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OZONE-INDUCED BIODEGRADABILITY OF DISINFECTION BY-PRODUCT PRECURSORS

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ABSTRACT

This research investigated the use of integrated ozone-biofiltration in treating a highly colored groundwater for drinking water purposes. Bench and pilot-scale experiments were conducted to assess the effects of ozone dose, media type, empty bed contact time (EBCT), and backwashing on the removals of dissolved organic carbon (DOC), color, and chlorination Disinfection By-Product (DBP) formation. Distribution system regrowth potential was evaluated using assimilable organic carbon (AOC) and assorted ozonation by-products (OBPs) as indices.

It was determined that the overall removals of color, DOC, and DBP precursors were increased with ozone dose, but possibly at the expense of regrowth potential and bromate formation. Granular activated carbon (GAC) performed superior to anthracite and sand media biofilters in terms of DOC, chlorination DBP formation, and AOC removals. An EBCT beyond 3.5 minutes did not provide much additional removal of the parameters measured, while backwashing had an insignificant effect on biofilter performance. Free chlorine and monochloramine, evaluated as post-disinfectants, exhibited markedly different reactivities with the raw and treated waters in terms of total chlorine demand and DBP formation. An attempt to simulate the DOC removals during larger-scale biofiltration using bench-scale methods did not provide a definable relationship.

This research illustrated that the use of ozone-enhanced biofiltration, as an independent process, is a viable technology for treating surface and groundwaters which possess low turbidity and moderate levels of color.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Introduction

It is well established that the chlorination of organic matter present in all natural waters results in the formation of organic contaminants, referred to as disinfection by-products (DBPs). Since these organic contaminants are potentially harmful to human health, the United States Environmental Protection Agency (USEPA) has, and continues, to promulgate regulations which specify the levels of particular DBPs permissible in drinking water supplies. These regulations represent the impetus behind the development of means in which to minimize the formation and distribution of DBPs during drinking water treatment. The current options available in attenuating DBP formation have been identified as the use of alternative disinfectants to chlorine and/or the removal of the natural organic matter (NOM) precursors prior to chlorination.

Ozone is the most promising alternative to chlorine as the primary microbial disinfectant for drinking water treatment processes. Ozone, however, is very unstable within natural waters, resulting in its inability to maintain a distribution system residual. Thus, the use of a post-disinfectant (i.e., applied at terminus of process train), such as chlorine and/or monochloramine, is required in combination with ozone to provide comprehensive disinfection. Furthermore, ozone has been observed to produced its own inorganic and organic by-product contaminants, some of which are of regulatory concern.

Ozone, as a strong oxidant, reacts readily with the electron-rich, unsaturated bonds which constitute a significant fraction of the NOM present in source waters. These oxidative reactions result in transformations of the NOM, manifested by decreases in color, chlorination

DBP formation, and chlorine demand. In addition, the ozone oxidation of NOM creates compounds, such as small aldehydes and ketoacids, which are more amenable to biodegradation. This enhancement of NOM biodegradability represents potential problems of bacterial regrowth if discharged into the distribution system.

Biofiltration, typically in the form of rapid filtration, is a technology in which biologically active media is employed to consume the biodegradable NOM (BOM) produced upon ozonation. The removal of BOM through biofiltration results in the mitigation of regrowth potential, as well as the removal of compounds which are reactive with chlorine and/or act as DBP precursors.

1.2 Project Objectives

The primary objective for this project was to assess the use of combined ozonation and biofiltration in treating Orange County Groundwater (OCGW), a highly colored groundwater found in southern CA. As a result, the project was expected to provide general insight on ozonation and biofiltration as an integrated technology, representing an alternative to other processes (i.e., membrane filtration and enhanced-coagulation) available in treating source waters which possess low turbidity and excessive quantities of color and organic matter. The project was separated into pilot and bench-scale efforts, each intended to contribute to the understanding of factors influencing the quality of the OCGW when subjected to certain treatment conditions. The following objectives were delineated to achieve the goals of the project:

bench-scale:

- evaluate the effects of ozone dose and biofiltration on the removals of dissolved organic carbon, color, UV_{abs}, chlorination DBP formation, and chlorine demand; determine optimum ozone dose/range to be examined more intensively at the pilot-scale
- evaluate the reactivity between raw OCGW and ozone
- characterize the OCGW organic matter and determine the raw water quality of OCGW as a basis for comparison with other source waters potentially treatable using ozone-enhanced biofiltration

pilot-scale:

- evaluate the effect of ozone dose and biofilter media type on the removals of dissolved organic carbon, color, UV_{abs}, chlorination DBP formation, and chlorine demand; compare color and DBP levels with current and proposed USEPA regulations
- evaluate the production and removal of distribution system regrowth potential
- evaluate the effects of design and operation parameters associated with biofiltration
- assess the use of free chlorine and monochloramine as post-disinfectants
- evaluate the use of bench-scale experiments in predicting larger-scale performance

CHAPTER II

BACKGROUND

2.1 Natural Organic Matter (NOM) and Dissolved Organic Carbon (DOC)

The term NOM refers to the naturally occurring organic material found in all surface and groundwaters. It is a collection of compounds ranging from complex, polyaromatic, high molecular weight molecules to simple amino acids and carbohydrates. NOM is typically quantified by its organic carbon content due to carbon's atomic predominance in the compounds which comprise NOM as well as the availability and feasibility of analytical methods. Specifically, the fraction of the total organic carbon (TOC) which is smaller than 0.45 μm, termed dissolved organic carbon (DOC), is commonly used to approximate the NOM of a given water body.

The DOC content of natural waters has been found to consist of 20 to 80 % hydrophobic acids (humic and fulvic acids) and 5 to 20 % hydrophilic acids, both operationally defined by fractionation techniques using XAD resins of different hydrophobic capacity (Aiken and Cotsaris, 1995). The hydrophobic acids, commonly referred to as humic substances, are highly complex, aromatic compounds, possessing various acidic functional groups, and representing 85 to 100 % of the color exhibited by natural waters (Owen et. al., 1995; Collins et. al., 1986). The hydrophilic acids are not as well defined, but are known to possess a greater density of acidic functional groups than the hydrophobic acids (Aiken et. al., 1992). The remaining portion of the DOC pool is comprised of compounds such as carbohydrates, proteins, and amino acids.

2.2 Disinfection By-Products (DBPs)

DBPs are halogenated organic compounds formed during the chlorination of natural waters. Specifically, DBPs are products of the reaction between chlorine, the primary microbial disinfectant used in the United States, and NOM, in particularly the humic substances fraction (Rook, 1977; Stevens et. al., 1976; Reckhow and Singer, 1990; Reckhow et. al., 1990). The primary DBP compound groups currently quantifiable are trihalomethanes (THMs) and haloacetic acids (HAAs). Due to findings which classify a majority of these compounds as either potential or known carcinogens, the USEPA has regulated the concentrations allowed in drinking water supplies. The current USEPA maximum contaminant level (MCL), the maximum concentration allowed at the consumer's tap, is 100 μg/L for total THMs [= chloroform ($CHCl_3$) + bromodichloromethane ($CHCl_2Br$) + dibromochloromethane ($CHClBr_2$) + bromoform ($CHBr_3$)]. Under a proposed Disinfectant/Disinfection By-products (D/DBP) Rule, Stage I, the MCL for total THMs would be lowered to 80 μg/L and the MCL for five HAAs [= monochloroacetic acid ($CH_2ClCOOH$) + dichloroacetic acid ($CHCl_2COOH$) + trichloroacetic acid (CCl_3COOH) + monobromoacetic acid ($CH_2BrCOOH$) + dibromoacetic acid ($CHBr_2COOH$)] would be set at 60 μg/L. Stage II of the D/DBP Rule would further lower the MCLs for THMs and HAAs to 40 and 30 μg/L, respectively (Pontius, 1996).

2.3 Ozonation

Since the first report on the presence of DBPs in drinking water supplies (Rook, 1974) and the subsequent promulgation of USEPA regulations, extensive effort has been expended to determine means in which to reduce the amount of these compounds formed during drinking water treatment. The primary options to remove DBPs are to use disinfectants alternative to chlorine and/or to remove the NOM precursors (i.e., humic substances) prior to chlorination.

Ozone, an extremely strong oxidant and biocide, is being considered as both an alternative disinfectant as well as a contributor to precursor reduction. Although ozone is an exceptional primary disinfectant (i.e., provides majority of microbial inactivation), its main deficiency as a comprehensive disinfectant is its inability to persist in natural waters due to its instability. Thus, a treatment process using ozone requires the addition of a secondary disinfectant (i.e., post-disinfectant), such as chlorine and/or monochloramine, used at end of the process train to enable the sustenance of a disinfectant residual throughout the distribution system.

As a strong oxidant, ozone readily reacts with NOM, particularly with the electron rich aromatic compounds comprising the humic substances fraction. The oxidation of these compounds involves the cleaving of unsaturated bonds, resulting in a decrease in the color and UV_{abs} attributed to these sites (Miltner et. al., 1992; Tan and Amy, 1991; Volk et. al., 1993). Furthermore, ozone oxidation has been found to reduce the average size (Amy et. al., 1992; Tan and Amy, 1991) and humic content of the DOC (i.e., less compounds adsorbed on XAD-8 resin after ozonation), as well as increase the relative acidity of the NOM compounds (Owen et. al., 1995). These transformations have typically been observed to occur with little (< 10 %) complete mineralization of the DOC to carbon dioxide (CO_2).

As a consequence of ozone's oxidative "dissection" of the complex fraction of the NOM pool, biodegradation of these compounds by microorganisms becomes more favorable. Some of the more smaller and simpler aldehydes (ex., formaldehyde), ketoacids (ex., glyoxylic acid), and carboxylic acids (ex., oxalic acid) have been commonly observed as products of ozonation (Najm and Krasner, 1995; Weinberg et. al., 1993; Carlson et. al., 1996). These compounds, in addition to many others, contribute to the overall enhancement of NOM biodegradability. A number of studies have shown that biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC), indices of DOC biodegradability (Huck, 1990), are

both increased markedly upon the ozonation of source waters (Murphy et. al., 1993; Amy et. al., 1992; Bradford et. al., 1994). This increase in biodegradability, if not attenuated during treatment, can potentially represent problems in terms of bacterial distribution system regrowth (Joret et. al., 1991).

Ozonation of natural waters has been observed to result in changes in the amount of DBPs formed during chlorination. Although there are some results which indicate otherwise, THMs formed during chlorination are generally found to decrease anywhere from 10 to 60 % for waters which have been ozonated (Chang and Singer, 1991; Shukairy et. al., 1994). This occurrence is attributed to conservative transformations of the precursor humic substances, and to a lesser degree, the complete oxidation (i.e., mineralization) of the precursor material. Related to DBP formation, ozonation has been found to affect the chlorine reactivity of the NOM, resulting in reductions of chlorine demand.

Ozone has also been observed to directly form by-products upon reaction with NOM and bromide (Br^-), a common ion present in drinking water supplies. Some of the brominated by-products measured include bromate ion (BrO_3^-), bromoform ($CHBr_3$), bromoacetic acids, and various other organic species (Haag and Hoigne, 1983; Siddiqui and Amy, 1993). Bromate is a suspected carcinogen and is proposed to be regulated under the D/DBP Rule at an MCL of 10 μg/L (Pontius, 1996). Bromoform ($CHBr_3$) and some of the bromoacetic acids are proposed to be regulated as part of the total THMs and five HAAs discussed in section 2.2. In addition to the formation of by-products directly, ozonation followed by chlorination can indirectly shift the speciation of the DBPs toward the heavier, brominated species (Amy et. al., 1991). Furthermore, some of the previously discussed aldehydes (i.e., formaldehyde and acetaldehyde), which are common by-products of ozonation, are suspected health risks and may be regulated upon further investigation (Krasner et. al., 1993).

2.4 Biofiltration

2.4.1 Overview

As discussed in the previous section, biodegradable organic matter (BOM) in drinking water supplies, particularly after ozonation, can be the source for bacterial regrowth in the distribution system. Biofiltration, typically in the form of rapid filtration (i.e., hydraulic loading rates between 2 to 10 gpm/ft^2) through (downward flow) biologically active media (i.e., bacterial biofilm residing on typical filtration media, such as granular activated carbon or sand), is a promising technology capable of removing BOM from ozonated waters. Numerous researches have found that specific compounds formed during ozonation (i.e., ozonation by-products-OBPs), such as some of the aldehydes, ketoacids, and carboxylic acids discussed previously, are readily removed (> 80 %) during biofiltration (Carlson and Amy, 1995; Krasner et. al., 1993). Others have observed that BOM as a composite, measured in terms of AOC and BDOC, is also effectively removed during biofiltration (Servais et. al., 1991; Huck et al., 1994; LeChevalier et. al., 1992).

The net result of increasing BOM during ozonation and then subsequently removing it during biofiltration is the reduction of DOC. As the precursor to chlorination DBP formation, the consequence of DOC removal is the corresponding removal of DBPs. Ozone-enhanced biofiltration has been shown to reduce THM and HAA formation 10 to 50 % beyond the reduction achieved with ozonation alone, as well as 5 to 50% reduction using solely biofiltration (Speitel et. al., 1993; Miltner et. al., 1992; Shukairy et. al., 1995). Some of these studies suggest that the precursors to HAA formation are more amenable to biodegradation than THM precursors. Related to DBP formation, chlorine demand has been found to be removed during biofiltration, attributed to DOC removal as well as to conservative transformations (i.e., incomplete biological oxidation) which alters DOC-chlorine reactivity (Shukairy and Summers, 1992).

2.4.2 Operation and Design Parameters

A few of the operation and design parameters necessary to consider in evaluating a biofiltration process have been recognized as media type, empty bed contact time (EBCT), and backwashing. The three primary media types utilized for biofiltration treatment are sand, anthracite, and granular activated carbon (GAC). Sand and anthracite are considered non-adsorbing, non-porous media, whereas GAC exhibits adsorptive capability and possesses a porous structure, representing a greater surface area relative to the other media types. Previous studies have illustrated that biologically active GAC (BAC) consistently performs better than biologically active sand and/or anthracite, in terms of AOC, THM formation potential, and DOC removals (LeChevallier et. al., 1992; Wang et. al., 1995). The superiority of BAC has speculatively been attributed to the following: 1) bioregeneration, the process in which sorbed compounds are de-sorbed due to complete or partial biodegradation, liberating sites for additional sorption, 2) more surface area relative to other media types, providing more area for bacterial attachment and growth, 3) porous structure protects biofilm from backwash scouring, 4) sorption of oxygen provides oxygen enriched environment which facilitates biodegradation (AWWA Committee Report, 1981).

EBCT is an important design parameter defined by the depth of the media bed divided by the hydraulic loading rate (HLR = flow rate/filter surface area). Previous research conducted by Krasner et. al. (1993) showed that EBCTs as low as 1.4 minutes for GAC biofilters were sufficient in removing the majority of AOC, TOC, and measured aldehydes from ozonated waters. However, as part of the same study, EBCTs of 4.2 minutes for anthracite biofilters were found to be required for effective removal of the aldehydes, glyoxal and methyl glyoxal. Other researches have observed an EBCT of 5.0 minutes for GAC-sand (combination of media) biofilters as providing effective AOC removals (LeChevallier et. al., 1992). Carlson and Amy (1995) determined that greater than 90 % of the total OBP and total

DOC removals were achieved within EBCTs of 2.0 and 3.0 minutes, respectively. They attributed the short EBCT requirements to the fact that measured biomass concentrations predominated at the top portion of the filter.

Backwashing, a necessary operation of rapid filtration, is postulated to have an effect on biofiltration due to scouring perturbations to the biomass and/or biomass inactivation when using post-chlorinated backwash water. Furthermore, biofiltration performance is suspected to deteriorate as the backwashing cycle (i.e., time from backwash to the next backwash) progresses due to particle accumulation resulting in decreases in effective media/water contact time (Carlson et. al., 1996). In a study by Miltner et. al. (1995), it was determined that media biomass concentrations were not affected by backwashing using non-chlorinated water, but were immediately decreased an average of 22 % when backwashed with chlorinated water. It required 40 hours of undisturbed run time for the biomass concentrations to rebound to pre-backwash levels. Correspondingly, removals of measured aldehydes and AOC were negatively affected by the chlorinated backwash, while uninhibited performance was observed for filters backwashed with non-chlorinated waters. Carlson et. al. (1996) found that DOC removals at various times during a filter run were discernibly different only at very low EBCTs (<10 seconds). They postulated that only small losses of biomass occurs during backwashing (non-chlorinated water) relative to the much greater steady-state biomass concentrations present on acclimated media.

2.5 Post-Disinfection

As discussed previously, ozone is an exceptional primary disinfectant, capable of providing the majority of microbial inactivation for a treatment process. However, ozone is an inadequate secondary, or distribution system, disinfectant due to its instability and resulting inability to maintain a required residual. Thus, post-disinfectants, such as chlorine and

chloramines, are required at the terminus of a process train employing ozone-biofiltration in order to provide a disinfectant residual throughout the distribution system. Although chlorine (i.e., free chlorine; HOCl/OCl$^-$) has been the most commonly considered post-disinfectant due to its reliability and effectiveness, other chemicals have been evaluated as alternatives to chlorine in order to circumvent the inherent problems associated with its use (i.e., DBPs). Chloramines, compounds formed during the reaction of free chlorine and ammonia (i.e., combined chlorine), are the most commonly utilized alternative to chlorine post-disinfection. Chloramines, particular in the form of monochloramine (NH_2Cl), have been observed to form significantly fewer DBPs (50 to 95 %) in the presence of NOM than free chlorine (Cowman and Singer, 1996; Amy et. al., 1987; Jacangelo et. al., 1989). Unfortunately, monochloramine is a much weaker oxidant than chlorine, requiring greater than 1000 times the concentration time (C x t; Chick-Watson Law) for inactivation of unattached microorganisms (i.e., microorganisms in solution). However, studies have shown that monochloramine may be more effective in inactivating attached microorganisms (i.e., biofilms) than free chlorine (LeChevallier et. al., 1988), a favorable property for a distribution system disinfectant.

2.6 Orange County Groundwater (OCGW)

The OCGW is a configuration of confined and unconfined aquifers underlying the Santa River Basin in southern California. The combined aquifer system is estimated to possess 6 to 12 million acre-feet of water, corresponding to approximately 30 years of drinking water supply for that region (Tan and Amy, 1991). Difficulty in treating OCGW for drinking water purposes is due to inherent elevated levels of color, TOC, and chlorination DBP formation potential, all attributed to the presence of naturally occurring organic matter. Various studies have evaluated the character of OCGW as well as potential treatment alternatives. Carey (1989) characterized OCGW sampled from numerous well sites

throughout the basin. He found that the humic fraction represented 57 to 94 % (average = 78%) of the DOC (total DOC = 0.3 to 14.4 mg/L; average = 11.8 mg/L) and 86 to 100 % of the color (total color = 5 to 210 cu; average = 64 cu) for the 16 sample locations investigated. He also measured bromide concentrations of 120 to 450 μg/L, post-chlorination THM concentrations of 24 to 328 μg/L, and average apparent molecular weights of 600 to 15,000 daltons. Other researchers have observed similar water quality for the OCGW (Tan and Amy, 1991; Amy et. al., 1992).

Some of the previous attempts to treat OCGW for removal of NOM have focused upon ozonation alone, membrane filtration, enhanced coagulation, and more recently, ozonation combined with biofiltration. Enhanced coagulation has been shown to produce adequate effluent quality, but requires significant coagulant quantities (> 60 mg/L $FeCl_3$), resulting in excessive amounts of sludge (Akiyoshi et. al., 1995; Noble et. al., 1996). Membrane processes have demonstrated effectiveness in terms of DOC, color, and THM formation potential removal (Tan and Amy, 1991), but have been shown to fail in removing AOC levels sufficiently (Noble et. al., 1996). Ozonation alone has been observed to remove 5 to 50% of chlorine THM formation and 50 to 90 % of the color from raw OCGW (Amy et. al., 1992). Limited ozone-biofiltration experimentation, using an economically reasonable ozone dose, suggests that color can potentially be reduced to acceptable levels, but reduction of THMs upon chlorination may be problematic (Akiyoshi et. al., 1995).

CHAPTER III

METHODS/MATERIALS

3.1 General Laboratory Methods

Unless otherwise noted, all glassware used for experimentation and analysis was cleaned using the following procedure: 1) soap rinsed and/or soaked overnight followed by a tap water rinse, 2) acid washed (typically overnight) in 15% (v:v) nitric acid (HNO_3), 3) rinsed with de-ionized (D.I.) water, 4) oven dried at 104 °C. Plastic containers were rinsed several times with soap and tap water, rinsed numerous times with de-ionized (D.I.) water, and air dried. De-ionized (D.I.) and Milli-Q (D.I. water purified additionally with ion exchange resins and granular activated carbon; Millipore Water Purification System, Bedford, MA) waters were used for all experimentation and preparation of reagents.

3.2 Analytical Methods

All analytics were conducted at the University of Colorado (CU)-Boulder, Environmental Engineering Laboratories, unless otherwise noted. All analyses were performed at room temperature (22 ± 2 °C), unless otherwise noted.

3.2.1 Organic Carbon

Dissolved organic carbon (DOC) and total organic carbon (TOC) were both measured using a Sievers Model 800 Total Organic Carbon Analyzer (Seivers Instruments, Boulder, CO) and a Shimadzu TOC-5000 Total Organic Carbon Analyzer (Shimadzu, Columbia, MD). The Shimadzu TOC-5000 utilizes a high temperature (680 °C) furnace and platinum catalyst to combust carbon to CO_2 which is detected by an non-dispersive infrared gas analyzer. Prior

to analysis, samples were manually acidified to pH < 2.0 using hydrochloric acid (HCl), and mechanically sparged of inorganic carbon using hydrocarbon free air. An organic carbon calibration curve was developed for every analysis group using standards of potassium hydrogen phthalate (KHP).

The Sievers Model 800 utilizes an ultraviolet/persulfate combination to oxidize total carbon to CO_2 which is detected using a CO_2 selective membrane and conductivity cell. Inorganic carbon is determined using internal acidification (H_3PO_4) to convert carbonate species to CO_2 which is also detected using a CO_2 selective membrane and conductivity cell. Organic carbon is calculated by taking the difference between the total and inorganic carbon fractions. To better resolve organic carbon measurement, the majority of inorganic carbon was removed from all samples after internal acidification (pH< 2.0) using a Sievers Inorganic Carbon Removal unit (principle: vacuum degassing). The Sievers Model 800 is internally calibrated and does not require external calibration for every sample group. However, KHP standards were run periodically throughout the project to confirm the accuracy of the instrument. The measured and predicted standards were consistently within 1.0 % of one another.

The DOC fraction of the TOC for a given sample was obtained by filtering through a 0.45 μm, hydrophilic, synthetic membrane filter (Millipore, Bedford, MA). Each filter was pre-rinsed with a sufficient volume of Milli-Q water to remove the carbon inherent to the filter membrane. All samples hereafter referred to as being "0.45 μm filtered" were done so using the filter and pre-cleaning procedure discussed above.

3.2.2 UV Absorbance (UV_{abs}) and Color

UV_{abs} was measured at λ = 254 nm using a Shimadzu UV-160A UV-Visible Spectrophotometer (Shimadzu, Columbia, MD) with a quartz cell of path length = 1.0 cm. All UV_{abs} samples were 0.45 μm filtered prior to analysis. Color was measured at λ = 408 nm also using the UV-160A. Platinum cobalt standards were used to develop a calibration curve relating UV_{abs} (@ 408 nm) and color. Apparent color is defined as the color exhibited by unfiltered samples, whereas true color is defined as the color exhibited for 0.45 μm filtered samples.

3.2.3 Trihalomethanes (THMs)

The four THM species, chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHBrCl_2$), and bromoform ($CHBr_3$), were analyzed using a modification of EPA method 551 (Hodgeson and Cohen, 1990). The following procedure was used to extract the THM species from the aqueous phase to a solvent phase which could be analyzed by a gas chromatograph (GC): 1) a 42 mL chlorinated sample was removed from incubation at the designated time (see section 3.4.5), 2) 10 mL was removed from the sample vial and placed in a separate container for chlorine residual measurement (see section 3.2.4), 3) 3 mL of HPLC grade methyl-tert-butyl ether (MTBE) and approximately 4.0 grams of sodium chloride (NaCl) were added to the sample vial, 4) the sample vial was recapped, inverted 30 times, and allowed to set for approximately 10 minutes, 5) approximately 1.5 mL of the THM containing MTBE extract was transferred to a 2 mL GC vial for analysis.

A Hewlett Packard 5890 Series II Gas Chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a Nickel electron capture detector (ECD) and a J & W Scientific DB-1 megabore column (J & W Scientific, Folsom, CA) was used to analyze the MTBE extract.

The GC carrier gas was ultra high purity nitrogen (>99.999%) at a flow rate of 28 cm/min. The injection volume was 1 μL at a temperature of 120 °C (injector temperature). The temperature program consisted of the following: 1) initial temperature of 40 °C held for 3 minutes, 2) 15 °C/min. temperature increase to 63 °C and held for 1.5 minutes, 3) 15 °C/min. temperature increase to 100 °C and held for 1.0 minute, 4) temperature increase to 180 °C and held for 2.0 minutes.

MTBE blanks, which contained a known concentration of $CHCl_3$, were run throughout a given sample run to assess the consistency of GC operation. The average concentration of $CHCl_3$ measured for the MTBE blanks was considered the baseline concentration. Calibration curves for each of the THM species were developed periodically using standards made from a stock solution of 2000 $\mu g/ml_{methanol}$ (Supelco, Bellefonte, PA) and the following procedure: 1) 500 μL of stock solution was added to a given aliquot of methanol and Milli-Q water (it was determined that a 15 % (v:v) methanol solution at 4 °C contained in a sealed, head-space free, 72-mL serum vial were the best conditions to maximize solubility of the THM stock solution), 2) the diluted stock solution was added to Milli-Q contained in volumetric flasks and/or other glass bottles to obtain at least five different concentrations of the THM species within the range of interest, 3) Milli-Q/THM solutions were added to 42 mL EPA vials with PTFE-faced silicone septas + open-top polypropylene caps and extracted/analyzed in duplicate (minimum) as described in the two preceding paragraphs.

3.2.4 Chlorine Residual (free and combined)

All chlorine residual measurements were made using a Hach Colorimeter with Hach reagent packets (Hach, Loveland, CO), utilizing a modified version of Standard Methods 4500-Cl, *N,N*-diethyl-*p*-phenylenediamine (DPD) Colorimeter Method (Standard Methods, 19th

ed., 1995). The sample volume was 10 mL and the measurement wavelength was 528 nm. For the residual associated with chlorination for THM formation (see section 3.4.5), total chlorine (free + combined) concentrations were measured using Hach reagent packets for total chlorine. For the free chlorine decay experiments (see section 5.3), free chlorine was measured using Hach reagent packets for free chlorine. For the combined chlorine decay experiments (see section 5.3), the various chlorine species were determined using the following protocol: 1) 10 mL of sample was added to a measurement cell, 2) a free chorine packet was added to the sample which was immediately measured to obtain the free chlorine concentration, 3) 100 μL of 1.0 g/L potassium iodide (KI) was added to the sample which was immediately measured to obtain the concentration of free chlorine + monochloramine (NH_2Cl) combined, 4) a total chlorine packet was added to the sample and immediately measured to obtain the concentration of free chlorine + monochloramine (NH_2Cl) + all other chorine species (assumed to be predominantly dichloramine-$NHCl_2$) combined, 5) each respective specie comprising the total chlorine concentration was determined by taking the difference of the above measurements.

3.2.5 Dissolved Ozone Residual (bench-scale)

Dissolved ozone in the absence of natural organic matter (NOM) was measured spectrophotometrically using the Shimadzu UV-160A UV-Visible Spectrophotometer (Shimadzu, Columbia, MD) discussed previously. An extinction coefficient of 3100 $M^{-1}cm^{-1}$ at λ = 258 nm was used to relate dissolved ozone concentrations to UV_{abs} (Westerhoff, 1995). Due to the UV_{abs} interference of NOM at λ = 258 nm, dissolved ozone in the presence of NOM was measured using the indigo method (Bader and Hoigne, 1981). Specifically, Hach reagent

ampules for dissolved ozone and a Hach DR2000 Spectrophotometer (Hach, Loveland, CO) were used at a wavelength of 600 nm.

3.2.6 Ozonation By-Products (OBPs)

The OBPs analyzed consisted of four aldehydes: formaldehyde (HCHO), acetaldehyde (CH_3CHO), glyoxal (OHCCHO), and methyl glyoxal (OCH_3CCHO); and three ketoacids: pyruvic (CH_3COCO_2H), glyoxylic ($C_2H_2O_3$), and ketomalonic ($C_3H_2O_5$). Aldehydes were analyzed using a modification of a method developed by Sclimenti et. al. (1990). The following procedure was used to extract the aldehyde species from the aqueous phase to a solvent phase which could be analyzed by a gas chromatograph (GC): 1) 22 mL was removed from 42 mL sample, 2) 1.0 mL of 15 mg/mL o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBOA-HCl) was added to the sample and shaken for 2.0 minutes, 3) the sample was incubated at 45 °C for 1.75 hours, 4) 100 μL of concentrated sulfuric acid (H_2SO_4; quenches PFBOA-HCl) and 4.0 mL of hexane (C_6H_{14}) were added to the sample after being allowed to cool to room temperature, 5) the sample vial was recapped, shaken for approximately 2 minutes, and allowed to set for 5 minutes, 6) approximately 1.5 mL of aldehyde containing hexane extract was transferred to a 2 mL GC vial for analysis.

Ketoacids were analyzed using a modification of a method developed by Xie and Reckhow (1992). The following procedure was used to extract the ketoacid species from the aqueous phase to a solvent phase, as well as to derivatize the compounds, enabling analysis by a gas chromatograph (GC): 1) 22 mL was removed from 42 mL sample, 2) 1.0 mL of 15 mg/mL PFBOA-HCl was added to the sample and shaken for 2.0 minutes, 3) 100 μL of concentrated sulfuric acid (H_2SO_4; quenches PFBOA-HCl) and 4.0 mL of MTBE were added to the sample, 4) the sample vial was recapped, shaken for approximately 2 minutes, and

allowed to then set for 5 minutes, 5) 2.0 mL of ketoacid containing MTBE extract was transferred to a 2.5 mL glass vial, 6) the extract was stored at 4 °C for approximately 20 minutes, 7) 250 µL of diazomethane was added to the extract (diazomethane preparation: using specific diazomethane synthesis reaction vessel, approximately 150 mg of solid methyl-nitro-nitroso guanidine (MNNG) and 0.8 mL of 5.0 N NaOH were reacted to form a gas which was allowed to dissolve into approximately 2.5 mL of MTBE at 4 °C), 8) the extract was allowed to react for 15 minutes at 4 °C followed by 15 minutes at room temperature, 9) approximately 100 mg of silica gel was added to extract (silica quenches excess diazomethane), 10) approximately 1.5 mL of extract was transferred to a 2 mL GC vial for analysis.

A Hewlett Packard 5890 Series II Gas Chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a Nickel electron capture detector (ECD) and a J & W Scientific DB-5 megabore column (J & W Scientific, Folsom, CA) was used for analysis of the aldehyde and ketoacid extracts. Ultra high purity helium (>99.999%) at a flow rate of 2 mL/min was used as the carrier gas while ultra high purity nitrogen (>99.999%) was used as the ECD make-up gas. The injection volume for both aldehydes and ketoacids was 1 µL at a temperature of 180 °C (injector temperature). The temperature program for aldehyde analysis consisted of the following: 1) initial temperature of 50 °C held for 1 minute, 2) 4 °C/min. temperature increase to 186 °C and held for 11.0 minutes, 3) 20 °C/min. temperature increase to 246 °C and held for 2.0 minutes. The temperature program for ketoacid analysis consisted of the following: 1) initial temperature of 50 °C held for 1.0 minute, 2) 4 °C/min. temperature increase to 140 °C and held for 15.0 minutes, 3) 4 °C/min. temperature increase to 185 °C and held for 5.0 min., 4) 35 °C/min temperature increase to 245 °C and held for 2.0 minutes.

Aldehyde and ketoacid calibration curves were developed periodically using diluted solution concentrates and/or solid compounds. Typically, aldehyde and ketoacid 'cocktails' were prepared, consisting of a composite of the various compounds diluted to a given stock concentration. Given volumes of the 'cocktails' were added to Milli-Q contained in volumetric flasks to obtain at least five different concentrations of aldehyde and ketoacid species within the range of interest. Milli-Q/(aldehyde or ketoacid) solutions were added to 42 mL EPA vials with PTFE-faced silicone septas + open-top polypropylene caps and extracted/analyzed in duplicate (minimum) as described in the previous two paragraphs.

3.2.7 Assimilable Organic Carbon (AOC)

AOC was measured at the Irvine Ranch Water District (IRWD) Laboratory using the following modified version of the van der Kooij method (1982): 1) a 500 mL water sample was collected and filtered through a 0.22 μm nylon membrane filter (pre-washed) and placed in a 1000 mL, 'AOC-free' flask (cleaned using acid wash method described by van der Kooij, 1982), 2) the sample was inoculated with 1.0 mL of a *Pseudomonas fluorescens* strain P17 stock to achieve a final concentration of 500 to 1000 CFU/mL and incubated as a stationary culture at room temperature, 3) on days 5, 6, and 7, the sample was diluted with a phosphate buffer and 50 μL was placed on an R_2A plate, 4) plate colonies were counted after 48 hours of incubation at room temperature, 5) the remaining water sample was filtered again (see step 1), placed in new, 'AOC-free' flask, inoculated with 1.0 mL of a *Spirillum* strain NOX stock to obtain a final concentration of 500 to 1000 CFU/mL, and incubated as a stationary culture at room temperature, 6) on days 4, 5, and 6, the sample was diluted with a phosphate buffer and 50 μL was placed on an R_2A colony plate, 7) the plate colonies were counted after 72 hours of incubation at room temperature. The maximum number of colonies recorded during the three

day sampling period for each respective bacteria strain is defined as N_{max} (CFU/mL). The sample AOC concentrations for the associated P17 and NOX strains are calculated by correlating the measured N_{max} to that which was previously determined using pure acetate and pure oxalate [i.e., $AOC_{acetate,P17}$ (μg C equivalents/L) and $AOC_{oxalate,NOX}$ (μg C equivalents/L), respectively]. The total AOC (i.e., AOC_{total} in μg C equivalents/L) is considered $AOC_{acetate,P17} + AOC_{oxalate,NOX}$.

3.2.8 Other Analyses (conducted at CU)

Ion chromatography (IC) was conducted by the Department of Geology at CU. A Dionex Series 4500 i (Dionex, Sunnyvale, CA) was used to analyze bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{-2}), and dibasic phosphate (HPO_4^{-2}) ions. A 2.7 mM Na_2CO_3 / 0.3 mM $NaHCO_3$ eluant was used in conjunction with an Ionpac column (AS-12A) and guard column (AG-12A). All samples were 0.45 μm filtered prior to analysis and multiple standards were run with each sample group to develop respective analyte calibration curves.

Alkalinity measurements were performed on 0.45 μm filtered samples using Standard Methods 2320 A (Standard Methods, 19th ed., 1995). pH was measured using an Orion EA920 pH meter (Orion Research) and glass probe (Corning). The pH meter was calibrated with two standards prior to each analysis. All ammonia (NH_3-N) measurements were made using a Hach DR2000 Spectrophotometer (Hach, Loveland, CO) with ammonium salicylate and sodium molybdate reagent packets. Turbidity was measured using a calibrated Hach 2100A Turbidity Meter (Hach, Loveland, CO).

3.2.9 Other Analyses (conducted at the Irvine Ranch Water District-IRWD)

Color, turbidity, dissolved oxygen (DO), temperature, pH, and dissolved ozone residual measurements were made at the IRWD pilot plant for samples generated during pilot plant experimentation (see section 3.5). Color was measured using a Hewlett Packard 8452A Diode Array Spectrophotometer (Hewlett Packard, Palo Alto, CA) at λ = 408 nm with a quartz cell of path length = 10 cm. Platinum cobalt standards were used to develop a calibration curve relating UV_{abs} (@ 408 nm) and color. Turbidity was measured using a calibrated Hach 2100P Turbidity Meter (Hach, Loveland, CO). DO was measured using a YSI Model 58 Dissolved Oxygen Meter with a YSI 5739 probe (YSI). pH was measured using a calibrated Cole Palmer Chemcadet pH Meter with a glass probe (Cole Palmer). Temperature was measured according to Standard Methods (Standard Methods, 19th ed., 1995). Dissolved ozone was measured according to the indigo method (Bader and Hoigne, 1981) using a Hach 100 Pocket Analyzer (Hach, Loveland, CO) at a wavelength of 600 nm.

Total dissolved manganese (Mn_{total}), total dissolved iron (Fe_{total}), NH_3-N, and total Kjendal Nitrogen (TKN) measurements were conducted at the IRWD Laboratory for samples generated during pilot-plant experimentation (see section 3.5). Fe_{total} and Mn_{total} were both measured using EPA Method 200.8, whereas TKN and NH_3-N were measured using EPA methods 351.2 and 350.3, respectively (EPA Methods, 1992).

Pilot-plant samples were not filtered or prepared in any manner prior to analysis, which was performed immediately after sampling. The preservation and storage of samples analyzed at the IRWD Laboratory is described in section 3.5.1.

3.3 Source Water

The source water used for all bench-scale and pilot-scale experimentation was obtained from an OCGW well located at the Irvine Ranch Water District pilot plant in Santa

Ana, CA. The well, which is part of the Dyer Road Well Field, accessed the two following aquifer regions: a region of high colored water (> 150 cu) located at a depth of ~ 1800 ft., and a region of low colored (<15 cu) water located at a depth of ~700 ft. After review of previous studies using this particular OCGW source, in addition to some preliminary experimentation, it was determined that a 50 cu blend composed of the high and low colored waters was representative of potential waters treatable using an ozone-enhanced biofiltration process. Thus, unless otherwise stated, all experimentation reported hereafter was conducted using the 50 cu blend as the raw water source.

3.4 Bench-Scale Experimentation

All bench-scale experimentation was performed at the University of Colorado (CU)-Boulder, Environmental Engineering Laboratories. All bench-scale experimentation was performed at room temperature (22 ± 2 °C), unless otherwise noted.

3.4.1 Sample Handling/Storage

All raw water samples used for bench-scale experimentation were obtained from the OCGW well located at the Irvine Ranch Water District (IRWD) pilot plant. Raw water samples were shipped overnight to CU and stored (2 week maximum) at 4 °C until experimentation. Unless otherwise stated, all samples generated during bench-scale experimentation were immediately 0.45 μm filtered and stored (72 hr. maximum) at 4 °C until analysis and/or further experimentation.

3.4.2 True Batch Ozonation (Ozone Decay)

True batch ozonation was used for decay experiments by applying a stock solution of dissolved ozone to a raw water sample contained in a batch reactor, proceeded by periodic measurements of dissolved ozone concentration (Westerhoff, 1995). The ozone stock solution was obtained by bubbling gaseous ozone through a coarse, stone diffuser into a 2.0 L glass flask which contained approximately 1500 mL of Milli-Q. The flask and Milli-Q were surrounded by ice and insulated to maintain the lowest temperature possible, and covered to prevent light penetration. Gaseous ozone (~ 5% ozone) was generated using an 0.25 lb/day OREC Model V5 Ozone Generator (OREC, Phoenix, AZ) and ultra high purity oxygen (>99.999%) as the source gas. Prior to entering the Milli-Q, the gaseous ozone was passed through a solution of 60 mM, pH = 6.0 phosphate buffer to strip potential contaminants.

To measure the dissolved ozone concentration of the stock solution, 1.0 mL was removed from the flask using a wide-mouthed (to prevent stripping) glass pipette and added to 2.0 mL of 1.0 N H_3PO_4 (to stabilize ozone decay) contained in a 3 mL quartz cell. The UV_{abs} of the solution was analyzed according to the method described in section 3.2.5.

The batch reactor consisted of a 1000 mL graduated cylinder with a bottom spout for sample collection and a top cover plate to minimize ozone volatilization. After the ozone stock concentration was measured, the appropriate volumes of 0.45 μm filtered raw water sample, phosphate buffer , and ozone-free Milli-Q were determined and added to the reactor in order to obtain the following ultimate solution (i.e., the solution after the addition of ozone stock): DOC = 3.0 mg/L, $[O_3]$ = 125 μM (6.0 mg/L), $[PO_4^{-3}]$ = 0.005 M, [Alkalinity] = variable, and pH = 7.5. The ozone stock solution was then expeditiously added to the buffered and diluted raw water sample, covered with the top plate, and stirred continuously using a magnetic stir bar. The sample was allowed to mix for a minimum of one minute prior to sampling to insure

complete mixing. Dissolved ozone was measured at given time increments according to the methods described in section 3.2.5.

All glassware used in this procedure was rinsed with ozone solution prior to use, satisfying the inherent ozone demand of the glassware. Alkalinity was removed from the raw water by acidifying (pH = 2.0 using HCl) a given sample and helium gas sparging vigorously for approximately two hours. Replication of true batch ozonation experiments was performed by repeating the process described above for a given sample, under identical conditions.

3.4.3 Semi-Batch Ozonation

Semi-batch ozonation was performed using a 2.75 L glass reactor apparatus equipped with a metal impeller and an air-tight, top cover plate. Gaseous ozone was generated using the OREC system described in section 3.4.2, and introduced directly into the reactor through a metal bubble diffuser. Applied ozone dose (mg/L/min) was determined using a modified version of Standard Methods 2350E, the Iodometric Method (Standard Methods, 19th ed., 1995). Sample transferred ozone dose (mg/L) was determined by taking the difference of the applied ozone dose (predetermined for a given application time) and the output ozone dose, which was also measured iodometrically. After discovering that the glass reactor possessed significant ozone demand, a 10 minute ozonation of D.I. water was performed prior to every raw water ozonation to maximize the oxidation of glassware contaminants.

Raw water samples were not filtered, buffered, or adjusted for pH prior to semi-batch ozonation. Ozonated samples used for bench-scale biofiltration experiments (see section 3.4.4) were allowed to set at room temperature for a minimum of two hours (typically overnight) before application to the biofilters, insuring the complete absence of ozone residual. Ozonated samples used strictly for analysis were stored at 4 °C overnight, 0.45 μm filtered, and analyzed immediately.

3.4.4 Biofiltration

The biofiltration system used for bench-scale experimentation, modeled after the original design of Mogren et. al. (1990), consisted of a series of semi-batch, glass reactors (8 total), configured in parallel. Each of the reactors (see Figure 3.1) was comprised of a 500 mL separatory funnel containing approximately 150 mL (bulk volume) of biologically acclimated sand (effective diameter = 0.8 mm) which was supported at the bottom of the reactor by glass wool. The sample water was recirculated through each reactor with the use of an air vacuum pump, which pulled a combination of air and water through a network of plastic (polypropylene), stainless steel, and glass tubing from the bottom exit of the reactor to the top entrance. The vacuum drawn air was ambient air which had been 'scrubbed' through the following system (in order of ambient air to reactor system): a 260 cm^3 granular activated carbon (GAC) filter, a 44 cm^3 GAC filter, a 0.3 μm hepa filter, and a 500 mL gas wash bottle containing Milli-Q. The constant contact of the sample water with the 'scrubbed' air insured aerobic conditions.

A biofilm was initially developed (i.e., biologically acclimated) on identical sand media using two different source waters, Silver Lake/Barker Reservoir (proportions unknown; Boulder, CO) and OCGW, the source for the current study. The intention of using two different source waters was to confirm some of the previous available findings (Mogren et. al., 1990) which suggest that biomass source origin does not influence biofilter performance (in terms of DOC removal) when testing natural waters.

The Silver Lake/Barker Reservoir sand was acclimated by continuously running raw Silver Lake/Barker Reservoir water through approximately 750 mL (bulk volume) of pre-washed (tap water to remove fine material) sand contained in a 1000 mL chromatography column (Spectrum, Los Angeles, CA). The water was introduced into the bottom of the column at a flow rate sufficient to fluidize the bed. The column was backwashed using high

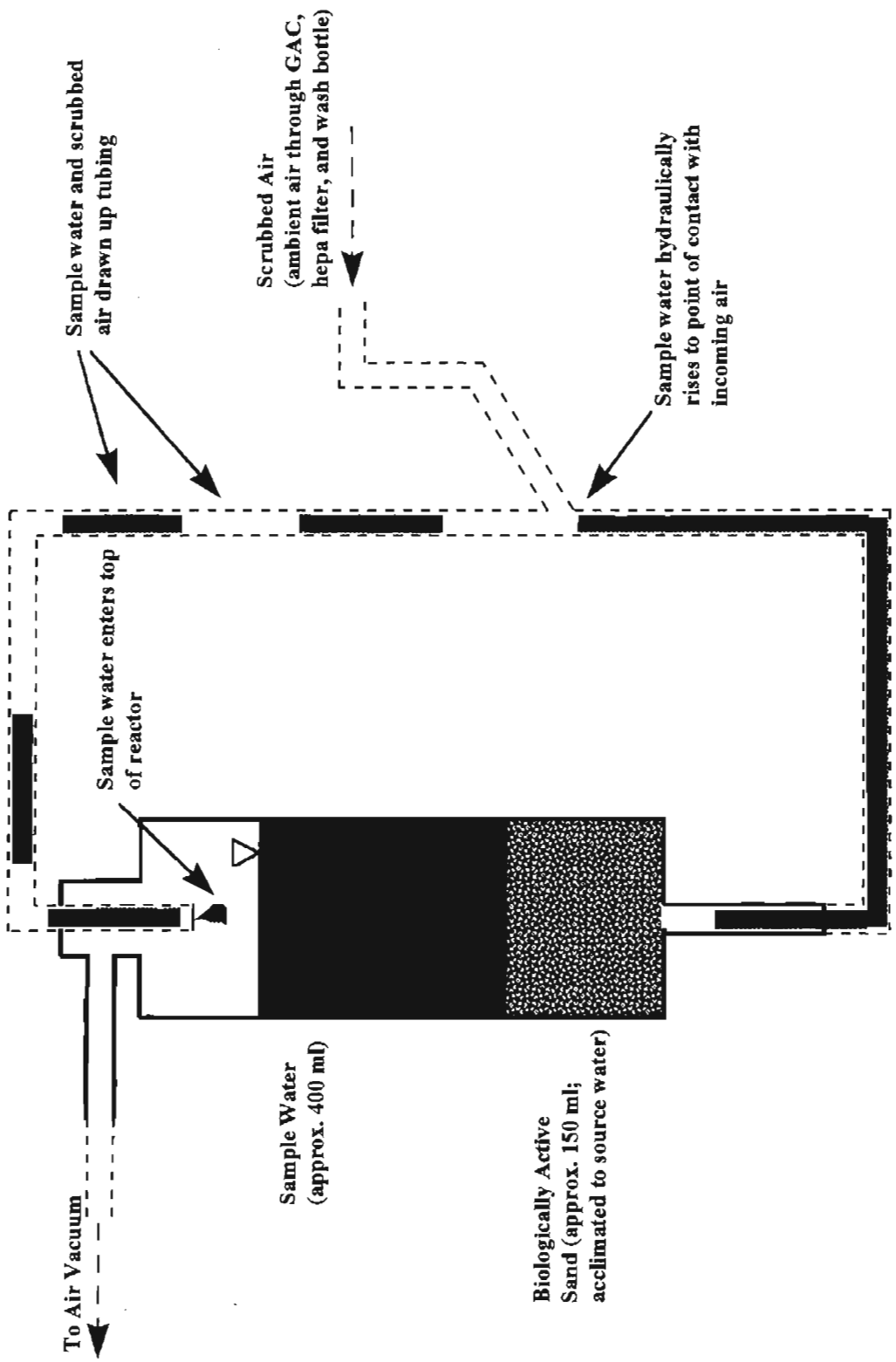

Figure 3.1 Bench-scale biofiltration reactor schematic (typical)

flow rates in the event of media clogging (typically, bi-weekly), and was covered with aluminum foil to prevent light penetration (to inhibit algal growth). After a 30 day acclimation period, the sand was transported to CU, washed gently with Milli-Q and loaded into four of the bench-scale biofilters.

The OCGW sand was acclimated by continuously running the high colored OCGW through approximately 10 L of pre-washed (backwashed several times with low colored OCGW to remove any residual fines) sand contained in an IRWD pilot plant filter column (see section 3.5.2) at a depth of 3.7 ft. Aerated (6.0 - 7.0 mg/L dissolved oxygen) raw water was introduced into the top of the filter at a constant loading rate of 4.0 gpm/ft^2 (~0.35 gpm), and backwashed with low colored OCGW every 24 hours. Upon completion of a 30 day acclimation period, approximately 3000 mL of the media was removed from the column, placed in plastic containers containing the source water, shipped overnight to CU, gently washed with Milli-Q, and loaded into four of the bench-scale biofilters.

After inconclusive preliminary experimentation was conducted on the effect of source water acclimation (DOC removals were too low to reconcile the differences in acclimation source), all eight reactors were subjected to ozonated (transferred dose: 1.0 - 2.0 mg O_3/mg DOC) 50 cu OCGW, using standard operating protocol, for several months prior to all other experiments. Before beginning the other experiments, all reactors were tested for consistency in terms of DOC removal.

Biofiltration experiments were typically conducted for a five day period using a sample recirculation rate of approximately 30 mL/min. The five day reaction period was chosen based upon numerous literature citings which have shown that the majority of biodegradable organic matter removal, under comparable conditions, occurs within this length of time (Murphy et. al., 1993; Mogren et. al., 1990). Prior to each experiment, the reactors were cleaned and prepared using the following procedure: 1) all sample contents were drained

from the bottom of each reactor, 2) the reactors were filled with a saline solution (Milli-Q + NaCl; equivalent conductivity of the source water), which was circulated through the reactors for a minimum of two hours, 3) the saline solution was drained from the bottom of each reactor, as well as from all the reactor tubing, 4) approximately 200 mL of experiment sample water was introduced into each reactor, and subsequently drained. After the above cleaning procedure was performed, approximately 400 ml of sample water was introduced into each of the reactors and operation begun. At the conclusion of the experiment, or at given sampling times, a sample was removed from the bottom (gravimetrically) or from the top (using needle with syringe) of each reactor, 0.45 μm filtered, and stored at 4 °C until analysis or further experimentation.

All samples used for the biofiltration experiments were not filtered and free of any ozone residual. Replication of biofiltration experiments was achieved by using multiple reactors to test a given sample.

3.4.5 Chlorination

Two primary chlorination protocols were used to measure THM formation and chlorine demand of bench and pilot-scale samples. THM Simulated Distribution System (THMSDS), a test evaluating THM formation and chlorine demand commensurate to a distribution system, consisted of the following conditions: Cl_2 dose (mg/L) = f x [DOC] (mg/L) + 7.6 x [NH_3-N] (mg/L) where f = 2.0 for raw water samples and 1.0 for all treated samples, pH = ambient, incubated at 20 °C in the dark, and a reaction time = 24 hours. An f constant of 2.0 was required for all raw water samples in order to maintain a chlorine residual ≥ 0.1 mg/L (minimum accepted) for the duration of the test. Average chlorine residuals for all THMSDS samples analyzed was 0.5 ± 0.2 mg/L.

THM Formation Potential (THMFP), a test evaluating THM formation and chlorine demand in the presence of excess chlorine, consisted of the following conditions: Cl_2 dose (mg/L) = 3.0 x [DOC] (mg/L), pH = ambient, incubated at 20 °C in the dark, and a reaction time = 72 hours. Ammonia breakpoint was not accounted for in this test due to the low ammonia concentrations (< 0.1 mg/L) present in all samples analyzed. Average chlorine residuals for all THMFP samples analyzed was 3.0 ± 0.8 mg/L.

All samples used for chlorination were contained in 42 mL EPA vials, head-space free with PTFE-faced silicone septas + open-top polypropylene caps. Samples associated with bench-scale experimentation were 0.45 μm filtered, whereas samples associated with pilot-scale experimentation were not filtered prior to chlorination. Samples were not adjusted for pH since all sample groups chlorinated exhibited a pH of close to the same value (± 0.2). Samples were not buffered due to the inherent buffering capacity (in the form of alkalinity) of all samples and the observation of negligible pH changes (± 0.1) during chlorination.

Free chlorine stock solutions were prepared using a concentrated sodium hypochlorite (NaOCl) solution and stored at 4 °C in the dark. Free chlorine concentrations of stock solutions were measured prior to use by methods described in section 3.2.4. Combined chlorine was prepared by mixing a free chlorine solution (~ 4.0 mg/L) with a pH = 8.5 - 9.0, buffered (100 mg/L Na_2CO_3) ammonium chloride (NH_4Cl = 0.5 g/L) solution to obtain a Cl/N molar ratio equal to approximately 0.7. The free chlorine was slowly added to the continuously mixed NH_4Cl solution to achieve the maximum monochloramine concentration possible. The various chlorine species were measured using the method described in section 3.2.4. Solutions of > 90% monochloramine were considered acceptable for use in experimentation.

Replication was conducted for chlorination experiments by chlorinating multiple aliquots of the same sample and analyzing all for THMs and chlorine residual.

3.4.6 Characterization

XAD-8 resin (Rohm and Haas, Philadelphia, PA) chromatography was used for fractionating the humic and non-humic DOC of a given sample. The resin used for experimentation was cleaned using a Soxhlet extraction method (Aiken et. al., 1992), in which methanol followed by acetonitrile were each administered for a 48 hour period. Clean resin was rinsed with warm (~ 60 °C) Milli-Q several times to remove residual solvents before being packed into a 9.0 mL chromatography column (Spectrum, Los Angeles, CA), achieving a final bulk volume equal to 8.0 mL of resin. After the resin was packed into the column, the following procedure was used to prepare the resin and fractionate a given sample: 1) Milli-Q was passed (flow rate = 10 to 15 bed volumes/hr.) through the resin for approximately 2 hours before the DOC of the influent and effluent were measured to insure equivalence, 2) the resin was rinsed (flow rate = 10 to 15 bed volumes/hr.) with five bed volumes of 0.1 N sodium hydroxide (NaOH), five bed volumes of Milli-Q, five bed volumes of 0.1 N HCl, and five bed volumes of Milli-Q, in that order, 3) step 2 was repeated before the DOC of the influent and effluent were measured to insure equivalence, 4) the resin was acidified by passing (flow rate = 10 to 15 bed volumes/hr.) five bed volumes of 0.1 N HCl through the column, 5) ~530 mL of pH = 2.0 (HCl acidified), 0.45 μm filtered sample was passed (flow rate = 10 to 15 bed volumes/hr.) through the resin as the column permeate was collected for analysis and the retentate was adsorbed onto the resin, 6) the flow direction was reversed and 5 to 10 bed volumes of 0.1 N NaOH was passed (flow rate = 5 to 7.5 bed volumes/hr.) through the resin as the retentate was de-sorbed and collected for analysis. The sample volume of 530 mL was

calculated using the following equation: $V_e = 2 \times V_o \times (1 + k'_{0.5r})$ where V_e is the sample volume, V_o is the resin volume, and $k'_{0.5r}$ is a resin capacity factor (Leenheer, 1981). A resin capacity factor of 50 was chosen based upon previous investigations (Leenheer, 1981; Aiken et. al., 1992). Upon experiment completion, the DOC of the raw water, resin permeate, and resin retentate (diluted) were analyzed to provide a complete carbon mass balance.

Ultrafiltration was used to characterize a given sample in terms of apparent molecular size (AMS). Amicon YM ultrafilters and 200 mL stirring cells (Amicon, Danvers, MA) were used for all experimentation. Ultrafilters of various pore sizes, previously soaked in Milli-Q for a minimum of 72 hours, were installed in parallel stirring cells, and pressurized to 55 psi using industrial grade nitrogen gas. Before application of the raw water sample, approximately 200 mL of Milli-Q was passed through each of the ultrafilters to insure removal of all residual DOC and verify correct permeation flow rates. Exactly 160 mL of a given sample (pH = 7.0 (HCl acidified), 0.45 μm filtered) was passed through each of the ultrafilters. Approximately 65 mL of the permeate was collected for analysis as approximately 80 mL of the retentate remained in the stirring cell (the first 15 mL of permeate was wasted). Upon completion of the experiment, the DOC of the raw water, permeate from all ultrafilters, and retentate (diluted) from all ultrafilters was analyzed to provide a complete carbon mass balance.

3.5 Pilot-Scale Experimentation

All pilot-scale experimentation was performed at the Irvine Ranch Water District (IRWD) Pilot Plant located in Santa Ana, CA, overlying the Dyer Road Well Field. All pilot-scale experimentation was performed at room temperature (22 ± 2 °C). The sample water was obtained from a well located on site (see section 3.3 for description).

3.5.1 Sample Collection/Handling/Storage

All samples associated with pilot-scale experimentation were collected and shipped overnight to CU and/or transported same day to IRWD laboratories for further experimentation and/or analysis. TKN and NH_3-N samples were preserved (pH < 2.0) with H_2SO_4, and Fe_{total} and Mn_{total} samples were preserved (pH < 2.0) with HNO_3, all during sample collection. Samples shipped overnight to CU were stored in a cooler packed with blue ice to maintain the lowest ambient temperature possible. Upon receipt of samples at CU laboratories, all samples were immediately refrigerated at 4 °C. DOC, UV_{abs}, and OBP samples were analyzed the same day of receipt, whereas samples used for chlorination experiments were stored at 4 °C for 24 to 72 hours. Samples used for bench-scale biofiltration experiments (i.e., kinetic experiments; see section 5.4) were used the same day of receipt. Samples for not aforementioned bench-scale analyses were used immediately or 0.45 μm filtered and stored (72 hr. maximum) at 4 °C. Upon receipt at IRWD laboratories, all samples were immediately refrigerated until analysis. AOC analysis was begun the day of sample receipt, whereas TKN, NH_3-N, Fe_{total}, and Mn_{total} were analyzed within two weeks.

Unless otherwise stated, all samples were collected approximately six hours after filter backwashing. All pilot plant analysis was conducted immediately proceeding sampling.

3.5.2 Process Train

The IRWD pilot plant process train consisted of a blend tank, a conventional counter-current ozone contactor, and three parallel filter columns (see Figure 3.2). The high and low colored waters were accessed from the on-site well and proportioned (~ 25% high and ~ 75% low (v:v)) in the blend tank (140 gallon) to achieve the 50 cu source water. From the blend tank, the source water was introduced to the top of the ozone contactor (diameter = 8 in.,

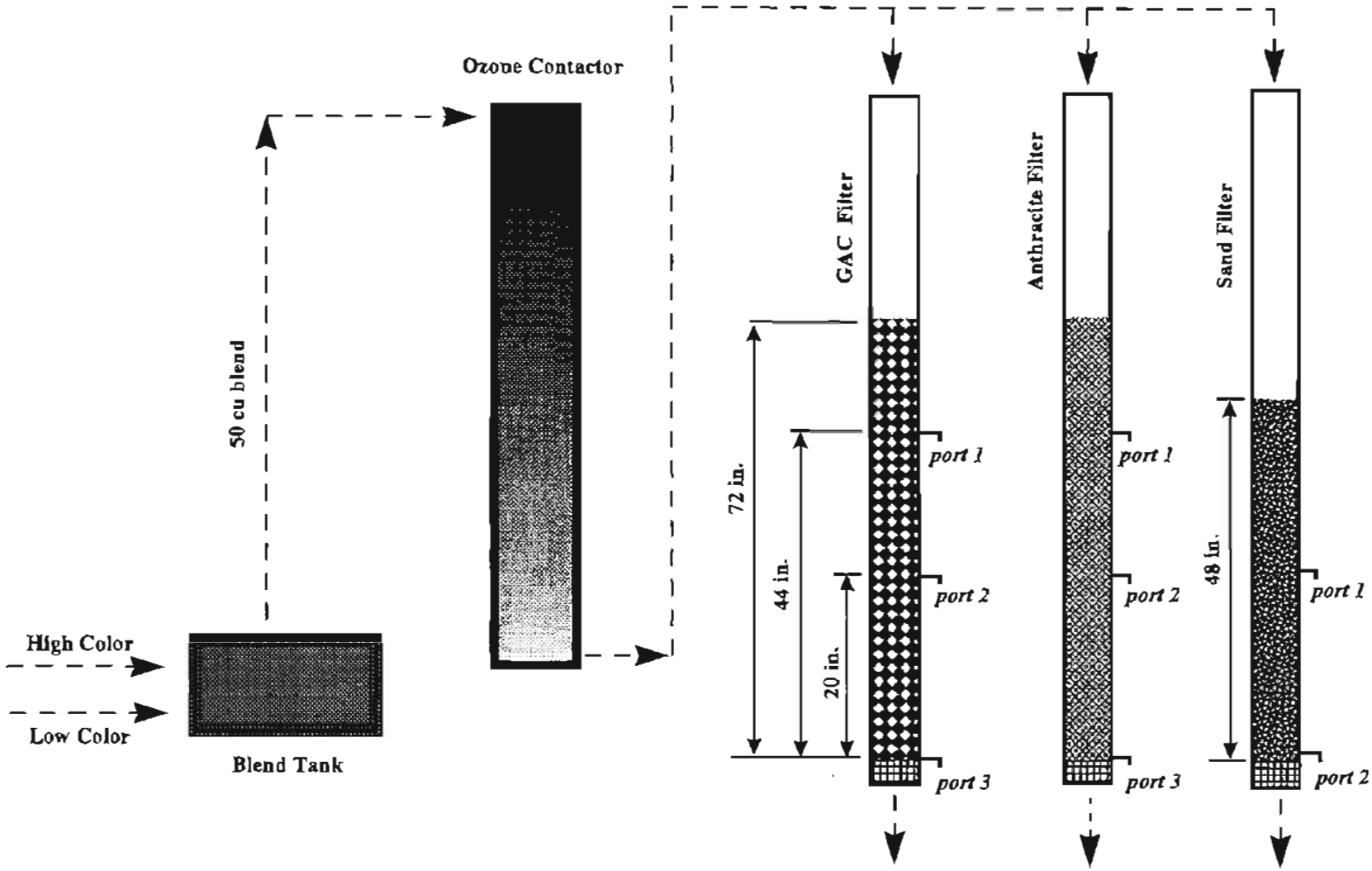

Figure 3.2 IRWD Pilot Plant Schematic

height = 15 ft.) and exited out the bottom. The flow rate through the ozone contactor was approximately 6.5 to 7.0 gpm, corresponding to a contact time of approximately 5.0 minutes. Ozone, generated using a 7 lb/day PCI ozone generator (PCI), was bubbled from the bottom of the contactor through a fine, stone diffuser. Transferred ozone dose was determined by taking the difference between ozone generated (i.e., applied) and the ozone concentration of the off-gas, both monitored mechanically. The ozone effluent was introduced to the three, parallel filter columns (diameter = 4 in., height = 20 ft.) at a constant flow rate of 0.45 ± 0.05 gpm (HLR = 5.0 ± 0.2 gpm/ft^2) which was allowed to decline as media headloss manifests. The three different filter media consisted of GAC (Calgon F-300, effective size = 0.8 to 1.0 mm, depth = 6.0 ft.), anthracite (effective size = 1.6 mm, depth = 6.0 ft.), and sand (effective size = 0.8 mm, depth = 4.0 ft.). The heavier sand media was not as deep as the other two media due to backwashing difficulties. Each column was supported by approximately 10 in. of gravel and contained multiple, vertically distributed sampling ports. All piping used for water transport consisted of PVC. All processes (i.e., flow rates, headloss, etc.) were monitored and controlled by a Wonderware Intouch (version 4) software package connected via a Modicon 984 PLC.

3.5.3 Standard Operation

The pilot plant was operated continuously, seven days a week. During the five day work week, all columns were backwashed when the sand media reached a point of terminal headloss. Terminal headloss being defined as the point in which the water above the media rises to a specific column overflow location (~ 16 ft. above gravel support), and backwashing consisting of 1.0 minute of air scour followed by 15 to 20 minutes of water (low color OCGW) fluidization at a flow rate of 2.5 gpm. Although the anthracite and GAC media consistently

exhibited longer run lengths (i.e., time from backwashing to terminal headloss) than the sand, it was decided to backwash all filters at once to be as operationally consistent as possible. During weekends and holidays, all filter columns were allowed to reach terminal headloss and overflow into the waste stream until the next work day.

At the initiation of pilot plant operation, it was observed that run lengths for all filter media were slowly decreasing with time. After considerable investigation, it was determined that biological growth and/or solids precipitation in the ozone contactor was seemingly accumulating over time and sloughing into the filter columns, causing an accelerated build-up of headloss. To circumvent this problem, a standard practice was initiated entailing the periodic "cleaning" of the ozone contactor, consisting of subjecting the contactor to a high ozone dose for a period of approximately 30 minutes. The filter columns were by-passed during this procedure. The "cleaning" procedure was performed two days a week and always one day prior to an experiment. It was found that consistent and sufficient run lengths were achieved by employing this protocol.

3.5.4 Experimentation

To initiate pilot-scale experimentation, virgin media was placed in each of the respective filter columns, proceeded by a two week application of high colored water (non-ozonated) followed by a two week application of 50 cu water (non-ozonated). Ozonation was then began at the first studied transferred ozone dose of 3.2 mg/L (average dose; ~1.0 mg O_3/mg DOC), and continued for approximately ten weeks until the realization of steady-state. DOC, UV_{abs}, color, pH, D.O., and turbidity of the raw, ozonated effluent , and filter effluents were continuously (typically weekly) monitored during this period to evaluate system dynamics and assess steady-state performance (steady-state was defined as the point in which consistent biofilter removals of the measured parameters was achieved). At steady-state, the cumulative

filter bed volumes for each of the GAC, anthracite, and sand filters was 8439, 11075, and 7388, respectively.

Following two weeks of extensive analyses at the 3.2 mg/L ozone dose, the transferred ozone dose was increased to 4.5 mg/L (average dose; ~ 1.4 mg O_3/mg DOC) for a period of approximately eight weeks. After achieving steady-state, as determined by the continuous monitoring described above, two weeks of extensive analyses were performed. At the 4.5 mg/L steady-state, the cumulative filter bed volumes for the GAC, anthracite, and sand filters was 16205, 19831, and 13518, respectively. The final transferred ozone dose of 6.1 mg/L (average; ~ 1.8 mg O_3/mg DOC) was applied for approximately seven weeks before steady-state was realized and five weeks of extensive analysis ensued. At steady-state, the cumulative filter bed volumes for each of the GAC, anthracite, and sand filters was 24297, 28048, and 19762, respectively.

Replication of pilot-scale experiments was achieved by conducting multiple day sampling/analysis efforts for a given set of operating conditions.

3.6 Data Analysis and Error Calculation

3.6.1 Data generation

To insure that the data generated throughout this project was dependable for use in interpretation, it was attempted to replicate as many of the experiments and/or analyses pragmatically feasible. Typically, all experimentation was triplicated using the approaches described previously for each respective experimental technique. The number of replicates analyzed for a given sample depended on the particular analytical method. The greater inherent variability of a particular method, the more analyses performed for a given sample or sample group.

3.6.2 Error Calculation and Representation

The standard deviation (σ) and coefficient of variance (c.v.) were used to represent and evaluate the error of the data generated. Analytical means and associated error were determined based upon replicate preparation and analysis of a given sample. Experimental means and associated error were determined using the analytical averages of replicate experiments. All graphical data points shown within this document represent the experimental averages. All graphical error bars shown within this document represent $\pm$ the standard deviation of the experimental averages. All graphical lines shown within this document are approximations of the relationships between data points.

The average analytical c.v.'s are provided in Table 3.1 to illustrate the variability inherent of the more frequently measured parameters. As mentioned above, all experimental error is represented in graphical form. For the majority of analytics and experiments performed, a c.v. of < 10 % was achieved and considered acceptable. For the THMFP, THMSDS, and OBPs analyses, a c.v. of < 15 % was achieved and considered acceptable. For the minor number of replicates which exceeded a 15 % c.v., the data was either discarded (if the number of samples analyzed was < 2) or the outlier was removed from the data set (if the number of samples analyzed was $\geq$ 3) and the mean recalculated.

Table 3.1 **Coefficients of variance of most frequently analyzed parameters**

Parameter	c.v., %	n
DOC	1.4	>100
UV_{abs}	<2.0	>25
Color	<2.0	>25
THMFP	2.2	>50
THMSDS	2.2	>50
Cl_2 Residual	<5.0	>25

n: number of samples used to calculate c.v.

CHAPTER IV

RAW WATER QUALITY

As previously discussed (see section 3.3), the source water used for this study was a composition of two different raw waters, a high colored water (~ 25% by volume) and a low colored water (~ 75% by volume), obtained from distinct OCGW aquifer regions located within the Dyer Road Well Field (Santa Ana, CA). Various water quality parameters of the high and low colored waters were monitored periodically throughout the project (see Table 4.1). As shown, both waters were found to possess typical groundwater quality, such as little particulate TOC, low turbidity levels, and high alkalinity. In terms of biodegradability, nitrogen and phosphorous levels for both waters represent potential nutrient limitations. Bromide concentrations for both waters suggest possible formation of bromate upon ozonation and/or brominated chlorination by-products.

The 50 cu water was monitored extensively during the operation period of pilot-plant experimentation (see Table 4.2). As indicated by the σ (i.e., range) values given in Table 4.2, the majority of measured water quality parameters were reasonably consistent throughout the duration of the project. Low dissolved oxygen levels were measured for the raw water, suggesting a requirement of pre-biofilter oxygenation or ozonation to enable the sustenance of oxidative biodegradation. The elevated (compared to most surface waters) temperature levels measured indicate potential facilitation of biodegradation kinetics.

Molecular size and humic/non-humic fractionation was conducted on the raw OCGW. The apparent molecular size (AMS) distribution of the high colored water was determined based upon color, DOC, and UV_{abs} (see Figure 4.1). The humic/non-humic distinction was determined for the raw 50 cu water. It was found that the humic fraction consisted of 51% of

the DOC, 64% of the UV_{abs}, and 54% of the color. This represents slightly lower humic content than that which was previously measured for other OCGW source locations (Carey, 1985).

Table 4.1 **Bench-scale raw water quality of high and low colored OCGW**

Parameter	Units	*Low Color*			*High Color*		
		mean	σ	n	mean	σ	n
TOC	mg/L	0.7	0.5	3	11.0	0.3	3
DOC	mg/L	0.7	0.4	5	10.9	0.6	5
UV_{abs}	cm^{-1}	0.042	0.026	4	0.617	0.006	4
Color	cu	12	7	4	182	10	4
Turbidity	NTU	0.15	0.04	2	0.71	0.15	2
pH	--	8.0	0.5	3	8.5	0.4	3
Alkalinity	mg/L as $CaCO_3$	148	6	2	214	1	2
NH_3-N	mg/L	<0.1	--	1	0.6	--	1
NO_3^-	µg/L	77	103	3	26	5	2
NO_2^-	µg/L	<25	--	3	<25	--	3
SO_4^{-2}	mg/L	50	10	3	26	14	3
HPO_4^{-2}	µg/L	46	43	2	83	15	2
Br^-	µg/L	58	10	3	162	19	3

n: number of independent occasions of sampling and analysis
<: below given detection limit

Table 4.2 **Pilot-scale raw water quality of 50 cu OCGW**

Parameter	Units	mean	σ	n
DOC	mg/L	3.3	0.4	42
UV_{abs}	cm^{-1}	0.170	0.018	39
Color	cu	50	7	49
Turbidity	NTU	0.51	0.09	49
pH	--	8.2	0.2	49
Dissolved O_2	mg/L	1.9	0.6	49
Temperature	°C	29	1	49

n: number of independent occasions of sampling and analysis

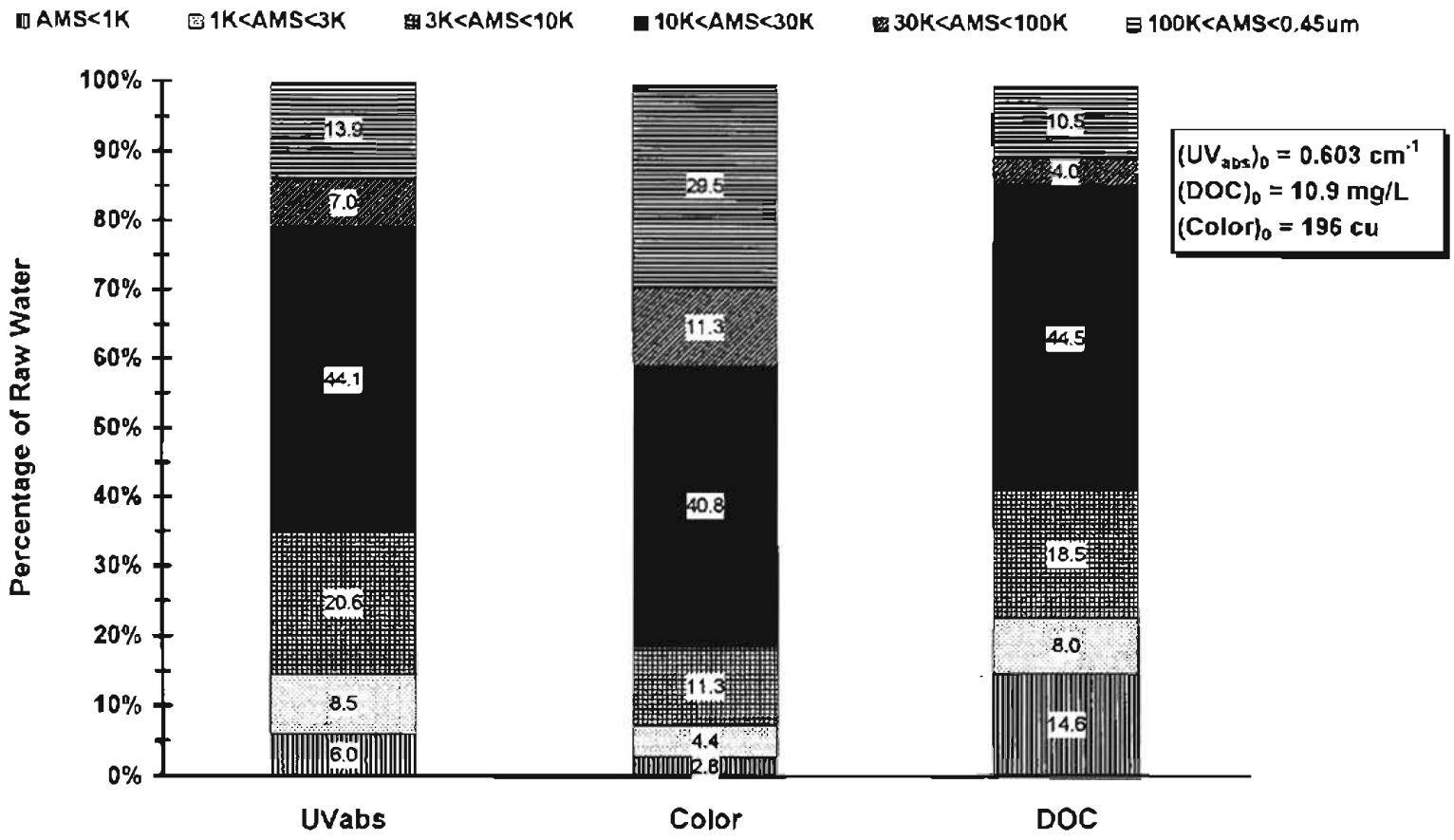

Figure 4.1 Apparent molecular size (AMS) distribution of color, UV_{abs}, and dissolved organic carbon (DOC) for raw high colored OCGW

CHAPTER V

RESULTS/DISCUSSION

5.1 Bench-scale

5.1.1 Ozone Reactivity

The ozone reactivity of the raw OCGW was evaluated by the development of ozone decay relationships (i.e., curves), which enabled the derivation of associated rate constants. Since alkalinity (i.e., bicarbonate) has been shown to retard the decomposition of ozone (Reckhow et. al., 1986), ozone decay for the raw OCGW was evaluated with and without alkalinity in order to differentiate between the ozone reactivity attributed to the composite water and the ozone reactivity attributed solely to the organic matter (see Figure 5.1). The presence of alkalinity was observed to slightly stabilize ozone decomposition within the raw OCGW. However, even in the presence of alkalinity, the reactivity of ozone with the OCGW was observed to be both rapid and extensive. Milli-Q (DOC < 0.1 mg/L) decay curves are also provided to illustrate ozone decay in the absence of organic matter, as well as to verify the consistency of methods used in this study with methods previously developed (Westerhoff, 1995).

Although ozone decay is a postulated first-order (pseudo) process, it is difficult to model the initial decay (t_0 to t_1) as such due to experimental limitations (Westerhoff, 1995). Therefore, two distinct rate constants were used to model ozone decay, a pseudo zero-order ($\Delta_{0\text{-}1}$) for t_0 to t_1 (0.0 to 1.0 minute), and a pseudo first-order (k_1) for $t \geq t_1$ ($t \geq 1.0$ minute). The respective rate constants for the OCGW are presented in Table 5.1, compared with constants previously determined (Westerhoff, 1995) for Suwannee River humic acid (SRH) and Suwannee River fulvic acid (SWF) isolates. The ozone reactivity of the OCGW, even in

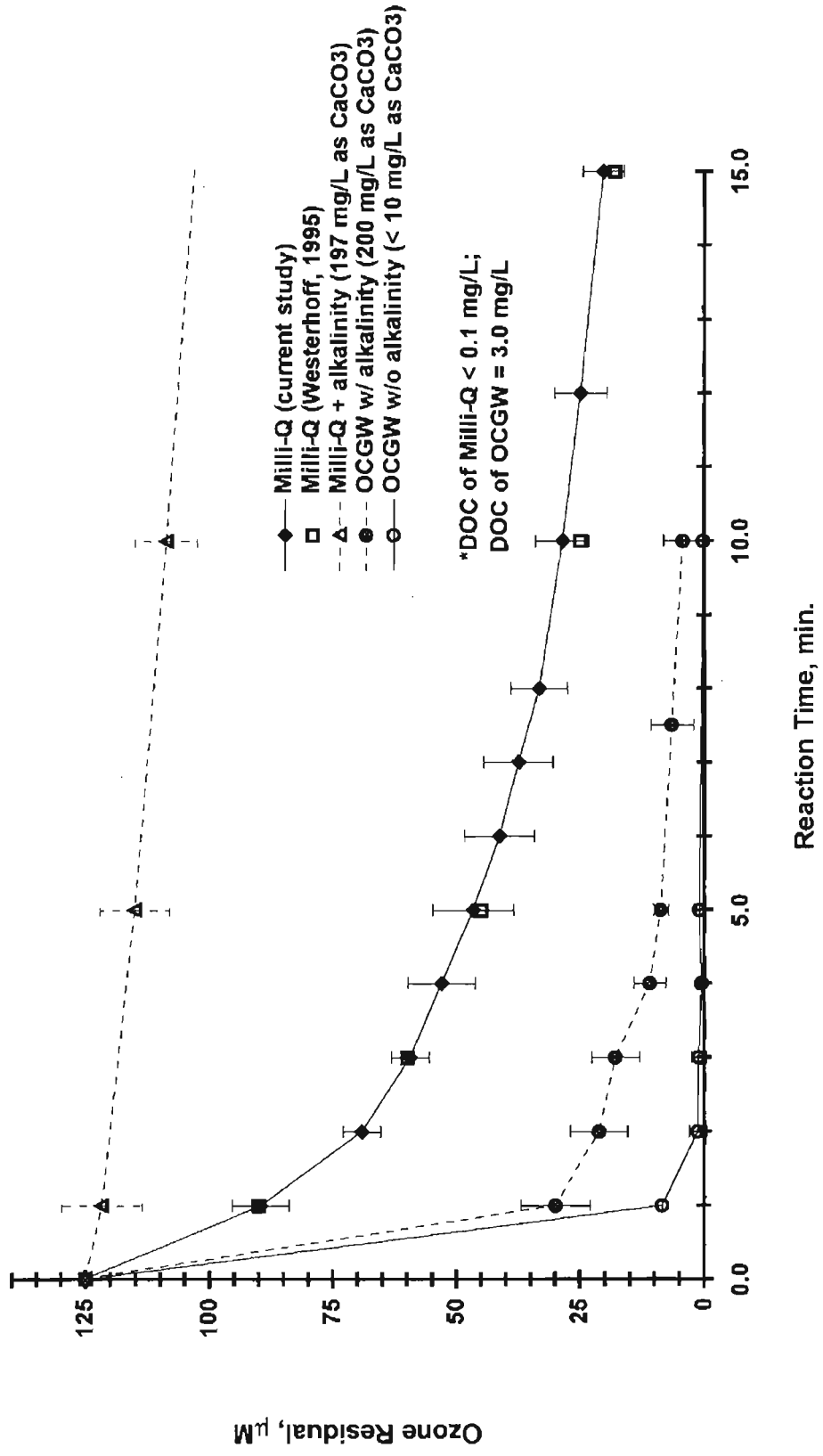

Figure 5.1. Ozone decay within Milli-Q and raw OCGW with and without alkalinity

the presence of alkalinity, was found comparable to that of the humic (humic and fulvic acids) isolates, which represent the most oxidant reactive fraction of the organic matter pool. This suggests that the majority of the OCGW organic matter is considerably reactive with ozone, presumably due to its aromatic and humic character.

Table 5.1 **Ozone decay rate constants for raw OCGW, Milli-Q, and Suwannee River humic (SRH) and fulvic (SRF) acid isolates [DOC =3.0 mg/L; pH =7.5, $(O_3)_0$ =125 μM]**

Source	$\Delta_{0,1}$ ($x10^5$ M)	k_1 ($x10^2$ sec^{-1})	r^2 (for k_1)
Milli-Q	3.53	1.24	0.93
Milli-Q*	3.27	1.14	0.92
OCGW (w/ alk.)	9.51	4.58	0.99
OCGW (w/o alk.)	11.7	t.r.	--
SRF*	8.38	9.67	0.96
SRH*	10.6	t.r	--

*: previous findings (Westerhoff, 1995); experimental conditions identical to current study
t.r.: reaction too rapid to calculate k_1 rate constant
alk: alkalinity
Milli-Q: DOC < 0.1 mg/L

5.1.2 Effect of Ozonation and Biofiltration on the Removal of Color, UV_{abs}, DOC, THMFP, and Chlorine Demand

Five day bench-scale biofiltration experiments were conducted to measure the removal of various raw water quality parameters as a function of transferred ozone dose. The removal of color and UV_{abs} was evaluated to determine how the compounds/moieties which cause these physical attributes are affected by ozonation and biofiltration (see Figures 5.2 and 5.3). As illustrated in Figure 5.2, greater than 90% of the total color removal achieved with the ozone doses considered was accomplished with 2.0 mg O_3/mg DOC (i.e., 2:1). Little additional total color removal was realized at ozone doses greater than 2:1, indicating that the majority of the interactions between ozone and the color causing compounds/moieties occurs within the 0 to 2:1 region. Furthermore, ozonation was found to be the treatment application which provided

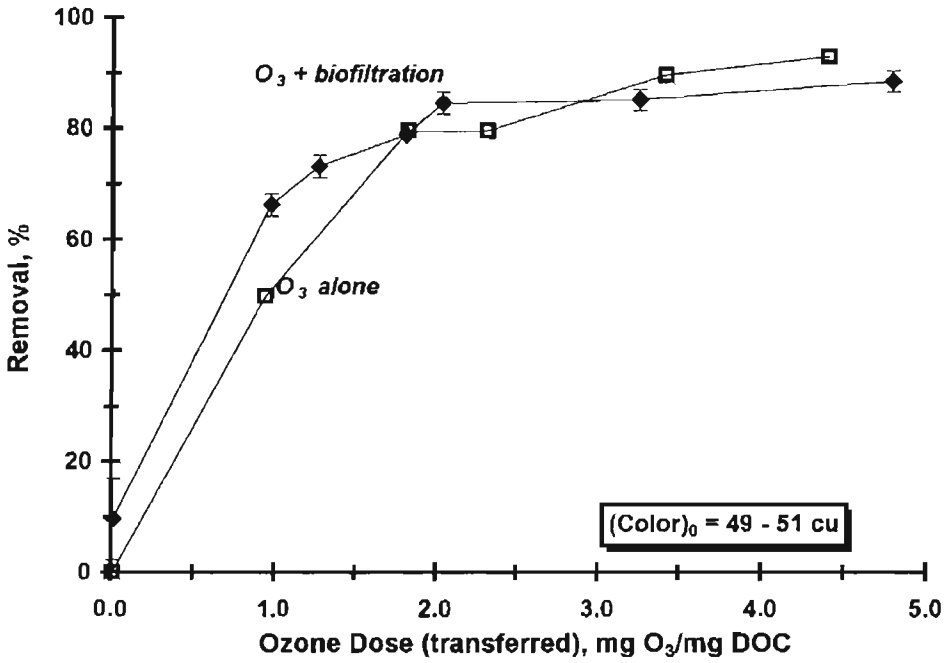

Figure 5.2 Effect of bench-scale ozonation and biofiltration (5-day) on the removal of true color

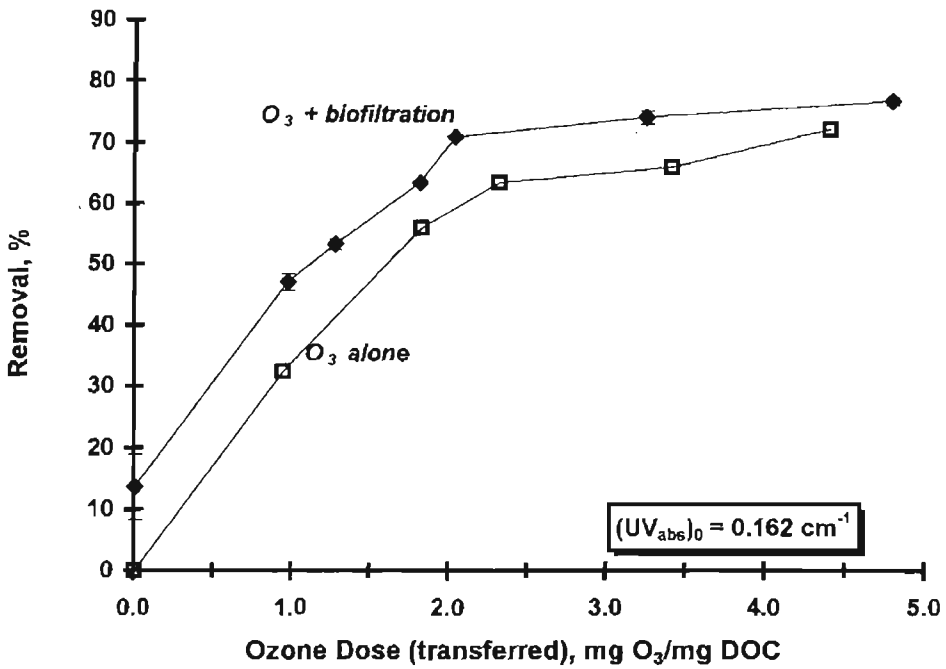

Figure 5.3 Effect of bench-scale ozonation and biofiltration (5-day) on the removal of UV_{abs}

predominant color removal, suggesting that the color causing compounds are refractory to biodegradation and/or are not amenable to removal by other potential biofiltration mechanisms (i.e., biosorption). The removal of UV_{abs} with ozone dose followed a trend similar to that for color removal, with the following exceptions: 1) UV_{abs} removal using ozone alone was not as significant as color removal, suggesting ozone reactivity disparities between color causing and UV_{abs} causing compounds/moieties, 2) biofiltration provided consistent removal of UV_{abs} throughout the entire ozone dose range evaluated, suggesting that the UV_{abs} causing compounds are slightly amenable to biodegradation and/or other removal mechanisms (i.e., biosorption).

Ozone was found to significantly enhance the amount of DOC which is removed during biofiltration, particularly within the 0 to 2:1 range of transferred ozone doses (see Figure 5.4). The trend of increased removal versus ozone dose was similar to the trends shown previously for UV_{abs} and color, suggesting that oxidation of the color and UV_{abs} causing compounds/moieties results in the formation of compounds more removable through biofiltration. Minor (< 8 %) DOC removals were achieved with ozonation alone, indicating that little mineralization of the DOC (i.e., complete conversion to CO_2) occurred, even at the higher ozone doses.

The effect of ozonation and biofiltration on DBP precursors was evaluated using THMFP as a surrogate parameter (see Figure 5.5). It was found that ozonation provided the majority of THMFP removal, even though little actual DOC removal (i.e., mineralization) occurred. This indicates that transformation, not complete removal, of the THM precursors represents the predominant mechanism in attenuating THMFP. Furthermore, the biofiltration removal of THM precursors, a fraction of the entire DOC pool, was not as significant as the removal of DOC, as a composite. This suggests that biofiltration, although potentially removing a portion of the precursor material, preferentially removes the compounds which do

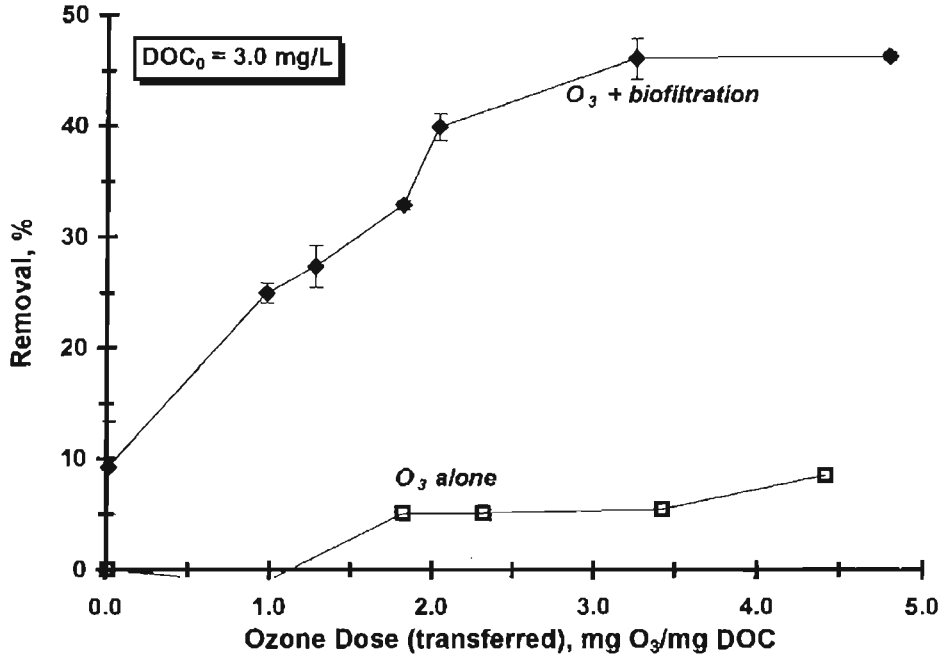

Figure 5.4 Effect of bench-scale ozonation and biofiltration (5-day) on the removal of dissolved organic carbon (DOC)

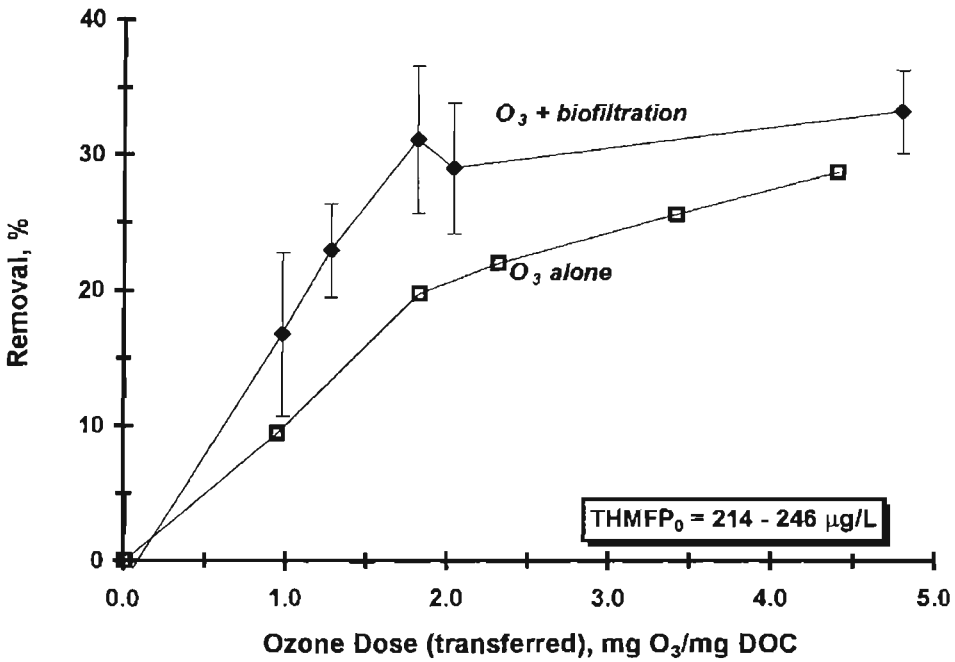

Figure 5.5 Effect of bench-scale ozonation and biofiltration (5-day) on the removal of THM formation potential (THMFP)

not form THMs upon chlorination. The normalization of THMFP to DOC (i.e., specific THMFP), an index of the THM forming properties of the organic matter, further illustrates the observations discussed above (see Figure 5.6).

The 72-hour chlorine demand associated with the THMFP experiments was also monitored (see Figure 5.7). Although ozonation alone did remove some chlorine demand, the combination of ozone and biofiltration represented the treatment process most effective in chlorine demand reduction. Interestingly, the ozone-enhanced biofiltration removals of DOC, the primary sink for chlorine, were significantly less than the corresponding removals of chlorine demand. This observation, best illustrated using specific chlorine demand (i.e., chlorine demand normalized to DOC), infers that possible conservative transformations of the DOC occur during biofiltration which alters chlorine reactivity (see Figure 5.6).

For illustration and clarification purposes, a composite of all the relationships discussed in this section, excluding color and UV_{abs}, is provided in Figure 5.8.

5.2 Pilot-scale

5.2.1 Effect of Ozone Dose and Biofilter Media Type on the Removal of Color, UV_{abs}, DOC, THMFP, THMSDS, and Chlorine Demand

Based upon the bench-scale results discussed in section 5.1, in addition to economic considerations, pilot-scale steady-state experimentation focused upon three ozone doses (transferred) within the range of 1:1 to 2:1 mg O_3/mg DOC (~3.0 to 6.0 mgO_3/L). The removal of various raw water quality parameters was measured as a function of ozone dose and biofilter media type. Similar to bench-scale experimentation, the removals of color and UV_{abs} were evaluated to determine how the compounds/moieties which cause these physical attributes are affected by ozone dose and biofilter media type (see Figures 5.9 and 5.10). Color was evaluated to also determine the ozone dose required to produce an effluent quality of

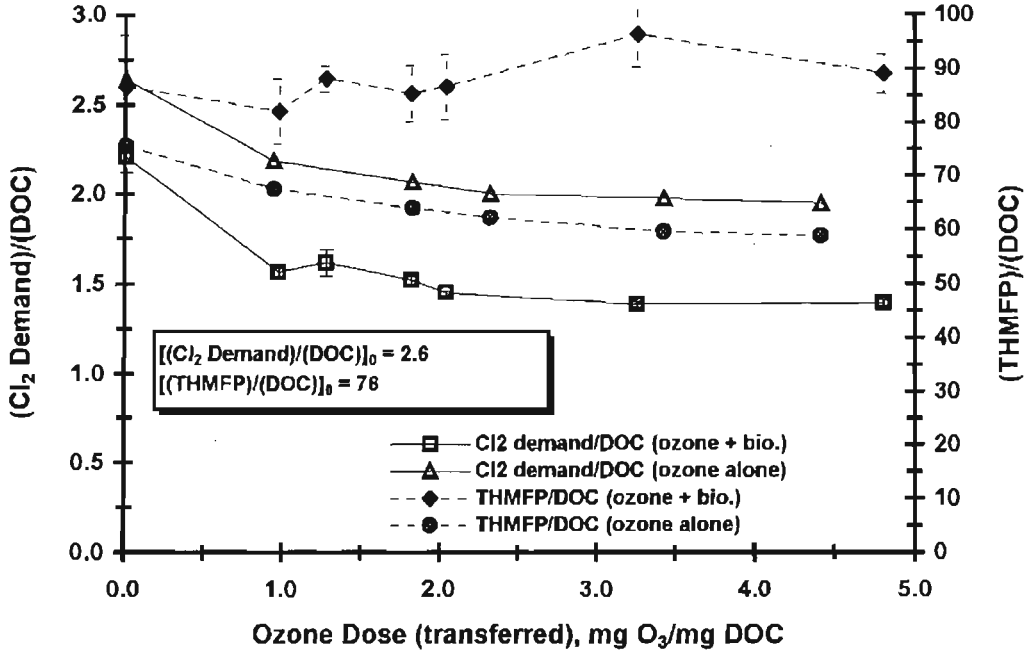

Figure 5.6 Effect of bench-scale ozonation and biofiltration (5-day) on specific chlorine demand (Cl_2 demand/DOC) and specific THMFP (THMFP/DOC)

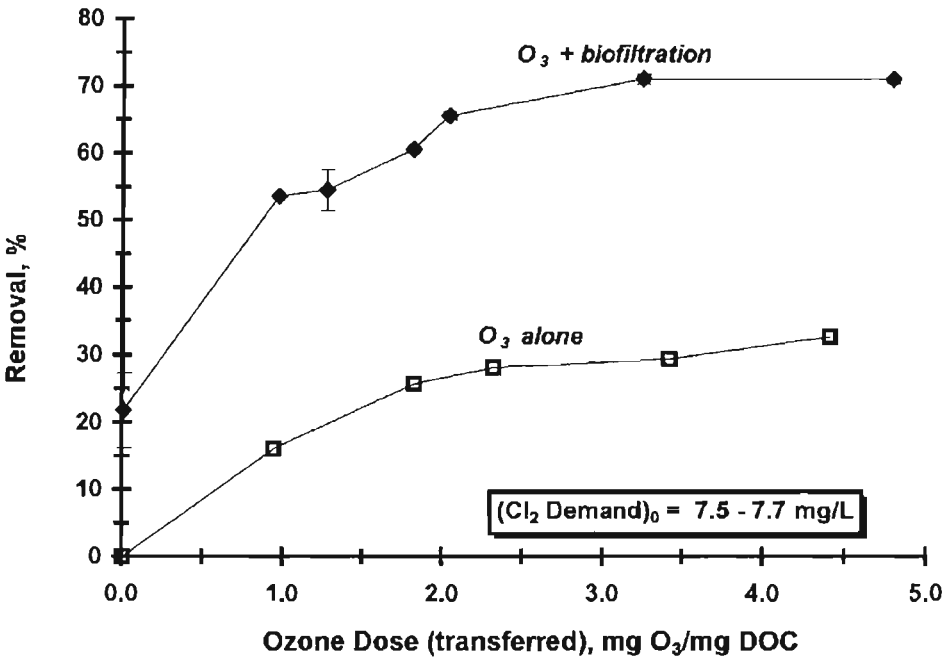

Figure 5.7 Effect of bench-scale ozonation and biofiltration (5-day) on the removal of chlorine demand (as total chlorine)

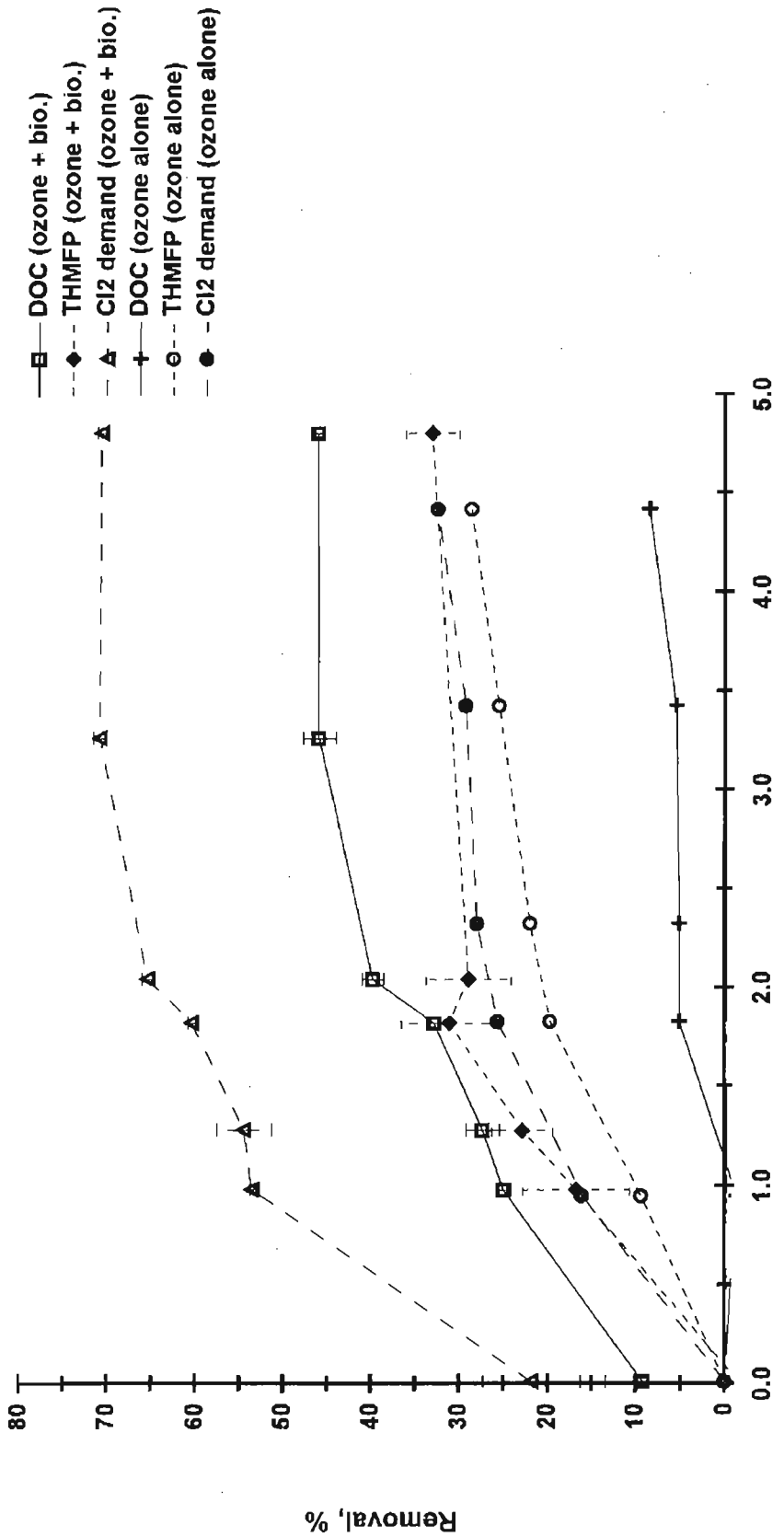

Figure 5.8 Effect of bench-scale ozonation and biofiltration (5-day) on the removal THM formation potential (THMFP), dissolved organic carbon (DOC), and chlorine demand (as total Cl_2)

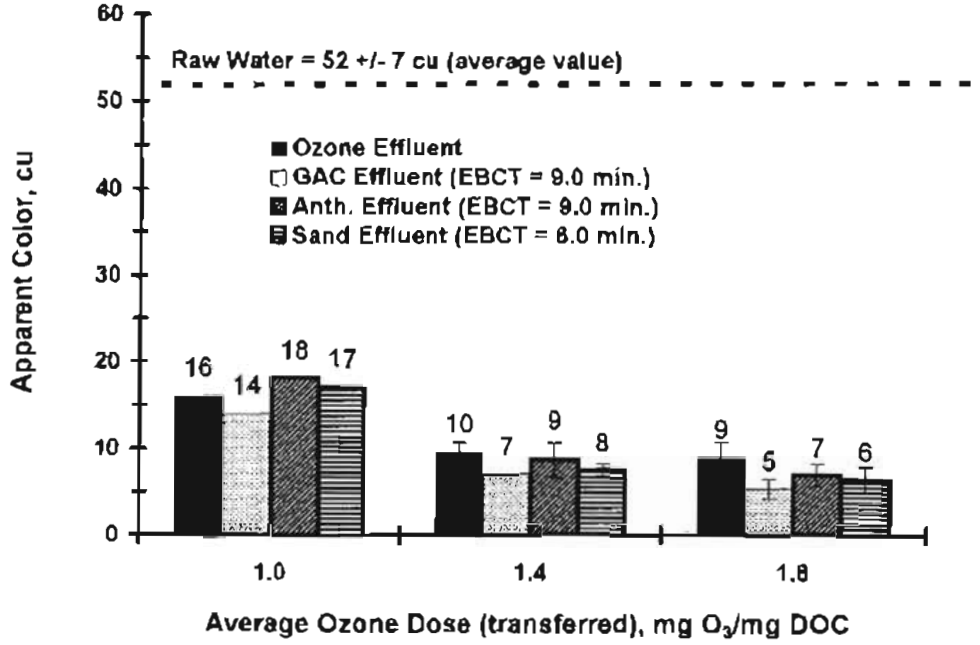

Figure 5.9 Effect of pilot-scale ozone dose and biofilter media type on apparent color

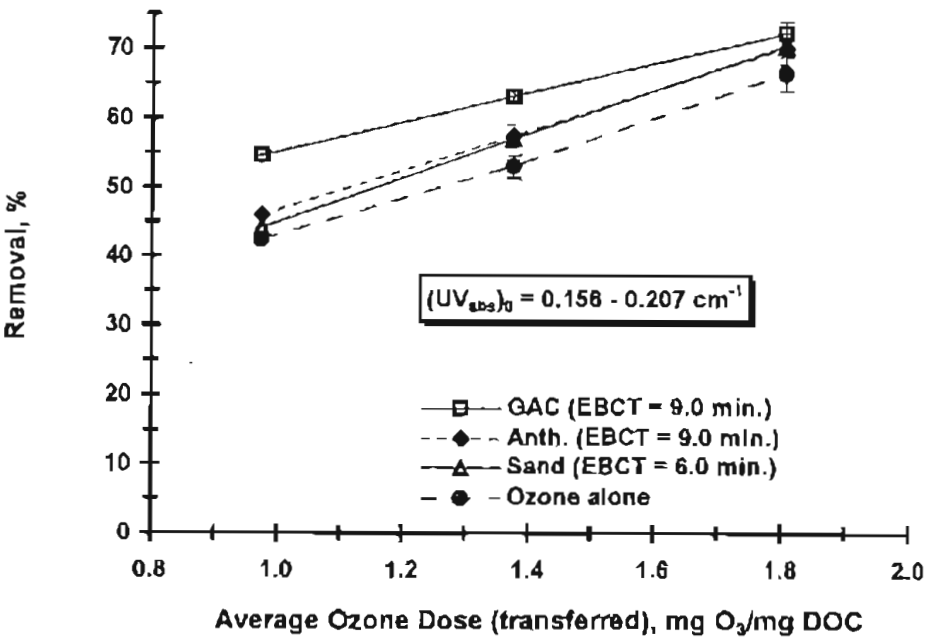

Figure 5.10 Effect of pilot-scale ozone dose and biofilter media type on the removal of UV_{abs}

less than 15 cu, the USEPA secondary standard. As shown in Figure 5.9, color removal was found to be achieved predominantly by ozonation, whereas neither of the three biofilters reduced color measurably. The 15 cu objective was met using a transferred ozone dose between 1:1 and 1.4:1 mg O_3/mg DOC.

It was found that the majority of UV_{abs} was removed by ozonation alone, and that the trend for removal versus ozone dose was similar to that developed at the bench-scale. Anthracite biofiltration and sand biofiltration were both found to remove UV_{abs} only slightly beyond ozonation effluent levels. GAC biofiltration was observed to remove considerable UV_{abs} at the lowest ozone dose, but progressively converged to the removal levels of the other media types as ozone dose was increased. The decrease in GAC UV_{abs} removal with ozone dose may be due to the following possibilities: 1) all the adsorption sites of the GAC likely to adsorb UV_{abs} causing compounds were not exhausted until the final ozone dose analysis (see section 3.5.4 for experimentation chronology), 2) UV_{abs} causing compounds which were less oxidized (potentially more hydrophobic) at the lower ozone doses were more interactive with the GAC surface.

DOC removal was found to increase with ozone dose and relatively little removal was found to occur with ozonation alone (see Figure 5.11). The anthracite and sand media filters exhibited identical DOC removal capabilities, whereas the GAC media was observed to be superior. The exceptional performance of GAC was again most pronounced at the lower ozone doses, likely associated with the removal of the UV_{abs} compounds discussed in the preceding paragraph. Although it is commonly postulated that GAC performs better than other media types due primarily to its greater biomass capacity and corresponding substrate utilization potential, this data suggests that the dominant factor is rather the additional removal of UV_{abs} causing compounds, most likely due to surface adsorption. This observation is further supported by the trends developed for specific UV_{abs} (SUVA = UV_{abs}/DOC), an index

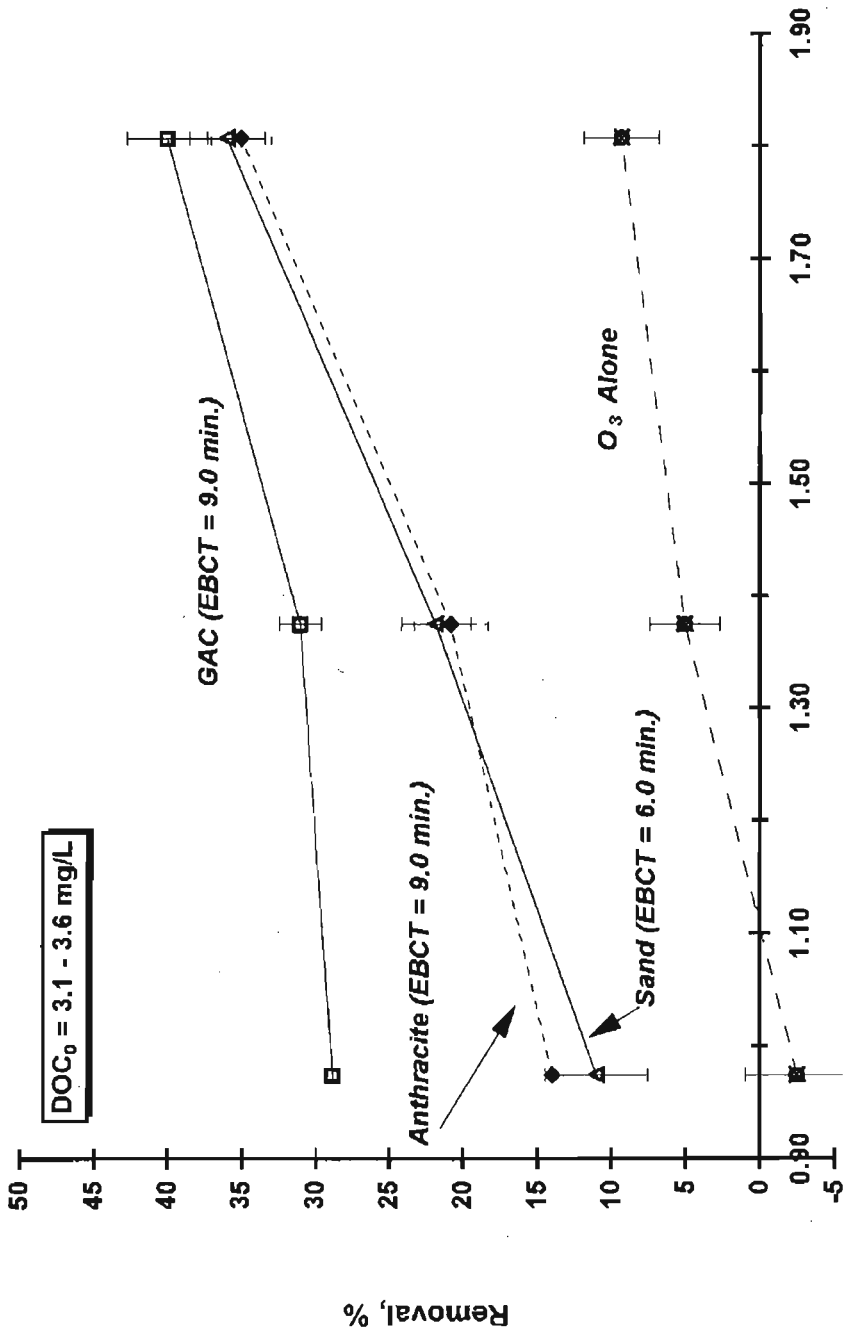

Figure 5.11 Effect of pilot-scale ozone dose and biofilter media type on the removal of dissolved organic carbon (DOC)

of the aromatic character of the DOC (see Figure 5.12). As illustrated, the SUVA removals for all media types are nearly equivalent, indicating that the aromatic character of all biofilter effluents is approximately the same. If the GAC media was removing more DOC than the other media due to greater biomass (i.e., more substrate consuming potential), assuming that non-UV_{abs} causing compounds (i.e., aliphatic compounds) are the most biodegradable (Goel et. al., 1995), the aromatic character of the GAC effluent should be more pronounced than the sand and anthracite effluents at all ozone doses. Since this is not the case, it is suggested that the superior performance of the GAC media, in terms of DOC removal, is attributed predominantly to adsorption rather than biodegradation.

THMFP reduction was evaluated as a surrogate for DBP precursor fate, whereas THMSDS was evaluated to assess the effect of ozone dose and media type on compliance with current and proposed THM regulations (see Figures 5.13 and 5.14). THMFP removal increased with ozone dose and GAC was observed to generally perform superior to the other media types. The GAC superiority can potentially be attributed to the additional removal of UV_{abs} causing compounds, the most likely precursors to THM formation (Edzwald et. al., 1985). In comparing the relative effects of ozonation and sand biofiltration (same media as bench-scale biofilters), ozonation was found to provide the majority of precursor attenuation at the 1.8:1 ozone dose. However, contradictory with the bench-scale results, at the other ozone doses, ozonation was seemingly not as significant of a factor.

THMSDS concentrations for the ozonated and biofiltered waters were observed to decrease with an increase in ozone dose. In general, it was found that ozonation provided the majority of THMSDS removal and that the GAC media produced the best effluent quality. Furthermore, the current USEPA MCL for total THMs (100 μg/L) was met at the ozone dose

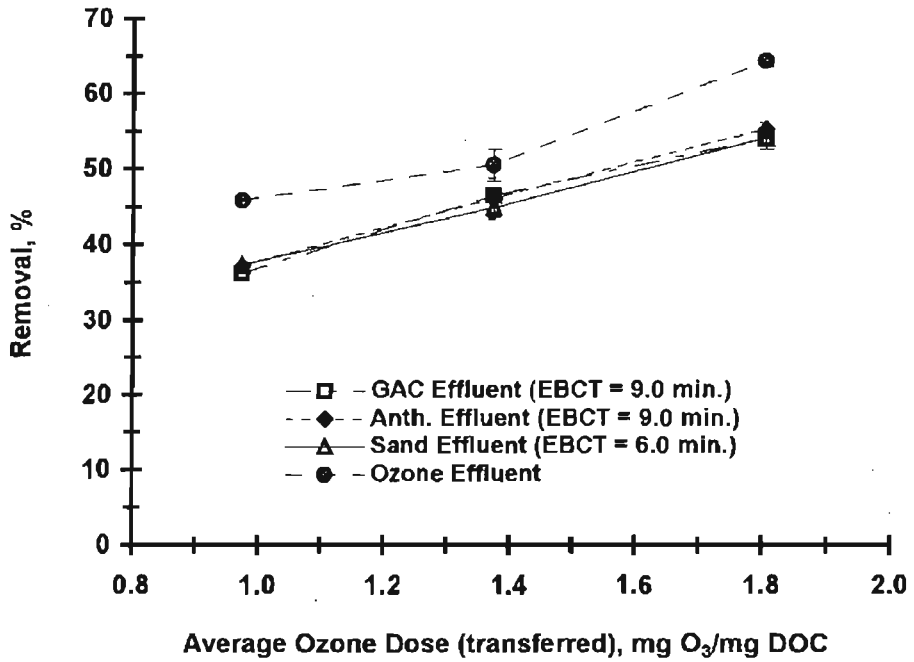

Figure 5.12 Effect of pilot-scale ozone dose and biofilter media type on the removal of specific UV_{abs} (SUVA)

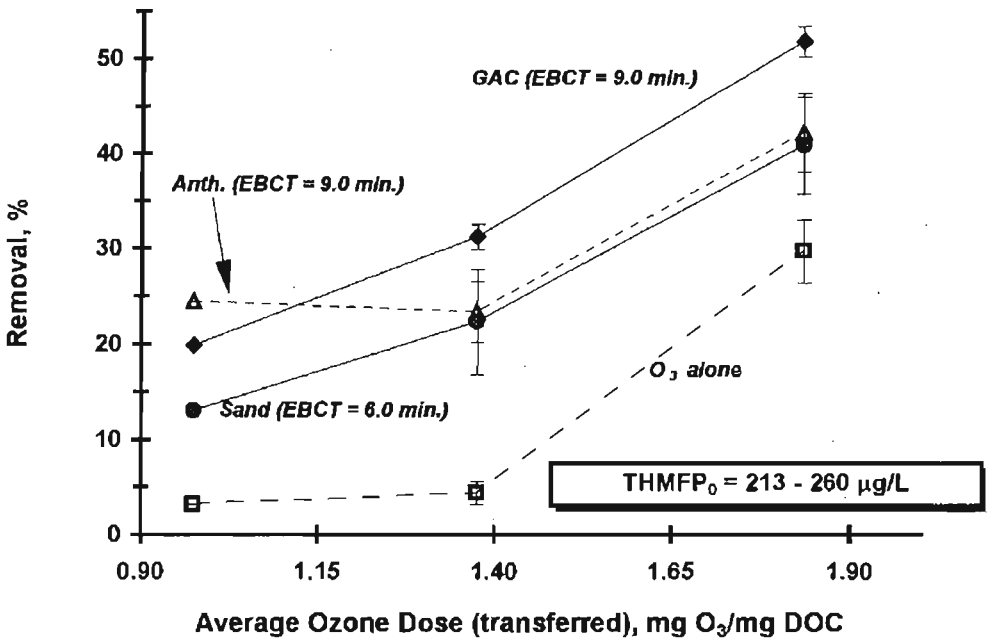

Figure 5.13 Effect of pilot-scale ozone dose and biofilter media type on the removal of THM formation potential (THMFP)

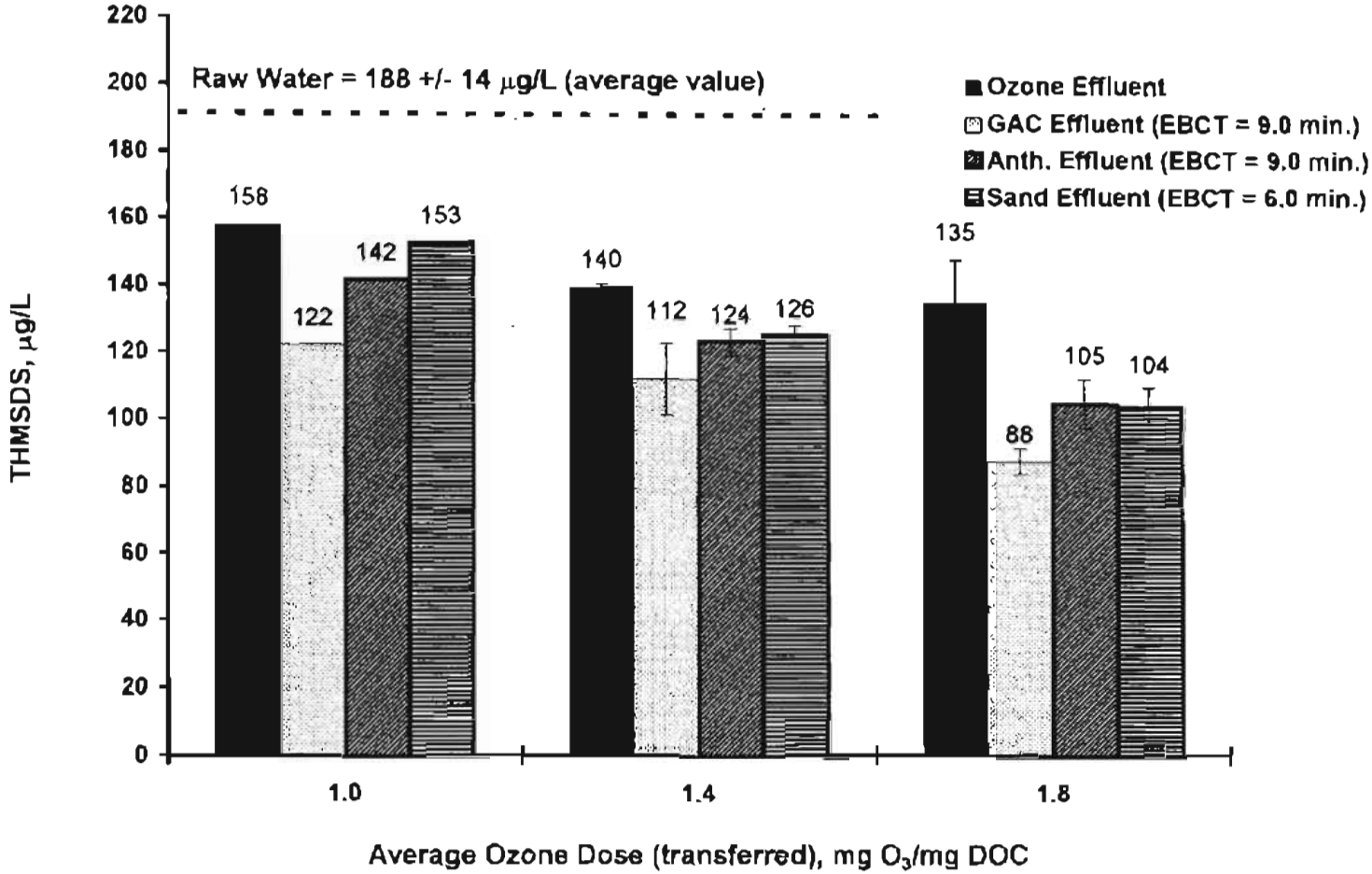

Figure 5.14 Effect of pilot-scale ozone dose and biofilter media type on THM simulated distribution system (THMSDS) concentration

of 1.8:1 for the GAC media only. The proposed D/DBP Stage I MCL for total THMs (80 μg/L) was not met for any of the media types at any of the ozone doses considered.

The 72-hour chlorine demand associated with the THMFP experiments was also measured, producing similar results to those observed at the bench-scale as well as following a similar trend as the other parameters discussed above (see Figure 5.15). Again, GAC displayed superior performance in removing chlorine demand, less pronounced as ozone dose increased.

For illustration and clarification purposes, as well as for comparison with the bench-scale results, a composite of the relationships discussed in this section, excluding color and UV_{abs}, is provided (see Figure 5.16). Furthermore, the relationship determined between THMSDS and THMFP is provided as a means of making any necessary conversions: THMFP = 1.35 x THMSDS + 4.31 (r^2 = 0.96).

5.2.2 Effect of Ozone Dose and Biofilter Media Type on OBPs and AOC

OBPs and AOC, used as surrogates to biological stability (i.e., distribution system regrowth potential), were monitored at steady-state to evaluate the effects of ozone dose and media type on the respective production and removal of these parameters (see Figures 5.17 and 5.18). The various OBPs measured represent some of the more abundantly formed compounds commonly identified in ozonated waters. As shown in Figure 5.17, the amount of OBPs produced upon ozonation increased with ozone dose, particularly between the ozone doses of 1.4:1 and 1.8:1. Consistently, more of the ketoacid species (dominant specie: glyoxylic) were produced than the aldehyde species (dominant specie: formaldehyde). At all ozone doses, it was found that each of the biofilters reduced the majority (> 85%) of both ketoacids and aldehydes to near raw water levels. Thus, in terms of OBPs, no detriment to biological stability was found with ozonation and with increasing the ozone dose.

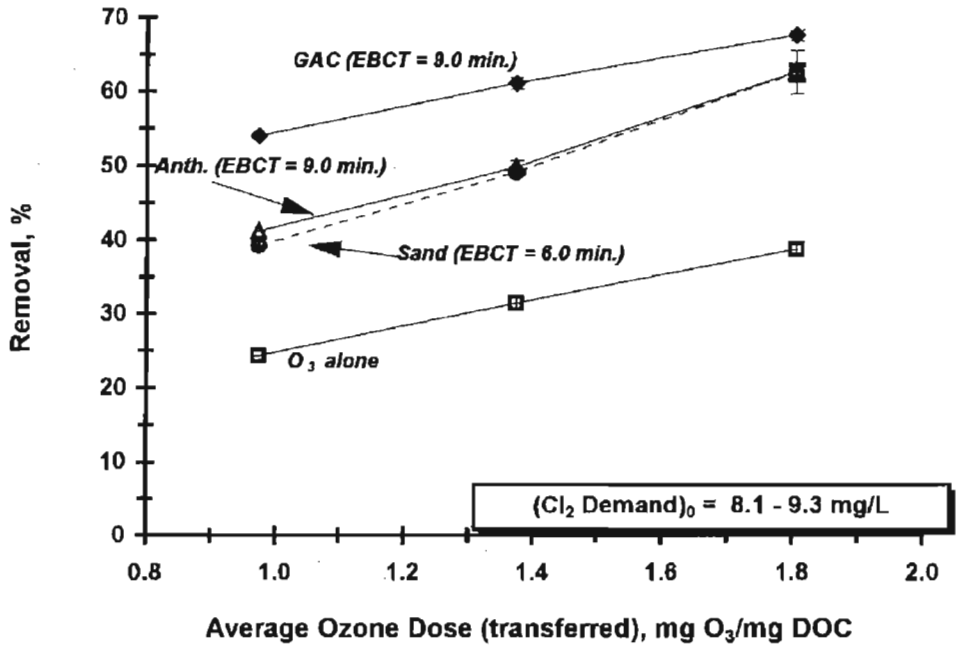

Figure 5.15 Effect of pilot-scale ozone dose and biofilter media type on the removal of chlorine demand (as total chlorine)

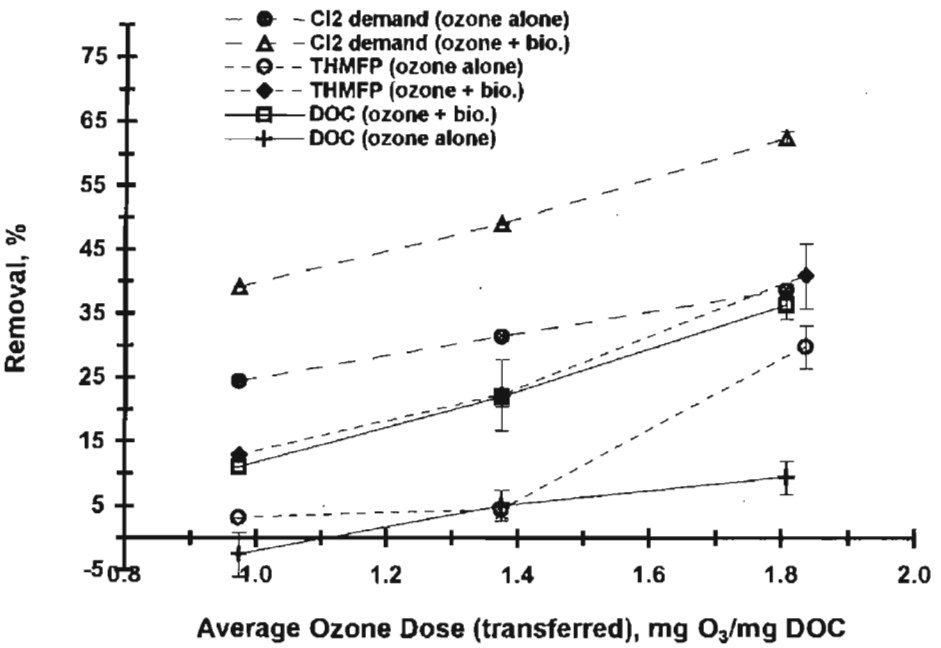

Figure 5.16 Effect of pilot-scale ozonation and biofiltration (sand filter) on the removal of THM formation potential (THMFP), dissolved organic carbon (DOC), and chlorine demand (as total chlorine)

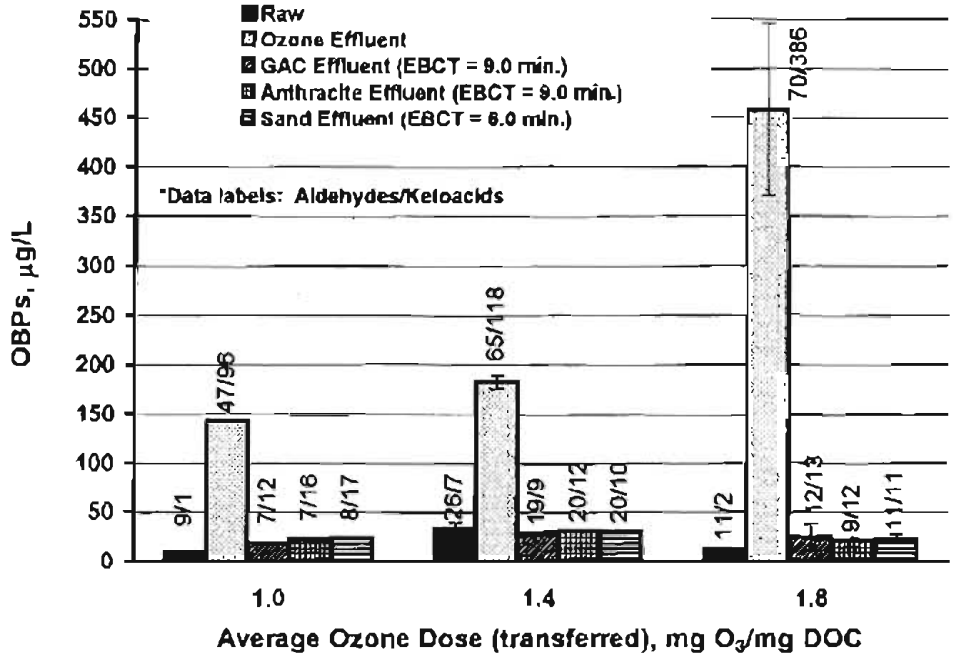

Figure 5.17 Effect of pilot-scale ozone dose and biofilter media type on ozonation by-products (OBPs)

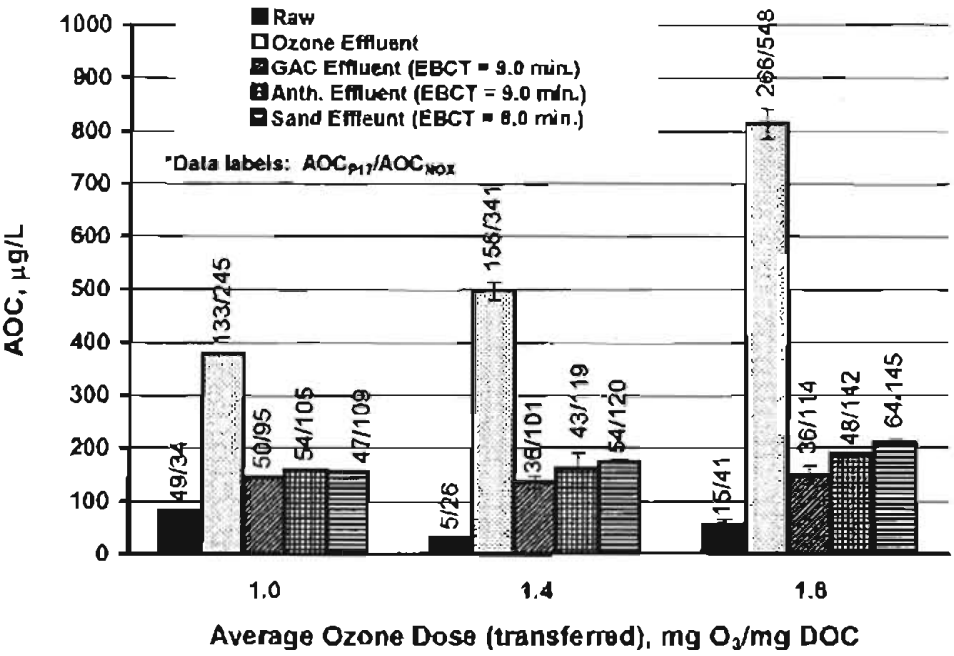

Figure 5.18 Effect of pilot-scale ozone dose and biofilter media type on assimilable organic carbon (AOC)

As with OBPs, AOC concentrations were found to increase significantly with ozone dose. However, it was observed that biofiltration did not reduce the AOC back to raw water levels. Although each of the biofilters' capacity to remove ozone produced AOC increased with ozone dose, the absolute effluent quality appeared to generally decrease. The GAC filter provided the best effluent quality which did not appear to deteriorate significantly with ozone dose increase. The amount of AOC_{NOX} produced upon ozonation was found to be approximately twice the concentration of AOC_{P17} at all ozone doses. Although AOC_{P17} is considered a measure of the more biodegradable compounds relative to the more recalcitrant AOC_{NOX}, there did not appear to be any discernible trends in terms of preferential removal. A strong relationship ($r^2 = 0.96$) was observed between AOC_{NOX} and AOC_{P17} for the raw ozonated, and biofiltered waters ($AOC_{NOX} = 1.98 \times AOC_{P17} + 12.7$).

5.2.3 Effect of Ozone Dose and Biofilter Media Type on Miscellaneous Analytes (Fe_{total}, Mn_{total}, NH_3-N, TKN, DO, pH, temperature, and turbidity)

Various miscellaneous parameters were measured, at steady-state, as a function of ozone dose and biofilter media type (see Table 5.2). Nitrogen, in the form of TKN and NH_3-N, was measured due to its role as a biological nutrient in biofiltration and its potential to contribute to regrowth in the distribution system. TKN concentrations of the raw water and throughout the entire process train were below detection, while NH_3-N was also close or below levels of detection. The data for the ozone doses 1.4:1 and 1.8:1 does indicate that NH_3-N was present at concentrations close to 100 µg/L and that a fraction of that was removed during biofiltration. Fe_{total} and Mn_{total} were monitored due to their potential as micronutrients. The data suggests that Fe_{total} was not affected by process treatment at the 1:1 and 1.4:1 ozone doses, but appears to have been partially removed during biofiltration at the 1.8:1 ozone dose. Mn_{total} was found to be removed to a certain degree through biofiltration.

Table 5.2 Effect of ozone dose and media type on TKN, NH_3-N, Fe_{total}, Mn_{total}, DO, temperature, pH, and turbidity

Parameter	Units	*Avg. Ozone Dose = 1.0 mgO₃/mgDOC*					*Avg. Ozone Dose = 1.4 mgO₃/mgDOC*					*Avg. Ozone Dose = 1.8 mgO₃/mgDOC*				
		Raw	O_3	GAC	Anth.	Sand	Raw	O_3	GAC	Anth.	Sand	Raw	O_3	GAC	Anth.	Sand
TKN	mg/L	<0.4	<0.4	0.8	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
NH_3-N	µg/L	<40	80	60	50	40	120	93	53	<40	60	130	140	<100	<100	<100
Fe_{total}	µg/L	142	140	123	133	130	190	200	199	196	193	121	115	67	72	84
Mn_{total}	µg/L	6.8	6.1	1.5	1.1	1.0	3.0	3.0	1.4	<0.5	0.6	6.2	6.0	1.4	1.4	2.0
DO	mg/L	2.4	6.9	4.8	6.0	5.5	2.3	6.8	5.0	6.0	6.3	2.1	7.2	4.2	5.4	5.5
Temperature	°C	27	27	27	27	27	28	28	28	28	28	30	30	30	30	30
pH	–	8.1	8.2	7.9	8.1	8.1	8.1	8.1	7.9	8.0	8.0	8.5	8.3	7.9	8.1	8.1
Turbidity	NTU	0.5	0.3	0.3	0.3	0.3	0.5	0.3	0.2	0.2	0.2	0.6	0.4	0.2	0.2	0.2

*all values presented are based upon experimental averages

Fe_{total} and Mn_{total}: sum of dissolved species for respective element

DO: dissolved oxygen

O_3: ozone effluent; GAC: GAC effluent; Anth.: anthracite effluent; Sand: sand effluent

<: below given detection limit

It was found that DO was greatly enhanced by ozonation and partially consumed during biofiltration. The GAC media biofilter was observed to reduce oxygen levels more than the other media types, possibly due to the addition of surface-oxygen interactions and/or greater biological consumption. There were no discernible trends observed between DO and DOC removals. Temperature and pH were found to change insignificantly throughout the process train. Turbidity levels were reduced upon ozonation and biofiltration to levels less than 0.5 NTU, the USEPA secondary standard.

5.2.4 Effect of Empty Bed Contact Time (EBCT) on the Removal of DOC, THMFP, THMSDS, Cl_2 Demand, OBPs, and AOC

The effect of EBCT on the removal of various raw water quality parameters was evaluated to assess the importance of this particular filter design consideration. Experiments were conducted by maintaining a constant filter hydraulic loading rate (HLR) and sampling from a series of vertically distributed filter ports (see Figure 3.2 for filter column port locations). All experiments were conducted at steady-state using a transferred ozone dose of 1.8 ± 0.1 mg O_3/mg DOC.

As illustrated in Figure 5.19, the majority (>90 %) of total DOC removal occurred at the top portion of each filter, equivalent to an EBCT of 3.5 minutes. THMFP removal was again observed to be achieved predominantly by ozonation alone (see Figure 5.20). The majority of biofiltration removal of THMFP appeared to occur within an EBCT of 3.5 minutes for the sand and anthracite filters, whereas the GAC filter continued to remove THMFP throughout the filter depth. The ability of the GAC media to continue removal of THMFP may have been attributed to a non-exhausted and/or bioregenerated filter bed capable of removing adsorptive compounds, which represent likely precursors to THM formation.

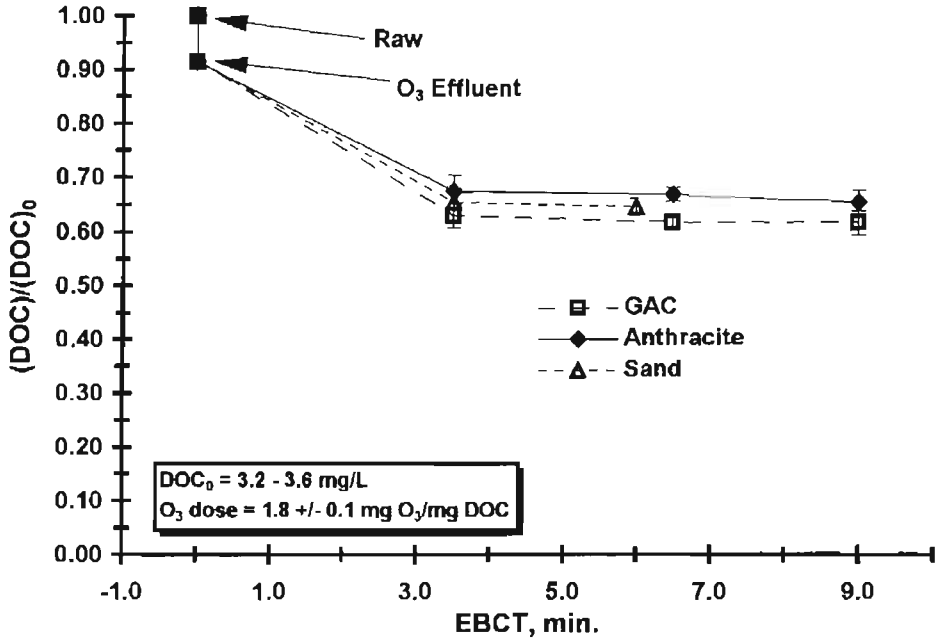

Figure 5.19 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on the removal of dissolved organic carbon (DOC)

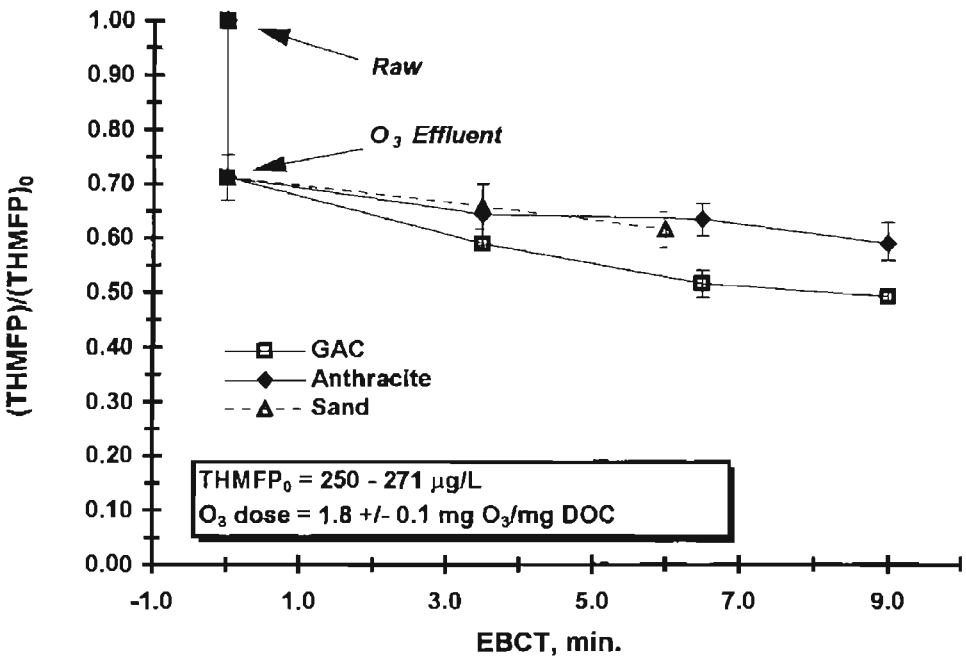

Figure 5.20 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on the removal of THM formation potential (THMFP)

THMSDS concentrations were observed to be reduced predominantly by ozonation with little additional reduction provided by a biofilter EBCT greater than 3.5 minutes (see Figure 5.21). The current USEPA MCL was not met for the anthracite or sand filters at any of the EBCTs considered. The GAC filter met the current USEPA MCL (100 μg/L) at an EBCT of 3.5 minutes, but did not meet the D/DBP Stage I MCL (80 μg/L) at any of the EBCTs considered. The majority of the 72-hour chlorine demand (associated with the THMFP experiments) removed during biofiltration occurred within an EBCT of 3.5 minutes for each of the media types (see Figure 5.22). Near complete removal of both the measured aldehyde and ketoacid species were found to occur within an EBCT of 3.5 minutes for all media types (see Figure 5.23). The majority of the AOC (AOC_{NOX} + AOC_{P17}) removal across the GAC biofilter (only filter monitored) occurred within an EBCT of 3.5 minutes, but the effluent still represented poorer quality than the raw water influent (see Figure 5.24). The relative concentrations of AOC_{P17} and AOC_{NOX} did not change significantly with EBCT.

5.2.5 Effect of Backwashing on the Removal of DOC, THMFP, and Cl_2 Demand

DOC, THMFP, and Cl_2 Demand were measured at three separate times (1, 6, and 24 hours) during the filter run to evaluate the effects of biofilter backwashing and headloss development on the removals of these parameters. The total run length of 24 hours was chosen based upon average run lengths for the sand media filter. As illustrated by Figures 5.25 thru 5.27, it was found that biofilter performance was consistent throughout the 24-hour filter run for each of the different media types. These results indicate, based on the parameters measured, that backwash perturbations are not significant and that filter run headloss development does not influence biofilter performance. The results also suggest that GAC pore protection (protection of biomass against backwash scouring due to inclusion in media pore

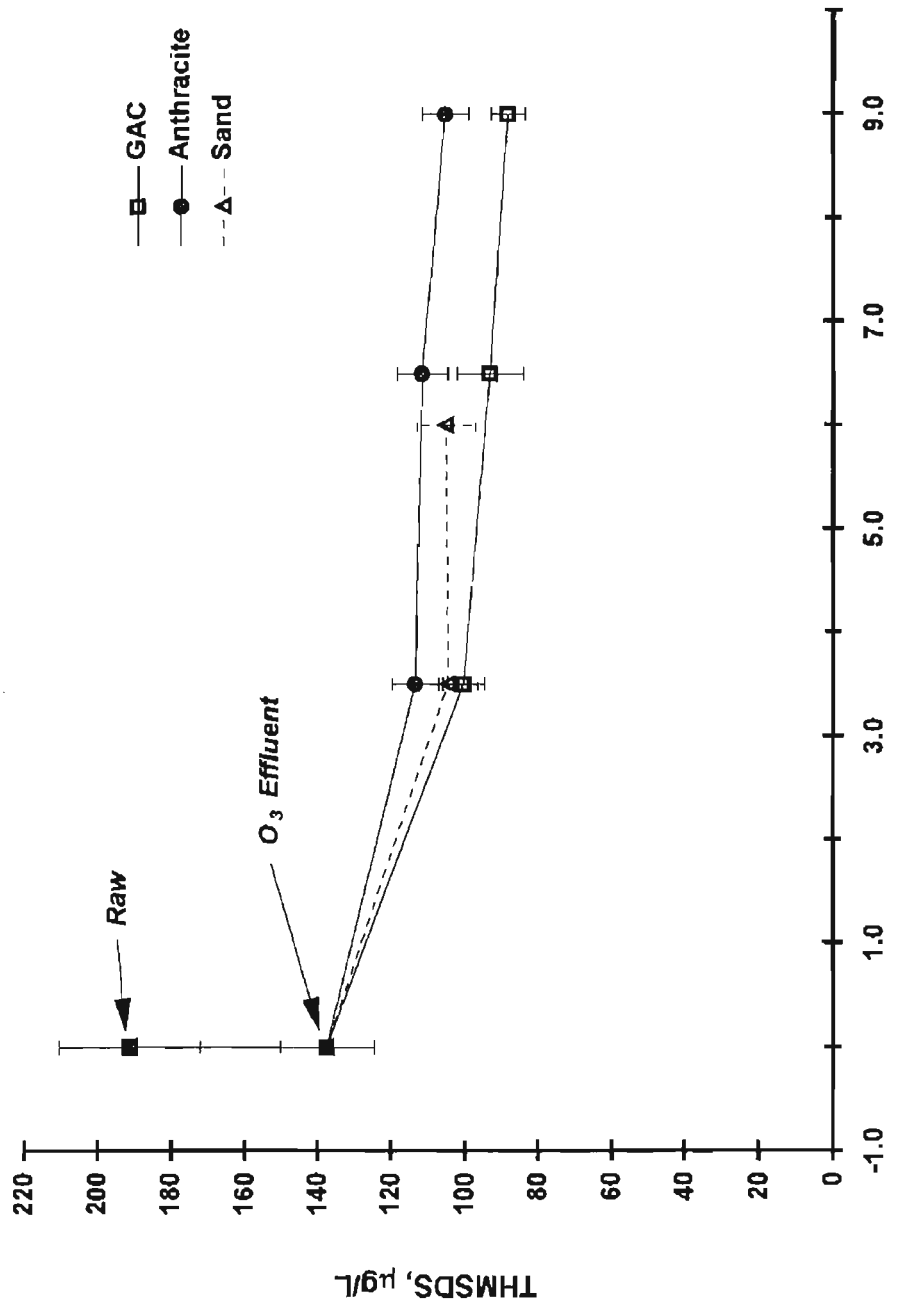

Figure 5.21 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on THM simulated distribution system (THMSDS) concentration

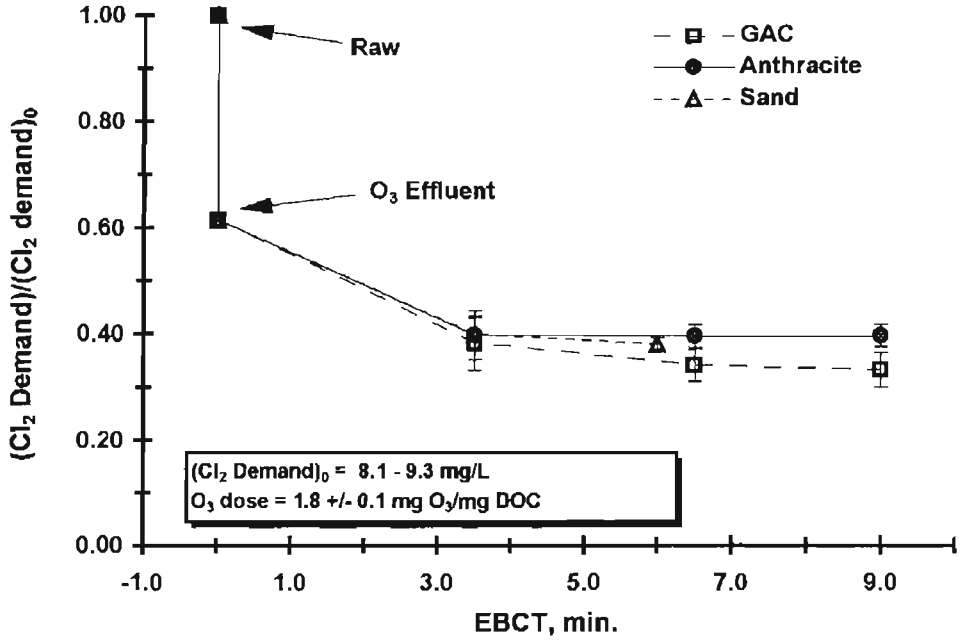

Figure 5.22 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on the removal of chlorine demand (as total chlorine)

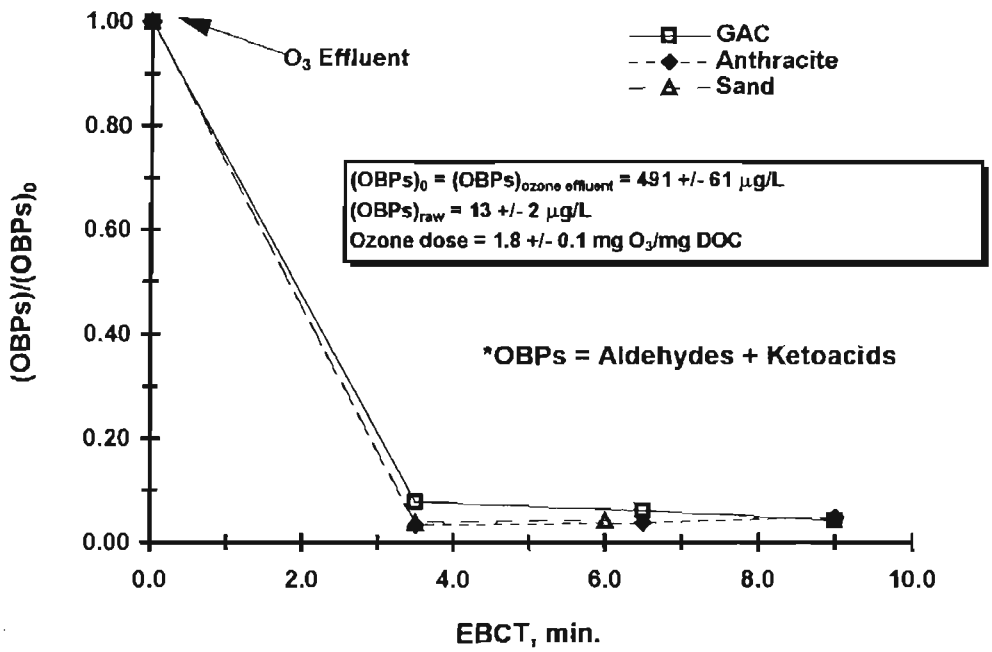

Figure 5.23 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on the removal of ozonation by-products (OBPs)

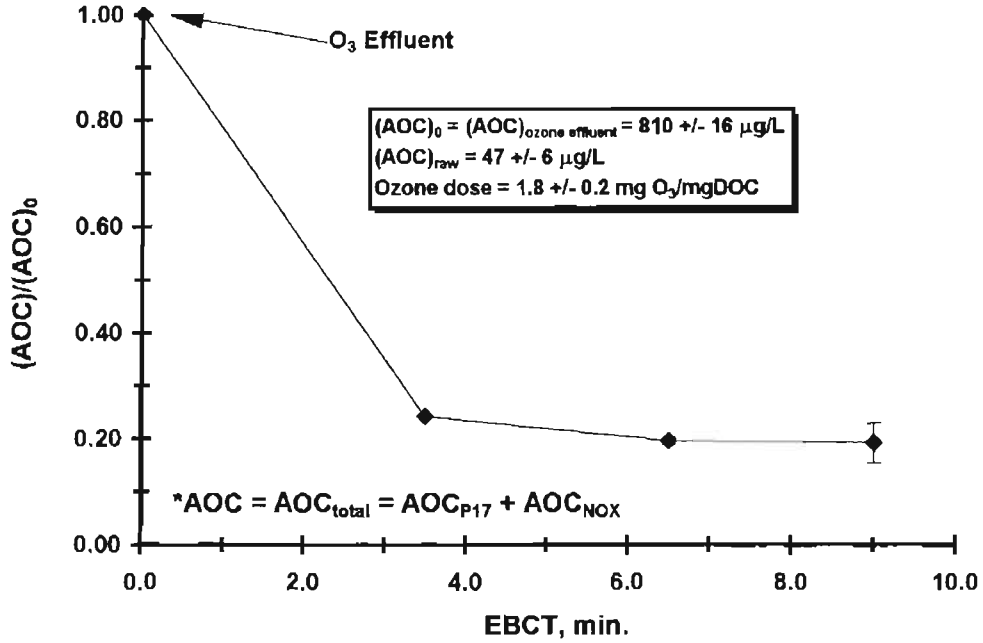

Figure 5.24 Effect of biofilter (pilot-scale) empty bed contact time (EBCT) on the removal of assimilable organic carbon (AOC)

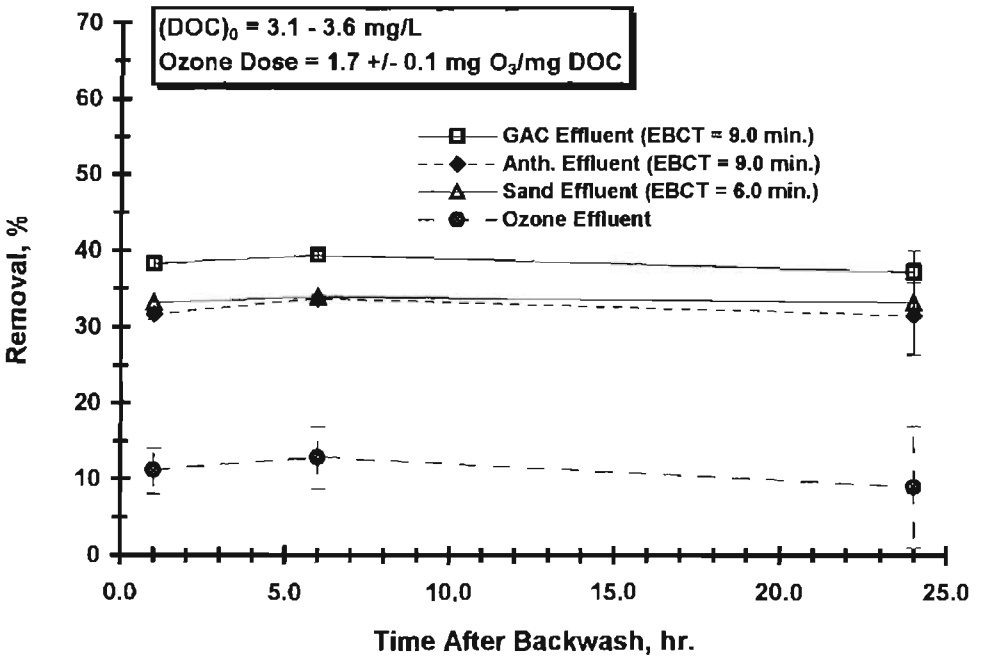

Figure 5.25 Effect of biofilter (pilot-scale) backwashing on the removal of dissolved organic carbon (DOC)

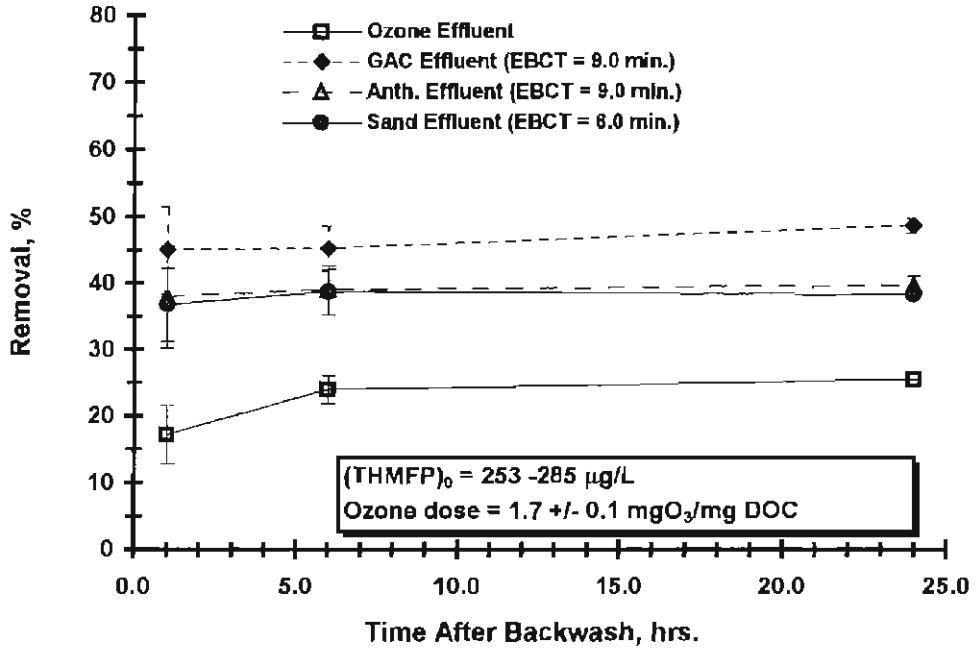

Figure 5.26 Effect of biofilter (pilot-scale) backwashing on the removal of THM formation potential (THMFP)

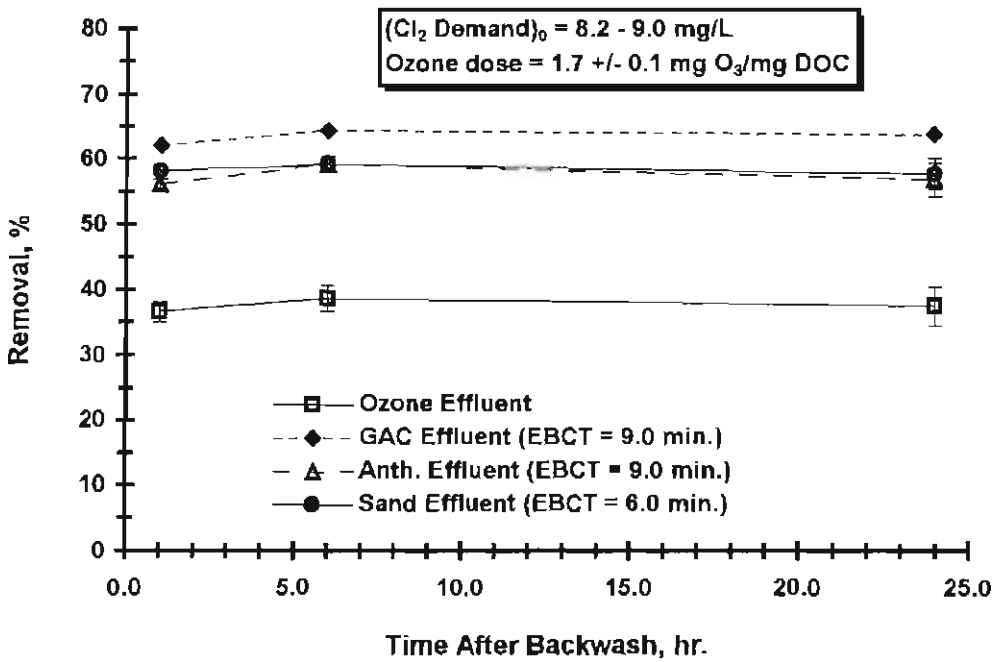

Figure 5.27 Effect of biofilter (pilot-scale) backwashing on the removal of chlorine demand (as total chlorine)

structure) is not the basis for the performance disparities between GAC and the non-porous media. If pore protection was substantial, it would be expected that the performance superiority of the GAC media would be most evident at the sample time immediately following backwashing (i.e., t = 1 hour).

5.3 Post-Disinfection

Free chlorine and monochloramine were considered as potential post-disinfectants for the studied ozone-biofiltration treatment process. Each disinfectant was evaluated based upon its reactivity with the pilot-scale raw, ozonated, and GAC biofiltered waters. All post-disinfectant experiments were conducted during pilot-scale steady-state at an ozone dose of 1.7 mg O_3/mg DOC.

Disinfectant kinetic decay relationships (i.e., curves) were developed as a basis for determining rate constants, chlorine demand, and THM formation. The decay experiments consisted of the following conditions: reaction time: 0 to 72 hours, temperature = 20 °C, pH = ambient, $(Cl_2)_0$ = $(Cl_2)_0$ required to obtain a 24 hour residual of 1.0 mg/L. A 1.0 mg/L Cl_2 residual (as total Cl_2) at a 24-hour reaction time was chosen as a representation of average United States distribution system conditions (Summers et. al., 1996). Although discrepancies exist between inactivation requirements (i.e., C x t) for the two disinfectants, the use of the uniform conditions described were assumed to be sufficient for purposes of comparison.

To determine the initial dose required to obtain the 24-hour, 1.0 mg/L residual, a series of chlorine doses was administered to the given samples under the conditions described above. After 24 hours, the chlorine residual was measured for each of the samples, resulting in a linear relationship between initial chlorine dose and chlorine residual (see Figures 5.28 and 5.29). The doses determined from the linear relationships were then used as the initial doses for the chlorine decay experiments (see Figures 5.30 and 5.31). Recognizable differences can

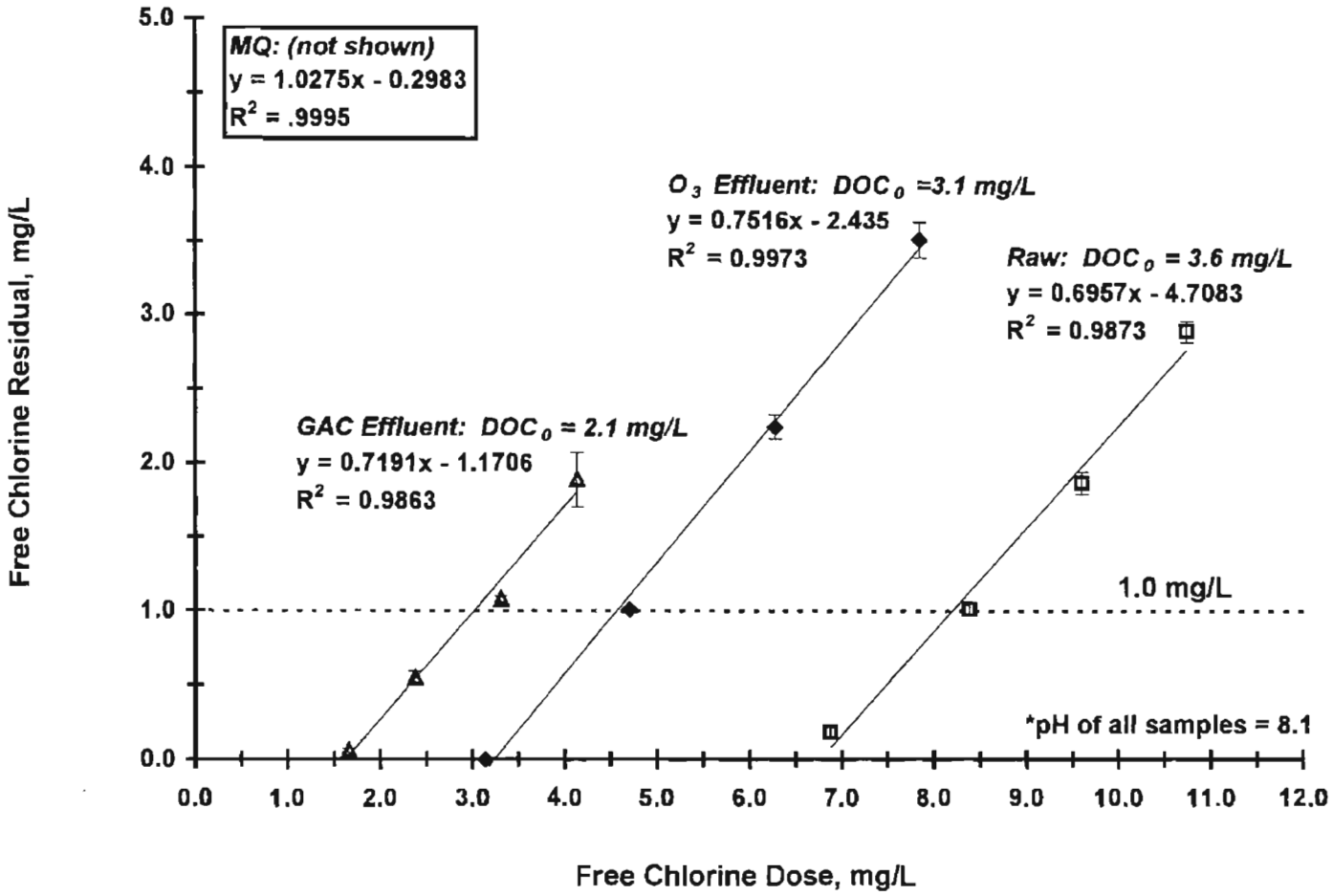

Figure 5.28 Twenty-four hour free chlorine residual vs. free chlorine dose for pilot-scale raw, ozonated (1.7 mg O_3/mg DOC), and GAC biofiltered waters

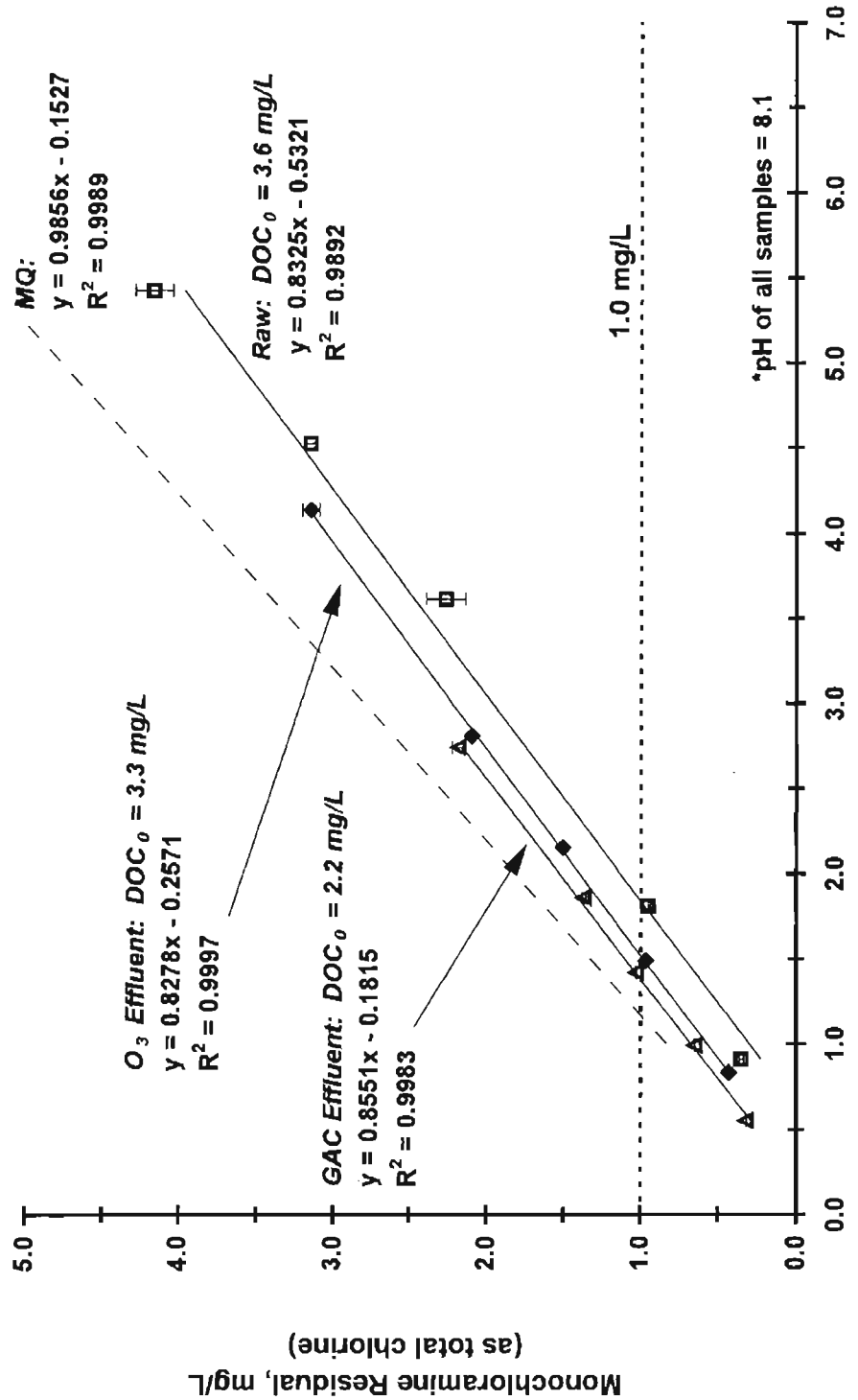

Figure 5.29 Twenty-four hour monochloramine residual vs. monochloramine dose for pilot-scale raw, ozonated (1.7 mg O_3/mg DOC), and GAC biofiltered waters

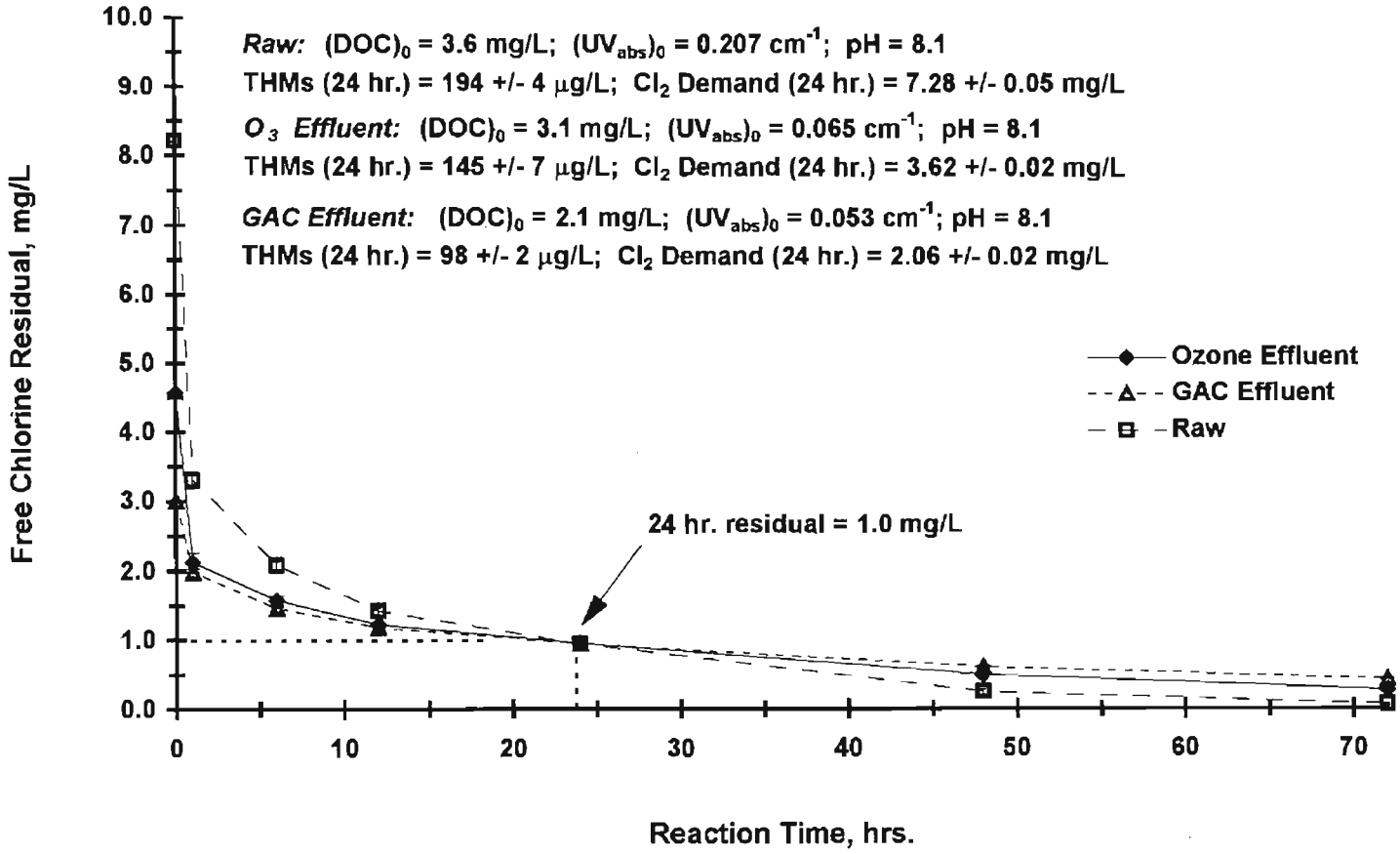

Figure 5.30 Free chlorine decay of pilot-scale raw, ozonated (1.7 mg O_3/mg DOC), and GAC biofiltered waters

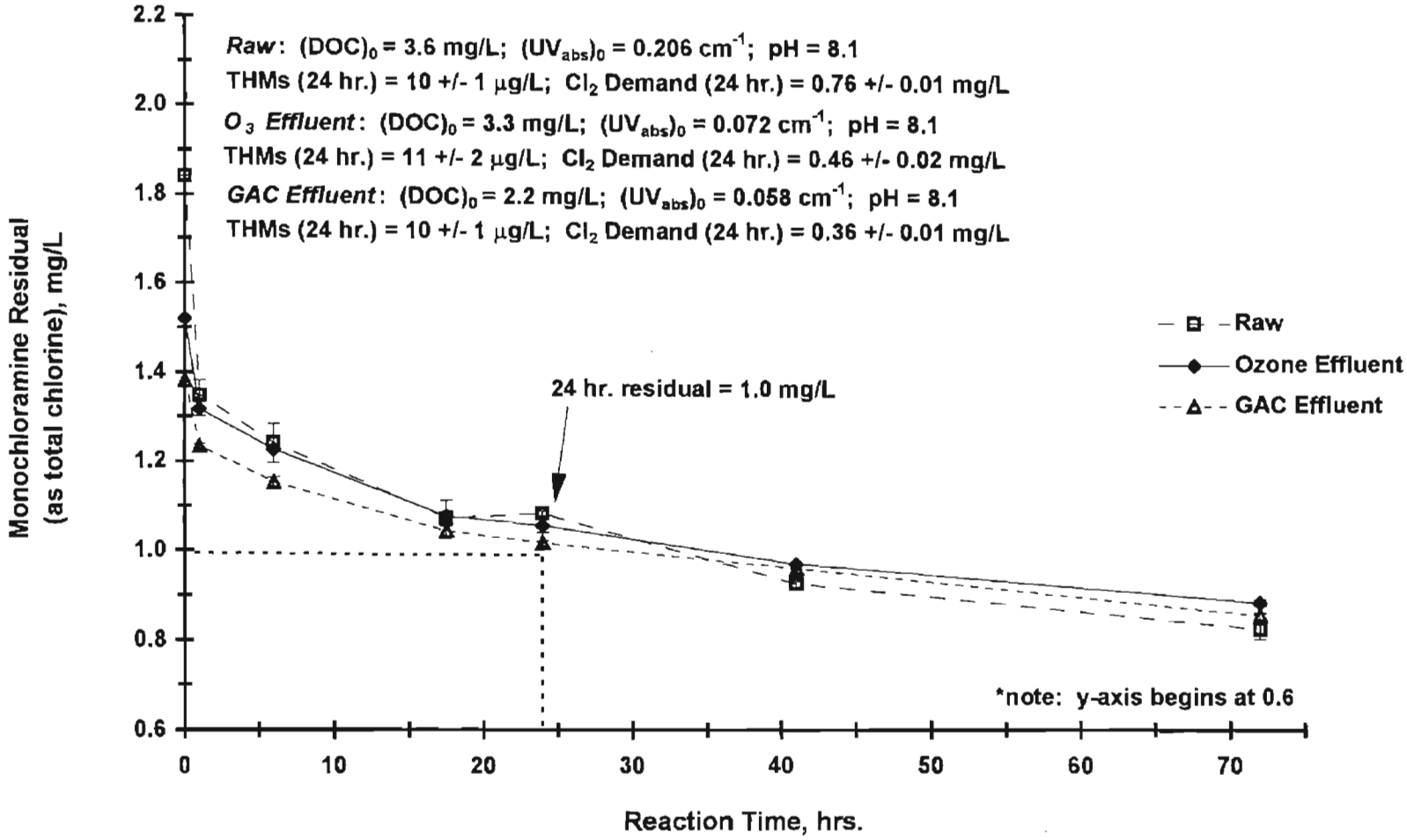

Figure 5.31 Monochloramine decay of pilot-scale raw, ozonated (1.7 mg O_3/mg DOC), and GAC biofiltered waters

be observed in the chlorine consumption rate and extent between the two oxidants as well as between the various process train samples.

Previous studies have found that chlorine decay can be modeled as a combination of two first-order (pseudo) processes, defined by an initially rapid reaction period followed by a slower reaction period (Qualls and Johnson, 1983; Zhu, 1995). However, perhaps due to limited data in the rapid reaction region, the data generated for this study was best modeled using a pseudo zero-order rate constant ($\Delta_{0\text{-}1}$) for t_0 to t_1 (0 to 60 minutes), and a pseudo first-order rate constant (k_1) for $t \geq t_1$ ($t \geq 60$ minutes). The rate constants for both disinfectants, in addition to 24-hour THM formation and Cl_2 demand, are presented in Table 5.3.

As indicated by the $\Delta_{0\text{-}1}$ and k_1 values given in Table 5.3, free chlorine was observed to generally be much more reactive with the tested waters than monochloramine. For both disinfectants, the raw water was more reactive than the ozonated and biofiltered waters. Thus, as observed with other results from this study, ozone oxidation and biofiltration alter and remove the organic matter, creating waters less reactive with post-disinfectants.

THMs formed after a 24-hour reaction period were markedly less for monochloramine relative to free chlorine. The THMs produced upon free chlorination were reduced 50 % by ozonation and biofiltration, but still represented ten times the THMs produced upon monochloramination. Treatment of the raw water was observed to have no effect on THMs formed with monochloramine. Chlorine demand (as total chlorine) over a 24-hour reaction period was significantly greater for free chlorine than monochloramine, another result of reactivity discrepancies. Raw water chlorine demand (as total chlorine) was reduced upon ozonation, and further by biofiltration, for both of the disinfectants.

Table 5.3 **Free chlorine and monochloramine reactivity with pilot-scale raw, ozonated (1.7 mg O_3/mg DOC), and GAC biofiltered waters [reaction time: 72 hr, temp. = 20 °C, pH = ambient, $(Cl_2)_0 = (Cl_2)_0$ required to obtain a 24 hr. residual of 1.0 mg/L]**

	Free Chlorine			*Monochloramine*		
	Raw	O_3	GAC	Raw	O_3	GAC
$\Delta_{0\text{-}1}$ (mg/L)	4.9	2.4	1.0	0.49	0.46	0.36
k_1** ($\times 10^{-6}$ sec^{-1})	14.8	7.4	5.7	2.4	2.1	1.7
THMs* (μg/L)	194	146	98	10	11	10
Cl_2 demand* (mg/L)	7.3	3.6	2.1	0.76	0.46	0.36

*: 24-hour measurement
**: average r^2 for k_1 determination = 0.96 ± 0.03
O_3: ozone effluent; GAC: GAC effluent
Cl_2 demand: reported as total chlorine

5.4 DOC Removal Kinetics

The kinetics of DOC removal using the bench-scale biofilters was performed on the raw, ozonated, and biofiltered waters obtained from the pilot-scale process train. The three primary objectives of the experiments consisted of the following: 1) to qualitatively compare the rate and extent of bench-scale DOC removal of the raw and post-treated pilot-scale waters, 2) to develop a relationship between the removal of DOC measured during pilot-scale biofiltration with DOC removal measured at a given time during bench-scale biofiltration, 3) to evaluate the effect of ozone dose on pilot-scale biofilter effluent quality in terms of the DOC available for biodegradation. The kinetic removals of DOC for the pilot-scale raw, ozonated (1.8 mg O_3/mg DOC), and biofiltered waters are illustrated in Figure 5.32. The results indicate that there is a fraction of the DOC rapidly removable (i.e., DOC_{rapid}) within the first 24 hours of bench-scale biofiltration, represented by the relatively steep initial portion of each kinetic curve. The essentially non-existent DOC_{rapid} of the raw water was found to be

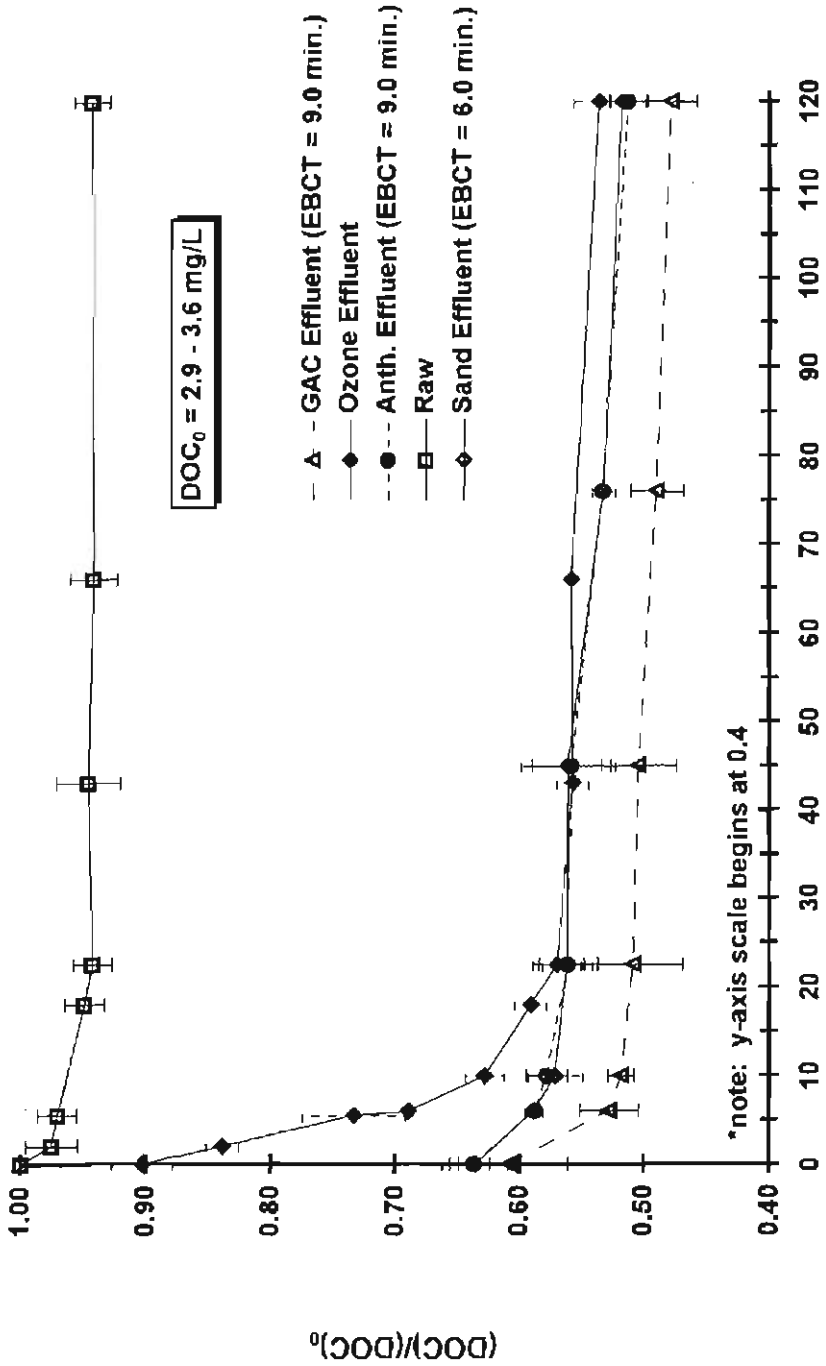

Figure 5.32 Dissolved organic carbon (DOC) removal kinetics of pilot-scale raw, ozonated (1.8 +/- 0.1 mg O_3/mg DOC), and biofiltered waters in bench-scale biofilters

significantly enhanced with ozonation. Pilot-scale biofiltration appears to have reduced the DOC_{rapid} formed through ozonation substantially, but not completely. These qualitative results correlate well with the results previously discussed regarding the fate of AOC through the pilot-scale process train.

In recent studies (Carlson et. al., 1996), it has been successfully determined that the bench-scale biofiltration DOC_{rapid} can be quantified by equating it to the DOC removable by a larger-scale biofilter (i.e., DOC_{filter}). In doing so, a relatively simple bench-scale experiment can provide quantifiable insight on the expected performance of a larger system. Therefore, as part of the current study, an attempt was made to relate the DOC_{filter} to DOC_{rapid} by determining the time during bench-scale biofiltration at which the two are equivalent and assessing whether that time is applicable to waters ozonated at various doses. The pilot-scale ozone effluent, at the three different ozone doses studied, was evaluated based upon DOC removal versus time in the bench-scale biofilters (see Figure 5.33). The DOC_{filter} for the pilot-scale sand biofilter (sand filter used in able to be consistent with media in bench-scale biofilters), at the respective ozone doses, was then superimposed on the bench-scale kinetic curves to determine the times of intersection. The following times determined for the 1:1, 1.5:1, and 1.8:1 ozone doses were approximately 1, 5, and 9 hours, respectively. Thus, a distinct time defining DOC_{rapid} could not be obtained from this data.. This is not unexpected when considering the obvious differences between the bench and pilot-scale biofiltration systems (i.e., flow rates, biomass concentrations, EBCTs, etc.).

In comparing the bench-scale DOC removal at the three ozone doses with the corresponding DOC_{filter}, it was observed that the DOC_{filter} fraction of the total removable DOC (i.e., DOC removed during five day bench-scale biofiltration; $DOC_{5\text{-}day}$) seemingly increased with ozone dose. In other words, $DOC_{filter}/DOC_{5\text{-}day}$ increased with ozone dose for this particular data set (see Table 5.4). This relationship has been observed in other studies

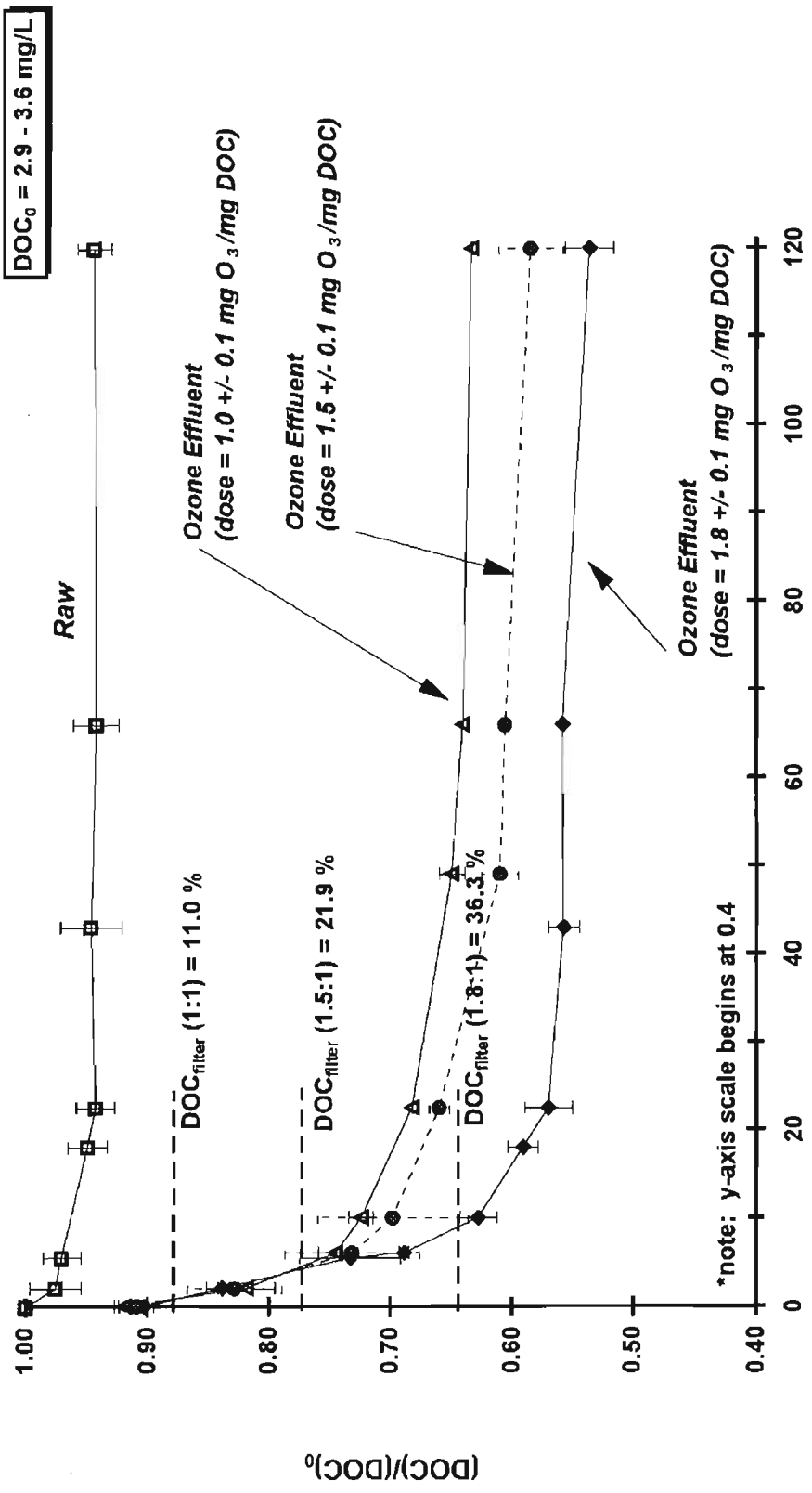

Figure 5.33 Dissolved organic carbon (DOC) removal kinetics of pilot-scale raw and ozonated waters in bench-scale biofilters

(Carlson et. al., 1996) in which the $DOC_{filter}/DOC_{5\text{-}day}$ fraction increased with ozone dose until a maximum was reached and maintained. In the current study, it appears that the maximum ozone dose was not yet reached. As a result of the continued increase in $DOC_{filter}/DOC_{5\text{-}day}$, the removable DOC remaining after pilot-scale biofiltration (i.e., $DOC_{slow} = DOC_{5\text{-}day} - DOC_{filter}$) was found to decrease with ozone dose, representing superior biofilter effluent (pilot-scale) quality as ozone dose increases. This contradicts the AOC data previously discussed which indicated that effluent quality, in terms of the presence of biodegradable compounds, decreased with an increase in ozone dose.

Table 5.4 **Effect of ozone dose on the DOC removable by bench and pilot-scale biofiltration**

O_3 Dose ($mgO_3/mgDOC$)	DOC_{filter}*	$DOC_{5\text{-}day}$*	$(DOC_{filter}/DOC_{5\text{-}day}) \times 100$	DOC_{slow}*	$AOC_{effluent}$
1.0 ± 0.1	11.0	36.5	30.1	25.5	156
1.5 ± 0.1	21.9	41.5	52.8	19.6	174
1.8 ± 0.1	36.3	46.3	78.4	10.0	209

*: represented as percentage of raw water concentration
DOC_{filter}: DOC removed by pilot-scale biofilter (sand media)
$DOC_{5\text{-}day}$: total DOC removed in 5 days by bench-scale biofilter
DOC_{slow}: $DOC_{5\text{-}day} - DOC_{filter}$
$AOC_{effluent}$: AOC_{total} of pilot-scale biofilter (sand media) effluent

5.5 Implications of Bromide

The concentrations of bromide in OCGW are concerning due to the potential formation of excessive levels of ozonation brominated by-products, in particularly bromate (BrO_3^-). Although bromate was not measured as part of this study, some speculations about its possible formation can be made. The dominant factors influencing the formation of bromate in natural waters are pH and DOC. pH affects the rate of ozone decomposition as well as the bromate formation pathway, in which a higher pH typically results in greater concentrations of bromate

(Siddiqui et. al., 1995; Westerhoff, 1995). The concentration and nature of the DOC for a source water can affect the rate of ozone decomposition and consequently the ozone available to react with bromide (Westerhoff, 1995). The relatively high pH (>8.0) of the OCGW is of concern in terms of bromate formation. However, as discussed in section 5.1.1, the reactivity of the OCGW organic matter with ozone is significant, indicating that the ozone available for reaction with bromide is small. Ozone residual, found in previous studies to be correlative with bromate formation (Krasner et. al., 1993; Shukairy et. al., 1994), was measured at the terminus of the pilot-scale contactor. For all ozone doses, the residual was measured to consistently be less than 0.10 mg/L (approximate detection limit), an encouraging level in terms of available ozone.

5.6 Biomass Concentrations of Pilot-scale Biofilter Media

5.6.1 Overview

This section describes the development of biomass depth profiles for the three pilot-scale biofilters. The objective was to compare the biomass contained on the different media types, as well as to evaluate the effect of biofilter EBCT on biomass. Biomass concentrations were measured using phospholipid analysis. Phospholipids are phosphate containing lipids located within the membranes of viable bacterial cell walls. The concentration of phosphate associated with a given sample of biomass can be correlated to the amount of cells present. This method allows for an indirect quantification of bacterial activity.

5.6.2 Methods and Materials

Phospholipids were measured using a modification of a method originally described by Findlay et. al. (1989) and revised by Carlson (1996). The phospholipid analysis was performed at the termination of pilot-scale experimentation, after steady-state conditions were

achieved for the 1.8 mg O_3/mg DOC transferred ozone dose. Media samples were obtained from each biofilter using a water vacuum which was introduced into the top of each filter column. As the media was removed by the vacuum, samples were collected at specific depths, enabling the development of a vertical profile of biomass. The media was placed in 42 mL EPA vials which was filled, head-space free with ozone effluent water. The samples were shipped in a cooler with blue ice, overnight, to CU. The samples were then transported, same day of receipt, to the Fort Collins Water Utility (Fort Collins, CO) where the analysis was performed.

Upon receipt of the samples, the ozone effluent water was decanted from the sample vials, and the following protocol was exercised to measure the phospholipid content of each sample (*note: the following protocol was derived from the dissertation of Carlson, 1996): 1) methanol, water, and chloroform were added to the media sample at a ratio of 1:2:0.8 (by volume) and a chloroform/media ratio of at least 7 (by weight), 2) after two hours at room temperature, chloroform and water were added to achieve a new ratio of 1:1:0.9 (by volume), 3) the sample was allowed to set at room temperature for a period of 24 hours, 4) the phospholipid containing chloroform phase was removed from the sample mixture and filtered through a Whatman 2V filter (Whatman, England), 5) the filtered chloroform was evaporated under a stream of nitrogen gas, 6) 0.45 mL of potassium persulfate solution (5 g in 100 mL of 0.36 N H_2SO_4) was added to the dried phospholipids and heated for two hours at 100 °C, 7) 0.1 mL of a ammonium molybdate solution (2.5% $(NH_4)_6Mo_7O_{24}*4H_2O$ in 5.72 N H_2SO_4) was added to the phospholipid sample and allowed to set at room temperature for ten minutes, 8) 0.67 mL of malachite green solution (0.111% polyvinyl alcohol dissolved in water at 80 °C, allowed to cool to room temperature, followed by the addition of 0.011% malachite green solid) was added to the sample and allowed to set for 30 minutes at room temperature, 9) the

absorbance of the sample was measured at $\lambda = 610$ nm using a Spectronic 600 (Milton Roy, Cambridge, MA).

The absorbance measurement described above was correlated to a phosphate concentration using a standard curve. The standard curve was generated by dissolving respective amounts of glycerol phosphate solid into D.I. water and analyzing the standards according to the procedure described above, with the exception that the liquid-liquid extraction was not required. The standard curve consisted of six points within a range of 5 to 50 nmoles phosphate.

5.6.3 Discussion

For each of the three media types, an exponential decrease in biomass versus either depth (see Figure 5.34) or EBCT (see Figure 5.35) was observed. Significantly greater amounts of biomass were found in association with GAC versus the anthracite or sand media. Graphical integration of the depth profiles (using Figure 5.34 in conjunction with media bulk densities and S.A. of columns) provides the following estimate of the total phospholipid mass: 4.9×10^5, 2.8×10^5, and 2.4×10^5 nmol PO_4^{-3} for GAC, anthracite, and sand, respectively. Using a conversion factor of 1.9 mg C/nmol PO_4^{-3} (Findlay et. al., 1989), total carbon masses were estimated to equal 9.4×10^5, 5.3×10^5, and 4.6×10^5 mg C/L, respectively, for the GAC, anthracite, and sand filters.

During one backwash event, volatile suspended solids (VSS), another measure of biomass, were measured in the backwash water under the following backwash conditions: 2.5 gpm over a duration of 15 minutes for both the GAC and anthracite; 5.0 gpm over a duration of 10 minutes for the sand. The VSS concentrations were determined to be 8.9, 1.7, and 4.6 for the GAC, anthracite, and sand, respectively; the total VSS masses using the backwash volumes of 142, 142, and 196 liters were calculated to be 1,300, 900, and 240 mg. Using an

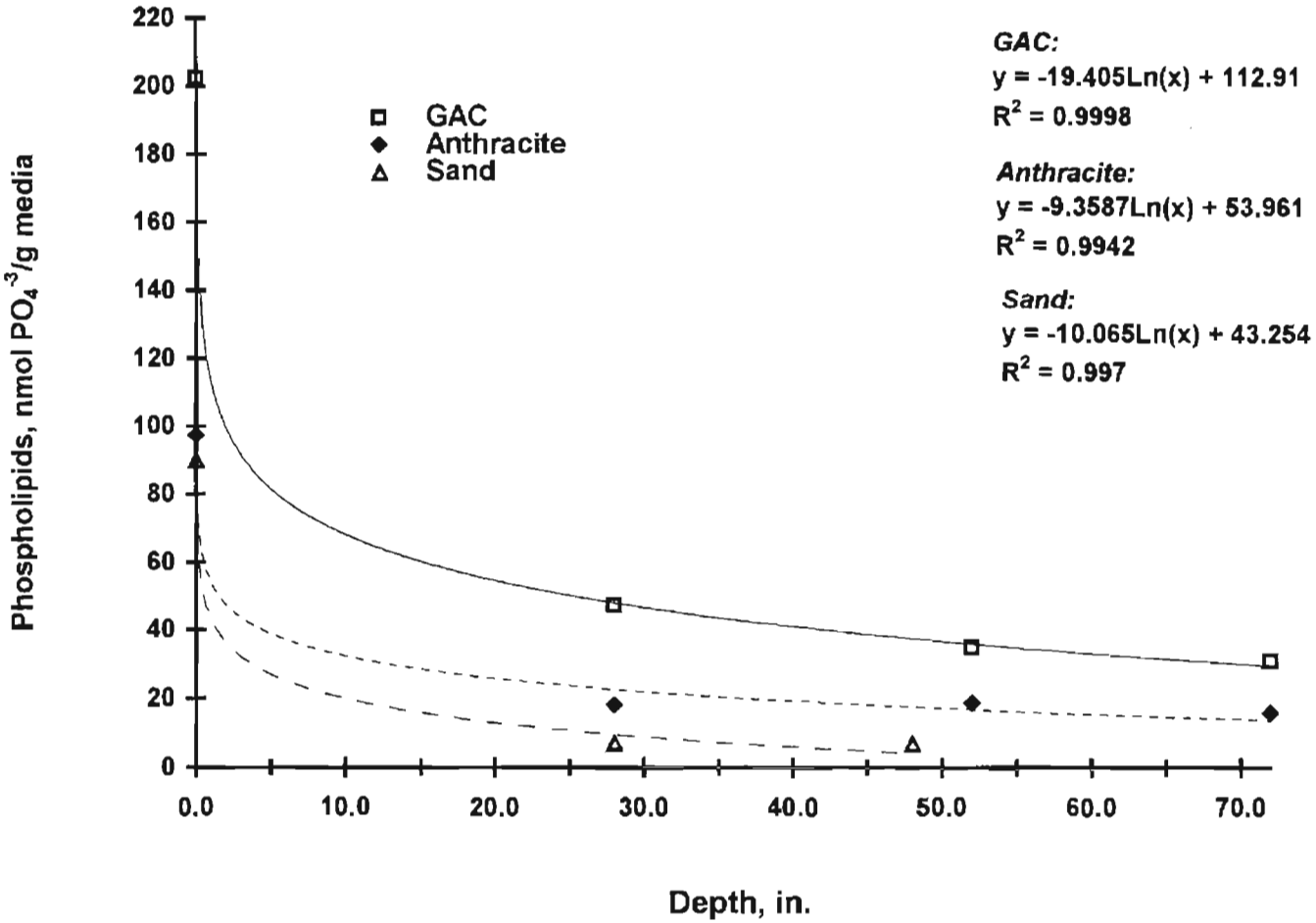

Figure 5.34 Effect of biofilter depth and media type on biomass (as phospholipids)

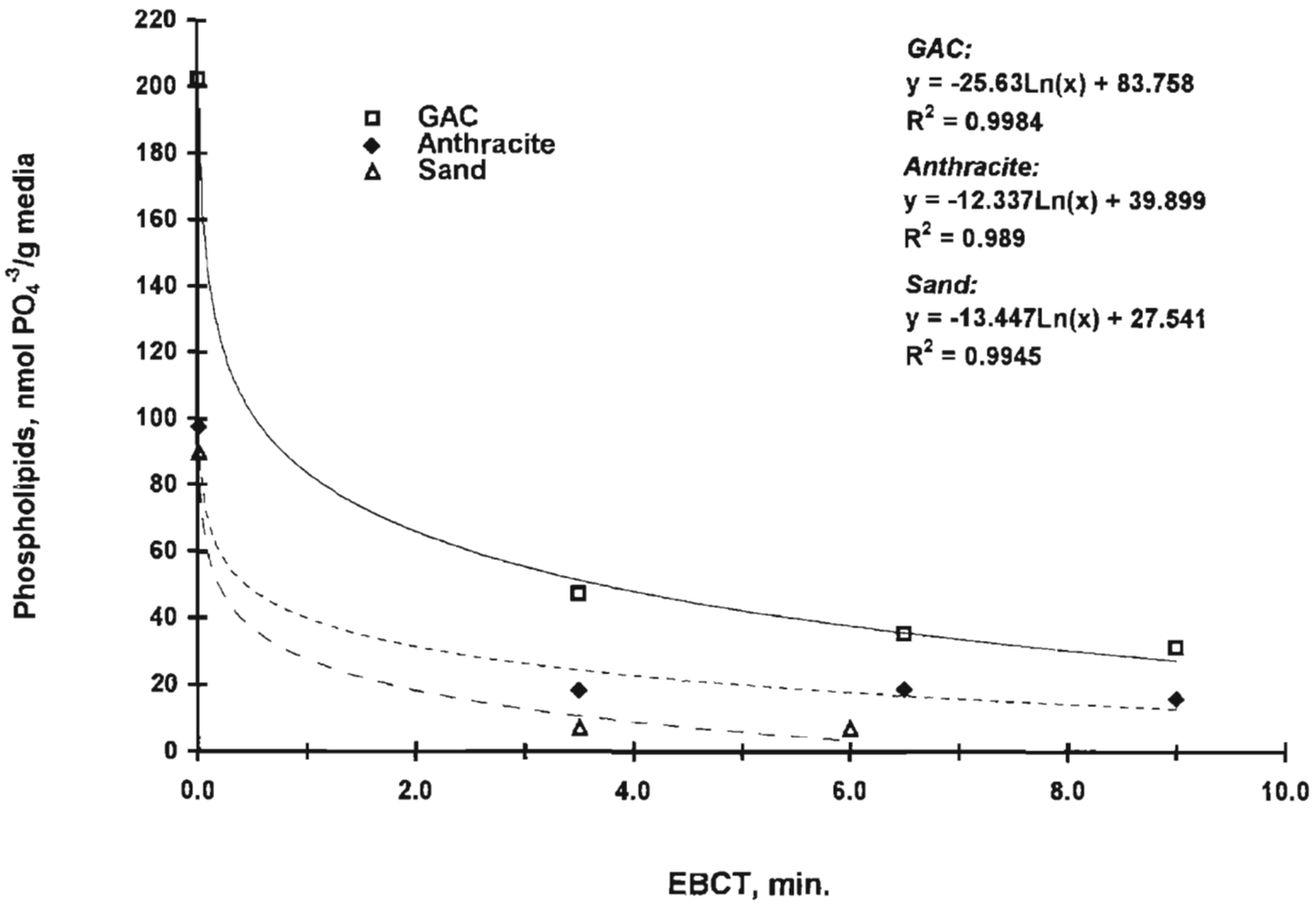

Figure 5.35 Effect of biofilter empty bed contact time (EBCT) and media type on biomass (as phospholipids)

assumed carbon cell content of 50% (by weight; 0.5 mg C/mg VSS), the total carbon masses were estimated to be 650, 450, and 120 mg C for GAC, sand, and anthracite filters, respectively.

A comparison of the biomass (as carbon) lost during backwashing versus the biomass (as carbon) associated with each media demonstrates that backwash perturbations to the biofilters' biomass are minor. This result is consistent with previously presented results (see section 5.2.5) which showed virtually no effect of backwashing on biofilter performance.

5.7 Comparative Assessment: OCGW Versus Other Source Waters

It is evident that the source water studied during this research is somewhat unusual in terms of its NOM properties (e.g., the high value for SUVA of 0.052 cm^{-1}); hence there is some concern about whether results obtained herein can be generalized. In order to contrast different source waters with the OCGW, the results of the current study are compared against those of Carlson (1996). Carlson (1996) studied the ozone-biofiltration treatment of the following low turbidity surface waters: Horsetooth Reservoir (SUVA = 0.017 cm^{-1}); the Poudre River (SUVA = 0.029 cm^{-1}); and College Lake (SUVA = 0.016 cm^{-1}). The bench-scale biofilter removals (5-day) are shown in Figure 5.36 for these source waters, in addition to the results obtained for the 50 cu OCGW. The OCGW results are most comparative with those of College Lake. This observation is somewhat surprising in light of their different SUVA values. In any event, the OCGW source can be considered to be amenable to ozone-biofiltration when contrasted to these other source waters.

Figure 5.37 shows OBP yields of the various source waters. The OCGW source, once again, behaves closest to that of College Lake. Furthermore, the OBP results, when compared to the biofilter DOC removals, suggest that the OBP composite is not a good surrogate of

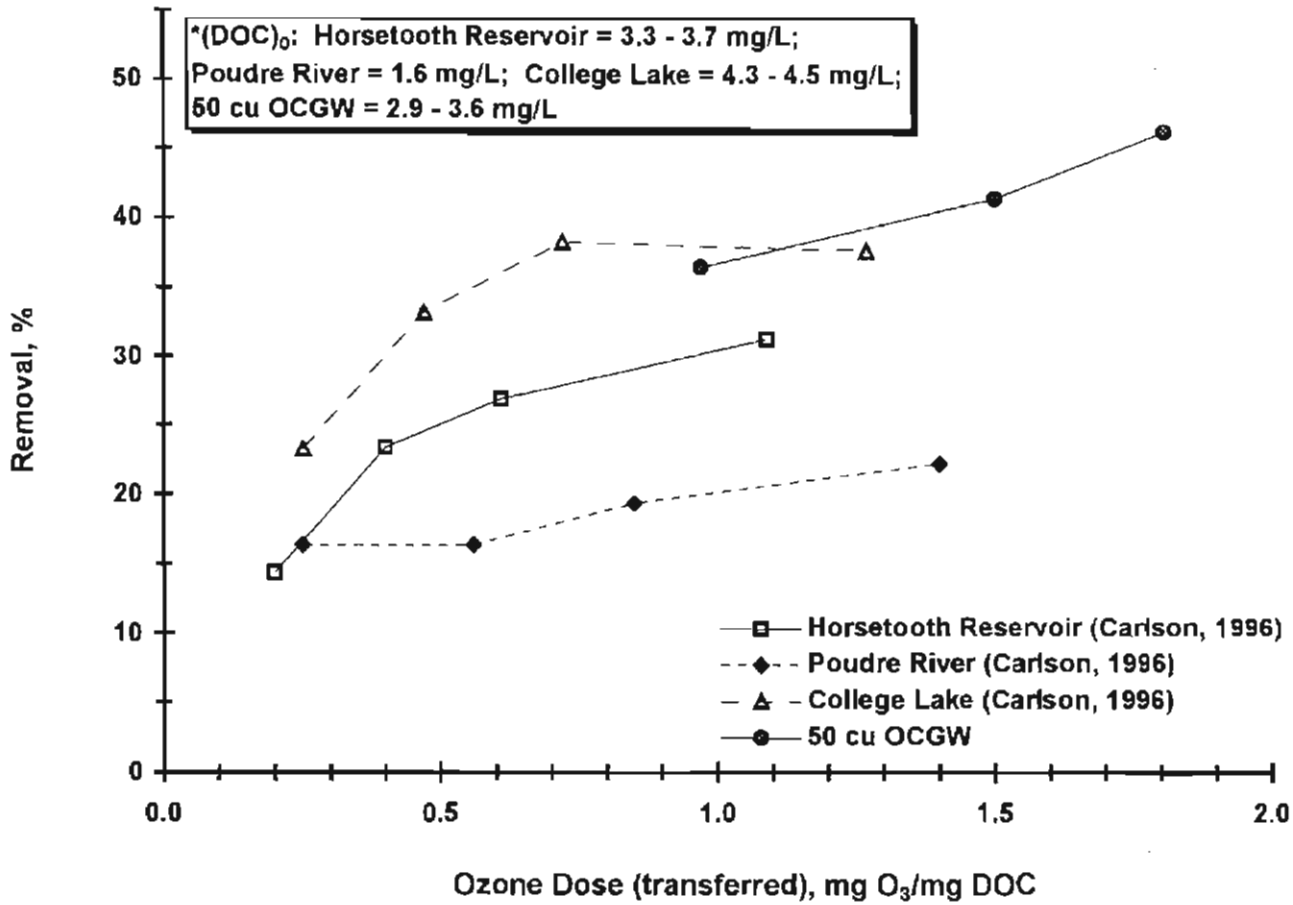

Figure 5.36 Removal of DOC in bench-scale biofilters (5-day) vs. ozone dose: comparison of 50 cu OCGW (current study) with Horsetooth Reservoir, Poudre River, and College Lake (Carlson, 1996)

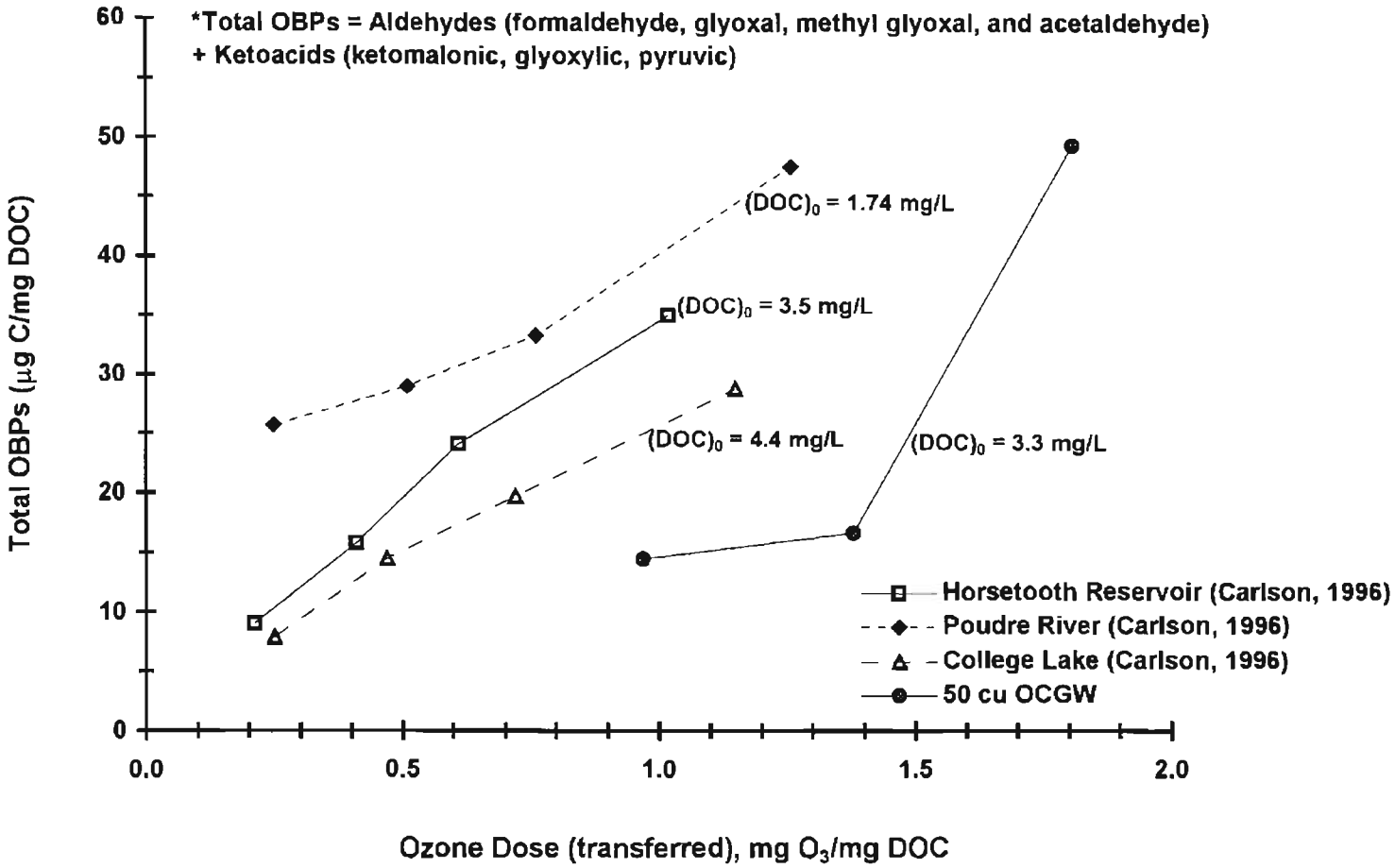

Figure 5.37 Formation of total OBPs vs. pilot-scale ozone dose: a comparison of 50 cu OCGW (current study) with Horsetooth Reservoir, Poudre River, and College Lake (Carlson, 1996)

biodegradability. This comparative assessment suggests that OCGW may be somewhat of an end member source water, but not an extreme outlier.

CHAPTER VI

SUMMARY

This research provided insight on the nature of a highly colored groundwater and its treatability using ozone-enhanced biofiltration. The use of ozone-enhanced biofiltration as an independent alternative for the drinking water treatment of low turbidity, moderately colored source waters was demonstrated. The process was observed to be effective in reducing color, DBP precursors, and chlorine demand, while providing adequate turbidity removals, filter operation times, and disinfection requirements. Some possible limitations were recognized in the form of inadequate stabilization of regrowth potential and production of brominated by-products. A detailed summary of the project results and associated observations are as follows:

- although stabilized due to the presence of bicarbonate, the ozone reactivity with OCGW was still significant, comparable to that found for Suwannee River humic and fulvic acid isolates
- an optimum ozone dose of approximately 2.0 mg O_3/mg DOC was observed for the removals of color, UV_{abs}, DOC, THMFP, and Cl_2 demand using bench-scale biofiltration; the trend of removal vs. ozone dose was similar for all the aforementioned parameters
- ozonation caused the majority of color and UV_{abs} removal, whereas bench-scale biofiltration generally provided little (< 5%) additional color removal and some (~ 5 to 10%) removal of UV_{abs}

- DOC removals during bench-scale biofiltration were increased (~ 15 to 35 %) by ozonation, whereas minor (<10 %) removals of DOC (i.e., mineralization) occurred using ozone alone
- ozonation was the source for the majority of total THMFP removal; specific THMFP (THM/DOC) was decreased (> 20%) upon ozonation, but increased (> 15%) during bench-scale biofiltration
- although some (> 30 %) Cl_2 demand was removed during ozonation, the addition of bench-scale biofiltration provided the majority of removal (> 70 %); specific Cl_2 demand (Cl_2 demand/DOC) was decreased (>20 %) upon ozonation and further reduced through biofiltration (>40 %)
- pilot-scale ozonation and biofiltration produced similar removal vs. ozone dose trends as observed at the bench-scale for DOC, color, UV_{abs}, THMFP, and Cl_2 demand
- the GAC media was superior to anthracite and sand media in removing the various parameters measured; the superior performance of the GAC media became less pronounced as ozone dose increased
- compliance with current USEPA regulations was achieved for color, THMs (GAC media only), and turbidity; none of the proposed USEPA regulations for THMs were met
- significant formation of OBPs (~ 150 - 400 μg/L) and AOC (~ 300 - 800 μg/L) occurred during ozonation; biofiltration reduced the majority of all OBPs to raw water levels; biofiltration did not remove all of the produced AOC and effluent quality was observed to deteriorate with increase in ozone dose
- the majority (> 80%) of biofilter removals for DOC, THMFP, THMSDS, Cl_2 demand, OBPs, and AOC were achieved with an EBCT equal to 3.5 minutes
- backwashing did not affect the biofilter removals of DOC, THMFP, and Cl_2 demand

- significant differences were observed between the reactivity of monochloramine and free chlorine with the OCGW; monochloramine produced significantly less THMs (~ 10 μg/L for GAC effluent) than free chlorine (~ 95 μg/L for GAC effluent) and required less initial dosage to maintain a given residual
- DOC rapidly removable during bench-scale biofiltration was qualitatively observed to be produced upon ozonation, and removed partially by pilot-scale biofiltration; a distinct relationship between the DOC removable during pilot-scale vs. bench-scale biofiltration was unable to be defined; the total (5-day) removable DOC present in the pilot-scale biofilter effluent was observed to decrease with ozone dose
- bromate is considered a potential concern due to raw water bromide levels and elevated pH; however, NOM reactivity and low measured ozone residuals during pilot-scale operation suggest the absence of available ozone for bromate formation
- greater biomass concentrations were observed to occur on the GAC media than the other media types; backwashing did not appear to perturb the biomass significantly
- the 50 cu OCGW was found to behave similarly to other given source waters, in terms of ozone-induced biodegradability and formation of OBPs

CHAPTER VII

FUTURE RECOMMENDATIONS

To further assess the use of ozone-enhanced biofiltration in treating OCGW, as well as other source waters, the future recommendations listed below should be considered:

- evaluation of the production of bromate and other brominated ozonation by-products, as well as the effect of ozonation and biofiltration on chlorination HAAs
- assessment of the amenability of other OCGW source locations, as well as low turbidity surface waters, to treatment using an independent ozone-enhanced biofiltration system; assessment of the benefit of combining ozone-enhanced biofiltration with other treatment processes (i.e., coagulation)
- determination of the post-disinfection requirements, using free and/or combined chlorine, considering inactivation credits achieved with ozonation and necessity to attenuate regrowth potential
- exploration of the possibility of simulating larger-scale biofiltration using bench-scale methods; reconciliation of pilot and bench-scale yield coefficients (Y = biomass produced/DOC removed) and mass loading rates
- investigation of the relationship between ozone dose and biofilter effluent quality in terms of distribution system regrowth potential; performance of other regrowth potential measurements, such as heterotrophic plate counts (HPC)
- investigation of the effect of nutrient (N and P) additions on biological performance

References

Aiken, G. and Cotsaris, E. Soil and Hydrology: Their Effect On NOM, *Journal AWWA*, 1:36 (1995).

Aiken, G.L., McKnight, D.M., Thorn, K.A., and Thurman, E.M. Isolation of Hydrophilic Organic Acids From Water Using Nonionic Macroporous Resins, *Organic Geochemistry*, 18:4:567 (1992).

Akiyoshi, E., Ruiz, H., Thompson, K., and Spangenberg, C. Removal of Natural Organic Matter and Disinfection By-Product Precursors in Groundwaters, *unpublished* (1995).

Amy, G., Chowdhury, Z., Green, R., Krasner, S., Owen, D., Paode, R., Rice, E.W., and Summers, R.S. Biodegradability of Natural Organic Matter: A Comparison of Methods (BDOC and AOC) and Correlations with Chemical Surrogates. Proceedings: AWWA Annual Conference, Vancouver, B.C. (1992).

Amy, G.L., Tan L., and Davis, M.K. The Effects of Ozonation and Activated Carbon Adsorption on THM Speciation, *Water Research*, 25:2:191 (1991).

Amy, G.L., Greenfield, J.H., and Cooper, W.J. Organic Halide Formation During Water Treatment Under Free Chlorine Versus Chloramination Conditions, Water Chlorination: Chemistry, Environmental Impact and Health Effects. Vol. 6, pp. 605-621 (1987)

Amy, G.L., Sierka, R.A., Bedessem, J., Price, D., and Tan, L. Molecular Size Distributions of Dissolved Organic Matter, *Journal AWWA*, 6:67 (1992).

AWWA Committee Report, An Assessment of Microbial Activity on GAC, *Journal AWWA*, 8:447 (1981).

Bader, H. and Hoigne, J. Determination of Ozone in Water By the Indigo Method. *Water Research*, 15:449 (1981).

Bradford, S.M., Palmer, C.J., and Olson, B.H. Assimilable Organic Carbon Concentrations in Southern California Surface and Groundwater, *Water Research*, 28:2:427 (1994).

Carey, T.J., Orange County California Groundwater Characterization and Treatability, Masters Thesis, University of Arizona (1989).

Carlson, K.H. Optimization of the Ozone and Biofiltration Processes for Multiple Drinking Water Objectives, Ph.D. Dissertation, University of Colorado-Boulder (1996).

Carlson, K.H. and Amy, G.L. The Relative Importance of HLR and EBCT on the Removal of BOM During Biofiltration, Proceedings: AWWA Water Quality Technology Conference, New Orleans, LA (1995).

Carlson, K.H., Amy G.L, Garside, J., and Blais, G. Ozone-Induced Biodegradation and Removal of NOM and Ozonation By-products in Biological Filters, Proceedings: Slow Sand/Alternative Biological Filtration Conference, London, England (1996).

Chang, D.S. and Singer, P.C. The Impact of Ozonation on Particle Stability and the Removal of TOC and THM Precursors, *Journal AWWA*, 3:71 (1991).

Collins, M.R., Amy, G.L., and Steelink, C. Molecular Weight Distribution, Carboxylic Acidity, and Humic Substances Content of Aquatic Organic Matter: Implications for Removal During Water Treatment, *Environmental Science and Technology*, 20:10:1028 (1986).

Compilation of EPA's Sampling and Analysis Methods. Lewis Publishing, New York, NY (1992).

Cowman, G.A. and Singer, P.C. Effect of Bromide Ion on Haloacetic Acid Speciation Resulting from Chlorination and Chloramination of Aquatic Humic Substances, *Environmental Science and Technology*, 30:1:16 (1996).

Edzwald, J.K., Becker, W.C., and Wattier, K.L. Surrogate Parameters for Monitoring Organic Matter and THM Precursors, *Journal AWWA*, 4:122 (1985).

Findlay, R.H., King, G.M., and Watling, L. Efficacy of Phospholipid Analysis in Determining Microbial Biomass in Sediments, *Applied and Environmental Microbiology*, 55:11:2888 (1989).

Goel, S., Hozalski, R.M., and Bouwer, E.J. Biodegradation of NOM: Effect of NOM Source and Ozone Dose, *Journal AWWA*, 1:90 (1995).

Haag, W.R. and Hiogne, J. Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate, *Environmental Science and Technology*, 17:5:261 (1983).

Hodgeson, J.W. and Cohen, A.L. (United States Environmental Protection Agency). Determination of Chlorination Disinfection By-products and Chlorinated Solvents in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography With Electron-Capture Detection, Methods for the Determination of Organic Compounds in Drinking Water: Supplement I (1990).

Huck, P.M., Zhang, S., Price, M.L. BOM Removal During Biological Treatment: A First-Order Model, *Journal AWWA*, 6:78 (1994).

Huck, P.M. Measurement of Biodegradable Organic Matter and Bacterial Growth Potential in Drinking Water, *Journal AWWA*, 7:78 (1990).

Jacangelo, J.G., Patania, N.L., Reagan, K.M., Aieta, M.E., Krasner, S.W., and McGuire, M.J. Ozonation: Assessing Its Role in the Formation and Control of Disinfection By-products, *Journal AWWA*, 8:74 (1989).

Joret, J.C., Levi, Y., and Volk, C. Biodegradable Dissolved Organic Carbon (BDOC) Content of Drinking Water and Potential Regrowth of Bacteria, *Water Science and Technology*, 24:2:95 (1991).

Krasner, S.W., Glaze, W.H., Weinberg, H.S., Daniel, P.A., and Najm, I.N. Formation and Control of Bromate During Ozonation of Waters Containing Bromide, *Journal AWWA*, 1:73 (1994).

Krasner, S.W., Sclimenti, M.J., and Coffey, B.M. Testing Biologically Active Filters for Removing Aldehydes Formed During Ozonation, *Journal AWWA*, 85:5:62 (1993).

LeChevallier, M.W., Becker, W.C., Schorr, P., and Lee, R.G. Evaluating the Performance of Biologically Active Rapid Filters, *Journal AWWA*, 4:136 (1992).

LeChevallier, M.W., Cawthon, C.D., and Lee R.G. Inactivation of Biofilm Bacteria, *Applied and Environmental Microbiology*, 54:10:2492 (1988).

Leenheer, J. A. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon form Natural Waters and Wastewaters. *Environmental Science and Technology*, 15:5:578 (1981).

Miltner, R.J., Shukairy, H.M., and Summers, R.S. Disinfection By-product Formation and Control by Ozonation and Biotreatment. *Journal AWWA*, 11:53 (1992).

Miltner, R.J., Summers, S.R., and Wang, J.C. Biofiltration Performance: Part 2, Effect of Backwashing, *Journal AWWA*, 12:64 (1995).

Mogren, E.M., Scarpino, P., and Summers, R.S. Measurement of Biodegradable Dissolved Organic Carbon in Drinking Water. Proceedings: AWWA Annual Conference, Cincinnati, Ohio (1990).

Murphy, B.M., Ozone Induced Conversion of DBP Precursors (DOC) to Biodegradable By-Products (BDOC), Masters Thesis, University of Colorado-Boulder (1993).

Najm I.N. and Krasner, S.W. Effects of Bromide and NOM on By-Product Formation, *Journal AWWA*, 1:106 (1995).

Noble, P.A., Clark, D.L., and Olson, B.H. Biological Stability of Groundwater, *Journal AWWA*, 5:87 (1996).

Owen, D.M., Amy, G.L., Chowdhury, Z.K., Paode, R., McCoy, G., and Viscosil, K. NOM Characterization and Treatability, *Journal AWWA*, 1:46 (1995).

Pontius, F.W. An Update of the Federal Regs, *Journal AWWA*, 3:36 (1996).

Qualls, R.G. and Johnson, D.J. Kinetics of the Sort-Term Consumption of Chlorine by Fulvic Acid. *Environmental Science and Technology*, 17:11:692 (1983).

Reckhow, D.A. and Singer, P.C. Chlorination By-products in Drinking Waters: From Formation Potentials to Finished Water Concentrations, *Journal AWWA*, 4:173 (1990).

Reckhow, D.A. Singer, P.C., and Malcolm, R.L. Chlorination of Humic Materials: By-product Formation and Chemical Interpretations, *Environmental Science and Technology*, 24:11:1655 (1990).

Reckhow, D.A., Legube B., and Singer, P.C. The Ozonation of Organic Halide Precursors: Effect of Bicarbonate, *Water Research*, 20:8:987 (1986).
Rook, J.J. Chlorination Reactions of Fulvic Acids in Natural Waters, *Environmental Science and Technology*, 11:5:478 (1977).

Rook, J.J. Formation of Haloforms During Chlorination of Natural Waters, *Water Treat. Exam.*, 23:234 (1974)

Sclimenti, M.J. Ozone Disinfection By-Products: Optimization of the PFBHA Derivation Method for the Analysis of Aldehydes. Proceedings: AWWA Annual Conference, San Diego, CA (1990).

Servais, P., Billen, G., Ventresque, C., and Bablon, G.P. Microbial Activity in GAC Filters at the Choisy-le-Roi Treatment Plant, *Journal AWWA*, 1:62 (1991).

Shukairy, H.M., Miltner, R.J., and Summers, R.S. Bromide's Effect on DBP Formation, Speciation, and Control: Part 1, Ozonation, *Journal AWWA*, 6:72 (1994).

Shukairy, H.M., Miltner, R.J., and Summers, R.S. Bromide's Effect on DBP Formation, Speciation, and Control: Part 2, Biotreatment, *Journal AWWA*, 10:71 (1995).

Shukairy, H.M. and Summers, R.S. The Impact of Pre-ozonation and Biodegradation on Disinfection By-Product Formation, *Water Research*, 26:9:1217 (1992).

Siddiqui, M.S. and Amy, G.L. Factors Affecting DBP Formation During Ozone-Bromide Reactions, *Journal AWWA*, 1:63 (1993).

Siddiqui, M.S., Amy, G.L., and Rice, R.G. Bromate Ion Formation: A Critical Review, *Journal AWWA*, 10:58 (1995).

Speitel, G.E., Symons, J.M., Cipparone, L.A., Diehl, A.C., and Sorenson, H.W. Effect of Ozone Dosage and Subsequent Biodegradation on Removal of DBP Precursors. *Journal AWWA*, 5:86 (1993).

Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, and WPCF, Washington, D.C. (19th edition, 1995).

Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., and Owen, D. Assessing DBP Yield: Uniform Formation Conditions. *Journal AWWA*, 6:96 (1996).

Tan, L. and Amy, G.L. Comparing Ozonation and Membrane Separation for Color Removal and Disinfection By-product Control, *Journal AWWA*, 5:74 (1991).

van der Kooij, D., Visser, A., and Hijnen, W.A.M. Determining the Concentration of Easily Assimilable Organic Carbon in Drinking Water. *Journal AWWA*, 10:540 (1982).

Volk, C., Renner, C., Roche, P., Paillard, H., Joret, J.C. Effect of Ozone On the Production of Biodegradable Dissolved Organic Carbon (BDOC) During Water Treatment. *Ozone: Science and Engineering*, 15:389 (1993).

Wang, J.C., Summers, S.R., and Miltner, R.J. Biofiltration Performance: Part 1, Relationship to Biomass, *Journal AWWA*, 12:55 (1995).

Weinberg, H.S., Glaze, W.H., Krasner, S.W., and Sclimenti, M.J. Formation and Removal of Aldehydes in Plants That Use Ozonation, *Journal AWWA*, 5:72 (1993).

Westerhoff, P. Ozone Oxidation of Bromide and Natural Organic Matter, Ph.D. Dissertation, University of Colorado-Boulder (1995).

Xie, Y., Reckhow, D.A. A New Class of Ozonation By-Products: the Ketoacids. Proceedings: AWWA Annual Conference, Vancouver, B.C. (1992).

Zhu, H.W., Modeling the Effects of Coagulation on the Chlorination of By-Product Formation, Ph.D. Dissertation, University of Colorado-Boulder (1995).