	0	--	0	0	0
26.8	2	0.299	8.28	0	0	0	--	0	0	0
26.9	4	0.231	8.29	0	0	0	--	0	0	0
27	6	0.190	8.28	0	0	0	--	0	0	0
27.1	8	0.124	8.28	0	0	0	--	0	0	0
27.2	--	--	8.27	0	80	0.6	0.181	0	0	0

Appendix C (continued)

Table C 22: Continued

27.3	--	--	8.28	0	40	1.4	--	0	0	0
27.5	--	--	8.29	0	40	1.9	0.202	0	0	0
27.8	--	--	8.30	0	40	2.6	--	0	0	0
27.9	--	--	8.29	0	40	3.4	0.238	0	0	0
28	--	--	8.29	0	40	4.1	--	0	0	0
28.2	--	--	8.30	0	40	5.4	0.245	0	0	0
28.6	--	--	8.43	0	0	--	--	148	0	0
28.6	--	--	8.43	0	0	4.9	0.238	0	0	4.35

Table C 23: Combined peroxide chlorine and ammonia runs at well 3 11/10/2004 at pH 7.8

		Initial Conditions:				
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)
25	400	-118	7.48	0.162	1.02	1.372

Set Parameters:

pH	Volume (L)	Peroxide ratio
7.8	2	0.5:1

Appendix C (continued)

Table C 23: Continued

Temp. (°C)	Time (min)	H ₂ S (mg/L)	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Residual Chloramine (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
--	0	1.715	7.8	57.5	0	0	0.162	0	0	0
--	1	1.407	7.8	--	0	0	--	0	0	0
--	2	1.177	7.8	--	0	0	--	0	0	0
--	2	--	7.8	--	280	1.7	0.336	0	0	0
--	--	--	7.83	--	--	0	--	0	0	0

Table C 24: Combined peroxide, chlorine and ammonia runs at well 3 11/10/2004 at pH 7.8

Initial Conditions:						
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)
25	400	-118	7.48	0.162	1.02	1.718

Set Parameters:

pH	Peroxide ratio
8.2	0.5:1
Volume (L)	
2	

Appendix C (continued)

Table C 24: Continued

Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Residual Chloramine (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
25	0	--	8.2	57.5	0	0	--	0	0	0
25	1	0.734	8.2	--	0	0	--	0	0	0
25.1	2	0.646	8.2	--	0	0	--	0	0	0
25.1	2	--	8.28	--	350	5.9	0.484	0	0	0
--	5 min after last chlorine dose	--		--	--	--	--	8.1	1.59	below detecti on limit (0.04)

Table C 25: Combined peroxide, chlorine and ammonia runs at well 4 11/11/2004 at pH 7.8

Initial Conditions:						
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)
25	424	-105	7.37	0.506	0.9	1.254 (probe)/1.000 (spec)

Appendix C (continued)

Table C 25: Continued

Set Parameters:		Peroxide ratio	
pH	Volume (L)	ratio	
7.8	2	0.5:1	

Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Chloramine formed (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
25	0	--	7.8	41.8	0	0	--	0	0	0
25	1	0.413	7.8	--	0	0	--	0	0	0
25.1	2	0.32	7.8	--	0	0	--	0	0	0
25.1	2	--	7.8	--	280	5	--	0	0	0
25.1	7	--	7.95	--	--	--	0.315	13.8	3.31	0.23

Appendix C (continued)

Table C 26: Combined peroxide, chlorine and ammonia runs at well 4 11/11/2004 at pH 8.2

Initial Conditions:						
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)
25	424	-105	7.37	0.506	0.9	1.254 (probe)/1.000 (spec)

Set Parameters:	
pH	Peroxide ratio
8.2	0.5:1

Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Chloramine formed (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
25	0	--	8.21	42	0	0	--	0	0	0
25	1	0.932	8.21	--	0	0	--	0	0	0
25.1	2	0.792	8.21	--	0	0	--	0	0	0
25.1	2	--	8.23	--	300	3	0.162	0	0	0

Appendix C (continued)

Table C 26: Continued

25.2	7	--	8.23	--	30	3.9	--	8.1	1.59	--
25.7	--	--	8.23	--	30	4.6	--	--	--	--
26.1	5 min after last chlorine addition	--	8.34	--	--	--	0.568	12.7	3.92	Below detection limit

Table C 27: Combined peroxide, chlorine and ammonia runs at well 8 10/19/2004 at pH 8.3

Initial Conditions:										
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)				
25.5	494	-34	7.27	6	0.8	1.06				
Set Parameters:										
pH	Volume (L)	Peroxide ratio								
8.3	2	0.5:1								

Appendix C (continued)

Table C 27: Continued

Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Chloramine formed (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
25.5	0	--	8.3	0	0	0				
25.5	0	1.048	8.3	34	0	0				
--	1	0.593	8.3	0	0	0				
26.4	2	0.482	8.29	0	0	0				
26.5	4	0.376	8.29	0	0	0				
--	6	0.319	8.29	0	0	0				
--	8	0.249	8.29	0	0	0				
--	--	--	8.27	0	120	0.8				
--	--	--		0	40	1.6				
27.4	--	--	8.28	0	40	2.6				
27.5	--	--	8.28	0	40	3.2				
27.7	--	--	8.28	0	40	4.5				
27.8	--	--	8.29	0	40	6				
28	--	--	8.41	0	0	0				
28	--	--	8.41	0	0	5				

Appendix C (continued)

Table C 28: Combined peroxide chlorine and ammonia runs at well 9 10/18/2004 at pH 8.3

Initial Conditions:										
Temp. (°C)	Conductivity (µS/cm)	ORP (mV)	pH	Turbidity (NTU)	DO (mg/L)	Sulfide (mg/L)				
24.9	479	-126	7.34	0.181	0.71	2.77				
Set Parameters:										
pH										
8.3	2	0.5:1								
Temp. (°C)	Time (min)	H ₂ S (mg/L) measured by probe	pH	H ₂ O ₂ added (µL)	Cl ₂ Added (µL)	Residual Cl ₂ (mg/L)	Turbidity (NTU)	NH ₃ Added (µL)	Chloramine formed (mg/L as Cl ₂)	Free NH ₃ (mg/L as N)
25.1	0	--	8.3	0	0	0	--	0	0	0
25.2	0	--	8.3	100	0	0	--	0	0	0
25.2	1	2.106	8.3	0	0	0	--	0	0	0
25.3	2	1.722	8.31	0	0	0	--	0	0	0
25.4	4	1.15	8.33	0	0	0	--	0	0	0
25.6	6	0.89	8.33	0	0	0	--	0	0	0
25.7	8	0.881	8.32	0	0	0	--	0	0	0
25.9	9	--	8.34	0	320	3	0.94	0	0	0

Appendix C (continued)

Table C 28: Continued

26	--	--	8.32	0	20	2.6	--	0	0	0	0
26.6	--	--	8.3	0	20	2.4	4.31	0	0	0	0
26.8	--	--	8.29	0	20	3.1	--	0	0	0	0
27	--	--	8.29	0	20	3.8	5.67	0	0	0	0
27.2	--	--	8.28	0	20	3.6	--	0	0	0	0
27.6	--	--	8.27	0	20	3.8	--	0	0	0	0
--	--	--		0	20	3.9	7.11	0	0	0	0
--	--	--		0	40	5.1(t)/4.7 (f)	--	0	0	0	0
28.3	--	--	8.36	0	0	0	--	14.1	0	0	0
--	--	--	8.36	0	0	0	8.2	0	0	3.69	0.05 (lower limit)

Appendix C (continued)

Table C 29: Field tests to test oxidant combinations at ambient pH 8/15/2005

Sample Number	Treatment	Temperature, °C	pH	Alkalinity, mg/L CaCO ₃	Conductivity, µS/cm	Dissolved Oxygen, mg/L O ₂
1	Raw Water	26.5	7.41	190	528	0.22
2	H ₂ O ₂ Only	26.8	7.42	200	531	0.11
3	H ₂ O ₂ /UV	27.7	7.45	190	539	0.64
4	H ₂ O ₂ /UV/NH ₂ Cl	28.5	7.83	220	635	0.86
5	H ₂ O ₂ /UV/NaOCl	28.7	7.49	190	618	0.82
6	H ₂ O ₂ /NaOCl	28.8	7.50	200	679	1.51
7	H ₂ O ₂ /NH ₂ Cl	29.1	7.85	200	697	0.63
8	UV Only	28.9	7.45	200	555	0.41
9	UV/NaOCl	29.4	7.48	190	694	0.95
10	UV/NH ₂ Cl	29.5	7.98	210	710	1.08
11	NaOCl Only	29.7	7.27	190	697	1.01
12	NH ₂ Cl Only	30.0	7.94	210	731	0.90

Appendix C (continued)

Table C 29: Continued

Sample Number	Treatment	ORP, mV	Turbidity, NTU	TOC, mg/L	Hydrogen Sulfide, mg/L S ²⁻	Sulfate, mg/L SO ₄ ²⁻	Hydrogen Peroxide Dose, mg/L H ₂ O ₂
1	Raw Water	-187	0.565	2.83	2.455	29	
2	H ₂ O ₂ Only	-192	0.121	2.71	1.865	30	1.25
3	H ₂ O ₂ /UV	-218	19.8	2.57	1.115	30	1.25
4	H ₂ O ₂ /UV/N H ₂ Cl	-36	26.3	2.67	0	33	1.25
5	H ₂ O ₂ /UV/N aOCl	-27	29	2.76	0	32	1.25
6	H ₂ O ₂ /NaO Cl	543	23	2.66	0	34	1.25
7	H ₂ O ₂ /NH ₂ C I	310	24.6	3.11	0	34	1.25
8	UV Only	-239	11.3	2.49	1.345	35	
9	UV/NaOCl	220	14.9	2.51	0	36	
10	UV/NH ₂ Cl	275	18.5	2.61	0	34	
11	NaOCl Only	295	2.81	2.6	0	36	
12	NH ₂ Cl Only	297	2.03	2.69	0	36	

Appendix C (continued)

Table C 29: Continued

Sample Number	Treatment	Residual Hydrogen Peroxide, mg/L H ₂ O ₂	UV Intensity	Sodium Hypochlorite Dose, mg/L Cl ₂	Residual Total Chlorine, mg/L Cl ₂	Residual Free Chlorine, mg/L Cl ₂
1	Raw Water					
2	H ₂ O ₂ Only	0				
3	H ₂ O ₂ /UV	0	13.1			
4	H ₂ O ₂ /UV/NH ₂ Cl		13.1	22.51	1.0	1.0
5	H ₂ O ₂ /UV/NaOCl		13.1	22.51	1.0	0.5
6	H ₂ O ₂ /NaOCl			22.51	2.8	2.3
7	H ₂ O ₂ /NH ₂ Cl			22.51	4.8	4.2
8	UV Only		13.1			
9	UV/NaOCl		13.1	22.51	1.8	0.4
10	UV/NH ₂ Cl		13.1	22.51	3.6	2.7
11	NaOCl Only			22.51	1.0	0.7
12	NH ₂ Cl Only			22.51	1.9	1.8

Appendix C (continued)

Table C 29: Continued

Sample Number	Treatment	Ammonium Chloride Dose, mg/L NH ₃ -N	Free Ammonia, mg/L NH ₃ -N	Residual Chloramine, mg/L Cl ₂
1	Raw Water			N/A
2	H ₂ O ₂ Only			
3	H ₂ O ₂ /UV			
4	H ₂ O ₂ /UV/NH ₂ Cl	2.63	0.9	0.35
5	H ₂ O ₂ /UV/NaOCl			
6	H ₂ O ₂ /NaOCl			
7	H ₂ O ₂ /NH ₂ Cl	2.63	0.54	4.38
8	UV Only			
9	UV/NaOCl			
10	UV/NH ₂ Cl	2.63	0.05	3.55
11	NaOCl Only			
12	NH ₂ Cl Only	2.63	0.4	1.61

Appendix C (continued)

Table C 30: Field tests to test oxidant combinations at pH 8.2 8/23/2005

Sample Number	Treatment	Temperature, °C	pH	Alkalinity, mg/L CaCO ₃	Conductivity, uS/cm	Dissolved Oxygen, mg/L O ₂
1	Raw Water	26.3	7.41	190	516	0.37
2	H ₂ O ₂ Only	27.0	8.23	220	550	0.53
3	H ₂ O ₂ /UV	27.5	8.25	220	561	0.25
4	H ₂ O ₂ /UV/NH ₂ Cl	28.6	8.81	240	670	0.52
5	H ₂ O ₂ /UV/NaOCl	29.4	8.25	230	703	1.01
6	H ₂ O ₂ /NaOCl	28.6	8.12	230	667	1.01
7	H ₂ O ₂ /NH ₂ Cl	28.9	8.81	230	672	1.23
8	UV Only	28.3	7.93	220	569	0.12
9	UV/NaOCl	29.0	8.10	240	666	0.95
10	UV/NH ₂ Cl	29.0	8.75	240	546	1.35
11	NaOCl Only	27.7	8.15	210	660	0.12
12	NH ₂ Cl Only	27.2	8.85	240	652	0.92

Appendix C (continued)

Table C 30: Continued

Sample Number	Treatment	ORP, mV	Turbidity, NTU	TOC, mg/L	Hydrogen Sulfide, mg/L S ²⁻	Sulfate, mg/L SO ₄ ²⁻	Hydrogen Peroxide Dose, mg/L H ₂ O ₂
1	Raw Water	-225	0.424	5.3	2.5	25	
2	H ₂ O ₂ Only	-254	0.22	3.29	1.71	26	1.19
3	H ₂ O ₂ /UV	-252	0.726	2.8	1.36	27	1.19
4	H ₂ O ₂ /UV/NH ₂ Cl	143	13.9	2.66	0	30	1.19
5	H ₂ O ₂ /UV/NaOCl	558	8.66	3.93	0	30	1.19
6	H ₂ O ₂ /NaOCl	287	6.6	2.58	0	30	1.19
7	H ₂ O ₂ /NH ₂ Cl	207	6.47	2.54	0	33	1.19
8	UV Only	-187	0.64	2.56	1.25	29	
9	UV/NaOCl	406	4.64	2.8	0	33	
10	UV/NH ₂ Cl	54	4.31	2.54	0	33	
11	NaOCl Only	265	5.58	2.66	0	33	
12	NH ₂ Cl Only	184	6.85	2.61	0	33	

Appendix C (continued)

Table C 30: Continued

Sample Number	Treatment	Residual Hydrogen Peroxide, mg/L H ₂ O ₂	UV Intensity	Sodium Hypochlorite Dose, mg/L Cl ₂	Residual Total Chlorine, mg/L Cl ₂	Residual Free Chlorine, mg/L Cl ₂
1	Raw Water					N/A
2	H ₂ O ₂ Only	0				
3	H ₂ O ₂ /UV	0	14.1			
4	H ₂ O ₂ /UV/NH ₂ Cl		14.1	21.59	5.3	3.9
5	H ₂ O ₂ /UV/NaOCl		14.1	21.59	4.9	4.2
6	H ₂ O ₂ /NaOCl			21.59	0.9	0.7
7	H ₂ O ₂ /NH ₂ Cl			21.59	0.9	0.7
8	UV Only		14.1			
9	UV/NaOCl		14.1	21.59	1.5	0.1
10	UV/NH ₂ Cl		14.1	21.59	2.07	0.1
11	NaOCl Only			21.59	0.6	0.1
12	NH ₂ Cl Only			21.59	0.54	0.5

Appendix C (continued)

Table C 30: Continued

Sample Number	Treatment	Ammonium Chloride Dose, mg/L NH ₃ -N	Free Ammonia, mg/L NH ₃ -N	Residual Chloramine, mg/L Cl ₂
1	Raw Water	N/A	N/A	N/A
2	H ₂ O ₂ Only			
3	H ₂ O ₂ /UV			
4	H ₂ O ₂ /UV/NH ₂ Cl	2.15	0.4	4.66
5	H ₂ O ₂ /UV/NaOCl			
6	H ₂ O ₂ /NaOCl			
7	H ₂ O ₂ /NH ₂ Cl	2.15	0.58	0.8
8	UV Only			
9	UV/NaOCl			
10	UV/NH ₂ Cl	2.15	1.04	2.21
11	NaOCl Only			
12	NH ₂ Cl Only	2.15	1.04	0.68

Appendix C (continued)

Table C 31: Field tests to test oxidant combinations at ambient pH 9/5/2005

Sample Number	Treatment	Temperature, °C	pH	Alkalinity, mg/L CaCO ₃	Conductivity, uS/cm	A. Color	T. Color
1	Raw Water	27.1	7.10	190	546	14	14
2	H ₂ O ₂ Only	28.2	7.39	180	537	12	20
3	H ₂ O ₂ /UV	28.5	7.41	190	534	127	38
4	H ₂ O ₂ /UV/NH ₂ Cl	29.8	7.66	200	958	206	52
5	H ₂ O ₂ /UV/NaOCl	29.5	7.60	230	741	187	29
6	H ₂ O ₂ /NaOCl	30.6	7.49	210	772	135	11
7	H ₂ O ₂ /NH ₂ Cl	30.4	7.56	190	757	221	10
8	UV Only	28.6	7.47	180	550	70	41
9	UV/NaOCl	29.3	7.57	230	722	158	22
10	UV/NH ₂ Cl	29.6	7.53	180	740	136	36
11	NaOCl Only	30.2	7.55	220	765	78	35
12	NH ₂ Cl Only	30.5	8.08	200	775	70	31

Appendix C (continued)

Table C 31: Continued

Sample Number	Treatment	ORP, mV	Turbidity, NTU	TOC, mg/L	Sulfide, mg/L S ²⁻	Sulfate, mg/L SO ₄ ²⁻	Hydrogen Peroxide Dose, mg/L H ₂ O ₂
1	Raw Water	-115	0.314	2.55	2.265	31.0	
2	H ₂ O ₂ Only	-192	0.48	4.21	1.675	31.0	1.24
3	H ₂ O ₂ /UV	-233	24	2.71	0.905	28.0	1.24
4	H ₂ O ₂ /UV/N H ₂ Cl	705	33.8	2.62		33.0	1.24
5	H ₂ O ₂ /UV/N aOCl	679	30.3	3.06		34.0	1.24
6	H ₂ O ₂ /NaO Cl	659	12.1	2.72		34.0	1.24
7	H ₂ O ₂ /NH ₂ C l	375	30.6	3.38		32.0	1.24
8	UV Only	-188	16.6	3.03	1.135	30.0	
9	UV/NaOCl	662	19.4	2.70		34.0	
10	UV/NH ₂ Cl	461	20.1	2.76		31.0	
11	NaOCl Only	673	5.77	2.62		34.0	
12	NH ₂ Cl Only	391	2.28	2.71		36.0	

Appendix C (continued)

Table C 31: Continued

Sample Number	Treatment	Residual Hydrogen Peroxide, mg/L H ₂ O ₂	UV Intensity	Sodium Hypochlorite Dose, mg/L Cl ₂	Residual Total Chlorine, mg/L Cl ₂	Residual Free Chlorine, mg/L Cl ₂
1	Raw Water					
2	H ₂ O ₂ Only	0.97				
3	H ₂ O ₂ /UV	0.87	13.7			
4	H ₂ O ₂ /UV/N H ₂ Cl		13.7	20.72	12.8	6.3
5	H ₂ O ₂ /UV/N aOCl		13.7	20.72	8.8	7.8
6	H ₂ O ₂ /NaO Cl			20.72	4.0	3.7
7	H ₂ O ₂ /NH ₂ C I			20.72	5.8	5.4
8	UV Only		13.7			
9	UV/NaOCl		13.7	20.72	6.9	6.9
10	UV/NH ₂ Cl		13.7	20.72	2.5	2.3
11	NaOCl Only			20.72	9.2	8.8
12	NH ₂ Cl Only			20.72	9.2	8.8

Appendix C (continued)

Table C 31: Continued

Sample Number	Treatment	Ammonium Chloride Dose, mg/L NH ₃ -N	Free Ammonia, mg/L NH ₃ -N	Residual Chloramine, mg/L Cl ₂
1	Raw Water			
2	H ₂ O ₂ Only			
3	H ₂ O ₂ /UV			
4	H ₂ O ₂ /UV/NH ₂ Cl	1.83	0.05	6.42
5	H ₂ O ₂ /UV/NaOCl			
6	H ₂ O ₂ /NaOCl			
7	H ₂ O ₂ /NH ₂ Cl	1.83	0.26	4.86
8	UV Only			
9	UV/NaOCl			
10	UV/NH ₂ Cl	1.83	0.05	0.47
11	NaOCl Only			
12	NH ₂ Cl Only	1.83	0.88	9.08

Appendix C (continued)

Table C 32: Field tests to test oxidant combinations at pH 8.2 9/10/2005

Sample Number	Treatment	Temperature, °C	pH	Alkalinity, mg/L CaCO ₃	Conductivity, uS/cm	A. Color	T. Color
1	Raw Water	28.2	7.58	200	532	10	9
2	H ₂ O ₂ Only	29.0	8.32	230	562	14	11
3	H ₂ O ₂ /UV	28.7	8.36	220	550	14	13
4	H ₂ O ₂ /UV/NH ₂ Cl	28.9	8.60	220	650	66	13
5	H ₂ O ₂ /UV/NaOCl	28.2	8.36	300	672	130	14
6	H ₂ O ₂ /NaOCl	28.6	8.35	240	690	116	16
7	H ₂ O ₂ /NH ₂ Cl	29.3	8.53	220	664	106	17
8	UV Only	29.0	8.40	230	564	15	13
9	UV/NaOCl	29.2	8.39	210	692	116	4
10	UV/NH ₂ Cl	28.8	8.56	240	661	120	19
11	NaOCl Only	28.8	8.39	240	688	133	11
12	NH ₂ Cl Only	29.2	8.59	230	682	131	16

Appendix C (continued)

Table C 32: Continued

Sample Number	Treatment	ORP, mV	Turbidity, NTU	TOC, mg/L	Sulfide, mg/L S ²⁻	Sulfate, mg/L SO ₄ ²⁻	Hydrogen Peroxide Dose, mg/L H ₂ O ₂
1	Raw Water	301	0.118	3.00	2.485	36.6	
2	H ₂ O ₂ Only	312	0.211	2.88	1.360	34.7	1.27
3	H ₂ O ₂ /UV	360	0.126	2.63	0.725	34.6	1.27
4	H ₂ O ₂ /UV/NH ₂ Cl	406	18.3	2.66		36.1	1.27
5	H ₂ O ₂ /UV/NaOCl	652	24.7	2.68		36.5	1.27
6	H ₂ O ₂ /NaOCl	609	21.4	2.67		37.3	1.27
7	H ₂ O ₂ /NH ₂ Cl	404	21.5	2.65		37.1	1.27
8	UV Only	330	0.095	2.71	0.985	36.9	
9	UV/NaOCl	238	22.5	2.71		37.2	
10	UV/NH ₂ Cl	353	21.4	2.69		37.8	
11	NaOCl Only	633	23.6	2.70		37.0	
12	NH ₂ Cl Only	396	22.2	2.79		36.1	

Appendix C (continued)

Table C 32: Continued

Sample Number	Treatment	Residual Hydrogen Peroxide, mg/L H ₂ O ₂	UV Intensity	Sodium Hypochlorite Dose, mg/L Cl ₂	Residual Total Chlorine, mg/L Cl ₂	Residual Free Chlorine, mg/L Cl ₂
1	Raw Water					
2	H ₂ O ₂ Only					
3	H ₂ O ₂ /UV	0	11.1			
4	H ₂ O ₂ /UV/NH ₂ Cl	0	11.1	17.59	6.88	0.6
5	H ₂ O ₂ /UV/NaOCl		11.1	17.59	4.0	3.9
6	H ₂ O ₂ /NaOCl			17.59	3.6	3.6
7	H ₂ O ₂ /NH ₂ Cl			17.59	6.64	1.96
8	UV Only		11.1			
9	UV/NaOCl		11.1	17.59	0.4	0.2
10	UV/NH ₂ Cl		11.1	17.59	6.6	0.26
11	NaOCl Only			17.59	3.7	3.6
12	NH ₂ Cl Only			17.59	3.96	2.34

Appendix C (continued)

Table C 32: Continued

Sample Number	Treatment	Ammonium Chloride Dose, mg/L NH ₃ -N	Free Ammonia, mg/L NH ₃ -N	Residual Chloramine, mg/L Cl ₂
1	Raw Water			
2	H ₂ O ₂ Only			
3	H ₂ O ₂ /UV			
4	H ₂ O ₂ /UV/NH ₂ Cl	1.99	0.82	5.9
5	H ₂ O ₂ /UV/NaOCl			
6	H ₂ O ₂ /NaOCl			
7	H ₂ O ₂ /NH ₂ Cl	1.99		
8	UV Only			
9	UV/NaOCl			
10	UV/NH ₂ Cl	1.99		
11	NaOCl Only			
12	NH ₂ Cl Only	1.99		

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Appendix D (continued)

Table D 3: Size distribution of raw water particles 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i , No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.27	0.30	2156	2156	1.1E+03	1.4E+03	7.3E+02	7.2E+03	3.6E+03	3.34
2	2	2.99	2.5	0.99	0.40	0.17	347	347	1.8E+02	1.4E+02	7.1E+01	2.0E+03	1.0E+03	2.54
3	3	3.99	3.5	0.99	0.54	0.12	212	212	1.1E+02	6.1E+01	3.1E+01	1.7E+03	8.7E+02	2.33
4	4	4.99	4.5	0.99	0.65	0.10	89	89	4.5E+01	2.0E+01	1.0E+01	9.2E+02	4.7E+02	1.95
5	5	5.99	5.5	0.99	0.74	0.08	92	92	4.7E+01	1.7E+01	8.5E+00	1.2E+03	6.0E+02	1.97
6	6	6.99	6.5	0.99	0.81	0.07	52	52	2.6E+01	8.0E+00	4.1E+00	7.8E+02	4.0E+02	1.72
7	7	7.99	7.5	0.99	0.87	0.06	48	48	2.4E+01	6.4E+00	3.2E+00	8.3E+02	4.2E+02	1.68
8	8	8.99	8.5	0.99	0.93	0.05	24	24	1.2E+01	2.8E+00	1.4E+00	4.7E+02	2.5E+02	1.38
9	9	9.99	9.5	0.99	0.98	0.05	28	28	1.4E+01	2.9E+00	1.5E+00	6.1E+02	3.1E+02	1.45
10	10	10.99	10.5	0.99	1.02	0.04	8	8	4.1E+00	7.7E-01	3.9E-01	2.0E+02	10.E+01	0.91
11	11	11.99	11.5	0.99	1.06	0.04	7	7	3.6E+00	6.2E-01	3.1E-01	1.9E+02	9.7E+01	0.86
12	12	12.99	12.5	0.99	1.10	0.03	8	8	3.9E+00	6.1E-01	3.1E-01	2.2E+02	1.1E+02	0.88
13	13	13.99	13.5	0.99	1.13	0.03	16	16	7.9E+00	1.2E+00	5.9E-01	4.9E+02	2.5E+02	1.20
14	14	14.99	14.5	0.99	1.16	0.03	8	8	4.1E+00	5.6E-01	2.8E-01	2.7E+02	1.4E+02	0.91
15	15	15.99	15.5	0.99	1.19	0.03	8	8	4.1E+00	5.2E-01	2.6E-01	2.9E+02	1.5E+02	0.91
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.0E+00	

Appendix D (continued)

Table D 4: Size distribution of particles after hydrogen peroxide treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i , No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./m $L-\mu\text{m}$
1	1	1.99	1.5	0.99	0.27	0.30	3204	3204	1.6E+03	2.1E+03	1.1E+03	1.1E+04	5.4E+03	3.5
2	2	2.99	2.5	0.99	0.40	0.17	266	266	1.4E+02	1.1E+02	5.4E+01	1.5E+03	7.8E+02	2.4
3	3	3.99	3.5	0.99	0.54	0.12	161	161	8.2E+01	4.6E+01	2.3E+01	1.3E+03	6.6E+02	2.2
4	4	4.99	4.5	0.99	0.65	0.10	111	111	5.7E+01	2.5E+01	1.3E+01	1.2E+03	5.9E+02	2.2
5	5	5.99	5.5	0.99	0.74	0.08	50	50	2.6E+01	9.1E+00	4.6E+00	6.4E+02	3.3E+02	1.7
6	6	6.99	6.5	0.99	0.81	0.07	111	111	5.6E+01	1.7E+01	8.7E+00	1.7E+03	8.5E+02	2.1
7	7	7.99	7.5	0.99	0.87	0.06	60	60	3.1E+01	8.1E+00	4.1E+00	1.1E+03	5.3E+02	1.8
8	8	8.99	8.5	0.99	0.93	0.05	70	70	3.6E+01	8.3E+00	4.2E+00	1.4E+03	7.1E+02	1.9
9	9	9.99	9.5	0.99	0.98	0.05	9	9	4.9E+00	1.0E+00	5.2E-01	2.1E+02	1.1E+02	9.9
10	10	10.99	10.5	0.99	1.02	0.04	20	20	1.0E+01	1.9E+00	9.8E-01	4.9E+02	2.5E+02	1.3
11	11	11.99	11.5	0.99	1.06	0.04	29	29	1.5E+01	2.6E+00	1.3E+00	7.9E+02	4.0E+02	1.5
12	12	12.99	12.5	0.99	1.10	0.03	19	19	1.0E+01	1.6E+00	8.1E-01	5.8E+02	2.9E+02	1.3
13	13	13.99	13.5	0.99	1.13	0.03	19	19	1.0E+01	1.5E+00	7.5E-01	6.2E+02	3.2E+02	1.3
14	14	14.99	14.5	0.99	1.16	0.03	10	10	5.2E+00	7.0E-01	3.6E-01	3.4E+02	1.7E+02	1.0
15	15	15.99	15.5	0.99	1.19	0.03	10	10	5.2E+00	6.5E-01	3.3E-01	3.7E+02	1.9E+02	1.0
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 5: Size distribution of particles after hydrogen peroxide-UV treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i , No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	264950	264950	1.4E+05	1.8E+05	9.0E+04	8.9E+05	4.5E+05	5.4
2	2	2.99	2.5	0.99	0.40	0.17	28270	28270	1.4E+04	1.1E+04	5.8E+03	1.6E+05	8.2E+04	4.5
3	3	3.99	3.5	0.99	0.54	0.12	23428	23428	1.2E+04	6.7E+03	3.4E+03	1.9E+05	9.6E+04	4.4
4	4	4.99	4.5	0.99	0.65	0.10	4847	4847	2.5E+03	1.1E+03	5.5E+02	5.1E+04	2.6E+04	3.7
5	5	5.99	5.5	0.99	0.74	0.08	7271	7271	3.7E+03	1.3E+03	6.7E+02	9.3E+04	4.7E+04	3.9
6	6	6.99	6.5	0.99	0.81	0.07	9694	9694	4.9E+03	1.5E+03	7.6E+02	1.5E+05	7.4E+04	4.0
7	7	7.99	7.5	0.99	0.87	0.06	4039	4039	2.1E+03	5.4E+02	2.7E+02	7.0E+04	3.6E+04	3.6
8	8	8.99	8.5	0.99	0.93	0.05	6463	6463	3.3E+03	7.6E+02	3.9E+02	1.3E+05	6.5E+04	3.8
9	9	9.99	9.5	0.99	0.98	0.05	3231	3231	1.6E+03	3.4E+02	1.7E+02	7.1E+04	3.6E+04	3.5
10	10	10.99	10.5	0.99	1.02	0.04	1616	1616	8.2E+02	1.5E+02	7.8E+01	3.9E+04	2.0E+04	3.2
11	11	11.99	11.5	0.99	1.06	0.04	807	807	4.1E+02	7.0E+01	3.6E+01	2.2E+04	1.1E+04	2.9
12	12	12.99	12.5	0.99	1.10	0.03	807	807	4.1E+02	6.5E+01	3.3E+01	2.4E+04	1.2E+04	2.9
13	13	13.99	13.5	0.99	1.13	0.03	807	807	4.1E+02	6.0E+01	3.0E+01	2.5E+04	1.3E+04	2.9
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	808	808	4.1E+02	5.2E+01	2.7E+01	2.9E+04	1.5E+04	2.9
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 6: Size distribution of particles after hydrogen peroxide-UV-chlorine-ammonia treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	347045	347045	1.8E+05	2.3E+05	1.2E+05	1.2E+06	5.9E+05	5.5
2	2	2.99	2.5	0.99	0.40	0.17	19733	19733	1.0E+04	7.9E+03	4.0E+03	1.1E+05	5.7E+04	4.3
3	3	3.99	3.5	0.99	0.54	0.12	13159	13159	6.7E+03	3.8E+03	1.9E+03	1.1E+05	5.4E+04	4.1
4	4	4.99	4.5	0.99	0.65	0.10	9047	9047	4.6E+03	2.0E+03	1.0E+03	9.4E+04	4.8E+04	4.0
5	5	5.99	5.5	0.99	0.74	0.08	5757	5757	2.9E+03	1.1E+03	5.3E+02	7.3E+04	3.7E+04	3.8
6	6	6.99	6.5	0.99	0.81	0.07	3289	3289	1.7E+03	5.1E+02	2.6E+02	5.0E+04	2.5E+04	3.5
7	7	7.99	7.5	0.99	0.87	0.06	5757	5757	2.9E+03	7.7E+02	3.9E+02	1.0E+05	5.1E+04	3.8
8	8	8.99	8.5	0.99	0.93	0.05	4112	4112	2.1E+03	4.8E+02	2.5E+02	8.1E+04	4.1E+04	3.6
9	9	9.99	9.5	0.99	0.98	0.05	8224	8224	4.2E+03	8.7E+02	4.4E+02	1.8E+05	9.2E+04	3.9
10	10	10.99	10.5	0.99	1.02	0.04	1645	1645	8.4E+02	1.6E+02	8.0E+01	4.0E+04	2.0E+04	3.2
11	11	11.99	11.5	0.99	1.06	0.04	4111	4111	2.1E+03	3.6E+02	1.8E+02	1.1E+05	5.6E+04	3.6
12	12	12.99	12.5	0.99	1.10	0.03	822	822	4.2E+02	6.6E+01	3.3E+01	2.4E+04	1.2E+04	2.9
13	13	13.99	13.5	0.99	1.13	0.03	822	822	4.2E+02	6.1E+01	3.1E+01	2.6E+04	1.3E+04	2.9
14	14	14.99	14.5	0.99	1.16	0.03	822	822	4.2E+02	5.7E+01	2.9E+01	2.8E+04	1.4E+04	2.9
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 7: Size distribution of particles after hydrogen peroxide-UV-chlorine treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	322674	322674	1.6E+05	2.2E+05	1.1E+05	1.1E+06	5.5E+05	5.5
2	2	2.99	2.5	0.99	0.40	0.17	16789	16789	8.5E+03	6.7E+03	3.4E+03	9.6E+04	4.9E+04	4.2
3	3	3.99	3.5	0.99	0.54	0.12	15595	15595	7.9E+03	4.5E+03	2.3E+03	1.3E+05	6.4E+04	4.2
4	4	4.99	4.5	0.99	0.65	0.10	2399	2399	1.2E+03	5.3E+02	2.7E+02	2.5E+04	1.3E+04	3.4
5	5	5.99	5.5	0.99	0.74	0.08	10797	10797	5.5E+03	2.0E+03	10.0E+02	1.4E+05	7.0E+04	4.0
6	6	6.99	6.5	0.99	0.81	0.07	4798	4798	2.4E+03	7.4E+02	3.8E+02	7.2E+04	3.7E+04	3.7
7	7	7.99	7.5	0.99	0.87	0.06	1199	1199	6.1E+02	1.6E+02	8.1E+01	2.1E+04	1.1E+04	3.1
8	8	8.99	8.5	0.99	0.93	0.05	3599	3599	1.8E+03	4.2E+02	2.2E+02	7.1E+04	3.6E+04	3.6
9	9	9.99	9.5	0.99	0.98	0.05	1199	1199	6.1E+02	1.3E+02	6.4E+01	2.7E+04	1.3E+04	3.1
10	10	10.99	10.5	0.99	1.02	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
11	11	11.99	11.5	0.99	1.06	0.04	1199	1199	6.1E+02	1.0E+02	5.3E+01	3.2E+04	1.6E+04	3.1
12	12	12.99	12.5	0.99	1.10	0.03	1199	1199	6.1E+02	9.6E+01	4.9E+01	3.5E+04	1.8E+04	3.1
13	13	13.99	13.5	0.99	1.13	0.03	1199	1199	6.1E+02	8.9E+01	4.5E+01	3.8E+04	1.9E+04	3.1
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 8: Size distribution of particles after hydrogen peroxide-chlorine treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	296270	296270	1.5E+05	2.0E+05	1.0E+05	9.9E+05	5.0E+05	5.5
2	2	2.99	2.5	0.99	0.40	0.17	18732	18732	9.5E+03	7.5E+03	3.8E+03	1.1E+05	5.5E+04	4.3
3	3	3.99	3.5	0.99	0.54	0.12	8197	8197	4.2E+03	2.4E+03	1.2E+03	6.6E+04	3.4E+04	3.9
4	4	4.99	4.5	0.99	0.65	0.10	10541	10541	5.4E+03	2.3E+03	1.2E+03	1.1E+05	5.6E+04	4.0
5	5	5.99	5.5	0.99	0.74	0.08	4684	4684	2.4E+03	8.5E+02	4.3E+02	6.0E+04	3.0E+04	3.7
6	6	6.99	6.5	0.99	0.81	0.07	1171	1171	6.0E+02	1.8E+02	9.2E+01	1.8E+04	9.0E+03	3.1
7	7	7.99	7.5	0.99	0.87	0.06	3513	3513	1.8E+03	4.7E+02	2.4E+02	6.1E+04	3.1E+04	3.6
8	8	8.99	8.5	0.99	0.93	0.05	4684	4684	2.4E+03	5.5E+02	2.8E+02	9.2E+04	4.7E+04	3.7
9	9	9.99	9.5	0.99	0.98	0.05	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
10	10	10.99	10.5	0.99	1.02	0.04	2342	2342	1.2E+03	2.2E+02	1.1E+02	5.7E+04	2.9E+04	
11	11	11.99	11.5	0.99	1.06	0.04	2341	2341	1.2E+03	2.0E+02	1.0E+02	6.3E+04	3.2E+04	3.4
12	12	12.99	12.5	0.99	1.10	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 9: Size distribution of particles after hydrogen peroxide-chlorine treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	159710	159710	8.1E+04	1.1E+05	5.4E+04	5.3E+05	2.7E+05	5.2
2	2	2.99	2.5	0.99	0.40	0.17	3842	3842	2.0E+03	1.5E+03	7.8E+02	2.2E+04	1.1E+04	3.6
3	3	3.99	3.5	0.99	0.54	0.12	3849	3849	2.0E+03	1.1E+03	5.6E+02	3.1E+04	1.6E+04	3.6
4	4	4.99	4.5	0.99	0.65	0.10	1925	1925	9.8E+02	4.3E+02	2.2E+02	2.0E+04	1.0E+04	3.3
5	5	5.99	5.5	0.99	0.74	0.08	1924	1924	9.8E+02	3.5E+02	1.8E+02	2.5E+04	1.3E+04	3.3
6	6	6.99	6.5	0.99	0.81	0.07	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
7	7	7.99	7.5	0.99	0.87	0.06	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
8	8	8.99	8.5	0.99	0.93	0.05	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
9	9	9.99	9.5	0.99	0.98	0.05	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	!
10	10	10.99	10.5	0.99	1.02	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
11	11	11.99	11.5	0.99	1.06	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
12	12	12.99	12.5	0.99	1.10	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 10: Size distribution of particles after UV treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	734	734	3.7E+02	4.9E+02	2.5E+02	2.5E+03	1.3E+03	2.9
2	2	2.99	2.5	0.99	0.40	0.17	53	53	2.7E+01	2.1E+01	1.1E+01	3.0E+02	1.5E+02	1.7
3	3	3.99	3.5	0.99	0.54	0.12	21	21	1.1E+01	6.0E+00	3.1E+00	1.7E+02	8.6E+01	1.3
4	4	4.99	4.5	0.99	0.65	0.10	7	7	3.5E+00	1.5E+00	7.8E-01	7.2E+01	3.7E+01	0.8
5	5	5.99	5.5	0.99	0.74	0.08	13	13	6.6E+00	2.4E+00	1.2E+00	1.7E+02	8.4E+01	1.1
6	6	6.99	6.5	0.99	0.81	0.07	6	6	2.9E+00	8.9E-01	4.5E-01	8.7E+01	4.4E+01	0.8
7	7	7.99	7.5	0.99	0.87	0.06	3	3	1.4E+00	3.7E-01	1.9E-01	4.8E+01	2.5E+01	0.5
8	8	8.99	8.5	0.99	0.93	0.05	3	3	1.4E+00	3.3E-01	1.7E-01	5.5E+01	2.8E+01	0.5
9	9	9.99	9.5	0.99	0.98	0.05	1	1	4.7E-01	9.8E-02	5.0E-02	2.0E+01	1.0E+01	
10	10	10.99	10.5	0.99	1.02	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
11	11	11.99	11.5	0.99	1.06	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
12	12	12.99	12.5	0.99	1.10	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	1	1	4.7E-01	6.9E-02	3.5E-02	2.9E+01	1.5E+01	
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	1	1	4.7E-01	5.6E-02	2.9E-02	3.6E+01	1.8E+01	

Appendix D (continued)

Table D 11: Size distribution of particles after UV-chlorine treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	204652	1.0E+05	1.4E+05	1.4E+05	7.0E+04	6.9E+05	3.5E+05	5.3
2	2	2.99	2.5	0.99	0.40	0.17	22384	1.1E+04	9.0E+03	9.0E+03	4.6E+03	1.3E+05	6.5E+04	4.4
3	3	3.99	3.5	0.99	0.54	0.12	10659	5.4E+03	3.1E+03	3.1E+03	1.6E+03	8.6E+04	4.4E+04	4.0
4	4	4.99	4.5	0.99	0.65	0.10	12791	6.5E+03	2.9E+03	2.9E+03	1.45E+03	1.3E+05	6.8E+04	4.1
5	5	5.99	5.5	0.99	0.74	0.08	7461	3.8E+03	1.4E+03	1.4E+03	6.9E+02	9.5E+04	4.8E+04	3.9
6	6	6.99	6.5	0.99	0.81	0.07	3198	1.6E+03	4.9E+02	4.9E+02	2.5E+02	4.8E+04	2.5E+04	3.5
7	7	7.99	7.5	0.99	0.87	0.06	3198	1.6E+03	4.3E+02	4.3E+02	2.2E+02	5.6E+04	2.8E+04	3.5
8	8	8.99	8.5	0.99	0.93	0.05	6395	3.3E+03	7.5E+02	7.5E+02	3.8E+02	1.3E+05	6.4E+04	3.8
9	9	9.99	9.5	0.99	0.98	0.05	2132	1.1E+03	2.3E+02	2.3E+02	1.1E+02	4.7E+04	2.4E+04	3.3
10	10	10.99	10.5	0.99	1.02	0.04	2132	1.1E+03	2.0E+02	2.0E+02	1.0E+02	5.2E+04	2.6E+04	
11	11	11.99	11.5	0.99	1.06	0.04	1066	5.4E+02	9.3E+01	9.3E+01	4.7E+01	2.9E+04	1.5E+04	3.0
12	12	12.99	12.5	0.99	1.10	0.03	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
14	14	14.99	14.5	0.99	1.16	0.03	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 12: Size distribution of particles after UV-chlorine-ammonia treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	61959	61959	3.2E+04	4.1E+04	2.1E+04	2.1E+05	1.1E+05	4.8
2	2	2.99	2.5	0.99	0.40	0.17	875	875	4.4E+02	3.5E+02	1.8E+02	5.0E+03	2.5E+03	3.0
3	3	3.99	3.5	0.99	0.54	0.12	623	623	3.2E+02	1.8E+02	9.1E+01	5.0E+03	2.6E+03	2.8
4	4	4.99	4.5	0.99	0.65	0.10	498	498	2.5E+02	1.1E+02	5.6E+01	5.2E+03	2.6E+03	2.7
5	5	5.99	5.5	0.99	0.74	0.08	250	250	1.3E+02	4.6E+01	2.3E+01	3.2E+03	1.6E+03	2.4
6	6	6.99	6.5	0.99	0.81	0.07	249	249	1.3E+02	3.8E+01	2.0E+01	3.8E+03	1.9E+03	2.4
7	7	7.99	7.5	0.99	0.87	0.06	500	500	2.5E+02	6.7E+01	3.4E+01	8.7E+03	4.4E+03	2.7
8	8	8.99	8.5	0.99	0.93	0.05	625	625	3.2E+02	7.4E+01	3.7E+01	1.2E+04	6.3E+03	2.8
9	9	9.99	9.5	0.99	0.98	0.05	375	375	1.9E+02	4.0E+01	2.0E+01	8.3E+03	4.2E+03	2.6
10	10	10.99	10.5	0.99	1.02	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
11	11	11.99	11.5	0.99	1.06	0.04	250	250	1.3E+02	2.2E+01	1.1E+01	6.7E+03	3.4E+03	2.4
12	12	12.99	12.5	0.99	1.10	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	125	125	6.4E+01	9.3E+00	4.7E+00	3.9E+03	2.0E+03	2.1
14	14	14.99	14.5	0.99	1.16	0.03	250	250	1.3E+02	1.7E+01	8.8E+00	8.4E+03	4.3E+03	
15	15	15.99	15.5	0.99	1.19	0.03	250	250	1.3E+02	1.6E+01	8.2E+00	9.0E+03	4.6E+03	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 13: Size distribution of particles after chlorine treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta d_{pi}$ log No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	12054	12054	6.1E+03	8.1E+03	4.1E+03	4.0E+04	2.1E+04	4.1
2	2	2.99	2.5	0.99	0.40	0.17	214	214	1.1E+02	8.6E+01	4.4E+01	1.2E+03	6.2E+02	2.3
3	3	3.99	3.5	0.99	0.54	0.12	51	51	2.6E+01	1.5E+01	7.5E+00	4.2E+02	2.1E+02	1.7
4	4	4.99	4.5	0.99	0.65	0.10	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
5	5	5.99	5.5	0.99	0.74	0.08	107	107	5.5E+01	2.0E+01	9.9E+00	1.4E+03	7.0E+02	2.0
6	6	6.99	6.5	0.99	0.81	0.07	107	107	5.4E+01	1.6E+01	8.3E+00	1.6E+03	8.2E+02	2.0
7	7	7.99	7.5	0.99	0.87	0.06	54	54	2.7E+01	7.2E+00	3.6E+00	9.3E+02	4.7E+02	1.7
8	8	8.99	8.5	0.99	0.93	0.05	54	54	2.7E+01	6.3E+00	3.2E+00	1.1E+03	5.4E+02	1.7
9	9	9.99	9.5	0.99	0.98	0.05	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
10	10	10.99	10.5	0.99	1.02	0.04	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
11	11	11.99	11.5	0.99	1.06	0.04	54	54	2.7E+01	4.7E+00	2.4E+00	1.4E+03	7.3E+02	1.7
12	12	12.99	12.5	0.99	1.10	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
13	13	13.99	13.5	0.99	1.13	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 14: Size distribution of particles after chlorine-ammonia treatment at ambient pH 8/16/2005

Channel No.	Lower Limit d_p μm	Upper Limit d_p μm	Mean Diam. d_{pi} μm	Δd_{pi} μm	$\log d_{pi}$ in μm	$\Delta \log d_{pi}$	Corrected Count	Number conc. ΔN_i No./mL	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$	$\Delta N_i/\Delta d_{pi}$ No./mL- μm	$\Delta V_i/\Delta d_{pi}$ $\mu\text{m}^3/\text{mL}-\mu\text{m}$	$\Delta N_i/\Delta \log d_{pi}$ No./mL	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm
1	1	1.99	1.5	0.99	0.17	0.30	9081	9081	4.6E+03	6.1E+03	3.1E+03	3.0E+04	1.5E+04	4.0
2	2	2.99	2.5	0.99	0.40	0.17	222	222	1.1E+02	8.9E+01	4.5E+01	1.3E+03	6.5E+02	2.4
3	3	3.99	3.5	0.99	0.54	0.12	101	101	5.2E+01	2.9E+01	1.5E+01	8.2E+02	4.2E+02	2.0
4	4	4.99	4.5	0.99	0.65	0.10	28	28	1.4E+01	6.3E+00	3.2E+00	2.9E+02	1.5E+02	1.5
5	5	5.99	5.5	0.99	0.74	0.08	74	74	3.8E+01	1.3E+01	6.8E+00	9.4E+02	4.8E+02	1.9
6	6	6.99	6.5	0.99	0.81	0.07	29	29	1.5E+01	4.4E+00	2.3E+00	4.4E+02	2.2E+02	1.5
7	7	7.99	7.5	0.99	0.87	0.06	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
8	8	8.99	8.5	0.99	0.93	0.05	15	15	7.5E+00	1.7E+00	8.4E-01	2.9E+02	1.5E+02	1.2
9	9	9.99	9.5	0.99	0.98	0.05	74	74	3.8E+01	7.8E+00	4.0E+00	1.6E+03	8.3E+02	1.9
10	10	10.99	10.5	0.99	1.02	0.04	15	15	7.5E+00	1.4E+00	7.2E-01	3.6E+02	1.8E+02	
11	11	11.99	11.5	0.99	1.06	0.04	30	30	1.5E+01	2.6E+00	1.3E+00	7.9E+02	4.0E+02	1.5
12	12	12.99	12.5	0.99	1.10	0.03	30	30	1.5E+01	2.4E+00	1.2E+00	8.6E+02	4.4E+02	1.5
13	13	13.99	13.5	0.99	1.13	0.03	15	15	7.5E+00	1.1E+00	5.6E-01	4.6E+02	2.4E+02	1.2
14	14	14.99	14.5	0.99	1.16	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
15	15	15.99	15.5	0.99	1.19	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	
16	16	16.99	16.5	0.99	1.22	0.03	0	0	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	

Appendix D (continued)

Table D 15: Size distribution of particles at elevated pH 8/23/2005

		Corrected Count for Treatments												
Lower Limit dp um	Upper Limit dp um	Raw Water	Hydrogen Peroxide	Hydrogen Peroxide -UV	Hydrogen Peroxide-UV-Chloramine	Hydrogen Peroxide -UV-Chlorine	Hydrogen Peroxide -UV-Chlorine	Hydrogen Peroxide -Chlorine	Hydrogen Peroxide-Chloramine	UV	UV-Chlorine	UV-Chloramine	Chlorine	Chloramine
1	1.99	3579	3536	1230	5066	18708	2740	6446	13233	31534	16868	1719	3083	
2	2.99	382	249	229	395	1471	289	589	1354	632	466	106	204	
3	3.99	239	158	131	257	276	104	515	1024	505	311	77	89	
4	4.99	111	65	49	83	276	98	230	396	168	249	49	62	
5	5.99	95	19	36	129	735	74	166	396	84	124	14	98	
6	6.99	72	46	42	110	368	86	120	165	211	93	35	27	
7	7.99	24	28	38	55	0	6	83	0	211	155	0	53	
8	8.99	16	19	13	83	92	18	74	66	84	31	7	71	
9	9.99	24	9	13	64	0	25	18	66	84	62	7	9	
10	10.99	8	9	13	55	0	6	74	0	0	31	0	9	
11	11.99	8	9	6	18	0	6	46	66	0	0	7	27	
12	12.99	0	0	6	9	0	0	9	0	0	0	0	0	
13	13.99	0	0	2	9	92	0	0	0	0	0	0	18	
14	14.99	8	0	4	18	0	0	0	0	0	31	0	0	
15	15.99	0	0	9	73	0	18	9	33	0	31	0	18	
16	16.99	0	0	6	28	0	0	0	0	42	0	0	0	

Appendix D (continued)

Table D 16: Size distribution of particles at ambient pH 9/5/2005

		Corrected Count for Treatments											
Lower Limit dp um	Upper Limit dp um	Raw Water	Hydrogen Peroxide	Hydrogen Peroxide -UV	Hydrogen Peroxide-UV-Chloramine	Hydrogen Peroxide -UV-Chlorine	Hydrogen Peroxide -Chlorine	Hydrogen Peroxide-Chloramine	UV	UV-Chlorine	UV-Chloramine	Chlorine	Chloramine
1	1.99	593	6701	8352	184	19623	22225	11100	9864	12843	28232	25353	46300
2	2.99	459	958	793	23	1309	2060	3089	806	917	2992	2187	2004
3	3.99	347	640	243	15	2156	3092	830	1209	459	2995	1537	801
4	4.99	139	292	59	9	1002	1619	361	537	184	2111	1181	401
5	5.99	125	167	120	9	1079	1398	605	739	275	2026	1655	1002
6	6.99	74	157	61	9	1079	1031	365	201	92	1499	887	801
7	7.99	84	83	0	7	462	734	243	336	92	2292	1004	400
8	8.99	50	94	0	3	617	1031	0	269	275	2204	531	400
9	9.99	36	42	60	2	463	589	0	336	0	1675	177	200
10	10.99	40	21	0	5	848	368	0	201	0	1410	0	100
11	11.99	34	35	61	2	617	589	0	134	184	882	58	100
12	12.99	17	35	0	1	231	221	0	0	92	353	0	0
13	13.99	15	30	0	1	231	295	0	201	184	264	59	0
14	14.99	13	7	0	1	0	74	0	67	92	88	59	0
15	15.99	20	5	0	0	308	295	0	0	0	617	0	0
16	16.99	4	0	0	1	77	74	0	0	184	88	0	100

Appendix D (continued)

Table D 17: Size distribution of particles at elevated pH 9/10/2005

		Corrected Count for Treatments									
Lower Limit dp um	Upper Limit dp um	Raw Water	Hydrogen Peroxide	Hydrogen Peroxide-UV	Hydrogen Peroxide-UV-Chloramine	Hydrogen Peroxide-UV-Chlorine	UV-Chloramine	Chlorine	Chloramine		
1	1.99	6265	3680	2564	10260	25895	21651	25575	30285		
2	2.99	797	331	612	144	1827	3474.8	4323.74	2484.66		
3	3.99	658	211	175	72	2108	2806.57	4779.31	1774.76		
4	4.99	312	151	29	72	552	1603.75	2729.22	532.427		
5	5.99	312	301	29	96	281	2004.69	2155.53	532.427		
6	6.99	243	30	29	72	281	1202.82	1594.51	177.476		
7	7.99	35	30	58	24	141	801.877	1809.62	0		
8	8.99	104	91	29	48	422	1069.17	1134.71	354.951		
9	9.99	35	91	0	24	0	267.292	1134.71	0		
10	10.99	0	91	0	0	281	801.877	1138.94	177.476		
11	11.99	35	60	0	0	0	267.292	911.15	177.476		
12	12.99	0	0	0	24	0	0	113.894	0		
13	13.99	0	0	0	0	0	133.646	227.788	0		
14	14.99	0	0	0	24	0	0	227.788	0		
15	15.99	35	0	0	0	141	267.292	569.469	0		
16	16.99	0	0	0	24	0	0	341.681	0		