6-25-2010

Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and EDCs from wastewater

Carson Odell Lee

Carson Odell Lee
Candidate

Civil Engineering
Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

, Chairperson

Ozone and Biofiltration as an Alternative to Reverse Osmosis for Removing PPCPs and EDCs from Wastewater

BY

Carson Odell Lee

B.S., Civil Engineering, University of New Mexico, 2007

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science
Civil Engineering

The University of New Mexico
Albuquerque, New Mexico

May 2010

Dedication

Although it would be impossible to list everyone here who has helped me to become who I am today, I shall give it a try.

To my Mom and Dad who showed me, each in their own way, the importance of an education and how to work hard

To my good friends over these many years who have stuck by my side in thick and thin. These great people include, but are not limited too; Brad (Bunny) Tausin, Tyson Ratliff, Jerry and Tonya Aragon, Steve Conway, Jason Clark, Jay Gonzales, Jay and Liz Olsen, Mathew Mulholland, Jared Roy, Josh Goldman, Chris Cumber, Rocky Norton, Aaron Ludewig, Tara Martin (Boozer), Fred and Linda Kellerup, the Chevers family, Gib, RW, Goldchain, Sunshine, and anyone else who I may have missed.

To Katy Blanke and Gloria for their big hearts and the wonderful work they do

To my fiancé, Danielle Kellerup (a.k.a. Daniellerup!), who I could not have done this without. Thank you for always having dinner ready and a smile to greet me, no matter how late I was working!!

In loving Memory of my Grandparents (Carson Odell and Dora Rogers) and my friend Ernie Tillerson

Acknowledgements

I would like to especially thank my advisor and committee chair, Dr. Kerry Howe, for all of the hard work and time he invested in both my research and education. His patience, knowledge, and dedication have not only made me a better engineer, but also a better person. I, like all of his previous students, value the opportunity to have worked with him and consider myself very fortunate in this respect.

My committee members, Dr. Bruce Thomson and Dr. Andrew Schuler, whose input and dedication to the project ensured its success and increased the quality of the science. A special thanks to Dr. Thomson for his time and his ability to throw a great party.

Thank you to Richard Rose and the New Mexico Environmental Department for their funding and support of this project. Their flexibility was especially appreciated in shaping the outcome of this project.

Thanks to Koch Membrane Systems for donating the microfilters and to Osmonics for donating the RO membranes and spacers used in this project.

Joey Nogales and the operators at the Albuquerque Bernalillo County Water Utility Authority (ABCWUA) Southside Water Reclamation Plant (SWRP) were extremely helpful in ensuring we had everything we needed to operate our pilot system. They were always quick to get us anything we needed and were very helpful when something went wrong.

A special thanks to Janet Leavitt, Emily Kowalchuk, Jeff Sampson, Josh Goldman, and Elizabeth Field for their assistance in this research project.

I would also like to thank the staff in the Civil Engineering office as well as the professors in the Civil Engineering department. Their hard work and dedication to the students makes the UNM Civil Engineering department one of the best around.

Ozone and Biofiltration as an Alternative to Reverse Osmosis for Removing PPCPs and EDCs from Wastewater

BY

Carson Odell Lee

ABSTRACT OF THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science
Civil Engineering

The University of New Mexico
Albuquerque, New Mexico

Ozone and Biofiltration as an Alternative to Reverse Osmosis for Removing PPCPs and EDCs from Wastewater

By

Carson Odell Lee

B.S., Civil Engineering, University of New Mexico, 2007

M.S., Civil Engineering, University of New Mexico, 2010

Abstract

A lot of attention has been paid to trace amounts of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in drinking water supplies. Current water and wastewater treatment techniques, such as coagulation, flocculation, and sedimentation for water treatment and the conventional activated sludge process for wastewater treatment, have shown only limited success in their removal. Although there is a lack of evidence linking these emerging microconstituents to adverse human health effects, not a lot is known about the effects of long term exposure to these compounds and more research is still needed. This study examined advanced wastewater treatment processes, such as membrane bioreactors (MBRs), along with processes that are not normally used for treating wastewater to remove these emerging contaminants.

The processes include oxidation with ozone coupled with biological active filtration (BAF) to increase the removal efficiencies of these compounds.

A pilot scale membrane bioreactor (MBR) was set up at the Albuquerque Bernalillo County Water Utility Authority (ABCWUA) Southside Water Reclamation Plant (SWRP). The MBR was continuously fed primary treated wastewater. The MBR effluent was used to feed an ozone contactor, which then fed a BAF column. The MBR was operated at an SRT of 10 days throughout the duration of the experiments. Three ozone doses where examined. The applied ozone doses were 2, 4, and 8 mg/L, which correspond to a ratio of 0.5, 1, and 2 mg ozone/mg TOC. After ozone treatment, the water was pumped to the BAF column. The BAF column used anthracite media that was seeded with MLSS and soaked in MBR feedwater for a week to establish a bio-growth prior to the experiments. The system was run for at least one week between sampling events to establish steady state conditions at each new ozone dose. To determine steady state conditions, TOC, UV_{254}, SUVA, and BDOC removal were evaluated. This study also investigated the removal of microconstituents using a reverse osmosis (RO) system that ran concurrent to the Ozone/BAF treatment train for two of the ozone doses. The concentrations of the compounds of interest were tested in the effluents of the MBR, ozone, BAF, and RO.

Significant removal of the selected compounds was observed at all selected ozone doses. Although removal of microconstituents increased with increasing ozone dose, little additional removal occurred at ozone concentrations greater than 4 mg/L. The change in percent removal of both organics and microconstituents was larger going from an ozone dose of 2 to 4 mg/L than going from 4 to 8 mg/L. The BAF column did not dramatically decrease the concentrations of these compounds after the initial decrease due to ozonation, although additional TOC removal was achieved. This can be contributed to oxidation breaking the compounds down to smaller, more biodegradable compounds. Bulk organic analysis such as TOC, UV_{254} absorbance, SUVA, and BDOC show that organic compounds are not mineralized to CO_2 and H_2O by ozonation alone.

However, the data also shows that additional destruction of TOC occurred in the BAF column following ozonation. Although the organic analyses do not indicate the fate of individual microconstituents, the microconstituents can be expected to have the same fate as other organics.

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

Of the many problems our country, and indeed the world, is facing today, a clean, safe, and abundant water supply is one that often gets little attention despite its importance to both the economy and quality of life. Of recent concern is the presence of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) that are being found in trace amounts in the nation's water supply. These microconstituents enter the water supply through many sources, although one of the most important is thought to be through wastewater treatment plants (WWTPs) [1, 2]. A large portion of these microconstituents enter the wastewater stream as human excretions of unmetabolized or partly metabolized pharmaceuticals [2, 3]. Conventional processes used in both wastewater treatment plants (WWTPs) [4] and drinking water treatment plants [5] have been found to be either ineffective at removing many microconstituents, or have large drawbacks to them.

Removing microconstituents in a wastewater treatment plant can be important in many ways. The effluent from WWTPs are usually discharged into surface waters, such as rivers. Contaminants from the treated wastewater have been shown to adversely affect surrounding wildlife and the aquatic environment [6, 7]. In addition, wastewater effluent has been shown to be a major source of pharmaceuticals and EDCs for water supplies that are downstream of these plants. Currently no evidence links PPCPs/EDCs to adverse human health problems at the concentrations being found in drinking water [7], but there is a lack of knowledge about the effects these microconstituents have on human health at these low levels. Until more research on the effect of these compounds is known, the precautionary principle should be applied and steps should be taken to decrease the amount of these compounds released into the environment.

Currently a lot of research has been focused on removing micropollutants from both drinking water and wastewater. Some of the more promising processes for removing microconstituents are oxidation, adsorption, and reverse osmosis. While these processes can remove many of these compounds to a relatively high degree, there are

drawbacks to these processes, especially in trying to incorporate them into wastewater treatment.

Oxidation can remove many compounds to a high degree although the oxidant dose and contact time required can be higher than that needed for disinfection. In the case of ozone, which is the most powerful oxidant used in water and wastewater treatment, the higher dose would require more energy than that required for disinfection, and may create higher concentrations of disinfection by-products (DBPs).

Adsorption processes, using granular activated carbon (GAC) and powdered activated carbon (PAC), can remove many micropollutants well although these processes also have drawbacks. Research has shown that hydrophilic compounds reach breakthrough in a column much faster than hydrophobic compounds [8, 9]. In addition, the presence of NOM can greatly reduce the removal efficiency of the carbon as well as exhaust the carbon faster. For wastewater treatment, which is expected to have much higher concentrations of NOM than most source waters, the activated carbon would have to be replaced or regenerated more often, which leads to higher operating costs.

Current research has shown that reverse osmosis (RO) is a very promising treatment technique that can remove most micropollutants to a high degree [8]. Although RO will remove these micropollutants, there are many drawbacks to using RO both in water and wastewater treatment. The RO process uses a lot of energy and also creates a concentrated wastestream that must be managed [8]. The RO process also wastes a portion of the water treated. This amount varies depending on the quality of the influent and the quality of the effluent desired. This loss of water can be a particular problem in places like New Mexico where sources of potable water are limited.

Some utilities treating wastewater for indirect potable water reuse are taking it upon themselves to remove as many of the emerging microconstituents as they can from the wastewater. This is due to not only the concern about future regulations regarding

these newly emerging compounds, but also because of the public perception of having microconstituents in the water.

Currently there are at least two communities in New Mexico that are looking to supplement their current water supplies through planned indirect potable water reuse. The village of Cloudcroft, New Mexico is currently constructing a state of the art water and wastewater treatment plant to deal with its ongoing water shortage problems. Cloudcroft will treat its wastewater using a membrane bioreactor (MBR), followed by RO, and advanced oxidation. The highly treated water will then be blended and stored in a reservoir for a period of time before it undergoes further water treatment to bring it to potable standards. These treatments include ultrafiltration followed by granular activated carbon and disinfection before the water is sent to the water distribution system.

The other community looking to supplement its current water supply is Rio Rancho, New Mexico. Currently a pilot scale system is investigating planned indirect potable water reuse using a different treatment train than the one in Cloudcroft. This pilot also involves the use of a MBR, but unlike the Cloudcroft facility, does not use reverse osmosis. Instead, the pilot study is examining the use of the advanced oxidation process (AOP) of ozone and H_2O_2 followed by GAC. Following this, the community plans to use the treated wastewater for aquifer storage and recovery where it will be removed in several years as potable water. One of the important parameters being monitored is the presence and removal of endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs). This treatment train has the potential to remove micropollutants to a high degree without the loss of water and high energy consumption associated with RO.

Because of the ongoing scarcity of water and the limitations of treatment processes like RO, this study examined the use of a combination of water treatment techniques to try to achieve a high degree of PPCP/EDC removal with no loss of water, minimal use of energy, and at the lowest cost possible. To gather the best possible data for the size and scope of this project, a pilot system was continuously operated at the

Albuquerque Bernalillo County Water Utility Authority (ABCWUA) Southside Water Reclamation Plant (SWRP). The pilot system consisted of an MBR, ozone contact chamber, and BAF column. The MBR received primary treated wastewater and operated at a flowrate of approximately 200 mL/min at an SRT of 10 days. The MBR effluent fed an ozone contactor at a flowrate of 100 mL/min. The effluent from the ozone contactor fed a biologically active filter composed of anthracite with an EBCT of approximately 20 minutes.

Due to the cost of the PPCP/EDC analysis, only three ozone doses were tested. To find the most effective ozone doses, the project was divided into two phases. In Phase 1 of the project, a series of analyses were done to examine the effects of various ozone doses on different organic parameters. The bulk organic analysis consisted of total organic carbon (TOC), UV_{254} absorbance, specific UV absorbance (SUVA), and biodegradable dissolved organic carbon (BDOC). These parameters were measured at varying ozone doses ranging from 0 to approximately 12 mg/L. It was determined that the widest array of data could be gathered by examining PPCP/EDC removal at ozone doses of 2, 4, and 8 mg/L.

Phase 2 of this research was also divided into two parts. Phase 2 examined both the removal of organics and the removal of microconstituents at the 3 applied ozone doses determined in Phase 1. TOC, UV_{254} absorbance, SUVA, and TOC removal were measured daily to establish steady state conditions and to predict PPCP/EDC removal. BDOC was measured 3 times for each applied ozone dose. The other part of Phase 2 examined the removal of microconstituents at the 3 applied ozone doses determined in Phase 1. A total of 16 samples were collected and analyzed for PPCPs/EDCs.

The purpose of this project was to evaluate the removal of these emerging contaminants from wastewater by a combination of these water treatment techniques. The average TOC concentration of the MBR effluent was approximately 4 mg/L, which corresponds to an ozone to TOC ratio of 0.5, 1.0, and 2.0 mg ozone/mg TOC. A concurrent RO process was also examined for PPCP/EDC removal and a field blank was

collected to establish confidence in the sampling process. Organic parameters were also collected and analyzed to determine if there is a correlation between the removal of organics and microconstituents.

The hypothesis in this research was that the combination of water treatment techniques employed in this study would be able to effectively remove a wide variety of compounds. Each of the treatment techniques employed is able to remove different compounds to various degrees due to the different properties of both the treatment techniques and the compounds to be removed. The various organic parameters should correlate to the degree of PPCP/EDC removal at the various ozone doses examined.

Objectives

The main objective of Phase 1 was to:

- Determine the three most effective ozone doses to examine the removal of PPCP/EDCs.
    - The ozone doses should give the widest array of removal data without being redundant

The main objectives of Phase 2 were to:

- Examine the removal of organics at the three ozone doses selected in Phase 1
- Examine the removal of PPCPs/EDCs at the three ozone doses selected in Phase 1
- Determine if there is a correlation between the removal of organics and PPCPs/EDCs

- Determine the effectiveness of the MBR-ozone contactor-BAF column treatment train and compare it to the effectiveness of the MBR-RO treatment train in removing PPCPs/EDCs from wastewater

Previous research has shown that MBRs have the ability to remove microconstituents as good as or better than the conventional activated sludge process used in many treatment facilities today [7, 10-12]. Because the MBR is a biological process, it is assumed that most biodegradable organics will be removed by this process. By using ozone, the nonbiodegradable portion that remains, can be oxidized into more biodegradable compounds. Following oxidation, the biological activity in the BAF column can use these newly formed, more biodegradable compounds as food and break them down even more. This combination of processes has the advantage of being able to remove microconstituents to a high degree without the high energy cost, loss of water, and production of a separate wastestream that is associated with using RO.

Chapter 2: Background and Literature Review

Throughout the world there is increasing demand for high quality potable water to support economic and population growth. As a result, indirect potable water reuse is of increasing interest to communities, particularly those in areas where water supplies are fully appropriated. Indirect potable water reuse can be planned or unplanned. Unplanned indirect potable water reuse occurs whenever wastewater effluent is discharged to a water body that is a source of supply for a downstream community. The city of Albuquerque, NM has recently begun using unplanned indirect potable water reuse with the opening of its new, state of the art, water treatment facility that treats water from the Rio Grande River. Planned indirect potable water reuse involves treating wastewater to a point where it can be used as a raw water supply, which is then further treated to potable standards [13]. Planned indirect potable water reuse has been practiced in the US since the 1970s [13]. This practice can be economically feasible for communities with limited water supplies, but several issues must be considered. These include:

- The treated water must be of high quality and must meet, state, and federal drinking water regulations.
- The water and wastewater treatment techniques must be reliable.
- The system must be economically feasible.
- An environmental barrier such as a reservoir or aquifer must be part of the system.
- The treated water must be acceptable to the public. A system may produce the cleanest, safest drinking water in the world but if no one trusts the water or if public sentiment towards the treated water is negative, then there is still a problem.

This last point, public acceptability, may ultimately be the factor that controls whether it is possible to implement a planned indirect potable water reuse system. Public perception may be sufficiently negative to restrict water reuse options even if health and treatment information suggests that a particular reuse strategy will be protective of human

health. For instance, an associated press story was published in early 2008 reporting that the drinking water supplies for at least 41 million Americans was found to have pharmaceuticals in them [14]. The story raised public awareness about the presence of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in the nation's water supply, and may generate public sentiment to regulate the removals of PPCPs and EDCs from drinking water.

PPCPs and EDCs are present in water at very low concentrations and therefore are frequently referred to collectively as microconstituents. PPCPs include but are not limited to fragrances, antibiotics, analgesics, insect repellants, lipid regulators, and antiepileptics. Many PPCPs are also EDCs, which are compounds that can disrupt an organism's endocrine system, often resulting in changes to its hormonal balance [15]. People have been aware of EDCs since the 1930s and they have been detected in surface and even treated drinking waters since the 1960s and 1970s [16]. There are three general classes of EDCs: estrogenic or anti-estrogenic (female sex hormones), androgenic or anti-androgenic (male sex hormones), and thyroidal compounds (hormones that control metabolism and many other systems in the body) [5, 6]. Although there is currently no comprehensive list of EDCs, efforts are underway to develop one. One problem in forming this list is that a huge number of chemicals are in use in commerce today and most of these chemicals have not been screened for endocrine function.

Pharmaceuticals have also been found in treated wastewater for decades. The first such report on the subject was released by the U.S. EPA in 1976 [17]. Although there are many different avenues by which EDCs and PPCPs can enter surface waters, the effluent from municipal WWTPs has been found to be a major source [6, 15, 17, 18]. EDCs can come from such sources as cleaning products, pesticides, plastics, household chemicals, and even hormones excreted by humans that end up in WWTP receiving waters [17]. Pharmaceuticals enter wastewater as human excretions of unmetabolized or partly metabolized pharmaceuticals and their metabolites as well as unused medications that are disposed of through the sink or toilet [3, 17, 19]. Personal care products can

enter the wastestream during rinsing while bathing or washing [17]. Other sources for EDCs and PPCPs include septic systems, combined sewer overflows, and untreated storm water flows to name a few. Current wastewater treatment processes, such as activated sludge, have shown to be inadequate at removing many microconstituents [4].

Much of the concern over microconstituents is fueled by the improved ability to detect them at very low concentrations. Current analytical methods can detect many organic compounds at concentration levels as low as 1 ng/L or 1 part per trillion (ppt) [16]. If these compounds had a detection limit in the µg/L range, or parts per billion (ppb), then few, if any microconstituents would be detected in water supplies [20]. Because it is very difficult to study the effects of these compounds on human health and the environment at these concentrations, there is limited data on the effects of long term exposure to these compounds with no concrete evidence thus far that there is a risk to human health, although more research is needed [17]. Even so, the precautionary principle should be used and more research should be done into investigating options for removing these micropollutants.

Treatment processes for PPCP/EDC Removal

To evaluate the overall effectiveness of a treatment process for removing microconstituents from wastewater, criteria, in addition to just removal efficiency, should be considered. First, any treatment train used to remove micropollutants from wastewater must meet all other regulatory guidelines including parameters such as total suspended solids (TSS), total organic carbon (TOC), ammonium, and chemical oxygen demand (COD). The treatment techniques should also be affordable, not just in the initial design and construction, but from an operational standpoint as well. In addition, the treatment processes should be as energy efficient as possible and avoid creating a separate waste stream. More energy consumption means more pollution, which in a way defeats the purpose. The last criterion for considering a process to remove microconstituents from wastewater is that the process should not waste water. This is especially important in regions where water is scarce.

The following sections examine the use of five different treatment processes for the removal of microconstituents from wastewater. These include MBRs (biological), RO, oxidation, activated carbon (adsorption), and biological filtration. Each process has benefits and drawbacks in removing microconstituents from wastewater, although some seem to work better than others. These five processes are examined due to their potential for advanced wastewater treatment or due to their frequent occurrence in the literature as processes being researched for removing microconstituents from wastewater.

Membrane Bioreactors

Membrane bioreactors are a relatively new technology with commercial use starting in the early 1970's [21]. With the increased use and reliability of these systems and the cost of the membranes and membrane processes decreasing, the use of this technology has become an increasingly attractive alternative to traditional processes like conventional activated sludge (CAS) [10, 21]. Stricter environmental regulations are making the MBR systems an even more attractive alternative due to their increased performance and cleaner effluent that is produced compared to conventional systems. Although the MBR process is very similar to the CAS process, there is a significant difference between the two processes.

Many WWTPs use the CAS process to treat wastewater. The CAS process is a biological process that involves aerobic biodegradation of suspended and dissolved organics in wastewater. The process involves developing a mixed culture of suspended microorganisms in an aeration basin. The microorganisms are separated from the treated wastewater by gravity settling and recycled back to the aeration basin. The supernatant from the clarifier becomes the treated wastewater effluent. The CAS process is highly effective at removing organic constituents; a well-operated plant will remove greater than 90 percent of both the suspended and dissolved material in the influent wastewater. Typical effluent limits on a CAS plant consist of maximum concentrations of 30 mg/L for both 5-day biochemical oxygen demand (BOD5) and total suspended solids (TSS).

A membrane bioreactor combines the processes of biological treatment and membrane separation [21]. The MBR process is a variation of the activated sludge process that utilizes membrane filtration to separate biological solids from the treated effluent rather than gravity settling. This modification produces a much higher quality effluent because the concentration of suspended solids is near zero [22]. The BOD_5 concentration of an MBR plant is also low because much of the effluent BOD_5 from a CAS plant is due to suspended solids. Diagrams of a CAS and an MBR plant are shown in Figures 2-1 and 2-2, respectively.

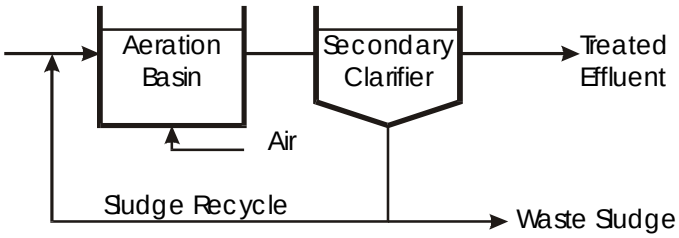

Figure 2-1: Flow diagram of the conventional activated sludge (CAS) process.

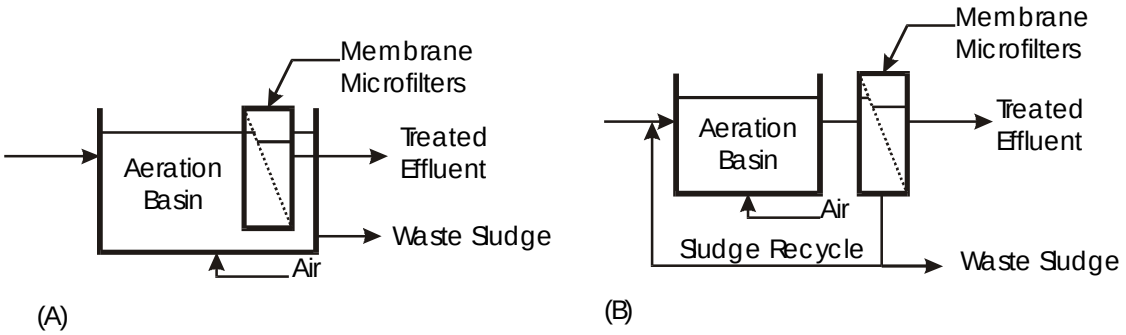

Figure 2-2: Flow diagram of the membrane bioreactor (MBR) process with (A) membrane microfilters located in the aeration basin and (B) membrane microfilters located outside of the aeration basin.

In an MBR plant, the membranes can be configured inside the aeration basin or externally [21]. Since solids separation does not depend on the settling characteristics of the biomass, separation with a membrane allows for higher concentration of biomass in

the aeration basin, which can reduce the size of treatment plant. The process can also be operated with a much longer solids retention time (SRT) which, in the CAS process, results in poor solids settling.

Mechanisms for microconstituent removal by biological processes

The removal of microconstituents by biological processes can be attributed primarily to two mechanisms, sorption and degradation [7, 10, 22]. Sorption is a term that includes adsorption, absorption, and ion exchange and is used when it is not clear which is occurring [23]. For the MBR process, sorption is the transfer of microconstituents from the water to either the sludge or the membrane [7, 24]. Biological solids in CAS and MBRs have large specific sorption capacities that can be attributed to the high specific surface area of the suspended microbial population [7]. Despite the large sorption capacity, current research is showing that the removal of many microconstituents by the MBR process is mainly due to biodegradation/biotransformation. Better biodegradation/biotransformation of compounds is due to the low concentration of TOC in a slow growing culture with long SRT. This forces organisms to develop degradation pathways for slowly degradable compounds in order to continue to recover energy to sustain microbial growth. Although there has been some contradicting research about the effect of SRT on some compounds [7], many reports have shown that a higher SRT increases biodegradation and therefore increases removal [7, 10, 22, 24]. The ability of MBRs to operate at long SRT values is one advantage of this process over CAS systems.

Some of the findings concerning MBRs and how well they perform in both traditional parameters as well as their ability to remove microconstituents are listed below. Many of the investigations studied only a small number of target microconstituents, in part because of the analytical challenges associated with measuring these compounds. Although many of the studies reviewed have varying ranges of compounds studied, some trends are evident in the findings. These include:

1. The studies confirm that MBRs achieved comparable or better removal of microconstituents than the CAS process. A couple studies found only slightly better performance [1, 22] while other studies reported much better removal for many more compounds [7, 10-12]. The conclusion of most of the investigations was that the MBR process can remove some microconstituents well but other compounds are left unaffected. Only a few microconstituents were removed to below the method reporting limit (MRL) [1, 4, 5, 7, 8, 10, 22].

2. The investigations confirm that longer SRTs in the MBR process produce a more diverse microbial population that enhances nitrification and removal of poorly degradable compounds [1, 7, 8, 21, 24].

3. Biodegradation and sorption to the sludge and membrane [24] were the main removal mechanisms for microconstituent removal by the MBR process [10, 22]. Although both of these mechanisms can remove microconstituents, biodegradation was found to be the most effective mechanism for microconstituent removal [7, 8, 15].

4. MBRs do an exceptional job of removing traditional wastewater parameters including TOC, TSS, ammonium, and COD [10, 21].

MBRs did not effectively remove some compounds. Several studies found that the antiepileptic medication carbamazepine is especially persistent with both the MBR and CAS process providing little to no removal [5, 10, 12, 22, 25]. Seven compounds that had no removal by at least one research group included carbamazepine, DEET, diclofenac, EDTA, hydrocodone, TCEP, and trimethoprim.

Indirect potable water reuse requires water to be treated to a particularly high quality because of public perception and concern about possible long-term health effects. Many researchers have agreed that a multi-barrier approach is the best way to achieve this and an MBR system can be a good first process. Although the MBR process is not effective at removing all microconstituents, they can provide subsequent systems with a high quality feed water that has low TSS and DOC. This will improve the performance

of subsequent advanced treatment by processes such as adsorption, advanced oxidation, or RO.

Reverse Osmosis

Reverse osmosis is a membrane-based treatment process that separates contaminants from water by forcing water through the membrane under pressure. Dissolved contaminants are separated from the water as the water passes through the membrane. The primary treatment mechanism in reverse osmosis is the physical separation of micropollutants from water because of differences in physicochemical properties that allow permeation through the membrane at substantially different rates. RO can effectively remove most microconstituents. Like the MBR process, removal depend on properties of the feedwater, membranes, and compounds to be removed [24]. Unlike the MBR process though, the RO feedwater must be of high quality to prevent fouling. In particular, this means that the feedwater for an RO system must be nearly free of solids.

Mechanisms for microconstituent removal by reverse osmosis

Many factors influence the removal mechanisms of microconstituents by the RO process. Because reverse osmosis is a diffusion-controlled process, solute separation occurs when constituents diffuse across the membrane slower than water does. Diffusion, and therefore removal efficiency is influenced by:

- Physical-chemical properties of the compound: These include the molecular weight, size, diameter, solubility, diffusivity, polarity, hydrophobicity, charge, and protonization of the compound [26, 27].
- Membrane properties: These include the membrane's surface charge, molecular weight cut off (MWCO), pore size, hydrophobicity, and surface roughness [26, 27].

- Membrane operating conditions: These include such parameters as flux, transmembrane pressure, and the fraction of water to be recovered [26, 27].
- Feedwater characteristics: The composition of the feedwater can play an important role in rejection efficiencies. These parameters include a feedwater's temperature, ionic strength, pH, hardness, concentration of microconstituents, and total organic matter concentration [26].

Conventional understanding of reverse osmosis dictates that removal efficiency will increase as the physicochemical properties of the micropollutant deviate from those of water. Drewes et al. (2006) developed the diagram shown in Figure 2-3 to estimate rejection of microconstituents by RO membranes [26, 28]. The objective of the diagram is to correlate removal efficiencies with solute and membrane properties. Although the diagram can be useful in the design of water treatment systems to remove certain microconstituents, the accuracy of this diagram has not been confirmed [26]. Figure 2-3 summarizes many types of interactions between the membrane, compound, and source water.

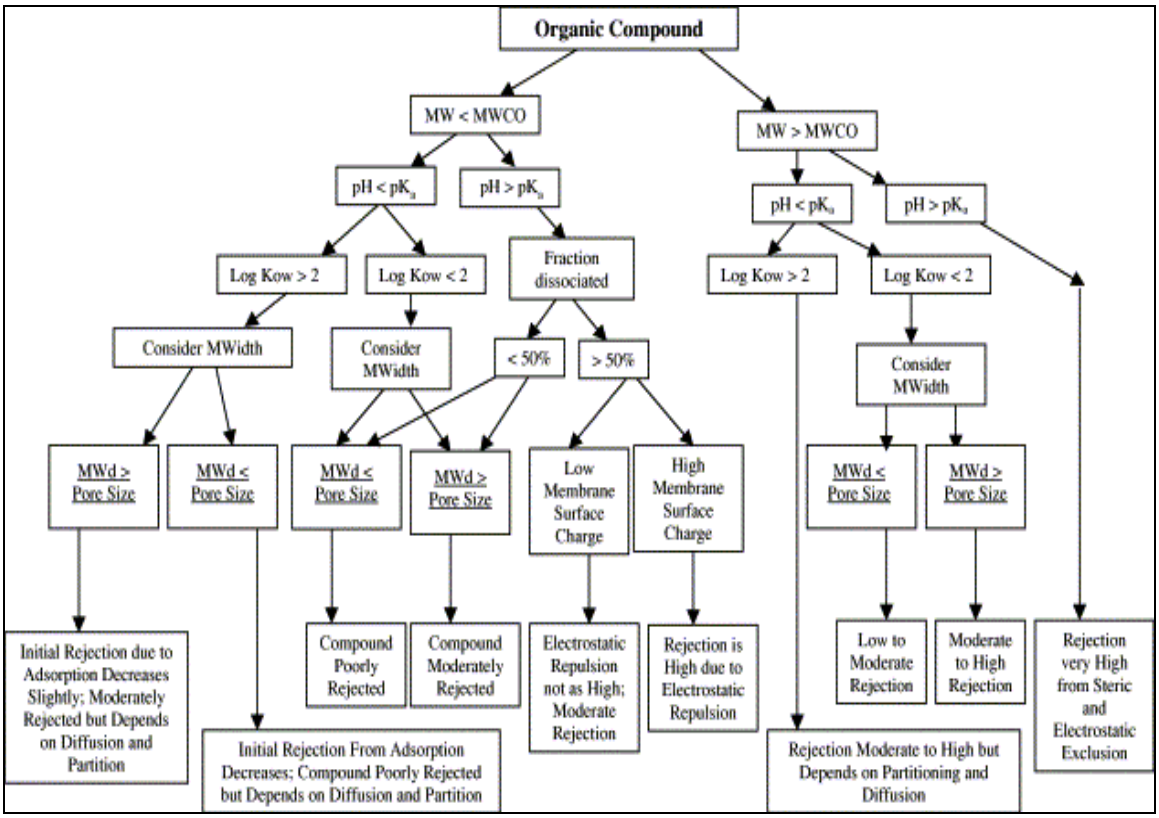

Figure 2-3: Rejection diagram for microconstituents using membrane processes as functions of both solute and membrane properties [26, 28].

Molecular size has been shown to be a major mechanism for solute rejection by RO and NF membranes [3, 8, 29, 30]. The density and molecular weight cut-off (MWCO) of the membrane greatly affect removal due to size exclusion, for both ionized and non-ionized compounds and is especially important for solutes that are not charged. Some studies have shown that the RO process removes uncharged organic compounds primarily through size exclusion [3, 29]. Compounds with a molecular weight greater than 200-300 Daltons (Da) are effectively rejected by RO/NF membranes although some larger compounds can still be detected in the permeate [27, 29]. For example, Kimura et al. (2004) reported the EDC, 17β-estradiol (MW: 279 Da), was found in RO permeate, although at very low concentrations [18].

Another important removal mechanism employed by the RO process is charge repulsion or electrostatic exclusion. This mechanism is explained by the repulsion between the negatively charged membrane surface and negatively charged solutes. Experimental results have shown that negatively charged compounds could achieve high rejection due to electrostatic exclusion [27, 31]. This was found to be true regardless of other physicochemical properties.

The concentration of microconstituents may also have an effect on how well they are rejected. Kimura et al. suggests that rejection efficiencies decrease with lower feed concentrations although they suggest further research should be done to determine its effects [27].

One factor that is not a property of either the membrane or solute but can still have a large effect on microconstituent removal is the fractional feed water recovery. Factors that can limit recovery are osmotic pressure, concentration polarization, and the solubility of sparingly soluble salts [23]. Higher recovery will result in increased permeate volume but will decrease its quality [23]. This can be important when trying to remove microconstituents. Verliefde et al. showed that at a recovery of 10 percent, a NF membrane was able to remove >75% of all target compounds with most achieving >90 percent removal and a few compounds being removed at >99 percent [28]. At 80% recovery, the same compounds were removed less effectively with one compound dropping to ~10 percent removal.

Membrane selection

Because solute removal efficiencies are closely linked to the chemical and physical properties of the membranes, material selection for RO membranes is important. A good RO membrane must meet many characteristics [23]. Ideally, an RO membrane material will produce a high flux that will not clog or foul easily while still maintaining high solute removal efficiency. The material should be affordable while being durable and stable. No commercial RO membrane can completely reject all solutes [26].

Membrane manufacturers have focused their efforts on developing membrane materials that achieve a high solute rejection while producing the highest fluxes at the lowest transmembrane pressures [26].

The two most popular materials used in RO membranes are cellulose acetate and polyamide. Although both materials have benefits and drawbacks, the polyamide seems to be better suited for many RO applications including the removal of microconstituents. One of the drawbacks of a polyamide membrane is that chlorine and other disinfectants will damage the membrane. Care must be taken in designing these systems to maintain feed water with proper disinfection while maintaining the integrity of the membrane.

Besides the membrane material, the decision to use either a NF or RO membrane can have important implications on different parameters. The classification of different membranes can be somewhat arbitrary. NF membranes can selectively remove divalent cations (hardness) and anions (e.g. sulfate) and NOM while leaving higher concentrations of the monovalent ions in the permeate. While traditionally many RO membranes removed ions indiscriminately, newer RO membranes have been developed that have similar selectivity.

Although RO membranes will achieve higher removal of microconstituents than NF membranes due to their tighter, denser material, NF membranes have some advantages. The RO process requires much higher pressures and is therefore more energy intensive [23]. NF membranes can be operated at lower pressures than RO, resulting in lower operating costs [29]. NF membranes are less susceptible to chemical and biological fouling and can be operated at higher fractional feed water recovery values.

Even though the RO process has shown to be very effective in the removal of microconstituents, there are several drawbacks to the process that make it an undesirable alternative in wastewater applications. As suggested earlier when considering criteria for selecting a wastewater treatment process for removing microconstituents, the process

should be relatively energy efficient. Although NF membranes can be more energy efficient that RO membranes, they still both consume a lot of energy. In addition, both RO and NF membranes create a separate, more concentrated waste stream that must be dealt with. Along with the concentrate from this stream is the water that cannot be recovered, which as mentioned earlier can be a very large drawback in areas where clean water is scarce. In addition, fouling of the RO membrane can be a serious problem, especially in wastewater applications.

Oxidation and Advanced Oxidation Processes

Oxidation and advanced oxidation processes (AOPs) achieve removal by chemical destruction rather than by separating chemicals from solution [23]. The most desirable outcome would be the complete oxidation of organic compounds to carbon dioxide, water, and mineral acids, but as this section will examine, few oxidants or AOPs achieve total mineralization of the constituents.

The Oxidation Process

A variety of water quality problems is amenable to treatment by chemical oxidation. These include disinfection, taste and odor control, and the removal of hydrogen sulfide, color, iron, and manganese, to name a few [23]. Oxidation processes have also been used to oxidize organic compounds.

The driving force behind all oxidation processes is the exchange of electrons between constituents and the corresponding decrease in the overall electrical potential [23]. Conventional oxidation processes use oxidants such as chlorine gas (Cl_2) and its dissolution products hypochlorous acid (HOCl) and hypochlorite (OCl^-), ozone (O_3), hydrogen peroxide (H_2O_2), permanganate ($KMnO_4$), and chlorine dioxide (ClO_2). In conventional oxidation processes, the oxidants are generally selective regarding which compounds they degrade. Although the use of oxidants such as chlorine is common in drinking water treatment, there are disadvantages. One of the largest concerns is the

production of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Advanced oxidation processes combine a chemical oxidant with UV radiation or sometimes use combinations of oxidants to increase the rate of the oxidation process. Advanced oxidation processes include various combinations of H_2O_2, Ozone, UV, TiO_2, and other oxidants. Common AOPs include UV-ozone, UV-peroxide, UV-titanium dioxide (TiO_2), and Fenton's reagent (H_2O_2 and an iron salt). Other processes such as wet air oxidation, super-critical oxidation, and catalytic oxidation require large amounts of energy in the form of high temperature and pressures. Because contaminant concentrations in drinking water are so low and the daily volume of water to be treated is so large, these processes are not used for drinking water treatment.

Although most AOPs that have commercial applications are actually a combination of two or more other processes, ozone is sometimes considered an AOP due to its ability to form hydroxyl radicals [23]. Ozone forms a variety of free radical species through a sequential decay cycle in water. Ozone also forms hydroxyl radicals when it reacts with NOM. This reaction is considered an important mechanism in destroying target compounds. At high pH (> 8.3) free radical scavengers such as carbonate ions (CO_3^{2-}) compete for these radicals with organic compounds, thus the effectiveness of ozonation processes diminishes at high pH.

Oxidation may occur through direct chemical oxidation of susceptible bonds in the target molecule or through generation of highly reactive free radicals such as the hydroxyl radical ($OH^{\bullet}$). AOPs, such as UV/O_3, UV/H_2O_2, UV/TiO_2, and Fenton's reagent are especially effective at generating free radicals which is the principal mechanisms responsible for their enhanced performance [30]. Hydroxyl radicals are reactive electrophiles that react with almost all electron-rich organic compounds [23]. For most compounds, their reaction rates are orders of magnitude faster than conventional oxidants.

The effectiveness of disinfection by oxidation processes is determined by a number of factors including the concentration of the oxidant or intensity of UV radiation, the reaction time, temperature, and the presence of competing reactants or free radical scavengers. For most oxidation reactions, there is a direct trade-off between oxidant concentration and reaction time. In other words, similar destruction can be achieved using a high oxidant concentration and short reaction time, or low oxidant concentration and long reaction time. Thus, design of disinfection processes are usually based on the parameter CT where CT is:

$$CT = \text{Oxidant Concentration} \times \text{Time}$$

CT usually has units of mg-min/L. The equivalent dose for UV oxidation is the product of light intensity (watts/m^2) and time (seconds) to give an exposure measured in Joules/m^2. Note that the energy of light is inversely proportional to its wavelength so that short wavelength light (i.e. ultra violet light) has more energy than visible light.

Chemical reactions are accelerated by higher temperatures, hence better oxidation or disinfection is achieved in warmer water. However, because of the large volume of water processed in a treatment plant it is not possible to control the temperature of water in a disinfection of oxidation process. Instead, the CT product is increased for lower temperatures to give similar removal.

Most AOPs are not specific to particular solutes and will react with any oxidizable compound in solution. This includes suspended solids as well as dissolved organic carbon, whether these compounds are natural or not. Therefore, it is important that the feed water have as low a concentration of TOC as possible to maximize destruction of microconstituents. Further, because suspended solids absorb light, it is important that the suspended solids concentration be as low as possible for oxidation processes that utilize UV light.

Summary of Oxidation Process Effectiveness for Microconstituent Removal

Water utilities have begun looking at oxidation and AOPs as a way to remove micropollutants due to the success of these processes in disinfecting drinking water [31]. Recently, significant advances in the understanding of the aquatic photochemistry of certain single compounds or classes of pharmaceuticals has been made, although specific data in this area is still needed [32].

Although most conventional oxidation processes work well for disinfection, they are not very effective at removing many micropollutants [33]. This is largely because lower oxidant concentrations and less powerful oxidants are needed to achieve disinfection than are needed to destroy trace concentrations of microconstituents. As a result, most studies have found relatively poor micropollutant removal by oxidation processes designed to achieve disinfection. In contrast, AOPs rely on higher oxidant doses, longer reaction times, and employ processes that maximize the production of highly reactive free radical compounds that will attack a wide variety of chemical bonds to destroy nearly all organic compounds [43, 44].

Although UV light irradiation has been shown to be an effective tool in drinking water disinfection, it achieves limited degradation of many micropollutants [7, 24, 34, 40, 42, 45], especially at doses used for disinfection (120-400 mJ/cm^2) [40, 43] (although one source cited typical disinfection doses of <5-30 mJ/cm^2 [6]). Either much longer exposure times or higher intensity UV light is required to destroy micropollutants than is required for disinfection [7, 34, 36, 43]. One author cited that the UV dose required for treating micropollutants would be orders of magnitude higher than that needed for disinfection [6], while another author cited the appropriate dose is about five times higher [34].

The combination of peroxide and UV light has been shown to be quite effective at degrading many micropollutants [37, 38, 41, 43, 44, 46]. This is believed to be due to enhanced production of free radical compounds. The studies by Muller and Jekel (2001)

and Muller, et al. (2001), found that the UV/H_2O_2 process had the highest degradation for atrazine (up to 99%), but it also used a lot of energy [36, 39].

Ozone and ozone-based AOPs are effective at removing many micropollutants [7, 46]. Ozonation by itself can reduce both the concentration and number of compounds detected after treatment [34, 44]. For example, Okuda, et al. (2008) found that ozone coupled with a biological activated carbon process reduced all residual pharmaceuticals to below quantification limits [33]. Although O_3 oxidation of microconstituents is highly effective, special considerations are needed for source waters with high bromide concentration to limit formation of brominated compounds [23, 34]. In addition, O_3 oxidation of microconstituents requires longer contact times and/or higher doses than that used for disinfection, which increase process costs [44].

Muller et al. (2001) found that the H_2O_2/O_3 process produced the best microconstituent removal in terms of energy use [35]. The energy used for this process was an order of magnitude lower than the UV based processes (UV/H_2O_2 and UV/O_3). Kim, et al. (2008) found this process to be very promising but did not pursue a full scale version due to the high bromide concentration in the source water [34]. Instead, the plant was built using the UV/H_2O_2 process. This system has been operating since 2004 and provides good destruction of both organic micropollutants and microorganisms.

Few AOPs have been built solely for removal of microconstituents; most have been designed solely to provide disinfection. One benefit to using an ozone or UV/H_2O_2 system is that they are widely used, have a high level of technical development in industrial applications, and their effectiveness is well established [36]. Ozone and UV/H_2O_2 have shown that they can destroy microconstituents and appear to be promising techniques although, like other oxidation processes, longer treatment is required for micropollutant removal than for disinfection [37].

Problem Compounds and Special Considerations

Ozone, ozone-based, and UV-based AOPs can effectively degrade most microconstituents but researchers have found some compounds are slowly oxidized. One study found that 2-QCA, DEET, and cyclophosphamide were poorly removed by these processes [38]. One study found that Ciprofloxacin was the most persistent target compound with only 16% degradation by ozone [9]. Carbamazepine [37, 38] and naproxen [39] were found to be poorly degraded with UV. UV/H_2O_2 showed better removal of these compounds [37, 38]. A couple studies found that clofibric acid was poorly removed by ozonation even at higher doses [10, 33].

Although oxidation processes can degrade many organic compounds, it is important to recognize that the products may not be not fully mineralized to H_2O and CO_2. The objective of an oxidation processes is to change the compound so that it is no longer biologically active [9]. While an oxidation process may destroy the parent compound, it may produce degradation products with unknown biological activity [9]. More research is still needed in determining the degradation products produced by oxidation and into the toxicity these compounds may have.

Although oxidation processes are not likely to completely mineralize organic compounds in water, considerable research has shown that partial oxidation of many recalcitrant compounds will substantially increase their biodegradability This principle is increasingly used in water and wastewater treatment plants where an oxidation step immediately precedes a biological process to facilitate removal of resistant compounds. A good example is the drinking water treatment plant recently completed by the Albuquerque Bernalillo County Water Utility Authority. This plant provides ozonation immediately prior to biological filters that contain granular activated carbon. Pre-ozonation achieves partial oxidation of refractory compounds that allows rapid biodegradation by organisms attached to the GAC surface.

Activated Carbon

This section examines the adsorption of microconstituents by granular activated carbon (GAC) and powdered activated carbon (PAC). Activated carbon is an effective adsorbent that is used for removing many dissolved compounds from water. GAC is used in a fixed-bed process like granular media filtration whereas PAC is added to water as a suspension, allowed to adsorb constituents from water, and then separated from the finished water. Activated carbon can be used at several scales, ranging from as large as full-scale municipal treatment systems to as small as water filters that can attach to the end of a plastic bottle or faucet. GAC is most commonly incorporated in water treatment facilities for (1) removal of trace contaminants and (2) removal of dissolved organic carbon (DOC) [23]. Activated carbon will effectively remove many organic compounds and the USEPA has designated GAC as a best available technology (BAT) for the treatment of many regulated organic pollutants [40].

Mechanisms for microconstituent removal by adsorption

Activated carbon removes dissolved constituents from solution by adsorption. Adsorption is a process in which compounds in the liquid phase accumulate on a solid surface [23]. The adsorption process is used in drinking water treatment to remove synthetic organic compounds (SOCs), disinfection by product (DBP) precursors, taste and odor-causing compounds, and some inorganic compounds. The process involves the adsorbate, the dissolved compound that undergoes adsorption, being transported via diffusion into the porous absorbent, the solid onto which the adsorbate adsorbs. The solute is attached to the absorbent surface thru either chemical bonds (chemisorption) or physical attraction (physical adsorption).

Adsorption is dependent on time and the amount of surface area (capacity) available for adsorption. Adsorption is an equilibrium process, so micropollutants in water will partition between the water and carbon surface until the two are in equilibrium with each other. Thus, presence of micropollutants on the carbon surface will also

indicate micropollutants remaining in the water, although in many cases the remaining micropollutant concentration in the water will be too low to measure.

Adsorption of microconstituents to activated carbon depends on properties of the water, activated carbon, and the microconstituents [23]. Physicochemical properties controlling adsorption are similar to those that control removal in reverse osmosis, although with the opposite effect in some uses. More nonpolar, more hydrophobic, and lower solubility compounds should be removed efficiently by carbon adsorption. For activated carbon, lower MW compounds are more efficiently removed because of increased accessibility to inner pores of the carbon, which is the opposite of reverse osmosis. In addition, uncharged molecules are more efficiently removed by adsorption (again, the opposite of reverse osmosis), because of the increased aqueous solubility of charged compounds. The pH of the solution affects adsorption for ionic solutes for several reasons. First, the charge on activated carbon is affected by pH. Generally, activated carbon has a negative charge above pH of about 5, and is neutral between a pH of 4 and 5. Adsorption of anionic constituents is thus greater below pH 4, but from an operational standpoint, is not practical. The pH is also an important parameter for the removal of acids and bases where the pH affects the charge of the solute.

Activated carbon has a nonpolar surface at a neutral pH [23]. Because water is a polar liquid, nonpolar organics are more hydrophobic and have lower aqueous solubility. Therefore, neutral hydrophobic compounds will have the strongest affinity to carbon surface, and organic compounds that are polar, hydrophilic, or charged will not be adsorbed as strongly due to strong water-adsorbate forces.

An implication of this removal mechanism is that compounds are not degraded or destroyed, just transferred to the activated carbon surface. If carbon were regenerated, compounds would then be destroyed during the regeneration process. If however, the carbon is just discarded when it reaches capacity, PPCPs could be released to the environment from the surface of the carbon.

A second mechanism for micropollutant removal by activated carbon is biodegradation by microorganisms living on the carbon surface. Ozone followed by activated carbon can be an effective removal strategy because the ozone chemically degrades compounds and makes them more biodegradable, and then the microorganisms living in the carbon bed complete the degradation process. This process is commonly called biofiltration.

Although activated carbon does have the potential to remove many microconstituents to a relatively high degree, it does come with some drawbacks. One of the drawbacks is that GAC must be regularly replaced or regenerated once breakthrough has occurred. Studies have found that for hydrophilic compounds, breakthrough can occur much more rapidly than in hydrophobic compounds [6, 34]. Vieno, et al. found that the hydrophobic compound, carbamazepine, could be effectively removed by GAC even after treatment of >70,000 bed volumes of water [34]. The same study found that the more hydrophilic compounds could pass GAC treatment after only 2,000 to 3,000 bed volumes of water. The regular regeneration or replacement of GAC could be quite expensive, especially if the breakthrough of hydrophilic compounds is a concern.

Another concern with using GAC in treating wastewater is the amount of NOM in the water. The presence of NOM can greatly reduce the removal efficiency of microconstituents by activated carbon due to competition for adsorption sites [8]. This is especially true for using GAC to treat wastewater due to the higher concentrations of NOM in wastewater as compared to many other surface water sources.

One of the concerns in developing the processes used in this research was in trying to develop a process that would both remove microconstituents well and be affordable and easy to maintain. The regular regeneration or replacement of the GAC in the process train would mean much more expense and maintenance. This goes against the initial criteria used in developing a treatment process. Another drawback to using GAC in the biofilter for this research project is in trying to account for which mechanism is contributing to microconstituent removal in the biofilter. This is because

biodegradation and adsorption are both present in the BAC column and it is difficult to account for the degree of removal of microconstituents by each mechanism [41].

Biological Filtration

Biologically active filters use microorganisms attached to the filter media in a column reactor to treat water. Biofiltration has shown that it can reduce chlorinated DBPs, bacterial regrowth, and chlorine demand as well as control other compounds of concern [42].

Biologically active filtration (BAF) is often follows an AOP such as ozonation to improve the biodegradability of recalcitrant compounds [42]. This process uses ozone to oxidize non-biodegradable organics into a biodegradable form that the active biomass on the filter media use as an energy and carbon source. The non-biodegradable organics are usually larger in MW. Ozone has the ability to oxidize and break down these larger organics into smaller, more biodegradable compounds. Although there are many different types of biological filters, this research is focused on single stage biological filtration [42]. This process incorporates both particulate and biodegradable organic matter removal into the same filter unit.

Because biologically active filters are a combination of two different processes, several factors can contribute to their effectiveness. The first factor is the ozone dose. Although it has been shown that a larger ozone dose will achieve a higher removal of microconstituents, there are problems associated with using an increased ozone dose. One problem is that most compounds do not exhibit a linear correlation between ozone dose and compound removal. A 2006 study by Snyder et al. shows that for many compounds additional removal was achieved with higher ozone doses, but the change in percent removal decreased at the highest dose for many of the compounds [43]. Higher ozone doses require more energy, which increases operating costs. Higher ozone doses also produce more ozonation by-products, which is especially a problem in bromide-rich waters. These disadvantages are examined further in the oxidation section.

Another factor that can contribute to the effectiveness of a biologically active filter in removing microconstituents is the type of filter media used. One of the most common biofilter media used is GAC. GAC has shown that it can remove many emerging micropollutants to a high degree, although as discussed in the section on activated carbon, there are drawbacks to using GAC in a wastewater application. One of the objectives of this research was to develop a process that can be operated for long periods with little maintenance and low costs. Another goal was to properly account for the microconstituent removal. In order to do this anthracite was used for the BAF media.

Anthracite is considered a non-adsorptive filter media [42]. It is frequently used in granular media filtration for water and wastewater treatment [23]. While GAC and anthracite are nominally the same material (pure carbon), the surface are of GAC is orders of magnitude higher than anthracite, which leads to orders of magnitude more adsorption capacity.

Both GAC and anthracite are used as biofilter media. Although GAC has a much greater surface area per unit volume than anthracite, it is thought that little biomass growth can occur inside the micropores of the GAC [42]. This makes the two medias much more evenly matched in growing a biomass. The GAC does have the advantage of being able to adsorb compounds; although once the adsorption capacity of the GAC is exhausted it cannot simply be backwashed. The GAC must be regenerated or replaced to regain its ability to adsorb compounds.

Another advantage of GAC is that it can quickly destroy any residual ozone. An ozone residual can quickly compromise the biological performance of BAF using anthracite. Because a GAC column quickly reduces the ozone residual, much of the biological activity in the column remains unaffected. This is why care should be taken in operating a BAF with anthracite to ensure that any ozone residual is removed before entering the column.

Although there are advantages to using GAC over anthracite, anthracite was used as the media in the BAF column for this research. This is due to the cost implications associated with using GAC and the ability to examine the contributions of biodegradation in removing microconstituents from wastewater. By eliminating adsorption as a contaminant removal mechanism, the project focus was on oxidation and biodegradation processes.

Chapter 3: Experimental Methods

A pilot system, consisting of an MBR, ozone contact chamber, RO system, and BAF column, was continuously operated at the ABCWUA Southside Wastewater Reclamation Plant (SWRP). The process flow diagram for the pilot system is shown in Figure 3-1. The system was used to examine the removal of PPCPs/EDCs from wastewater using two different treatment trains. One of the treatment trains consisted of an MBR that fed an ozone contactor that then fed the BAF column. The other consisted of the MBR followed by RO.

The MBR system was continuously fed primary treated wastewater throughout the duration of the experiments and operated at an SRT of approximately 10 days. The MBR produced an average of 175 mL/min of effluent, of which 100 mL/min was used to feed the ozone contactor. The ozone contactor consisted of three chambers with each chamber providing 5 minutes of contact time. The ozone contactor fed the BAF column, which had an EBCT of 20 minutes. From here the water was stored in a reservoir with an overflow. The reservoir was used to store enough water to backwash the BAF column for 10 minutes at a flowrate of 1.6 L/min.

Due to the cost of each PPCP/EDC analysis, only 16 samples were analyzed. The first PPCP/EDC sample was an MBR effluent sample collected on 8/18/09 that was used to determine what compounds were in the wastewater. It was determined that 3 ozone doses could be examined for PPCP/EDC removal. Each ozone dose sampling event tested for PPCPs/EDCs in the MBR, ozone, and BAF effluents. Two of the three sampling events also included samples from the RO effluent. A field blank and duplicate samples of the MBR, ozone, and BAF effluents were collected for quality assurance purposes. MWH laboratories performed the PPCP/EDC analysis, which included 83 compounds. In order to determine the ozone doses to analyze PPCP/EDC removal at, the project was divided into two phases.

Phase 1 of the project determined the ozone doses used to examine the removal of PPCPs/EDCs. A series of analyses were done to examine the effects of various ozone doses on different organic parameters. The bulk organic analysis consisted of TOC, UV_{254} absorbance, SUVA, and BDOC. These parameters were measured at varying ozone doses ranging from 0 to approximately 12 mg/L. Phase 2 of the project examined the removal of both organics and PPCPs/EDCs. The bulk organic analysis in Phase 2 was used to both determine steady state conditions and to monitor organic removal at the various ozone doses. At least one week was allowed for the BAF column to come to steady state. The RO system was run for at least one day to allow the system to achieve steady state conditions.

Besides the bulk organic and PPCP/EDC analysis, several other parameters were monitored to ensure proper performance of all systems. Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) samples were collected throughout the duration of the experiments to ensure proper MBR performance. Dissolved oxygen (DO) measurements were taken daily to ensure proper performance of both the MBR and the BAF column. Other system parameters were measured daily to ensure proper performance of all the systems including pH, conductivity, temperature, flowrates, and pressure. The indigo method, described in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2005), was used to measure both the ozone dose and ozone residual, which were measured daily to ensure proper operation of the ozone contactor. Detailed descriptions of each analysis can be found later in this chapter. A full description of the design of each treatment process is given in the following sections.

Process Design

For this research project, four pilot scale treatment processes were designed and built from scratch. These processes consisted of a membrane bioreactor, an ozone

contactor, a biologically active filter, and a reverse osmosis system. Initially, the project was used by another graduate student and was further modified to meet the research goals of this project. A schematic of the modified system used in this research can be found in Figure 3-1.

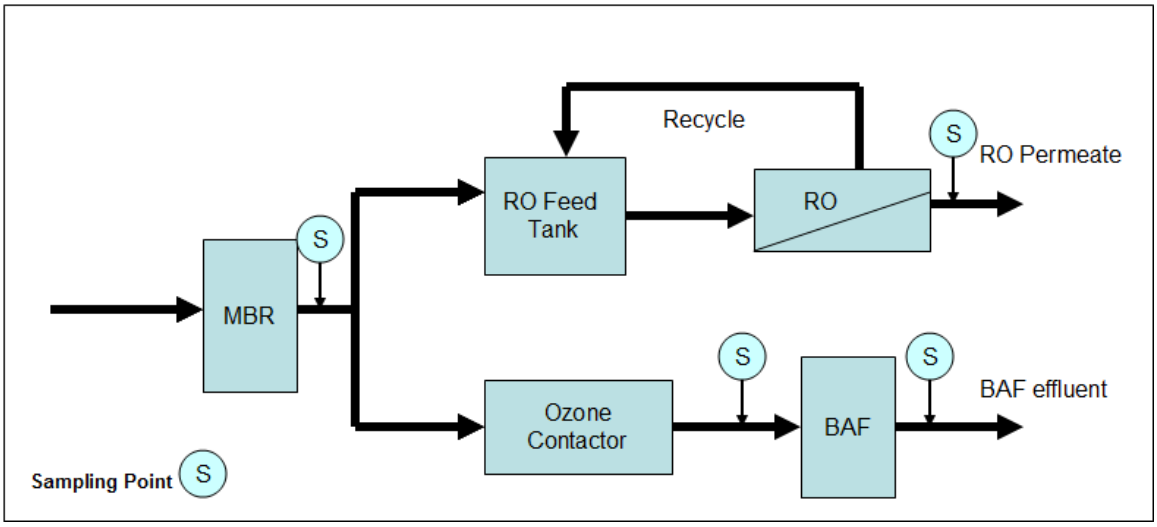

Figure 3-1: Schematic of project setup for pilot system at the ABCWUA SWRP

The system was set up at the SWRP. The MBR effluent was split with 100 ml/min feeding the ozone contactor and BAF systems and the rest feeding into an RO feed tank which then fed an RO system. The advantages of operating the system this way is that it allowed for a side-by-side comparison of the oxidation/biofiltration process and the RO process. Splitting the flow from one MBR ensures that both columns are receiving a similar water quality and that the concentrations of the selected compounds are similar for both effluents. Further detail about the design and operation of each of the systems is described below.

MBR System Design

The MBR unit was first constructed and tested in the environmental engineering lab at the University of New Mexico. The microfiltration units were constructed and donated by Koch and consist of hollow fiber microfilter tubes. The membranes are designed for submerged use with outside-in flow. The Koch microfilter was equipped with an air feed that allowed for both air scrubbing of the membrane and proper aeration of the tank. A Pondmaster model AP-40 that delivered approximately 1350 L/min was used to provide air to the Koch microfilter. Due to insufficient aeration of the tank, a second air pump was needed. A Pondmaster model AP-100 with a flow of 4300 L/min was used to supply air to a system of fine air diffusers that kept the DO in the tank at around 6 mg/L. Figure 3-2 shows a picture of the supplemental air delivery system.

Peristaltic pumps were used for both the MBR effluent and the wasting lines. The flow rates were calibrated with a graduated cylinder and stopwatch as described in the flowrates method and procedures section. The system used a ChronTrol-XT table top timer to shut off the peristaltic pump for the effluent. The pump was shut off every 10 minutes for one minute in order to relax the membrane and keep pressure from building up. This allowed the membrane to maintain a higher flux for longer periods of time between cleanings. To measure the pressure and calculate the flux through the membrane, a pressure gauge and transducer were used. The pressure transducer was monitored by a LabView data collection system, which also monitored the RO feed pressure, and temperature.

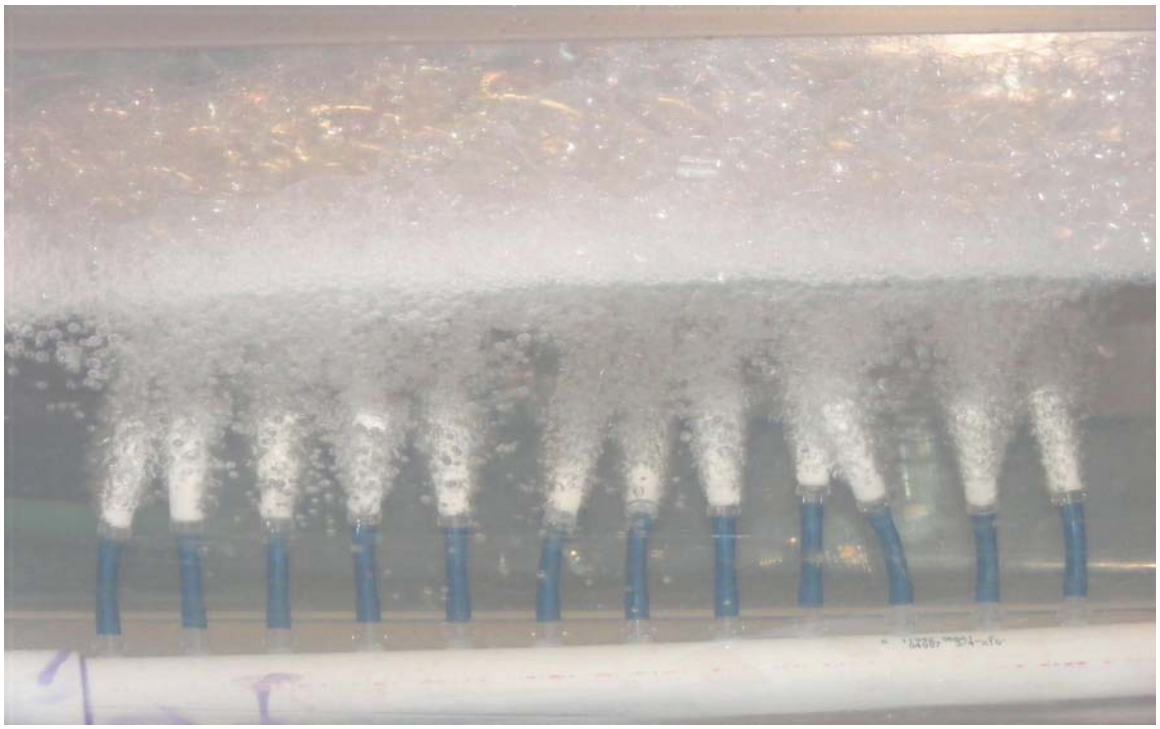

Figure 3-2: Photo of supplemental air supply system for MBR tank

The MBR influent flow was controlled by a float valve that kept the volume of wastewater in the tanks constant. A second float valve was installed to ensure that if the first one clogged, the system could keep running. Due to problems with high pressure and solids in the influent feed, a standpipe was used to keep the influent flowing into the tank consistent and stable. A low flow switch was installed in the tank just above the top of the membrane. If the water level in the tank became too low, the low flow switch would shut off the pump, which would keep the membrane from drying out. The volume of the tank, as well as the effluent and wasting flow rates used to establish the solids retention time (SRT) and hydraulic retention time (HRT) can be found in Table 3-1 below.

Table 3-1: MBR design parameters

Design Parameter	Value
SRT	10.0 days
HRT	9.0 hours
Effective Tank Volume	23.2 gallons (87.9 L)
MF surface area	16.1 ft^2 (1.5m^2)
Flowrates	
Waste	0.0016 gpm (6 mL/min)
Influent	0.048 gpm (181 mL/min)
Effluent	0.046 gpm (175 mL/min)

A wasting tank was used to collect all overflow and final effluent streams from the system as well as the wasting flow from the MBR tank. From the wasting tank the flow was diverted through a hose, down to a sump. Prior attempts to waste streams separately through hoses failed due to clogging of the hoses. The wasting tank provided an easy and reliable way to collect and waste the various sources of water.

In order to maintain a constant and accurate flow to the ozone contactor a standpipe was installed after the MBR effluent pump. From the standpipe a peristaltic pump fed the ozone contactor at 100 mL/min and the overflow fed the RO feed tank. This configuration kept the flow to the ozone contactor steady, even when the MBR effluent pump was shut off to relax the membrane.

Ozone Contactor Design

The ozone contactor consisted of three columns. This system is similar in design to the one used by Huber et al. (2005) [44]. A schematic of the system is presented in Figure 3-3. Effluent from the MBR is pumped into the top of the first column where it runs countercurrent to the ozone being bubbled in at the bottom through a glass diffuser. The ozone is generated with an Ozone Lab OL80W ozone generator that uses compressed USP oxygen to create the ozone.

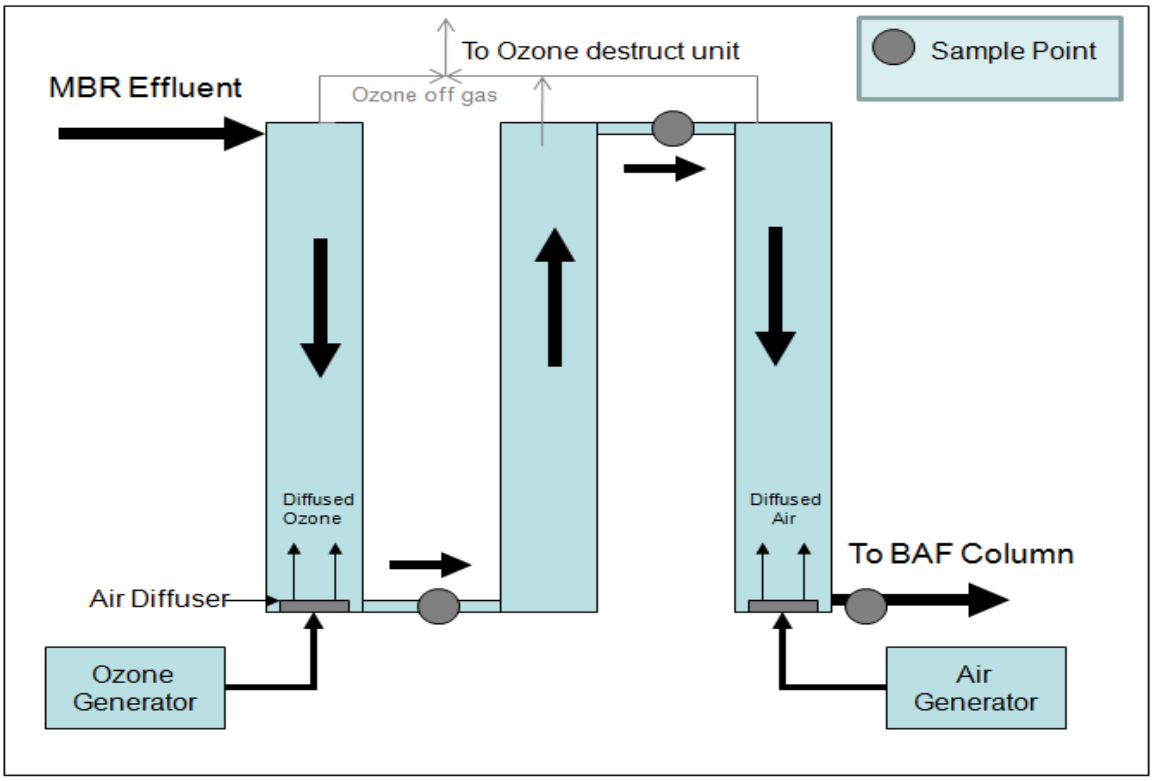

Figure 3-3: Diagram of ozone contactor

The water then flows up the second column for additional contact time. From here, the water flows into the top of the third column while air is being diffused into the bottom of the column in a countercurrent direction. The air is supplied by an Aquaculture 20-60 gallon aquarium air pump and is provided to strip off any residual ozone still in the water. This is important because the ozone could inactivate microbes in the BAC column. The column diameter, height, and total volume give a total hydraulic detention time of 5 minutes for each column. The parameters for this design can be found in Table 3-2.

Table 3-2: Ozone contactor design parameters

Design Parameter	Value
Flowrate	100 mL/min (0.026 gpm)
HRT	5 min
Column Height	0.44 m (1.44 ft)
Column diameter	0.038 m (0.125 ft)
Column area	0.0011 m^2 (0.0123 ft^2)
Column Volume	0.0005 m^3 (0.0177 ft^3)

All components used in the ozone contactor were composed of glass, stainless steel, or other ozone resistant materials. This precaution is necessary because ozone is very corrosive to many materials. This can not only corrode any non ozone resistant materials, but also contaminate the water with ozone byproducts caused by interactions between the ozone and the components.

The Ozone Lab OL80W ozone generator has an adjustable gas rotameter and a 10 turn, high precision, ozone output regulator that allowed for more precise control of the amount of ozone produced. The flow of oxygen was controlled by an oxygen flow regulator with a CGA 540 connection from Responsive Respiratory Inc. Since the rotameter was found to be inaccurate, ozone production was controlled by measuring the flow of air and adjusting the ozone output regulator.

This design offers a simple yet effective way to introduce ozone into the system. The three different sampling ports at the end of each column allow for ozone residual measurements at 5, 10, and 15 minute intervals, as well as TOC and microconstituent sampling. The three way valves in the off gas allow minimal interruption to the ozone gas flow while measuring the applied ozone dose.

The effluent from the ozone contactor flowed into a small reservoir where it was pumped to the top of the BAF column using a peristaltic pump. The reservoir and pump were required because the top of the BAF column was much higher than the ozone contactor. The flowrate on the peristaltic pump was set slightly higher than the 100

mL/min going into the reservoir. This was done to ensure that all of the water leaving the ozone contact chamber would be sent to the BAF column. As a precaution, an overflow was built into the reservoir that fed directly into the wasting tank so if the flow from the reservoir dropped below 100 mL/min, the system would not back up.

Biologically Active Filter Design

Following the ozone contactor, the water was pumped to the top of the BAF column, which was the last process in the treatment train. The media in the BAF column consisted of anthracite that was first seeded with MLSS and soaked in MBR feedwater for a week to establish a bio-growth prior to the experiments. The system was run for at least one week between sampling events to establish steady state conditions at each new ozone dose.

The BAF column consisted of a 2" diameter, clear PVC pipe. In order to get an EBCT of 20 minutes the height of the anthracite media was 3.24 feet (0.99 m) for a total volume of 0.071 ft^3 (0.002 m^3). An EBCT of 20 minutes was chosen to allow for the maximum amount of biodegradation by the BAF column, which is comparable to that in the GAC-biological filters used in the ABCWUA's San Juan Chama drinking water treatment plant. The dimensions and parameters for the BAF column are listed in Table 3-3 below.

Table 3-3: BAF column design parameters

Design Parameter	Value
Flowrate	100 ml/min (0.026 gpm)
Carbon Height	0.99 m (3.24 ft)
Column diameter	0.051m (0.167 ft)
Column area	0.002 m^2 (0.022 ft^2)
Carbon Volume	0.002 m^3 (0.071 ft^3)
EBCT	20 min
Column loading rate	2.96 m/hr (1.12 gpm/ft^2)
Backwash flow rate	1.6 L/min (0.42 gpm)
Backwash loading rate	47.4 m/hr (19.4 gpm/ft^2)

A standpipe was used to ensure the BAF media was constantly submerged. The flow from the BAF column would enter the bottom of the standpipe. The flow would exit the top of the standpipe which was situated a couple of inches higher than the anthracite media ensuring the media stayed submerged. This can be seen in the schematic of the BAF column found in Figure 3-4. After exiting the standpipe, the water would flow to a 12-gallon reservoir to store treated water for backwashing the column.

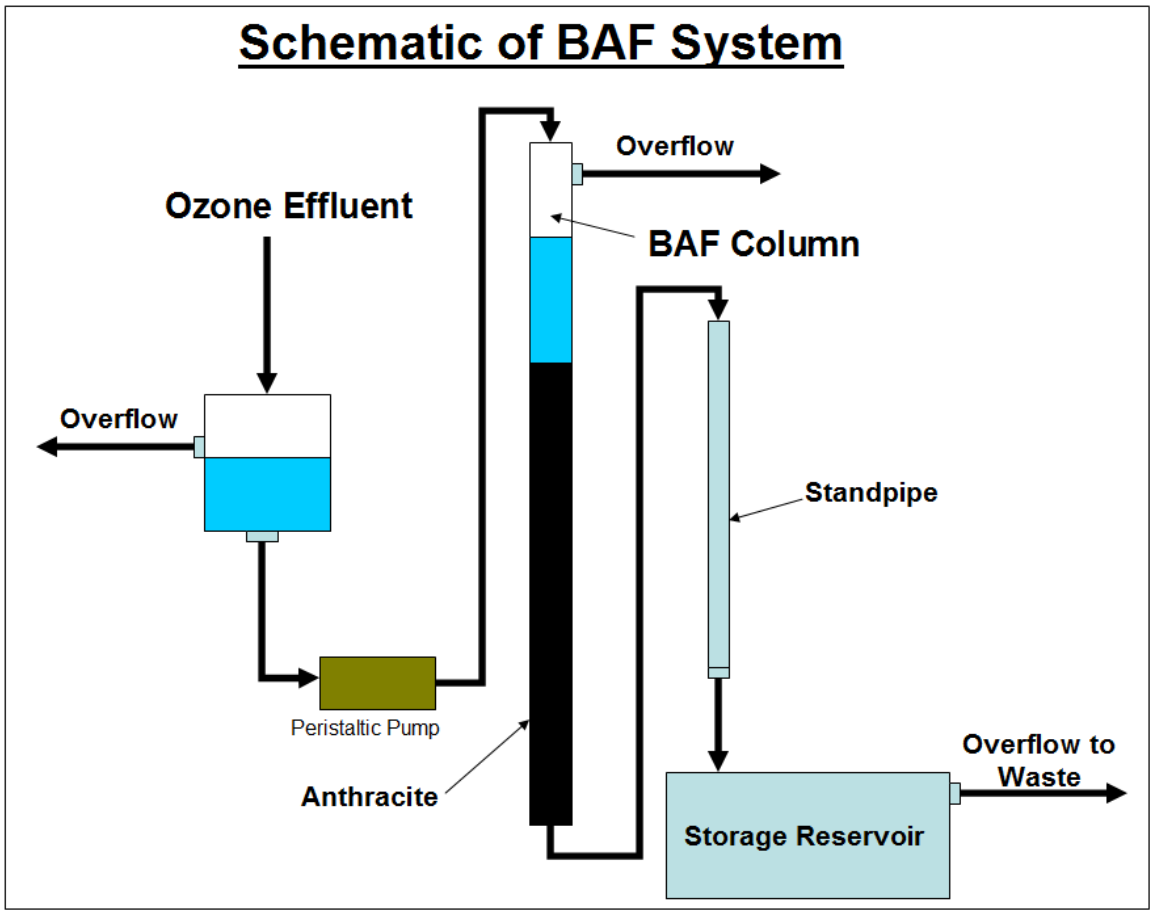

Figure 3-4: Schematic of BAF system

The column was backwashed between each ozone dose to maintain performance. Prior to the first two backwashes, the head on the column was over 30 inches, which was almost to the overflow near the top of the column. To reduce the head the column was backwashed with a peristaltic pump using water stored in the final effluent reservoir. Using the average values for anthracite and the design equations found in *Water Treatment Principles and Design*, Crittenden et al. (2005), a backwash flowrate of 1.6 L/min, which corresponds to a backwash loading rate of 47.4 m/hr (19.4 gpm/ft^2), was used to achieve 50% bed expansion during backwashing. The backwash was done for 10 minutes, which reduced the head to between 8 and 9 inches above the anthracite media.

One of the major obstacles in using a BAF column for research purposes is ensuring the column is at steady state. Toor et al. (2007) tried to validate that the BAC columns operated under steady state conditions through a heterotrophic plate count (HPC) and visual inspections of bacterial colonies [45]. Similar methods were used by Liang et al. (2003) [41]. The decision was made not to use these methods but instead to examine the TOC, UV_{254} absorbance, SUVA, and TOC removal of each process. The results for these parameters are found in the Results section. It was decided that the HPC method was too vague, and that there were too many variables to account for, even while following the procedures in Standard Methods.

Reverse Osmosis

The alternative process train to the MBR-ozone-BAF column was the MBR-RO treatment train. Literature has shown the RO process to be very effective in removing most micropollutants to a high degree although there are a few compounds that are still present in the RO effluent at highly reduced concentrations. A better understanding of how well the proposed process treatment train effectively removes microconstituents can be achieved through a side-by-side analysis with a process that the literature has shown to be effective in removing microconstituents from wastewater.

The RO unit was designed by Dr. Kerry Howe and constructed in the machine shop in the Physics department at the University of New Mexico. A picture of the unit is shown in Figure 3-5. The unit consists of six machined plates where up to five flat sheet RO membranes could be run in series. Osmonics AG RO membranes (proprietary polyamide thin film membranes) were cut to size and fitted between the plates. The unit was designed so that the system could run with as many as five and as few as one membrane. For this project, the RO unit was operated with 3 membranes.

Figure 3-5: Picture of the RO Unit

For this research project, feedwater from the RO feedtank was pumped into the bottom RO cell where it flowed across the membranes. Permeate passed through the membrane at an average rate of 3.2 mL/min per membrane for a total unit permeate flow of 9.5 mL/min. The concentrate passed through the series of plates until it is recycled back into the RO feed tank. Due to the low flux of permeate across the membranes, the system recycles concentrate into the feed tank allowing for the water to become more

concentrated which simulates conditions associated with higher recovery. Design parameters for the RO unit are found in Table 3-4. All parameters except permeate flow and recovery are actually average values taken by Elizabeth Field during her master's thesis research.

Table 3-4: Table of RO parameters

Design Parameter	Value
RO membrane length	0.200 m
RO Membrane width	0.080 m
Channel depth	0.000508 m
Effective membrane area	0.016 m^2
Feed channel cross sectional area	4.06E-5 m^2
Feed flow velocity	0.015 m/s
Permeate flux	20 (L/m^2-hr)
Feed flow	0.366 L/min
Permeate flow (average per membrane)	0.0032 L/min
Concentrate flow	.356 L/min
Average Recovery	78.7%
Flow to feed tank	0.075 L/min
Average system recovery	21.3%

The RO unit was turned on the day before microconstituent samples were taken. The day before that the RO feed tank was filled by diverting the overflow from the standpipe feeding the ozone contactor. The RO feedtank filled at an average flowrate of 75 mL/min.

Sampling and Analysis Procedures

With any research, one of the most important aspects is ensuring that sampling, analysis, and system operations are performed consistently and properly throughout the experimental process. This research called for most parameters to be measured daily

including system parameters such as flowrates, DO, and pH, and lab analysis such as TOC and UV_{254}. A list of these parameters along with testing frequency and location are found in Table 3-5.

Table 3-5: System parameters, testing frequency and location, and data use

Parameter	Frequency	Location	Data use
pH	Everyday	MBR, Ozone, BAF, and RO effluent	Proper system operation
DO	Everyday	MBR, Ozone, BAF, and RO effluent	Proper system operation
Temperature	Everyday	MBR, Ozone, BAF, and RO effluent	Proper system operation
EC	Everyday	MBR, Ozone, BAF, and RO effluent	Proper system operation
Pressure	Continuously	MBR effluent and RO feed	Proper system operation
Flow	Everyday	MBR, Ozone, BAF, and RO effluent	Proper system operation
MLSS	3 times per sampling event	MBR tank	Proper system operation
MLVSS	3 times per sampling event	MBR tank	Proper system operation
TOC	Everyday	MBR, Ozone, BAF, and RO effluent	Analysis of treatment train
BDOC	3 times per set ozone dose	MBR, Ozone and BAF effluent	Analysis of treatment train
Ozone dose	Everyday	Ozone contactor	Proper system operation
Ozone residual	Everyday	Ozone contactor	Proper system operation
PPCP/EDC concentrations	3 times (once at end of every ozone dose)	MBR, Ozone, BAF, and RO effluent	Analysis of treatment train
UV_{254} absorbance	Everyday	MBR, Ozone, BAF, and RO effluent	Analysis of treatment train

Sampling and Cleaning Procedures

To achieve the most accurate and reliable results possible, extreme care was taken to ensure all lab and sampling equipment was as clean as possible. This was achieved by adhering to the methods and procedures described in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2005). A list of procedures, instruments, and parameters is shown in Table 3-6.

Table 3-6: Measured parameters, instruments, and procedures

Parameter	Instrument	Procedure
pH	Oakton pH/CON 10 Series Meter	SM 4500-H+ B
EC		SM 2510 B
Temperature		SM 2550 B
DO	HACH HQ40d DO Meter	SM 4500-O G
Ozone dose	HACH DR 890 Colorimeter	See Ozone procedure
Ozone residual		SM 4500-O_3 B
TOC	Tekmar Dohrmann Phoenix 8000	SM 5310 C
BDOC		See BDOC procedure
MLSS/MLVSS	NA	2540 G
UV_{254} absorbance	Varian Cary 50 Conc UV/Vis Spectrophotometer	5910 B

Sampling was done with plasticware that was thoroughly washed with soap and water. The plasticware was then rinsed with DI water and inverted while drying to ensure dust did not collect in the container. The glassware cleaning procedure includes the same procedure for the plasticware with an additional soak in a 10% nitric acid bath for at least one hour. The TOC vials followed the same procedure except they were soaked for 24 hours in the acid bath and then capped with aluminum foil. The vials were then baked at 550 ºC for an hour and wrapped in foil to keep them from being contaminated. The TOC vial cleaning procedure follows Standard Methods 5310 B.1d except that the vials are baked at 550 ºC instead of 400ºC.

TOC Sampling and Analysis Procedure

The TOC data gathered for this research was used for many different reasons and ended up being one of the most important parameters examined. The TOC data was used to not only check the performance of the MBR system, but was also used to ensure the system was at steady state, measure BDOC, and to examine the amount of degradation of organics in each process. Because of this, the methods and procedures for sampling and analyzing TOC follow those in Standard Methods and care was used to ensure consistent, accurate data.

Sampling for TOC was done every day at several different locations in the treatment train. These locations can be found in Table 3-5. Grab samples were collected with clean plasticware and brought back to the lab for filtering and pH adjustment shortly following sampling. The samples were vacuum filtered through a 0.7 μm binder-free glass fiber filter (GF/F Whatman). Samples of 250 mL were collected every day except on days that included a BDOC analysis. In that case, 500 mL samples were collected instead. All samples were analyzed within 6 days of collection with most being analyzed in 3 days or less.

TOC analysis was done in accordance with Standard Method 5310 C (persulfate-ultraviolet oxidation method) using a Tekmar-Dohrmann Phoenix 8000 TOC analyzer. To ensure accuracy, two sets of standards (2 mg/L and 10 mg/L TOC) were run at the beginning and end of each set of analysis. Due to slight discrepancies in these standards before the experiments began, a new calibration curve was developed using KHP in concentrations of 0, 2, 6, 10, and 20 mg/L TOC.

UV_{254} Sampling and Procedures

Another important parameter examined in this research was UV_{254} absorbance. Like TOC, UV_{254} absorbance is often used as a surrogate for the concentration of NOM [23]. In addition, a recent study by Bahr et al. (2007) concluded that there is a good

correlation with UV_{254} absorbance between the specific ozone consumption and the removal of micropollutants [46]. The analysis for UV_{254} absorbance for this project followed the procedures in Standard Methods 5910-B using a Varian Cary 50 UV/Vis spectrophotometer. Sampling for UV_{254} absorbance was taken every day for the MBR, ozone, and BAF effluents as well as for the days the RO system was operating. For the RO system, samples were collected in the RO tank and permeate effluent. All samples were collected in clean TOC vials and tested within hours of collection.

SUVA

The specific UV absorbance (SUVA) parameter is the ratio of the UV_{254} absorbance to the TOC concentration. The formula is given by Equation 1:

$$SUVA = 100 * UV_{254}/TOC \quad \textbf{[1]}$$

The SUVA parameter was used to determine how well a treatment process may work in removing NOM [23]. SUVA can be used to measure how easily degradable organics are. Because of these factors, the SUVA parameter was found to be very important for many aspects of this research including its use in determining steady state conditions, how well the system treated TOC, and in predicting the removal of micropollutants based on the applied ozone dose.

BDOC Procedure

Unlike many of the other parameters used in this research the BDOC procedure is not listed in Standard Methods. Biodegradable dissolved organic carbon (BDOC) is a parameter that is widely used to quantify biodegradable organic matter (BOM) in drinking water [47]. In 1998, Khan et al. (1998) developed a modified batch procedure for determining BDOC in wastewater [47, 48]. The development of this procedure allowed BDOC analysis to be done on municipal water reclamation and secondary treated wastewaters with relatively low DOC concentrations. Although this procedure reduces variability and increases precision compared to BOD and COD, the 28-day incubation

period required can be a large drawback, especially if results are needed much sooner. In 1999, Khan et al. (1999) described a modified method so that the procedure could be done in just 5 days and included both ozonated and non ozonated secondary effluent samples [47]. This refined procedure was used in these experiments to determine the BDOC for the MBR, ozone, and BAF effluents, although further modifications were made.

The refined procedure in Khan et al. (1999) calls for the concurrent determination of $SBOD_5$ with BDOC. It was determined that the $SBOD_5$ parameter was not needed. Because of this, modifications to the procedure could be further made to ensure better accuracy and consistency. Instead of using 300 mL BOD bottles that were water sealed, glass bottles of at least 500 mL of volume were used. In addition, the modified bottles were only filled with 250 mL of undiluted sample. This was to ensure that there was enough oxygen in the bottles to allow for maximum biodegradation. Initial tests that followed the original method described by Khan et al. (1999), showed that after 5 days most of the samples, including those diluted by a factor of 4:1, were below the final dissolved oxygen concentration limit of 1 mg/L. This means that biodegradation of the organics could have been incomplete due to a lack of oxygen. Further testing showed that reliable BDOC measurements could be achieved using the 500 mL bottles with no dilution and 250 mL of sample.

BDOC Equipment

- 500 mL bottles, preferably with airtight lids or glass stoppers
- 0.7 µm glass-fiber filter (GF/F Whatman, Whatman International Ltd.)
- DI water (containing less than 0.20 mg/L TOC)
- Incubator at 37 ºC
- Clean 500 mL and 250 mL plasticware for sampling

- TOC vials and TOC analyzer
- Freshly collected MLSS (used as inoculum)
- Pipettes with wide mouthed tip

Methodology

The modified BDOC procedure used in this study is based on the method described in "Method development for measuring biodegradable DOC in reclaimed and treated wastewater" by Khan et al. (1998) [48]. Included is the refinements made in "Factors influencing biodegradable dissolved organic carbon measurement" by Khan et al (1999) [48] as well as the in house modifications mentioned above.

The cleaning method for all TOC vials, plasticware, and glassware used in this procedure can be found in the section on sampling and cleaning procedures. All glassware was thoroughly washed with soap and water, rinsed with DI water, soaked for at least 1 hour in a 10% nitric acid bath, and then rinsed again with DI water. The step by step procedure is as follows:

- Rinse a 0.7 μm glass fiber filter (GF/F Whatman) with 300 mL DI water, containing a TOC content of <0.2 mg/L.
- Filter sample through a 0.7 μm glass fiber filter (GF/F Whatman)
    - Waste first 50 mL of sample.
- Place samples in a washed glassware with at least 20% gas volume.
- Saturate the sample with DO by shaking.
- After shaking, collect two, 40 mL samples in clean TOC vials and measure TOC.
    - Record as TOC_i.
- Next, place mixture in washed glassware that is at least 500 mL in volume.
- Add 2 mL of unfiltered inoculum (2 mL of MLSS). This is part of the modified version by Khan et al. (1999). The MLSS should be used, without pre-rinsing,

within 24 hours. The well mixed inoculum should be added with a wide tipped pipette.

- Incubate in the dark for 5 days at 37° C.
    - Note: The original procedure calls for 28 days at 20° C, but the modified version from Khan et al. (1999) gives these variations.
- The samples are then filtered through GF/F filters and two, 40 mL samples collected and measured as DOC_f.
- A seed control, sample b, was prepared in the same way except that the 2 mL seed was added to 250 mL of DI water (TOC <0.2 mg/L) with no sample and the values were recorded as DOC_{bi} and DOC_{bf}. The DOC_{bi} measurement does not include the 2 mL of MLSS.
- The BDOC can then be found using Equation 2 below.

$$BDOC\ (mg/L) = [(DOC_i - DOC_f) - (DOC_{bi} - DOC_{bf})] \quad \textbf{[2]}$$

Ozone Residual and Applied Dose Procedure

One of the challenging aspects of this research was to develop an accurate, reliable, and inexpensive procedure to measure both the applied dose of the ozone and the residual ozone at different points in the ozone contactor columns. One of the complicating aspects was that the ozone measurements needed to be done in the field. This means that any apparatus used would have to be not only portable, but also able to hold up to the harsh environment at the pilot system set up at the SWRP. After reviewing Standard Methods, as well as several journal articles, a technique was found and further developed that meets all the criteria stated above.

A HACH DR 890 colorimeter was purchased and tested in the lab to ensure its accuracy. This instrument was chosen because it could accurately measure ozone and was portable, reliable, and affordable.

One of the key elements in developing a procedure to measure ozone was that it had to measure ozone in the feed gas and off gas as well as in the ozone contactor effluent. There are a couple of different methods that could have been used to measure the ozone residual in the chambers. One of them included using HACH AccuVac ampuls and a calibration curve that was preprogrammed into the HACH DR 890 Colorimeter. The problem with this method is that it could not be used to measure ozone concentrations in the gas. The other method involved programming a calibration curve into the instrument and following Standard Methods 4500-O_3 B, the indigo colorimetric method. This method was chosen because it could be further modified to measure ozone concentrations in the off gas.

Equipment

The following equipment was used to measure ozone in the off gas as well as residual concentrations in the water.

- 5 mm Precision Seal® rubber septa cap
- 1” piece of ozone resistant tubing with 5 mm ID
- 3 way, luer lock valve (Kynar or other ozone resistant material)
- 5 ml Gastight®, Hamilton syringe with 22 gauge, noncoring needle
- Indigo Reagent II (SM 4500 O_3 B)
- Glass 50 mL graduated cylinder
- 5 mL pipette

- Parafilm
- Two, 25 mL HACH sample vials
- Two, 100 mL volumetric flasks
- 50 mL, Erlenmeyer flask

Before using the HACH DR 890 series colorimeter, a calibration curve was made and entered as a program into the instrument. To ensure the accuracy of this program and the procedure used to measure the ozone in both the residual and off gas, side-by-side analyses were done in the lab with procedures and instruments known to be accurate. Confidence in both procedures was established before using them in the field.

For ozone residual measurements, the ozone concentrations produced by the HACH instrument were compared to analysis done following Standard Methods 4500 O_3 B using a Varian Cary Conc UV/Visible Spectrophotometer. The procedure developed closely follows the indigo colorimetric method in Standard Methods and is described in detail below.

For gaseous ozone, concentrations were measured in the lab using the Varian Cary 50 Conc UV/Visible Spectrophotometer. A molar absorptivity of E = 2950 M/cm was assumed and the absorbance was measured at 258 nm, as suggested in Standard Methods 4500 O_3 B. The data was then compared to the measurements taken by the HACH DR 890 Colorimeter using the method described below. A 1:1 stoichiometric ratio is assumed for the reaction between the ozone and the indigo for both the residual and off gas measurements [49].

Ozone Residual Procedure

To measure the ozone concentration in the residual, two 100 mL volumetric flasks were prepared with 10 mL each of indigo reagent II added with a clean pipette. The first volumetric flask is then filled to the mark with DI water. This blank can be used

repeatedly for up to four hours. The volumetric flask for the residual sample may need to be diluted with DI water depending on the concentration of the residual ozone in the sample. This dilution is factored into equation 3, which is used to calculate the concentration of ozone in the residual. After adding the correct amount of DI for dilution, the volumetric flask was filled to the line with sample water, being careful not to let the sample run down the side of the flask. The top of the flask was quickly covered with parafilm and inverted repeatedly for 30 seconds. Next, the blank sample was added to a clean 25 mL HACH sample vial. The vial was pre-rinsed with a small amount of the sample first. After that, at least 10 mL of the sample is added. After ensuring the vial was free of air bubbles, dust, or any other material, an accurate absorbance reading was taken. This procedure was repeated with another 25 mL HACH sample vial for the residual sample. The HACH instrument was turned on and set to the user-entered program. The sample vial was inserted into the HACH DR 890 colorimeter, and the cap closed to ensure there was no light interference. The "Blank" button on the control panel was then pressed. Note: Because the ozone bleaches the indigo solution, the actual sample was read as the blank. The sample was then taken out and replaced with the blank, again ensuring the cap was on correctly. The "Read" on the instrument panel was then pressed. An ozone concentration, C_H, was taken and used in equation 3 to find the ozone residual, C_{OR}.

$$C_{OR} = C_H * V_T / V_S \quad \textbf{[3]}$$

Where:

C_{OR} = Concentration of ozone residual (mg/L)

C_H = Concentration of ozone reported by the HACH instrument

V_T = Total volume of sample with DI water, usually 90 mL (mL)

V_S = Volume of sample added (mL)

This measurement was taken twice and averaged for each chamber in the ozone contactor, except when there was no ozone in the preceding chamber. Then the chamber was assumed to have zero residual, although occasional measurements were taken to ensure this was true.

Ozone feed and off gas procedure

Measuring the concentrations of ozone in the feed gas and off gas was used to find the applied ozone dose, the mass of ozone per volume applied to the reaction chamber. Some of the methods described in an article by Chiou et al. (1995) were used to develop ozone gas concentration measurements used in this research [49]. This measurement uses the same user-entered calibration curve used to measure the ozone residual. A ratio of 9:1 of DI water to indigo was used. This means that if 2 mL of indigo solution was used, 18 mL of DI water was also added. This was done to ensure all ozone gas measurements were consistent and so that the same calibration curve used to measure residual ozone could be used. The same 9:1 ratio was used in measuring the residual ozone.

The first step in measuring the ozone gas concentration was to prepare the syringe. A clean 5 ml Gastight® Hamilton syringe was first prepared by adding the proper amount of indigo solution. The amount of indigo solution varied by 0.5 mL increments and was chosen so that the ozone measurement with the HACH colorimeter read between 0.1 and 0.5 mg/L with optimal readings at the higher end. Initial test results in the lab showed readings greater than 0.5 mg/L were not reliable due to the indigo solution becoming too bleached for the HACH colorimeter to reliably measure.

Next, the proper amount of DI water was measured in a clean 50 mL graduated cylinder and added to a 50 mL Erlenmeyer flask. As mentioned earlier, a 9:1 ratio of DI water to indigo solution was used. After this was complete, the ozone gas was ready for sampling. The syringe was inserted into the septa to where the tip of the syringe is just visible past the luer lock connection. After that, the tubing with syringe was attached to

the 3-way valve via the luer locks. A picture of the tubing, syringe, and three-way valve are shown in Figure 3-6. Next, the 3-way valve was quickly and smoothly turned to where the ozone gas was open to all 3 ports. At the same time, the syringe was inserted as far as it would go. As soon as this happened, gas was immediately pulled through the syringe. Care was taken to do this in a smooth motion and as quickly as possible. The syringe was then filled with the predetermined amount of gas. Care was also taken in this step since being off by as little as 0.1 mL can mean a difference of up to 20% for some measurements. Next, the syringe was carefully pulled out of the septa and gently shaken for one minute. At the same time, the 3-way valve was switched back to its original position and the tubing with the septa was detached. After the minute of shaking, the contents of the syringe were injected into the Erlenmeyer flask with the predetermined amount of DI in it. The flask was then covered with parafilm and inverted several times to ensure the sample was properly mixed and diluted. Next, the 25 mL HACH sample vials were prepared the same way as when measuring the ozone residual. The vials were pre-rinsed with a small amount of sample. Then, at least 10 mL of sample was added to the vials and the ozone concentration measured. Equation 4 was used to get the true ozone off gas concentration, Y. The same procedure was used to measure the ozone concentration in both the feed gas and off gas.

$$Y = V_{DI} * C_H / V_g \quad \textbf{[4]}$$

Where:

Y = Concentration of ozone measured in the gas (mg/L)

V_{DI} = Volume of DI water (mL)

C_H = Concentration of ozone reported by the HACH instrument

V_g = Volume of off gas added

To find the applied ozone dose, a mass balance was done around the first ozone contact chamber. This can be seen in Figure 3-7. The volumetric water flowrate was

measured daily and the volumetric flow rate for the gas was measured at least every other day to ensure accuracy. The procedures for measuring the flow rates can be found below in the section on flowrate method and procedures. The applied ozone dose is given by Equation 5.

$$C_f = Q_g/Q_w*(Y_i-Y_f) \quad \textbf{[5]}$$

Where:

Q_g = Volumetric flow of gas (L/min)

Q_w = Volumetric flow of water (L/min)

C_f = Applied ozone dose (mg/L)

C_i = Initial ozone concentration in water = 0 (mg/L)

Y_i = Initial ozone gas concentration (mg/L)

Y_f = Final ozone gas concentration (mg/L)

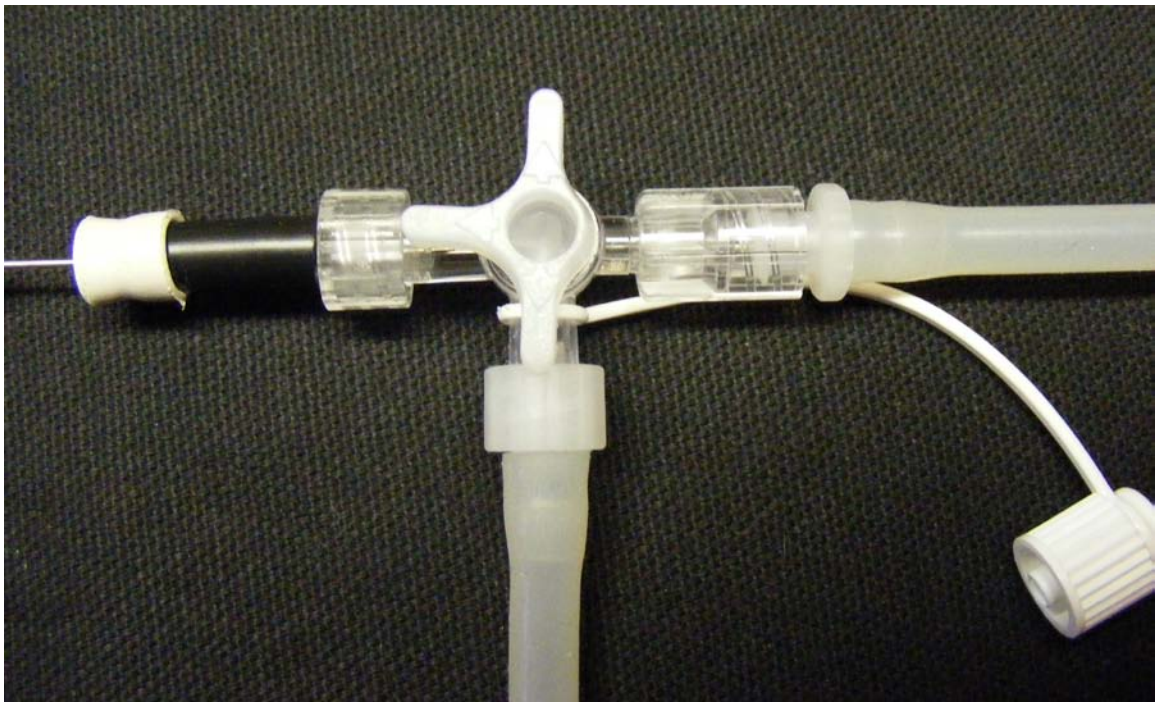

Figure 3-6: Picture of gas tight tubing with syringe and 3 way valve

To ensure accuracy, both the feed gas and off gas were measured three times and the average of the three measurements was used for each. This was done for several reasons. As described below, several small measurements must be taken in order to calculate the concentration of the off gas. These include measuring out the amount of DI water, indigo solution, and ozonated gas. Although the errors in each one of these is quite small, they can add up. In addition, the precision of the HACH DR890 colorimeter is less than that of the UV/Vis spectrophotometer. The HACH instrument is precise to 2 significant digits while the UV/Vis spectrophotometer in the lab reports 4 significant digits. This difference alone can cause inaccuracies of a few percent. The initial lab results showed that a more reliable and accurate value is achieved by averaging the ozone gas concentrations measured with the HACH instrument.

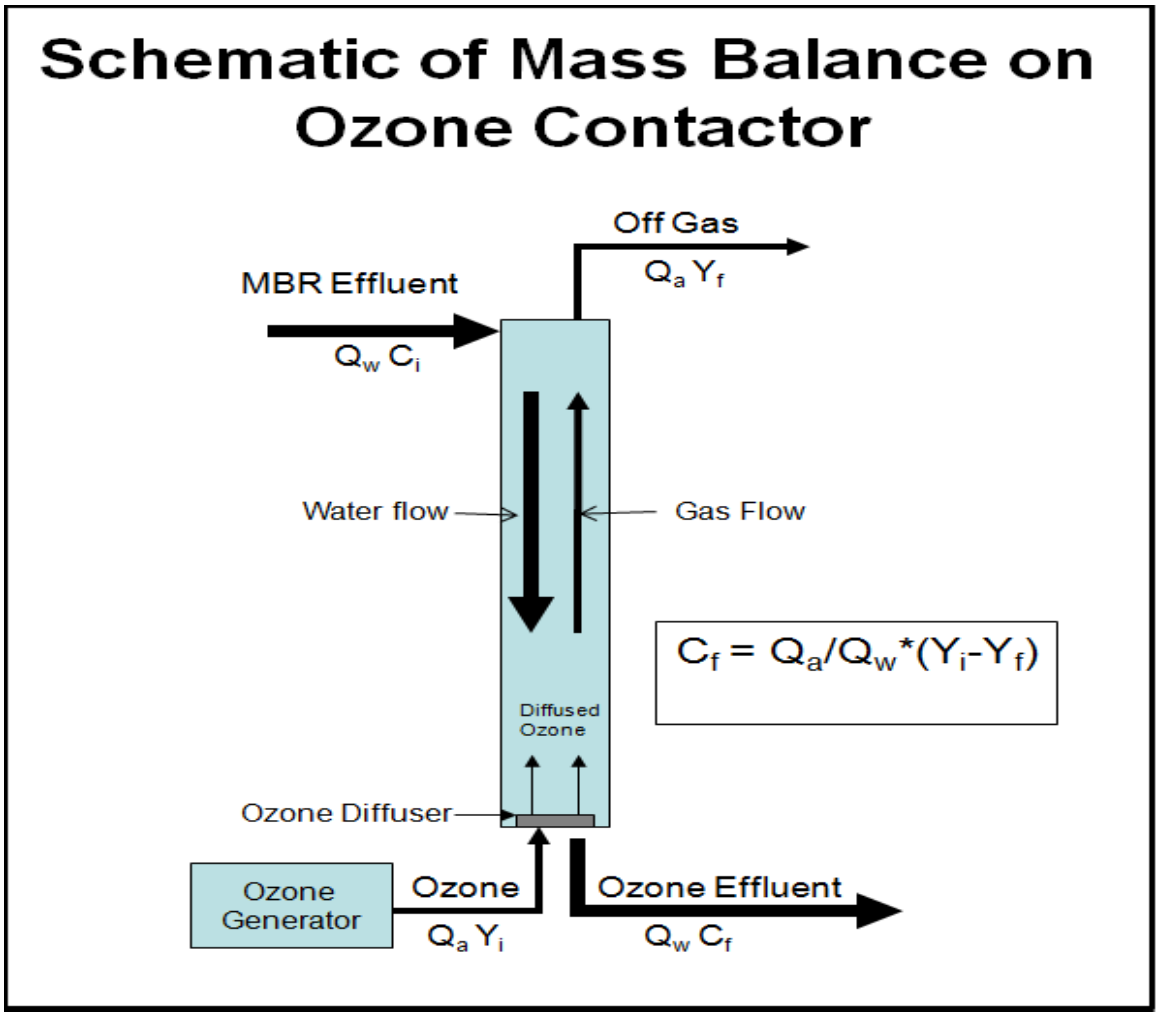

Figure 3-7: Schematic of mass balance around the first ozone contact chamber

Flowrate method and procedures

For this project, measuring and recording accurate flow rates was crucial in providing proper system operation. Accurate flow rate measurements are vital to calculating the SRT, HRT, and applied ozone dose. This ensures the data collected for this research project is both reliable and reproducible and that the system is running properly.

Because of the harsh environment at the pilot system, the initial flow meters used to monitor the MBR effluent flow did not last long. In addition, the flow rates

established by the peristaltic pumps and used to measure the wasting and MBR effluent flows were found to be inconsistent and unreliable over time. Because of this, it was established early on that the flow rates would have to be measured by hand with a stopwatch and graduated cylinder.

The flow rates for the MBR, ozone, and BAF effluents were established with a stopwatch and 100 ml graduated cylinder. This can be found in Equation 6. For the wasting flow rate, the volume was measured after 3 minutes of wasting flow into a 50 mL graduated cylinder. The flow rate for the RO permeate was measured using a calibration column were the initial and final volumes were measured over time using a stopwatch.

$$Q = V/t \quad \textbf{[6]}$$

Where:

Q = Volumetric flow rate

V = Volume

t = Time measured with stopwatch

The flow rate for the volumetric gas flow was found by diverting the flow of gas from the ozone generator to the ozone contact chamber. The diverted flow was used to fill an inverted 100 mL graduated cylinder that was full of water. The air would fill up the cylinder over time and a flow rate could be established. The flow rate was measured twice and the results averaged. Because the results for this method varied little from day to day, this flowrate was occasionally measured every other day although most of the time this measurement, along with the other volumetric flowrates listed in this section, were taken daily. This is because small changes in either the volumetric gas or water flowrate could change the applied ozone dose by a few percent.

PPCP/EDC sampling

Due to the extremely small concentrations of microconstituents and the complexity of the treated wastewater, the PPCP/EDC analysis was done by an outside lab. MWH labs was contracted to do the PPCP/EDC analysis for sixteen samples including one field blank and one initial sample from the MBR effluent used to determine what compounds might be found in future sampling events. The sampling schedule, including sampling locations, can be found in Table 3-7.

Table 3-7: Sampling schedule for PPCP/EDC analysis

Date	Sample Location	Data Use	# Samples
18-Aug-09	MBR effluent	Initial sample	1
29-Oct-09	MBR, BAF, and ozone effluent and the field blank	Samples for 8 mg/L ozone dose	4
6-Nov-09	Duplicates for MBR, BAF, and ozone effluents and 1 sample for RO effluent	Samples for 4 mg/L ozone dose	7
13-Nov-09	MBR, BAF, RO, and ozone effluents	Samples for 2 mg/L ozone dose	4

The analysis done by MWH labs uses LC-MS-MS by electrospray positive and negative modes to analyze 83 microconstituents using samples of less than 40 mL. Most of the compounds can be quantified in concentrations of 5 ng/L. A list of the compounds tested for and their detection limits can be found in Table 3-8.

Samples were shipped to MWH labs via next day air. The samples were grab samples collected in 40 mL vials sent by MWH labs. The sample vials came ready to use with the preservatives already inside. For each sample, two vials were filled. Before taking the samples, hands were thoroughly cleaned with soap and water. Gloves could not be worn while sampling and special precautions such as not wearing fragrances, or

smoking were done to prevent contamination. The vials were wrapped in protective plastic and put in a cooler with pre-frozen cooling packs to keep the samples preserved while shipping.

Table 3-8: PPCPs and EDCs analyzed by MWH laboratories

Analyte	Detection Limit (ng/L)	Analyte	Detection Limit (ng/L)	Analyte	Detection Limit (ng/L)
1,7-Dimethylxanthine	5	Dilantin	20	Progesterone	5
4-Nonylphenol	10	Erythromycin	10	Propylparaben	5
4-tert-Octylphenol	10	Estradiol	5	Sucralose	100
Acetaminophen	5	Estrone	5	Sulfachloropyridazine	5
Albuterol	5	Ethinyl Estradiol - 17 alpha	5	Sulfadiazine	5
Amoxicillin	20	Ethylparaben	20	Sulfadimethoxine	5
Andorostenedione	5	Flumeqine	10	Sulfamerazine	5
Atenolol	5	Furosimide	10	Sulfamethazine	5
Bendroflumethiazide	5	Gemfibrozil	5	Sulfamethizole	5
Bezafibrate	5	Ibuprofen	10	Sulfamethoxazole	10
BPA	10	Iohexal	10	Sulfathiazole	5
Butalbital	5	Iopromide	5	TCEP	5
Butylparaben	5	Isobutylparaben	5	Theobromine	5
Caffeine	10	Ketoprofen	5	Theophylline	10
Carbadox	5	Ketorolac	5	Triclosan	10
Carbamazepine	5	Lidocaine	5	Trimethoprim	10
Carisoprodol	5	Lincomycin	10	Warfarin	5
Chloramphenicol	10	Lopressor	20	Simazine	5
Chloridazon	5	Meclofenamic Acid	5	Propazine	5
Cimetidine	5	Meprobamate	5	Chlorotoluron	5
Cotinine	10	Metazachlor	5	Atrazine	5
DACT	5	Methylparaben	20	Cyanazine	5
DEA	5	Naproxen	10	Bromacil	5
DEET	2	Nifedipine	20	Diuron	5
Dehydronifedipine	5	Norethisterone	5	Linuron	5
DIA	5	Oxolinic acid	5	Isoproturon	20
Diazepam	5	Pentoxifylline	5	2,4-D	5
Diclofenac	5	Primidone	5		

A field blank was used to ensure proper sampling, preservation, and shipping protocol. The field blank procedure was the same as the sampling procedure except that instead of taking a sample, water provided by MWH labs was poured into the sample vials. The field blank water was free of any of the compounds being tested for and showed if there was a source of contamination in the sampling procedure.

Chapter 4: Experimental Results

To determine which applied ozone doses to evaluate PPCP/EDC removal at, the project was divided into two phases. Phase 1 analyses examined the effects of ozone dose on several organic parameters. The bulk organic analysis were TOC, percent TOC removal, UV_{254} absorption, SUVA, and BDOC with the applied ozone dose ranging from 0 to approximately 12 mg/L. Due to the cost of each PPCP/EDC analysis and the limited budget for testing, only three applied ozone doses could be examined for PPCP/EDC removal. Phase 1 examined the bulk organic analysis at varying ozone doses to determine the most effective ozone doses for microconstituent removal.

Phase 2 examined the removal of microconstituents at the 3 different applied ozone doses determined in Phase 1. In addition, some samples were collected and analyzed for PPCPs/EDCs for quality assurance purposes. Because the detection limits for PPCPs/EDCs are low (5 ng/L for most compounds), and the wastewater matrix so complex, there is inherent variability expected in the detection of these compounds. To increase confidence in the sampling procedures and PPCP/EDC analysis, some of the samples were used for quality assurances purposes. The quality assurance samples included one set of duplicates for the MBR, ozone, and BAF effluent, as well as a field blank to insure contamination was not an issue.

Phase 1: Evaluation of selected parameters at varying ozone doses

In Phase 1, MBR effluent was fed to the ozone contactor at a flowrate of 100 mL/min. Bulk organic analyses were performed at 13 applied ozone doses ranging from 1.3-11.9 mg/L. The bulk organic analysis included TOC, percent TOC removal, UV_{254}, SUVA, and BDOC. These parameters were examined to establish applied ozone doses for micropollutant removal.

To generate different ozone doses an oxygen flow rate and a power setting on the ozone generator was set. Once a day, before the ozone generator was turned on, the air and water flow rates were measured, as detailed in the flowrate method and procedures

section. The ozone generator was then turned on and allowed to run for at least half an hour to allow both the ozone generator to establish 100% output and to allow steady state conditions to develop in all the chambers.

Once the system came to steady state, measurements were taken for the influent gas concentration and the off gas ozone concentration. Several attempts were needed to establish the correct amount of indigo solution and gas volume to ensure accurate gas measurements of ozone. The average of three measurements for both the influent and off gas ozone concentrations was used to establish an applied ozone dose as described in the ozone procedure. The next step was to measure the residual ozone at different points in the ozone contactor.

The procedure for measuring the ozone residual is described in the ozone residual procedure section. To ensure the system was at steady state, the system was allowed to run uninterrupted for twenty minutes after the last ozone gas measurement. This was because opening and closing the three-way valve, when measuring ozone gas, could affect the ozone residual measurements because of the potential interruption of the ozone gas flow. In addition, the ozone residuals were measured from back to front, with the third chamber being measured first. This was done to ensure there was no interruption of flow to the chambers that had yet to be measured. Residual measurements were usually taken twice and averaged, except when no residual was detected. Residual data can be seen in Figure 4-1.

The instantaneous ozone demand of the treated wastewater occurred at an ozone dose of 2.6 mg/L. This is the ozone dose above which an ozone residual was first detected in chamber 1. An ozone residual was not detected in chamber 2 until an ozone dose of 5.8 mg/L. No residual ozone was detected in chamber 3, even at an ozone dose of almost 12 mg/L. The lack of detection of an ozone residual in chamber 3 showed the effectiveness of bubbling air into the bottom of chamber 3 any remove the residual ozone. The R^2 values of 0.95 and 0.76 for chambers 1 and 2, show a linear relationship between the ozone dose and residual ozone, although it is not a one-to-one relationship.

The slope for chamber 1 is 0.3. This shows that after the ozone demand is met, a 0.3 mg/L ozone residual is formed for every 1 mg/L of ozone added. The slope for chamber 2 is 0.16. An average of 1 mg/L of ozone is added for every 0.16 mg/L of ozone residual detected in chamber 2. This shows that ozone is being consumed as it goes through chambers.

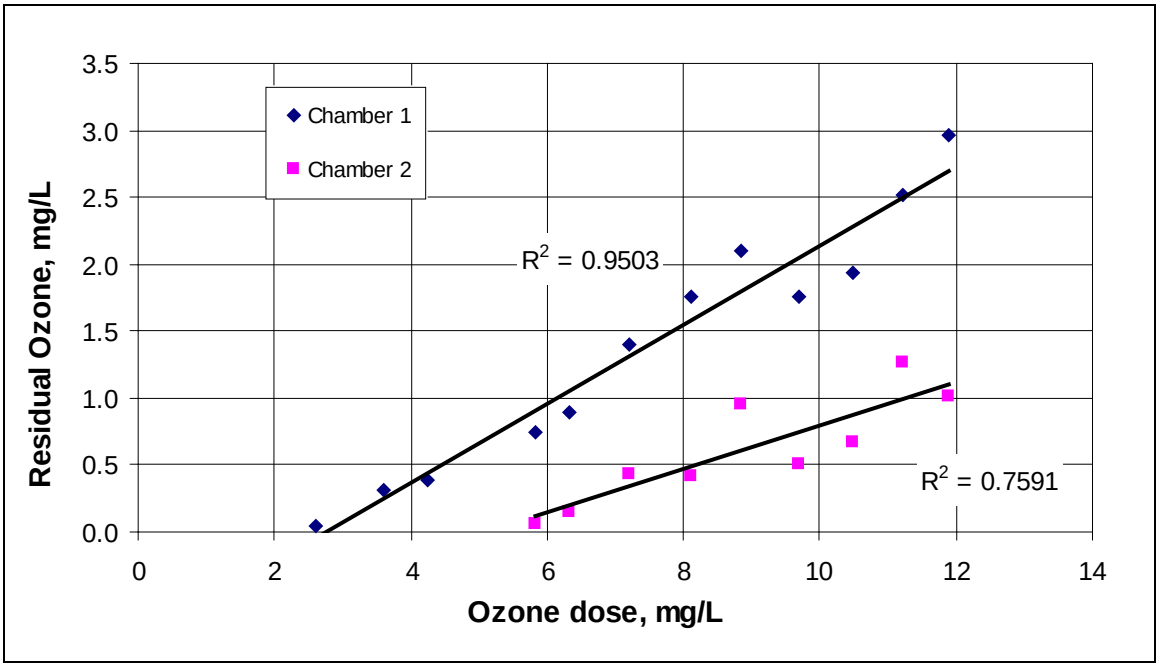

Figure 4-1: Residual ozone dose as a function of applied ozone dose in columns 1 and 2

After residual measurements were taken, 500 mL samples were collected from the ozone and MBR effluents for bulk organic analysis. The dial on the ozone generator was changed and the next set of measurements and samples were taken. Two or three different ozone doses were examined each day. After collecting the samples, a bulk organic analysis was done to find the most effective ozone dose based on TOC, % TOC removal, BDOC, UV_{254}, and SUVA.

TOC

TOC was analyzed at varying applied ozone doses to evaluate the effectiveness of ozone in removing TOC. The TOC samples collected for the ozone contactor were taken from the end of the third chamber. TOC removal by ozone is due to the complete

mineralization of organics to CO_2 and H_2O. Figure 4-2 shows that little to no organic removal is achieved through ozonation alone. The 11 samples analyzed for TOC removal ranged from +8% to -8% removal, with an overall average removal of -0.03%. The negative removals in Figure 4-2 may be the result of three possible causes. First, if no removal is occurring, the TOC measured in the ozone contactor effluent may be slightly different from the influent measurements because of instrument variability. A higher measurement in the ozone contactor effluent would cause negative removal. Second, it is possible that extremely recalcitrant compounds are not oxidized by the persulfate-ultraviolet oxidation method used by the TOC analyzer, and therefore not measured as TOC in the ozone influent. Ozone may be able to partially degrade the recalcitrant compounds to a point to where they can be mineralized and measured by the TOC analyzer. The third reason is that there may have been variability in influent TOC over time, so a particular sample of the effluent may not be paired with an influent sample that represents the actual influent the column received at the time. As mentioned earlier there were 2 or 3 different applied ozone doses examined each day during Phase 1. Each applied ozone dose took between 2 to 3 hours to measure and sample. Only one MBR effluent sample was taken per day and the concentration of TOC in the MBR effluent could have shifted between examined ozone doses.

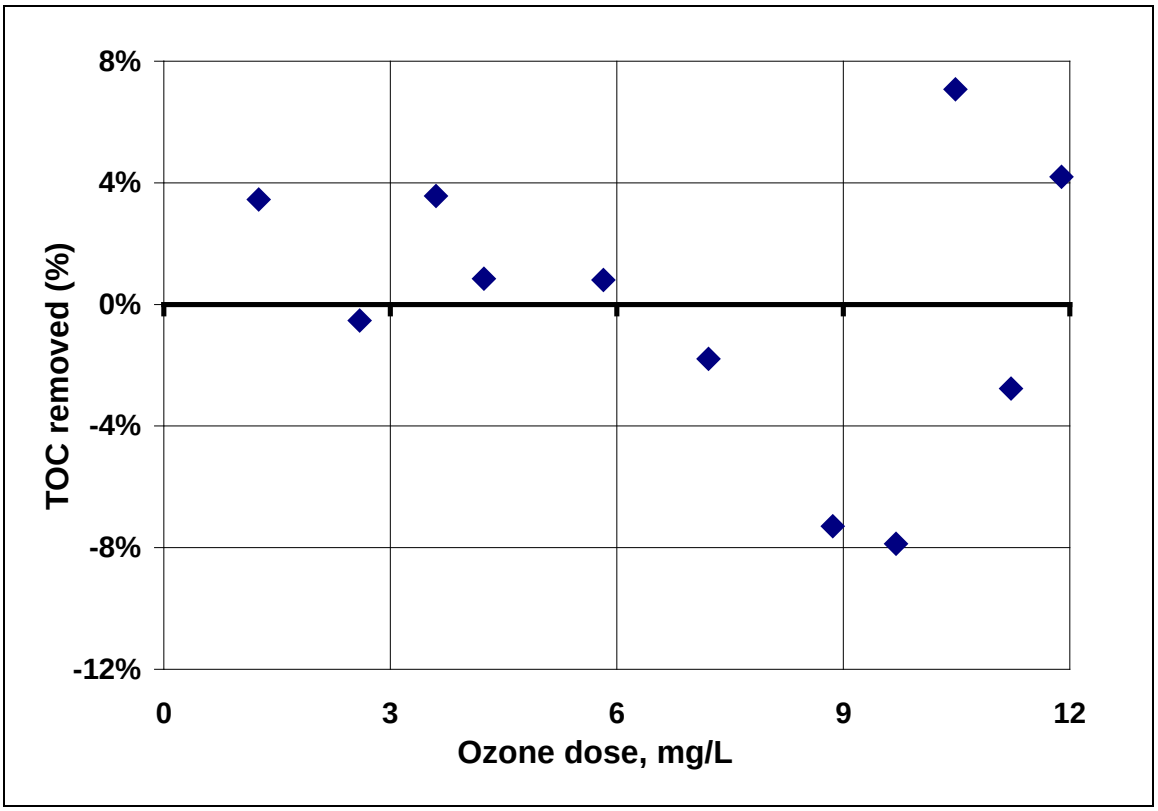

Figure 4-2: Percent of TOC removed as a function of applied ozone dose for Phase 1

UV_{254} Absorbance and SUVA

UV_{254} absorbance is often used as a surrogate for NOM. UV Absorbance at this wavelength is attributed to double bonded carbon groups in unsaturated and aromatic organics. These compounds tend to be more hydrophobic and recalcitrant. Increasing the applied ozone dose decreases the UV_{254} absorbance, although there is a limit as illustrated in Figure 4-3. The UV_{254} absorbance begins to level off at an applied ozone dose of around 8 mg/L. This is also seen in the SUVA data illustrated in Figure 4-4.

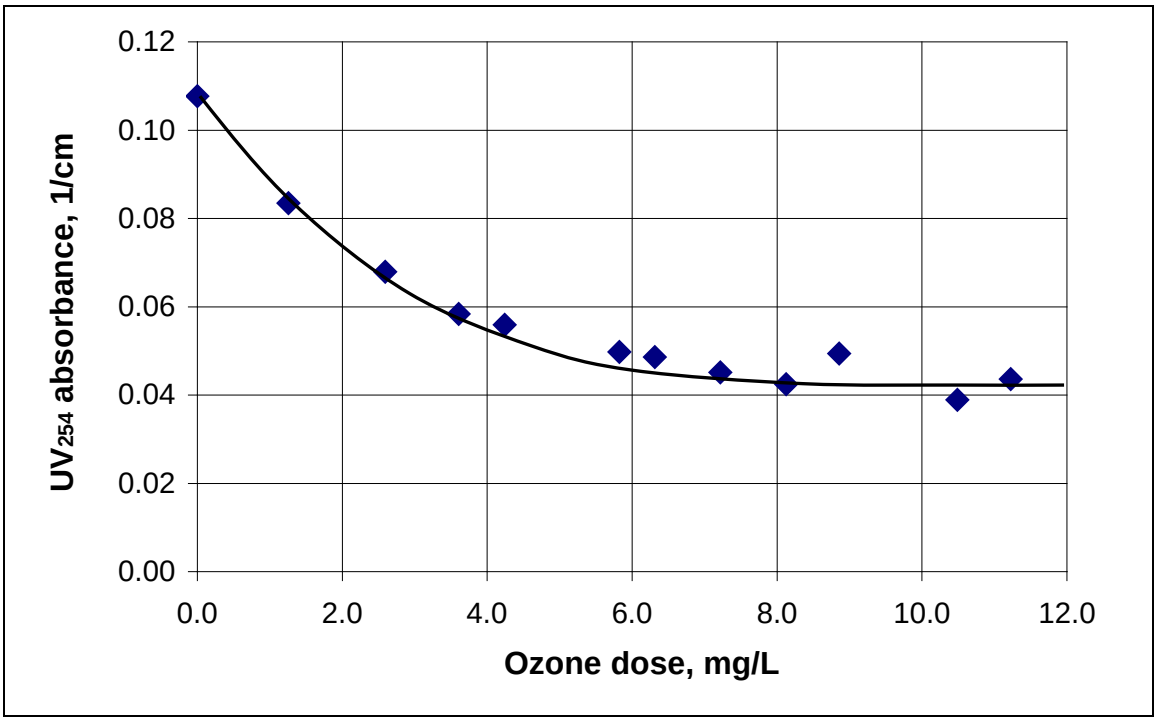

Figure 4-3: UV_{254} absorption as a function of applied ozone dose for Phase 1

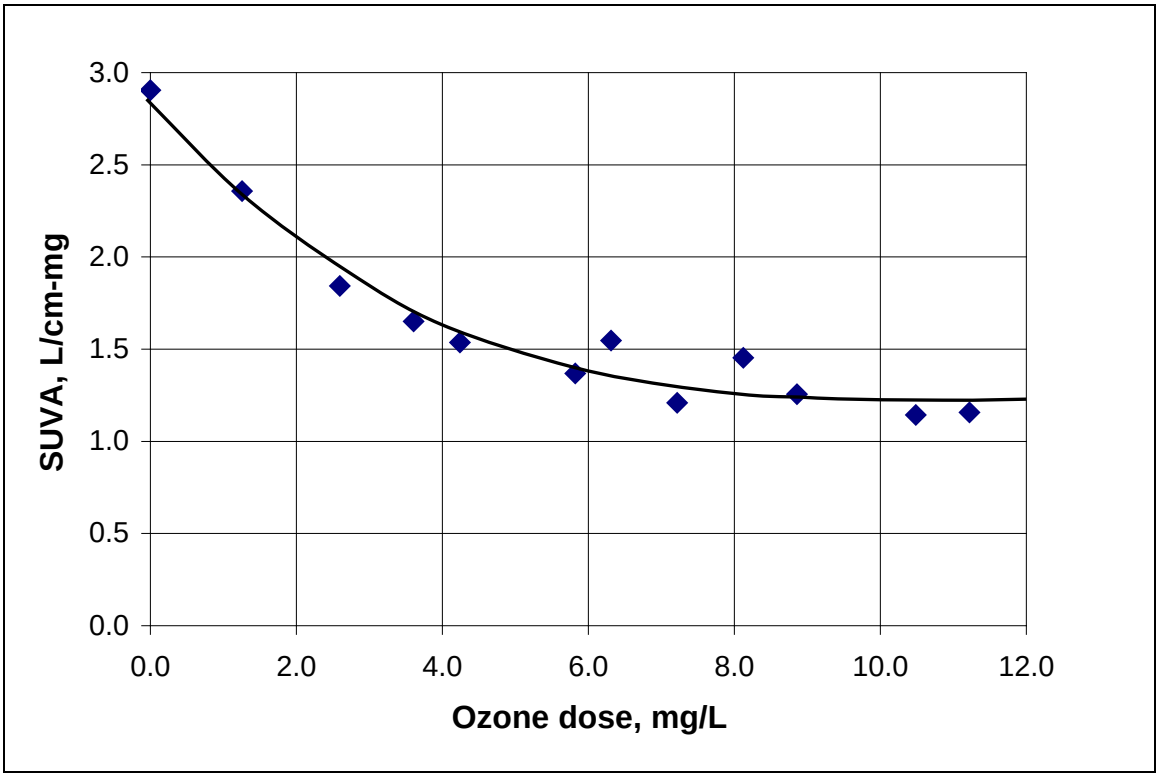

Figure 4-4: SUVA values for initial samples

The SUVA parameter is an indicator of the hydrophobicity of organics in water. SUVA is the ratio of UV_{254} absorbance to the TOC concentration and is calculated according to Equation 1. The SUVA values decrease with increasing applied ozone doses as seen in Figure 4-4. This suggests that as the applied ozone dose increases, the aromatic fraction is oxidized to more biodegradable forms. As with the UV_{254} absorbance measurements, the SUVA values begin to level off at around 8 mg/L, which leads to the conclusion that higher applied ozone doses have little to no effect on converting non-biodegradable organics into biodegradable forms.

BDOC

The last of the bulk organic analysis analyzed in Phase 1 was BDOC. BDOC is a parameter that measures the fraction of biodegradable organics present in water. Because the wastewater is being treated by a biological process prior to being ozonated, almost all the biodegradable organics are consumed. Only a small amount of biodegradable material is left in the MBR effluent when it enters the ozone contact chamber. The remaining organics consist of larger, recalcitrant compounds. As seen in the TOC, UV_{254} absorbance, and SUVA data, the non-biodegradable organics are not completely mineralized by the ozone, but are instead oxidized enough to increase the fraction of biodegradable organic matter. The fraction of biodegradable organics increases with increased ozonation as seen in Figure 4-5. Although, the initial concentration of TOC in the BDOC test varies over the range of samples taken (the initial TOC concentration is the total height of each column in Figure 4-5), the fraction of non-biodegradable dissolved organic carbon (NBDOC) in the BDOC test (which is indicative of the recalcitrant organic carbon) appears to level off at around 8 mg/L. This can be clearly seen in Figure 4-6, which plots the NBDOC as a function of ozone dose. This also suggests that the effectiveness of the ozone to covert non-biodegradable organics into a more biodegradable form is limited.

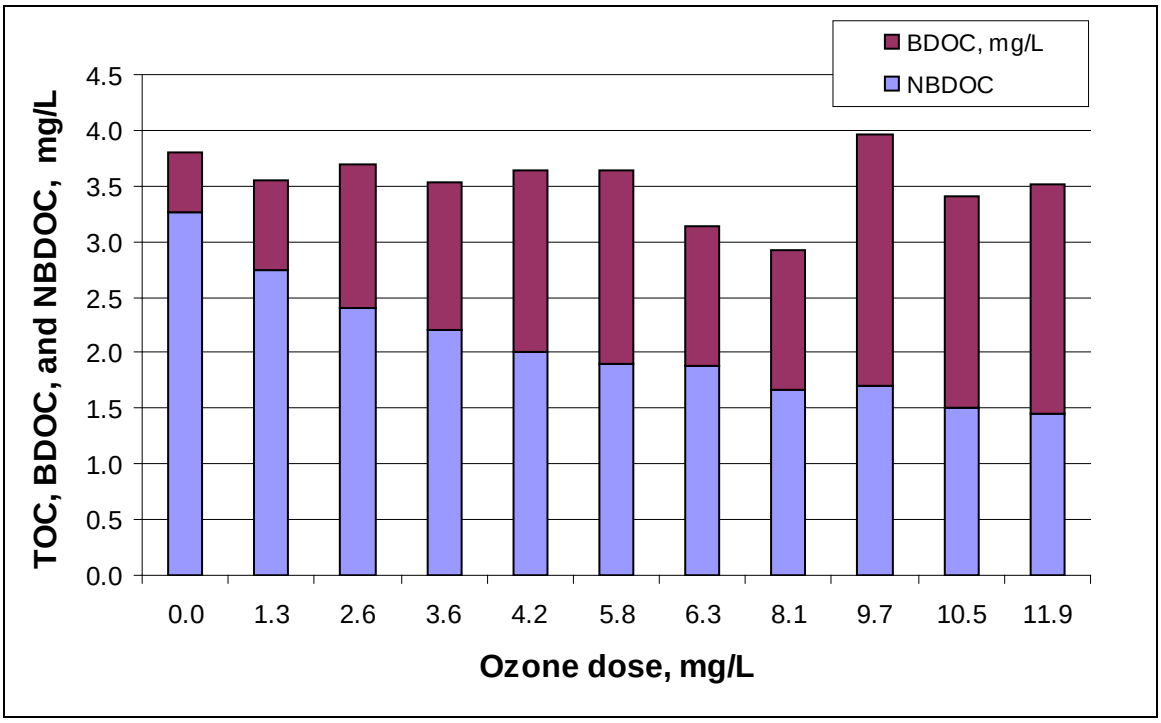

Figure 4-5: BDOC as a function of applied ozone dose for Phase 1. The total column height is the initial TOC concentration

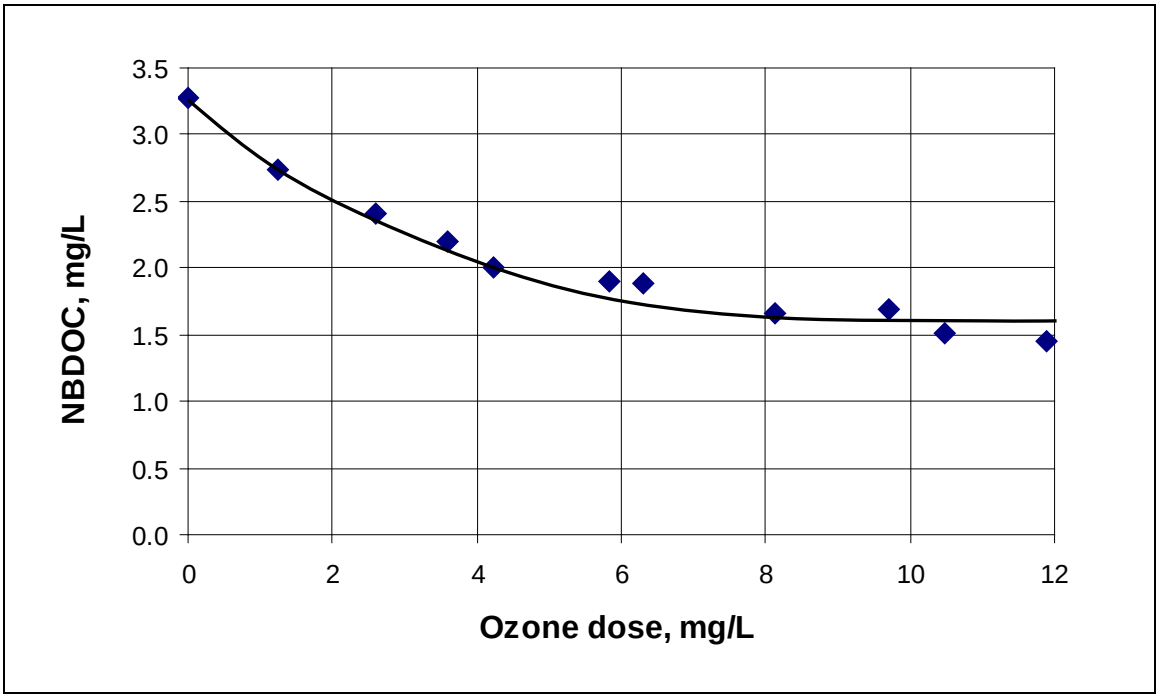

Figure 4-6: NBDOC as a function of applied ozone dose for Phase 1

Selection of Ozone Doses for Microconstituent Removal

Due to the expense of analyzing these samples, the ozone doses were selected to give the widest set of experimental conditions used in the project. Three different ozone doses were examined for their effectiveness in removing PPCPs and EDCs. The organic analyses in Phase 1 were done to determine the most effective ozone doses to use. The preliminary data showed that any ozone dose higher than 8 mg/L would not convert additional non-biodegradable organics into biodegradable forms. This dose was chosen as the maximum ozone dose to be examined. It was expected that any ozone dose higher than 8 mg/L would not achieve any additional microconstituent removal and so this was considered the best-case scenario for what this process could accomplish. The minimum ozone dose was correlated with the instantaneous ozone demand of the MBR treated water. An ozone residual in the first ozone chamber first starts to appear at an applied ozone dose of around 2.6 mg/L, as seen in Figure 4-1. Another consideration is in examining an ozone dose that oxidizes recalcitrant compounds the most efficiently. The largest percent decrease in UV_{254} absorbance occurs in the ozone dose range between approximately 1 to 4 mg/L as seen in Figure 4-7. Although absorbance still decreases at higher ozone doses, the effects are not nearly as pronounced. Because ozone doses of 3 and 4 mg/L might have only marginal differences in PPCP removal, ozone doses of 2 and 4 mg/L were selected. Since the MBR effluent TOC was around 4 mg/L, these ozone doses also give an approximate applied ozone dose to TOC ratio of 0.5, 1.0, and 2.0 mg ozone/mg TOC for ozone doses of 2, 4, and 8 mg/L.

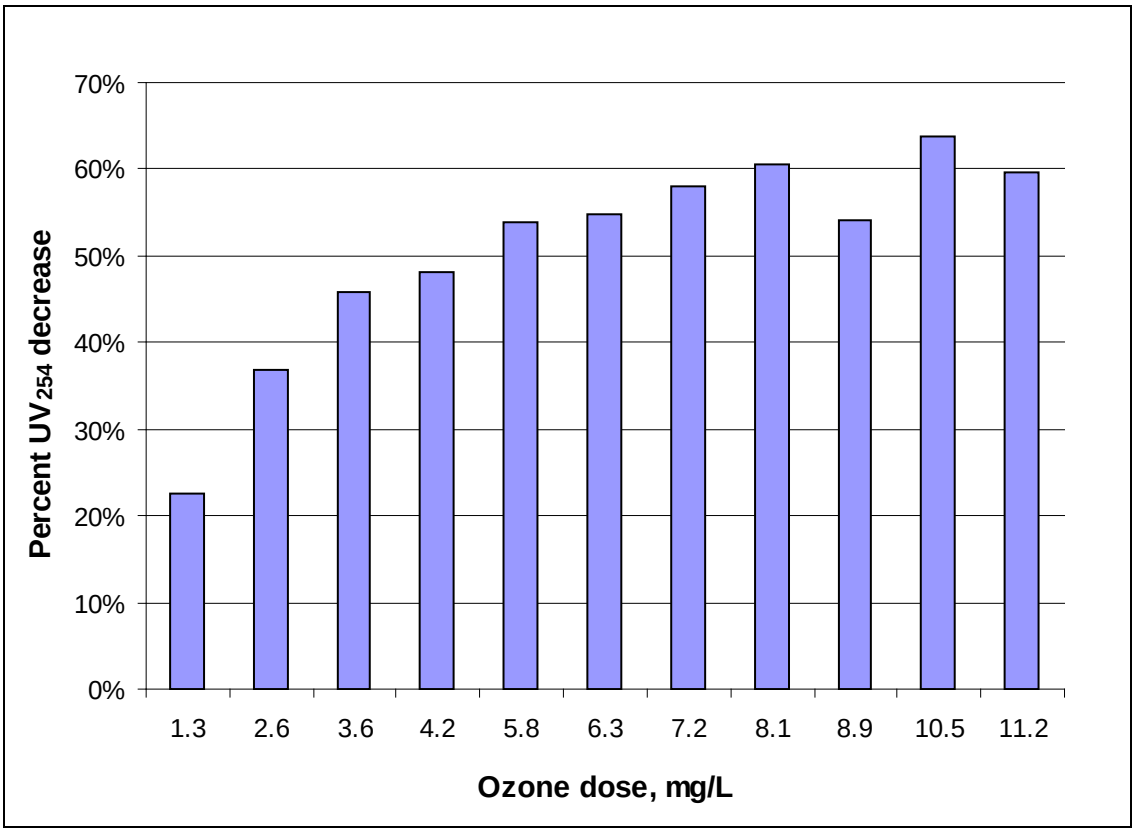

Figure 4-7: Percent decrease of UV_{254} absorbance with increasing applied ozone doses

TOC Removal in the BAF without Ozonation

As seen in the Phase 1 organic analysis, organic matter is not completely removed by the ozone process; however, the fraction of biodegradable organics is increased. To remove this fraction from the water, the BAF column uses biodegradation by microbes growing on the anthracite media in the column. Initially, GAC was used as the media in the BAF column, but as discussed earlier, was changed to anthracite. This was done in part because the adsorption capacity of the GAC could not be exhausted. To measure the amount of adsorption occurring in the column, TOC concentrations were measured in the influent and effluent of the column of GAC. The influent to the column was MBR effluent, which after having just undergone a biological process, should consist of mostly non-biodegradable organics. Therefore, any additional TOC removal is attributed to the adsorption process. The TOC concentrations for the GAC influent and effluent, as well

as the TOC percent removal are shown in Table 4-1. The results show that adsorption by the GAC removed from 30-65% of the TOC. To ensure that adsorption was not occurring in the BAF column, the media was changed to anthracite.

After the initial seeding of the anthracite, the media was put in the BAF column fed MBR effluent for a week prior to beginning the experiments. The anthracite was used in part because the mechanism for the removal of microconstituents is biodegradation whereas biologically activated carbon (BAC) uses both biodegradation and adsorption. To ensure there was no contribution of organic removal by adsorption in the BAF column, TOC was measured several times before starting Phase II. The MBR fed the BAF column, without ozonation, and TOC was measured in the BAF influent and effluent to ensure that the concentrations of TOC did not change as it passed through the column. The data in Table 4-1 shows little change in TOC as it passes through the BAF column, demonstrating that adsorption is not a mechanism in removing organics in the BAF column.

Table 4-1: TOC results for preliminary analysis of BAF column

Date	MBR effluent TOC, mg/L	BAF effluent TOC, mg/L	Percent Removal
BAF Column Using GAC as Media Filter			
23-Aug	4.43	2.34	47%
30-Aug	4.70	3.28	30%
6-Sep	4.38	2.95	33%
23-Sep	3.81	1.33	65%
26-Sep	3.67	2.12	42%
27-Sep	3.65	1.73	53%
BAF Column Using Anthracite as Media Filter			
17-Oct	4.04	3.97	1.6%
19-Oct	4.09	4.05	1.0%
21-Oct	3.75	3.96	-5.6%

Phase 2: PPCP and EDC Removal by Ozone/BAF

After analyzing the Phase 1 results from the MBR and ozone processes and determining the effect of ozone doses on microconstituent removal, Phase 2 of the project was begun. Just like Phase 1, the MBR effluent was fed to the ozone contactor at a flowrate of 100 mL/min. The applied ozone dose was set to one of the three doses determined in Phase 1. For Phase 2, the effluent from the ozone contactor was fed to the BAF column, which completed the treatment process. The system was operated continuously at the predetermined ozone dose until steady state in the BAF column had been established, which took between 7 and 8 days. At this point, samples were collected for PPCP/EDC analysis. The BAF column was backwashed, a new ozone dose was set, and the process was repeated until steady state in the BAF column was reached again.

MBR Performance

The MBR used in these experiments had been operating at an SRT of approximately 10 days for approximately 50 days prior to the initiation of these experiments, and was maintained throughout the duration of these experiments. Several other MBR parameters were monitored to ensure that the MBR process was functioning properly. These include the effluent and wasting flowrates, MLSS/MLVSS, pH, DO, and EC. MBR effluent parameters, such as TOC, UV_{254}, and SUVA were analyzed to provide a basis for comparison of the subsequent treatment processes. These parameters were also examined as possible surrogates for prediction of removal efficiencies of microconstituents and to analyze organic removal by each process.

During the Phase 2 experiments, large fluctuations in TOC, UV_{254} absorption, and SUVA were observed for all processes. Two large drops in TOC concentration occurred during Phase 2 on October 22nd and November 1st, as seen in Figure 4-8. These large decreases are also seen in the UV_{254} absorption and to a lesser degree in the SUVA data as illustrated in Figures 4-9 and 4-10 respectively. These sharp decreases in TOC and SUVA correspond to a sharp increase in conductivity and a drop in pH, as illustrated in

Figures 4-11 and 4-12 respectively. Because SUVA is a ratio of UV_{254} absorption to TOC and the values for both decreased, the SUVA values on these dates are not nearly as pronounced.

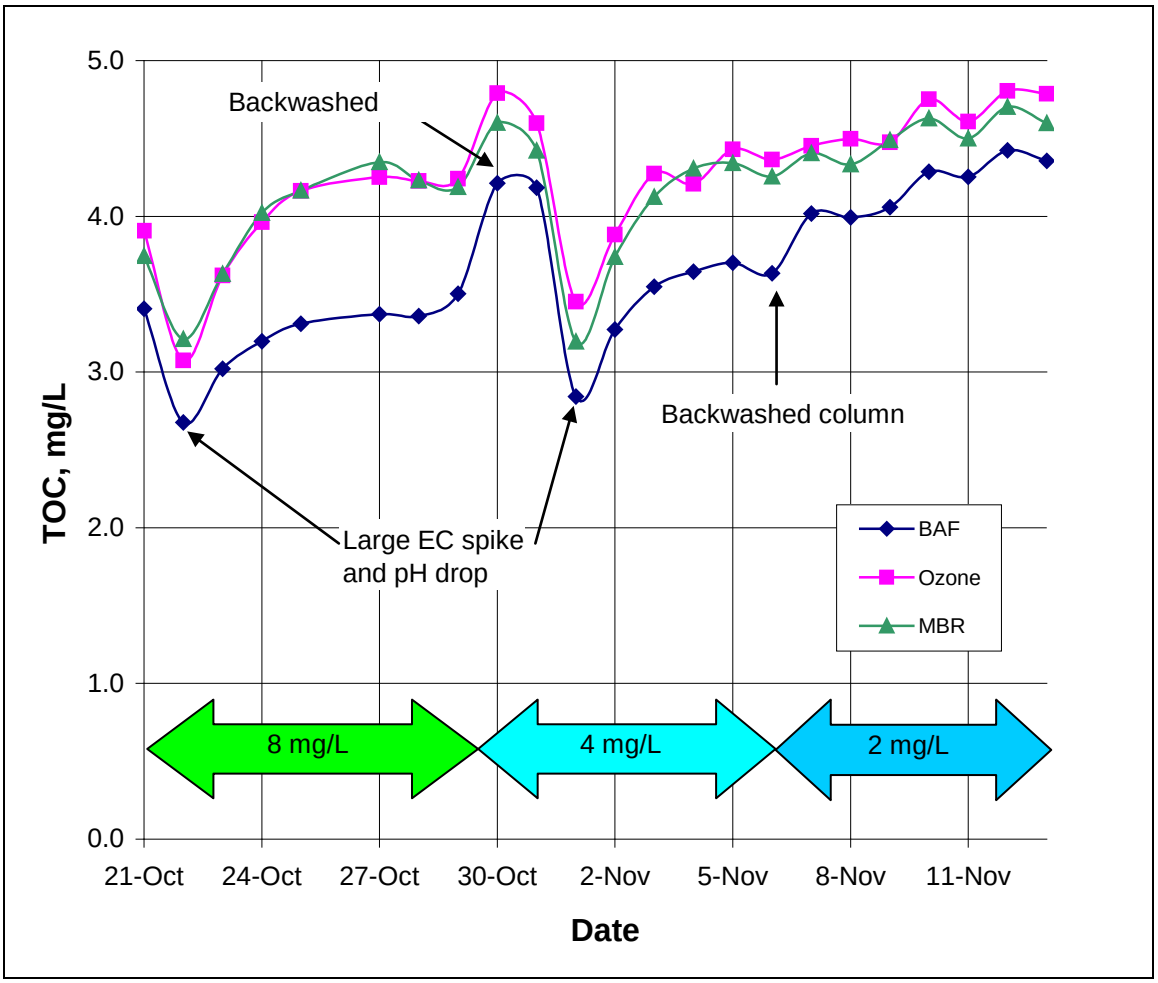

Figure 4-8: Phase 2 TOC values for MBR, ozone, and BAF effluent at applied ozone doses of 2, 4, and 8 mg/L

Even with the large changes to the MBR feedwater, the MBR still produced effluent with TOC concentrations less than 5 mg/L throughout Phase 2 of the experiments, as seen in Figure 4-8. Because MBRs can be resilient to such shock loadings, the measured parameters stabilized within a couple of days. Even with these

changes, TOC, UV_{254}, and SUVA rebounded quickly and steady state conditions were observed in each of these parameters before PPCP/EDC sampling. This will be explored in more detail later.

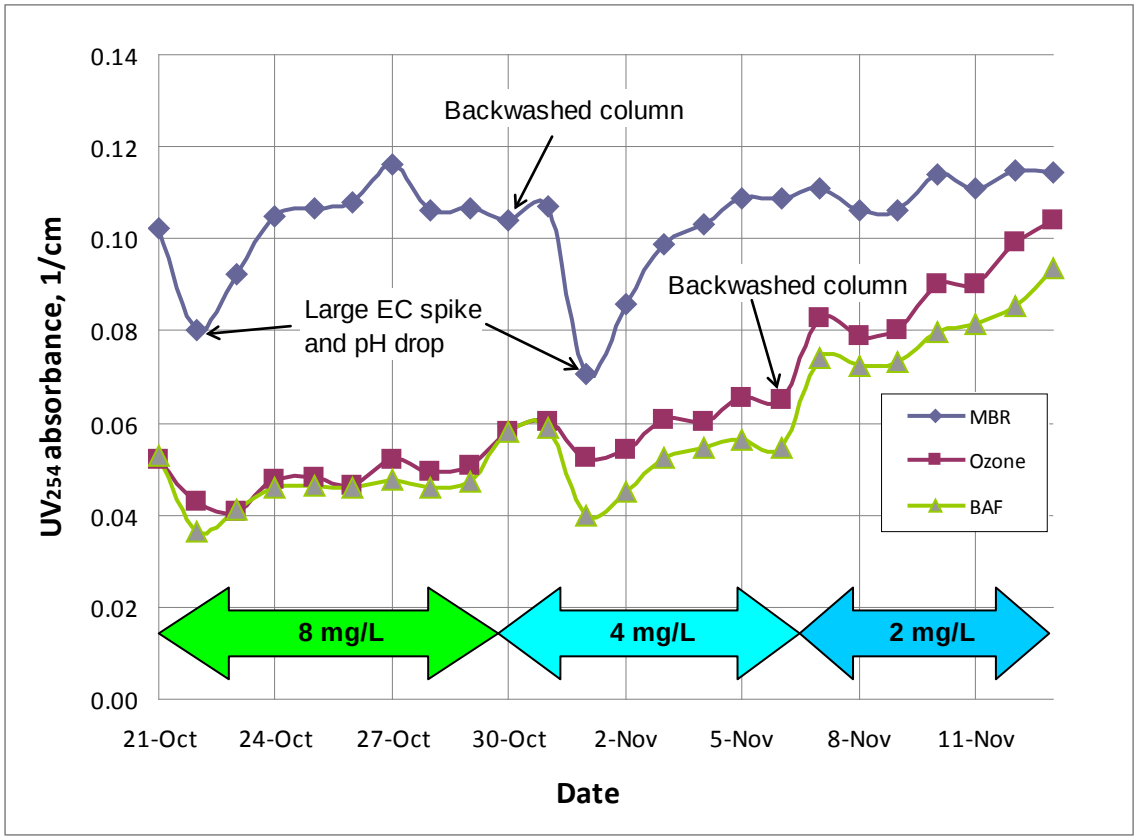

Figure 4-9: Phase 2 UV_{254} data for MBR, ozone, and BAF effluent at applied ozone doses of 2, 4, and 8 mg/L

The fluctuations in these parameters can be attributed to unstable conditions in the feedwater from the SWRP. Total suspended solids (TSS) and carbonaceous biochemical oxygen demand (CBOD) data from the SWRP primary effluent pump house sampling station, which sampled the same water used to feed the MBR, is shown in Figures 4-13 and 4-14 respectively. The data shows TSS for the MBR influent is much greater than the normal range of values typically observed by plant operators (90–150 mg/L) for the

entire duration of Phase 2. At one point, the TSS is over an order of magnitude higher than the normal maximum value. The CBOD data also shows several instances where the values are well above the normal range (90-130 mg/L) as illustrated in Figure 4-14.

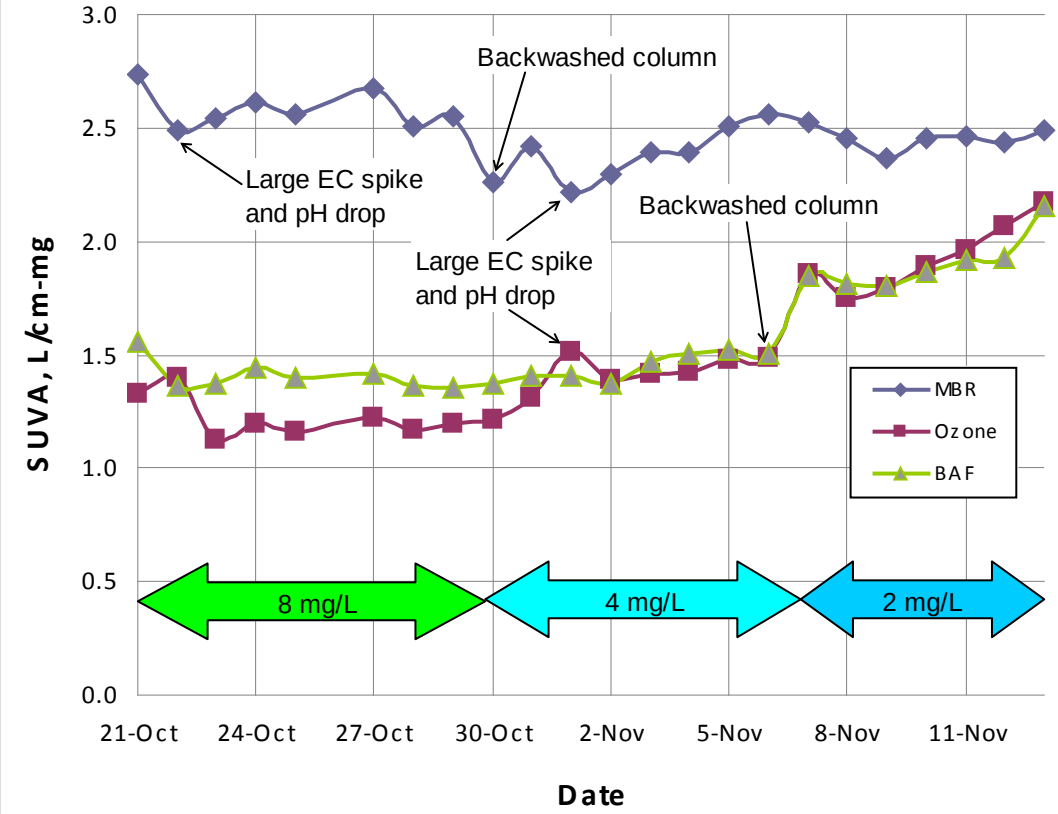

Figure 4-10: Phase 2 SUVA values for MBR, ozone, and BAF effluent at ozone doses of 2, 4, and 8 mg/L

According to plant operators, one or more of the primary settling basins that fed though the pump house where the pilot system operated, was continuously malfunctioning over the duration of Phase 2 of the experiments. The settling basins would then have to be drained, the problem repaired, and the basins filled again. As soon as the basin would fill up, another problem occurred that would take it off line again.

The basin would again have to be drained, repaired, and filled. The high TSS and CBOD values shown in Figures 4-13 and 4-14, are the result of the malfunctioning settling basins.

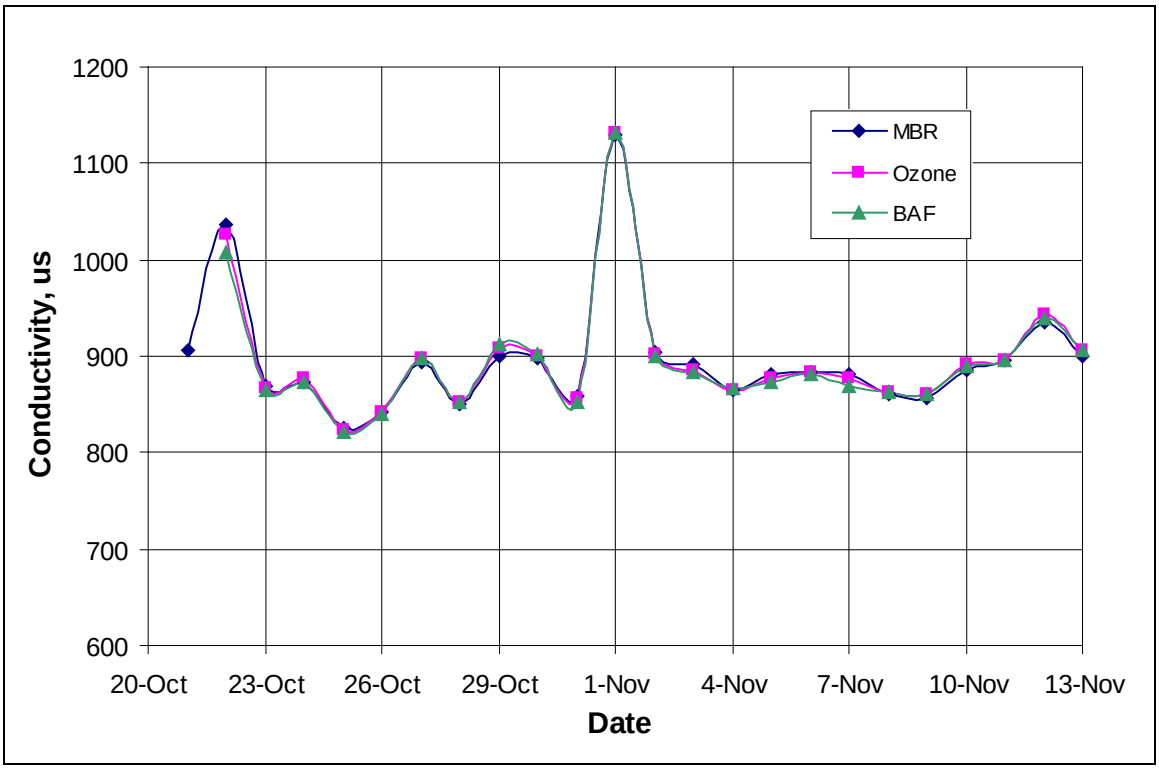

Figure 4-11: Conductivity values for all processes for Phase 2

Even though there is a clear connection between the quality of the wastewater being fed to the MBR, and the sharp spikes or drops in the parameters measured, the large spikes in TSS and CBOD do not quite match the spikes in TOC and conductivity and drops in pH, UV_{254} absorbance, and SUVA. The changes in water quality observed on October 22nd and November 1st, do not correlate with any sharp increases in the TSS and BDOC data shown in Figures 4-13 and 4-14 respectively. This could be due to a couple of possible causes. First there could be a change in the makeup of the feedwater that is not accounted for in any of the parameters measured. The events on October 22nd

and November 1st could also be attributed to a build up of solids over several days instead of being caused by one single event. The TSS values are consistently many times the typical values observed by plant operators throughout the duration of the Phase 2 experiments. Instead of the Events on October 22nd and November 1st being caused by one single large event, the changes in water quality could be due to a build up of solids over several days.

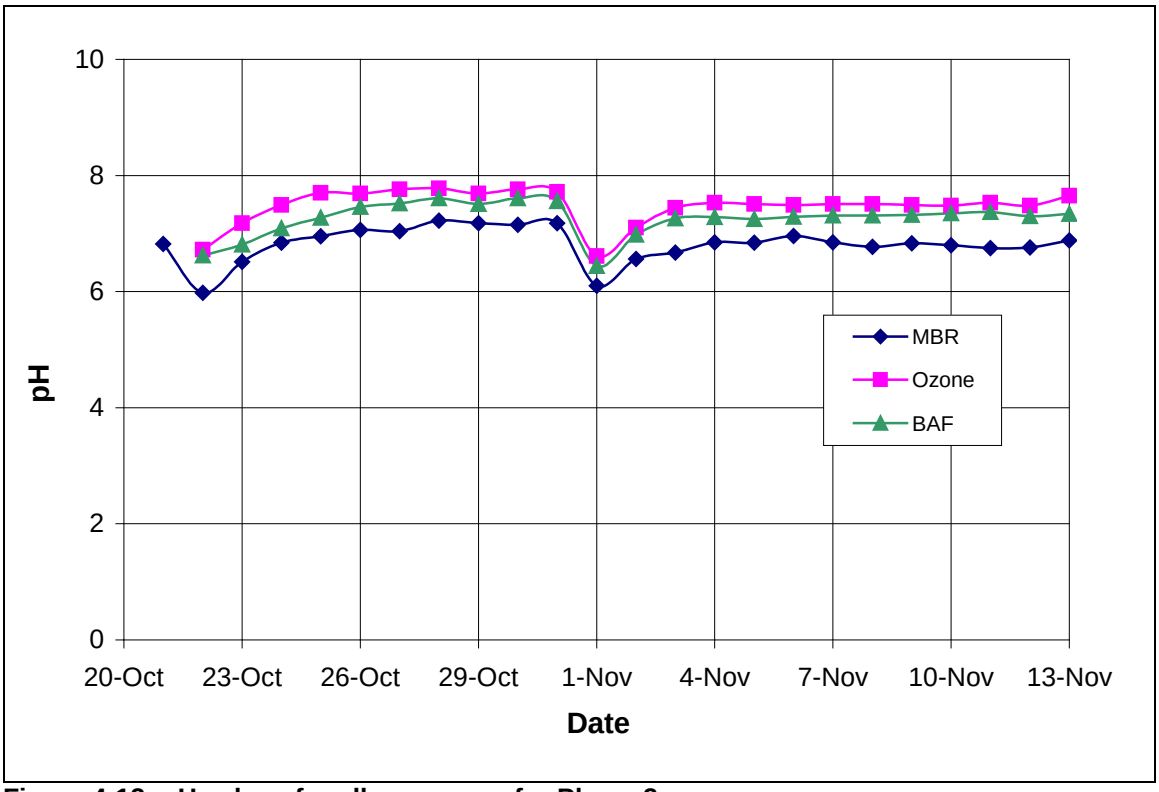

Figure 4-12: pH values for all processes for Phase 2

This build up of solids can be seen in the MLSS/MLVSS data shown in Figure 4-15. The figure shows MLSS/MLVSS data from September 10th to November 11th, 2009. During this period of time, the MBR was running at steady state with an SRT of 10 days. Up until October 14th, one week prior to the start of Phase 2, the average MLSS and

MLVSS for the system was approximately 6,000 and 4,000 mg/L respectively. By the start of Phase 2 on October 21st, the MLSS and MLVSS had spiked to 10,700 and 7,315 mg/L respectively. By November 3rd, the values had gradually tapered off to 8,205 mg/L for MLSS and 5,670 mg/L for MLVSS. Over the next 8 days, though, the values more than double. On November 11th, the MLSS was at 17,520 mg/L and the MLVSS was at 12,125 mg/L.

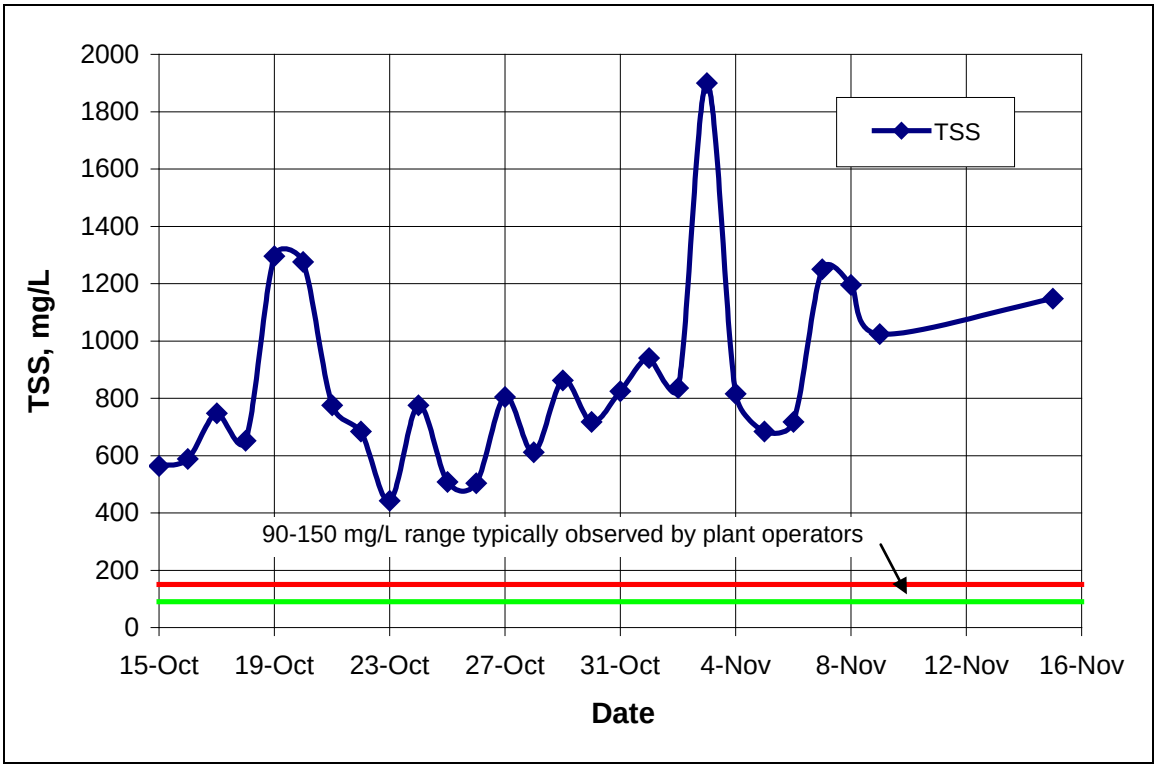

Figure 4-13: Pump House data for TSS from October 15 to November 15, 2009. Data used as influent MBR TSS

The MLSS/MLVSS data does correlate well with the TSS data. The TSS data shows values of over 550 mg/L starting on the 15th of October as shown in Figure 4-14. There is a sharp spike in TSS on the 19th and 20th of October with TSS measured at 1,296 and 1,276 mg/L respectively. This correlates well to the first spike in MLSS/MLVSS

that peaked on the 21st of October. After the spike in TSS the values fall sharply but are still well above the typical range. On November 3rd the TSS values spike again with a measurement of 1,900 mg/L. The values fall for a few days after this but jump to 1,250 mg/l on November 7th where they stay above 1,000 mg/L for the duration of the experiments. This correlates to what is seen in the MLSS/MLVSS data, and helps to explain the large drop in DO in the MBR effluent observed over the last few days of Phase 2 as shown in Figure 4-16.

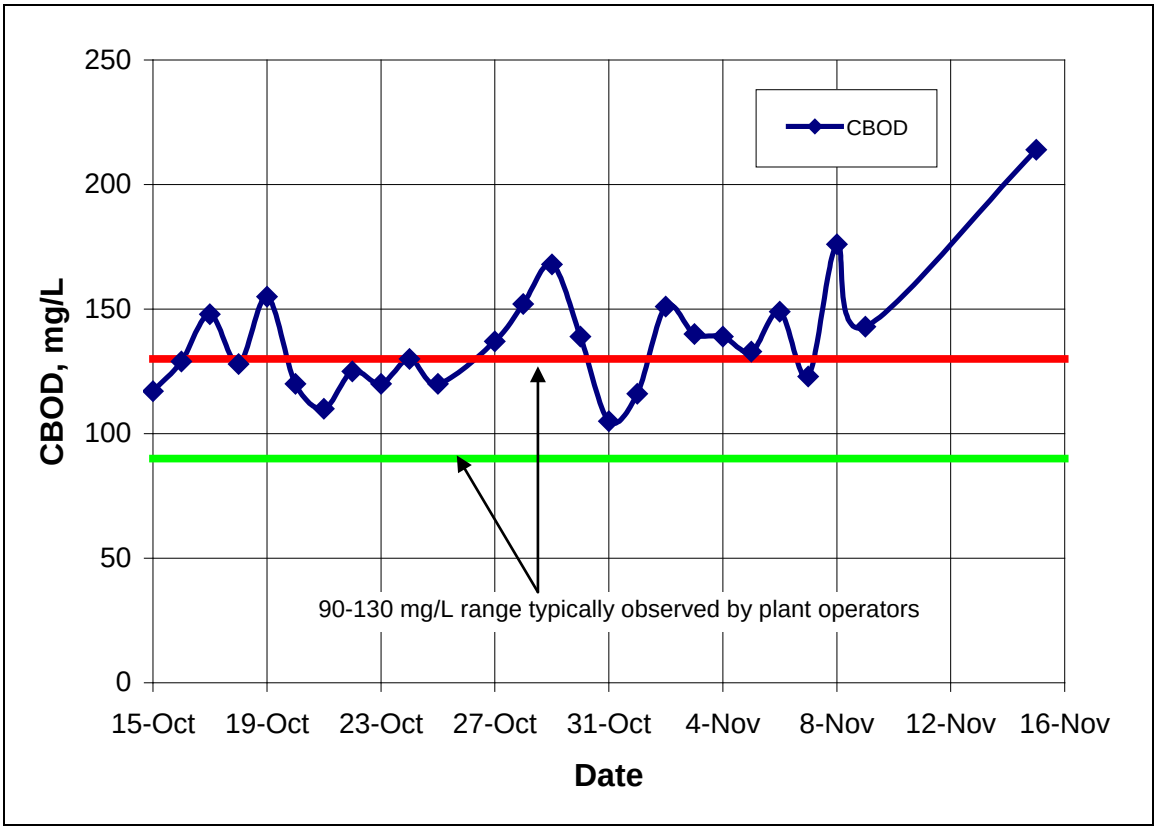

Figure 4-14: Pump House data for CBOD from October 15 to November 15, 2009. Data used as influent MBR CBOD

Unlike the other parameters, the DO remained constant through much of Phase 2 with average values between 5 and 7 mg/L in the MBR effluent as illustrated in Figure 4-

16. The values dramatically drop though during the last three days of Phase 2 experiments. The DO values on the 11th, 12th, and 13th of November are 4.99, 3.87, and 2.27 mg/L respectively. This large drop in DO is attributed to the large increase in solids in the MBR during this time as measured in the TSS and MLSS/MLVSS. The large increase in solids causes a large increase in microbes that use the solids for food. The increase in microbial activity increases the oxygen demand in the MBR tank, which decreases the DO. This decrease in DO over the last three days of Phase 2 is not observed in the ozone and BAF effluent. This is because the ozone supersaturates the wastewater with oxygen. This is why the DO readings measured in the ozone effluent are always much higher than the MBR effluent as illustrated in Figure 4-16. The DO measurements are always lower in the BAF effluent than in the ozone effluent. The DO in the BAF effluent is between 1 and 2 mg/L lower than the ozone effluent with an average difference of 1.3 mg/L. This difference is caused by the microbial activity in the BAF column and is a good indicator that biodegradation by microbes is occurring and that the BAF is operating properly.

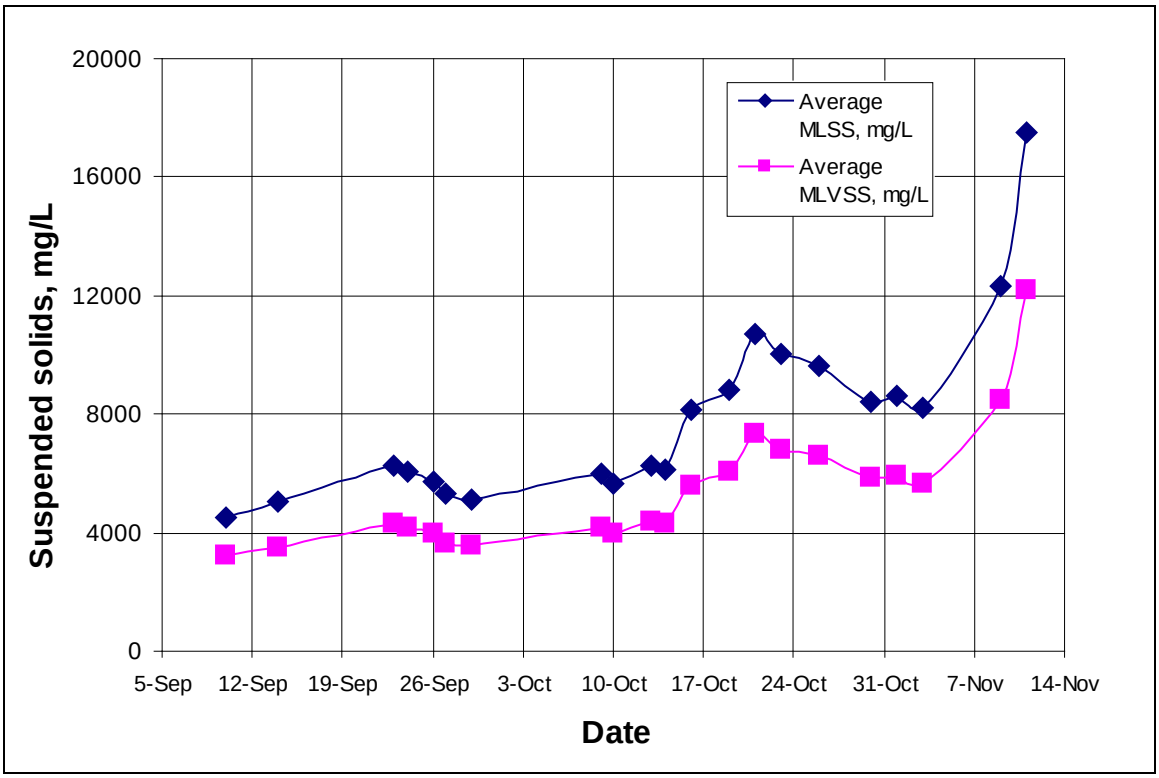

Figure 4-15: MLSS and MLVSS values from September 10 to November 11, 2009 for 10 day SRT

The pH measurements also show different values between processes as seen in Figure 4-12. The pH increases in the range of 0.51 to 0.77 from the MBR effluent to the ozone effluent with an average increase of 0.66. The pH also decreases an average of 0.22 from the ozone effluent to the BAF effluent. Unlike pH, the conductivity shows little variation between processes as illustrated in Figure 4-11. This was expected because the ozone and BAF processes are not expected to increase or decrease the concentration of ionic species in the water unless a significant fraction of the TOC was mineralized, which did not occur. Other parameters that show different values between processes are TOC, SUVA, BDOC, and UV_{254} absorption. These will be discussed in more detail later.

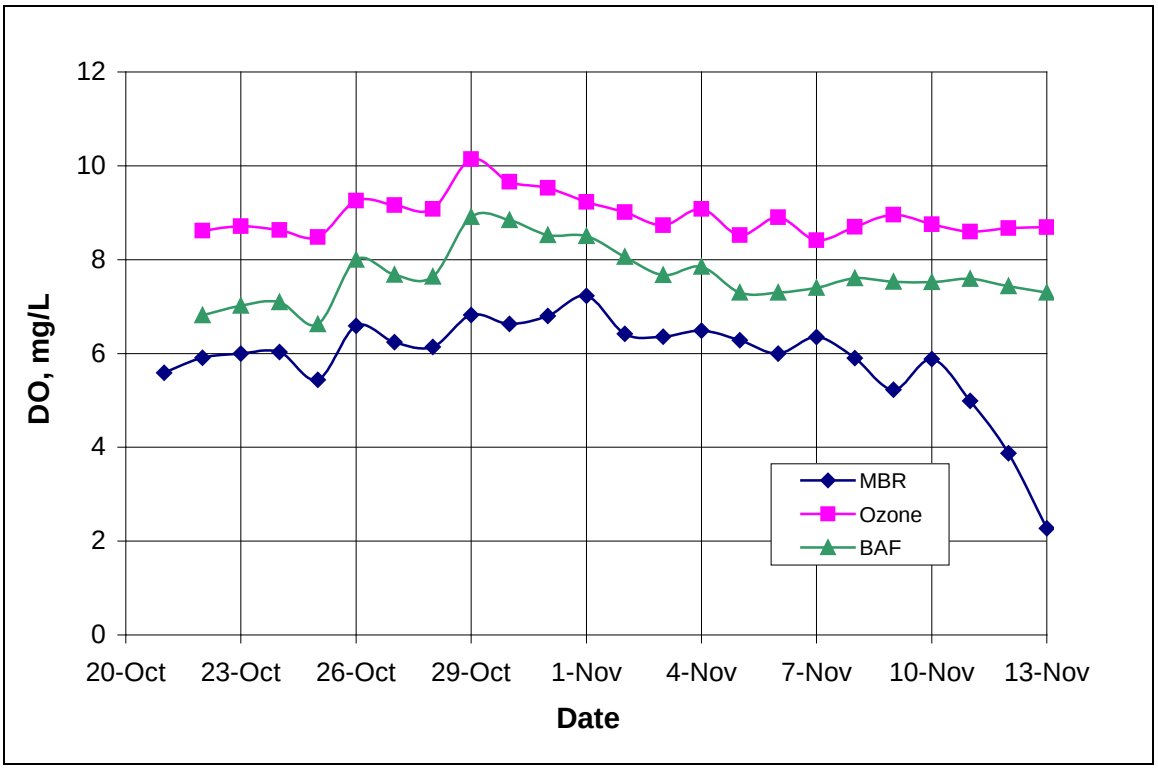

Figure 4-16: DO values for all processes for Phase 2

Performance of Ozone Contactor

The ozone contactor was operated to produce applied ozone doses of 8, 4, and 2 mg/L for the PPCP/EDC removal experiments. The applied ozone dose was stable once the dose was set, as illustrated in Figure 4-17. Due to the complex composition of the wastewater, the ozone residual was more variable, as seen in Figure 4-18. This variability could be attributed to the unstable conditions in the MBR feed that can contribute to variations in the makeup of the wastewater. High ozone residuals correlate with the drop in pH and spike in conductivity on October 22nd and November 1st, as illustrated in Figures 4-9 and 4-10 respectively. These variations could include increases or decreases in compounds that react with ozone. The large drops in ozone residual on October 30th and November 7th are due to changing the applied ozone dose from 8 to 4 mg/L and from 4 to 2 mg/L.

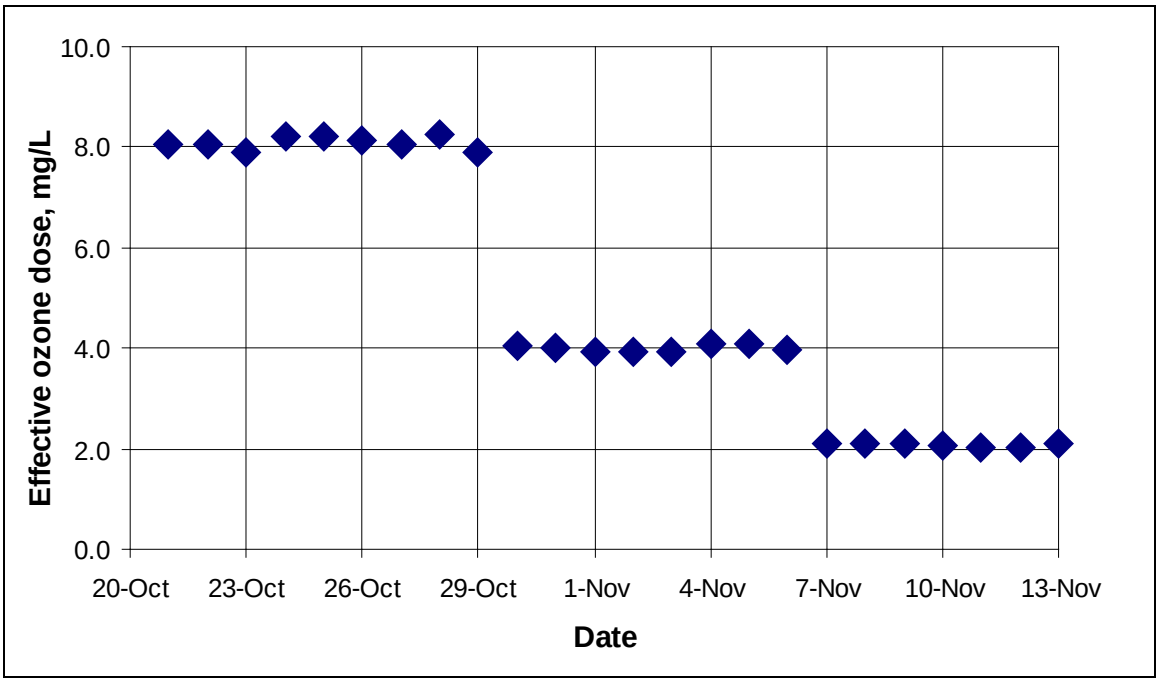

Figure 4-17: Applied ozone dose measurements for Phase 2

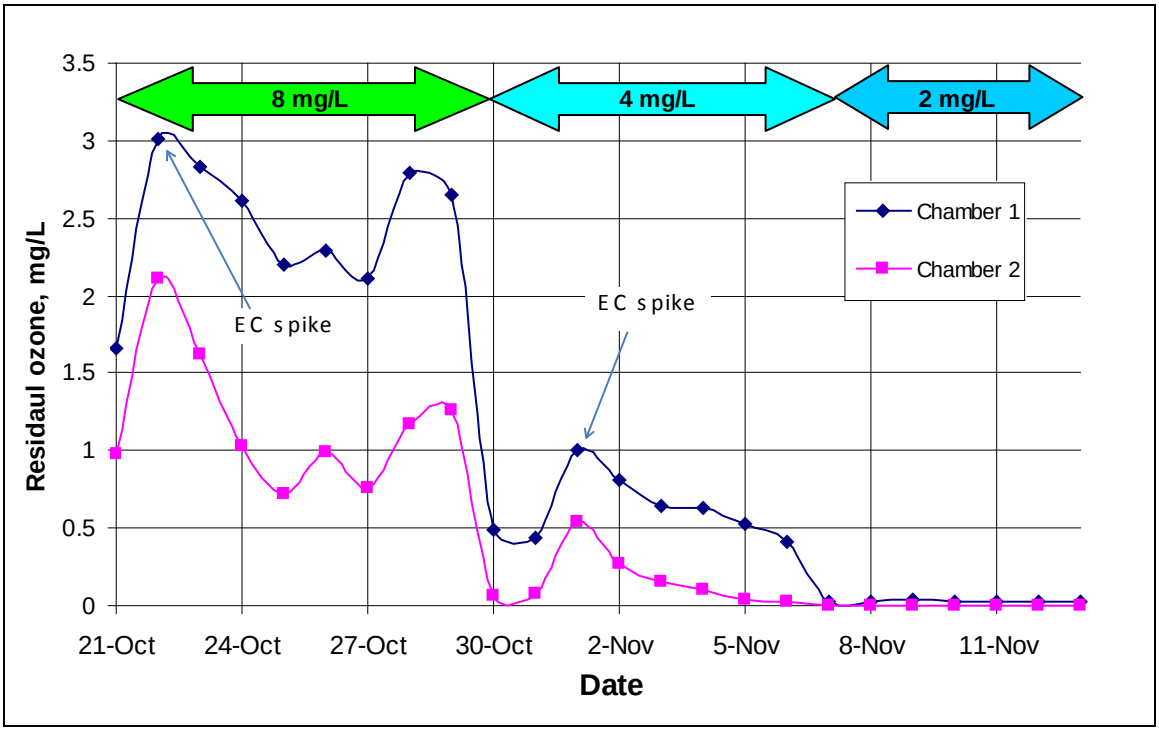

Figure 4-18: Residual ozone measurements from chambers 1 and 2 for Phase 2

To adjust the applied ozone dose, the power setting on the ozone contactor could be adjusted. The ozone dose could also be changed by adjusting the gas or water flowrates. The gas flowrate was set low to ensure maximum performance by the glass ozone diffuser. When the gas flowrate was increased, larger bubbles formed in the diffuser and the gas to liquid transfer efficiency decreased. A gas flowrate of 32 mL/min was used because it allowed for a good ozone transfer efficiency, between 79 and 93 percent as illustrated in Figure 4-19, and because it was large enough to supply an applied ozone dose of up to 8 mg/L. The average transfer efficiency was 91.1 percent for the 2 mg/L ozone dose, 88.2 percent for the 4 mg/L dose, and 82.3 percent for the 8 mg/L ozone dose. The transfer efficiency decreased as the applied ozone dose increased. This was probably due to a reduced concentration gradient between the gas and liquid streams as the ozone concentration in solution increased. The water flowrate in the ozone contactor was set at 100 mL/min. This flowrate was used in the design of the ozone contactor so that each contact chamber gave 5 minutes of contact time.

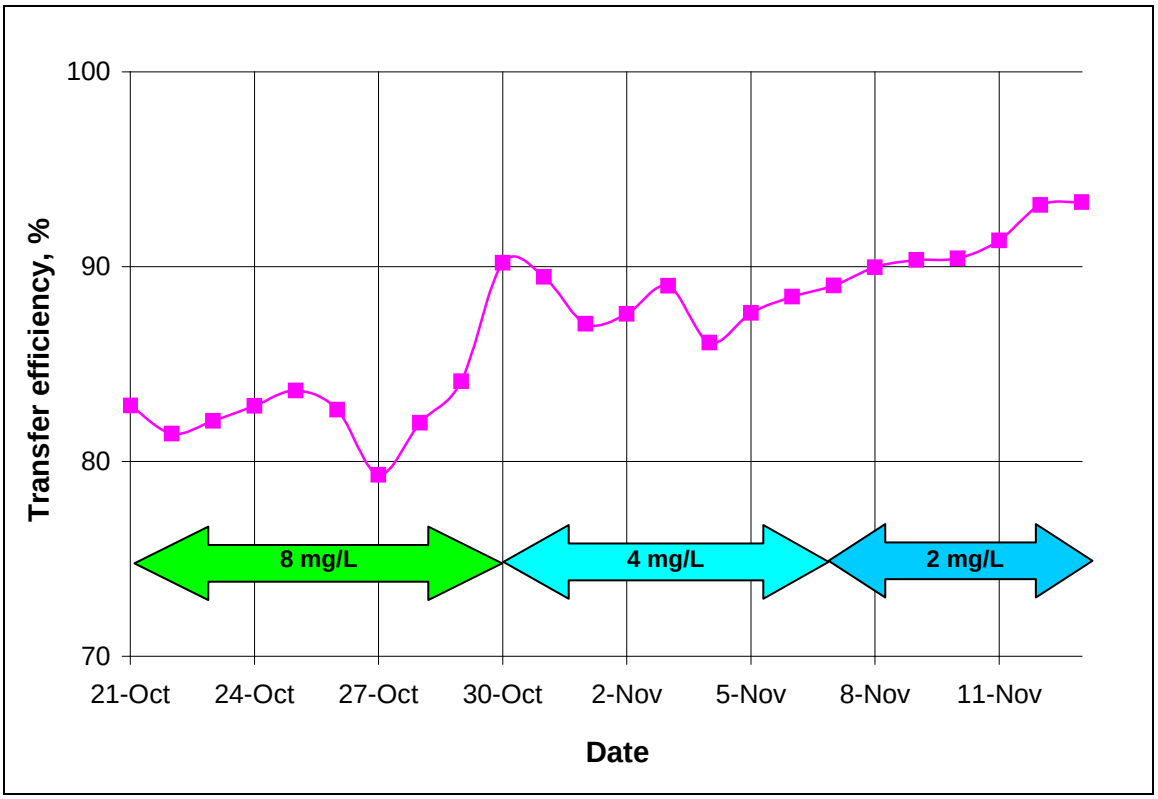

Figure 4-19: Gas transfer efficiency for ozone doses of 2, 4, and 8 mg/L from 10/21-11/13

BAF Performance

The BAF column ran continuously from October 16th, until the last day of sampling on November 13th. The column was initially fed by MBR effluent. This was done immediately following the seeding process that established microbial growth on the anthracite as described in the experimental methods section. On October 21st, Phase 2 of the experiments started and the feed for the BAF column was changed to ozone effluent. The initial head on the column at the beginning of Phase 2 was 10 inches as shown in Figure 4-20. By October 29th, the end of the 8 mg/L sampling event, the column had approximately 30 inches of head, which is close to capacity. The column was backwashed and the head decreased to approximately 9 inches. The head steadily increased on the column during the duration of the next sampling event, from October

30th to November 6th. At the end of the sampling event the column had approximately 31 inches of head. The column was backwashed again for the next sampling event and the head decreased to approximately 8.5 inches. Unlike the previous two cycles, the head on the column remained steady and never got above 9 inches.

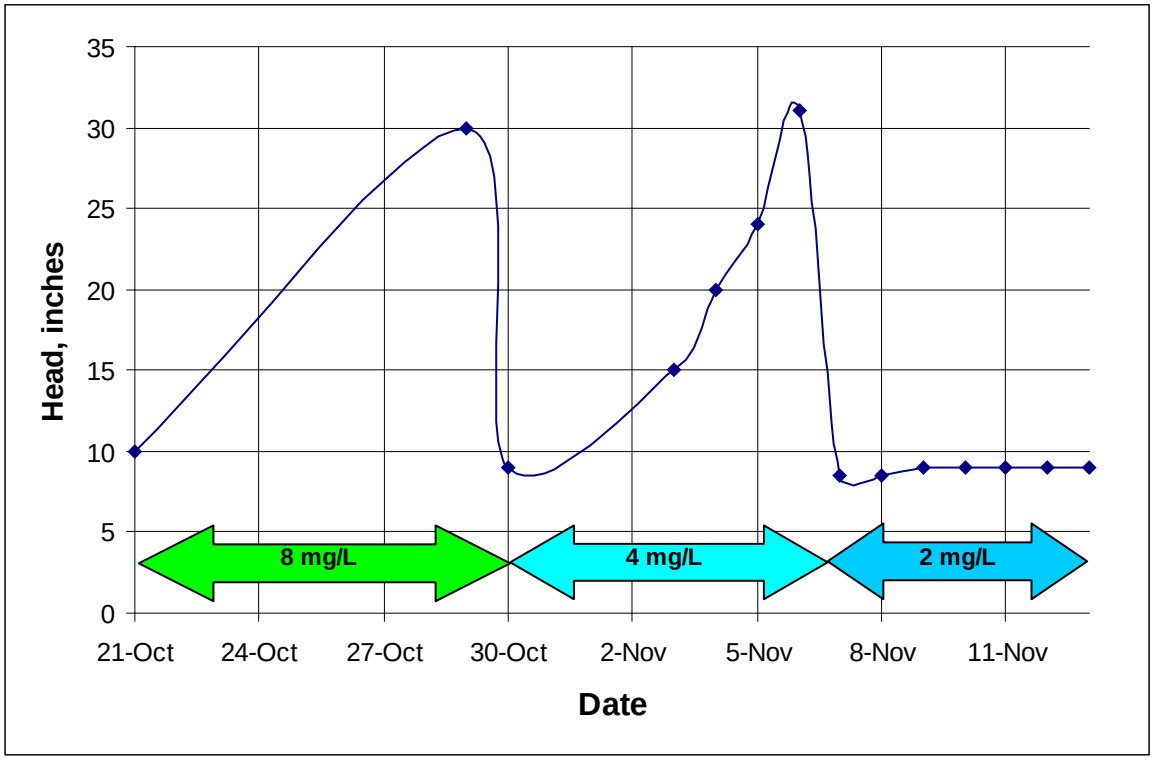

Figure 4-20: Head build up in the BAF during Phase 2

One of the parameters used to ensure microbial activity in the BAF column was dissolved oxygen. As discussed earlier, there was a decrease in DO of approximately 1.3 mg/L from the ozone to the BAF effluent. This decrease is attributed to the microbial activity in the BAF column. This was one of the parameters used to ensure the BAF column was operating correctly.

The bulk organic analysis also showed microbial activity in the BAF column. Decreases in TOC, SUVA, BDOC, and UV_{254} absorption, between the ozone contactor

and BAF column, show that organics are being consumed in the BAF column. These decreases are attributed to recalcitrant compounds being partially oxidized in the ozone contact chamber and then removed through biodegradation in the BAF column. The decrease in organics between the ozone contactor and BAF column is further examined in the next section.

Bulk Organic Analysis for Phase 2 Experiments

Samples for TOC, UV_{254} absorbance, and SUVA analysis were taken every day during Phase 2 of the study. BDOC analysis was done three times for each applied ozone dose examined. These analyses were used to both determine steady state conditions and to examine whether a correlation exists between these parameters and microconstituent removal.

Bulk Organic Analysis for 8 mg/L Ozone Dose

The first testing was done at an applied ozone dose of 8 mg/L. The system operated for 9 days at this ozone dose, from October 21-29. Samples were collected and analyzed daily for UV_{254} adsorption, TOC, SUVA, and TOC/TOC_0 as shown in Figures 4-21 to 4-24. The bulk organic analysis was performed to establish that the system was operating at steady state before sampling for PPCPs/EDCs.

The TOC values seen in Figure 4-21 were virtually the same in the MBR and ozone effluents. This shows that even at the highest ozone dose examined, 8 mg/L, organics are not being removed through ozonation alone. Although organic removal is not achieved in the ozone contactor, the BAF effluent showed consistent removal of TOC. The BAF column removed around 20 percent of the TOC for the last five days of the 8 mg/L ozone samples as shown in Figure 4-22. This shows that recalcitrant compounds are partially oxidized in the ozone contact chamber where they are broken down into more biodegradable forms. These are then consumed by the microbial culture in the BAF column.

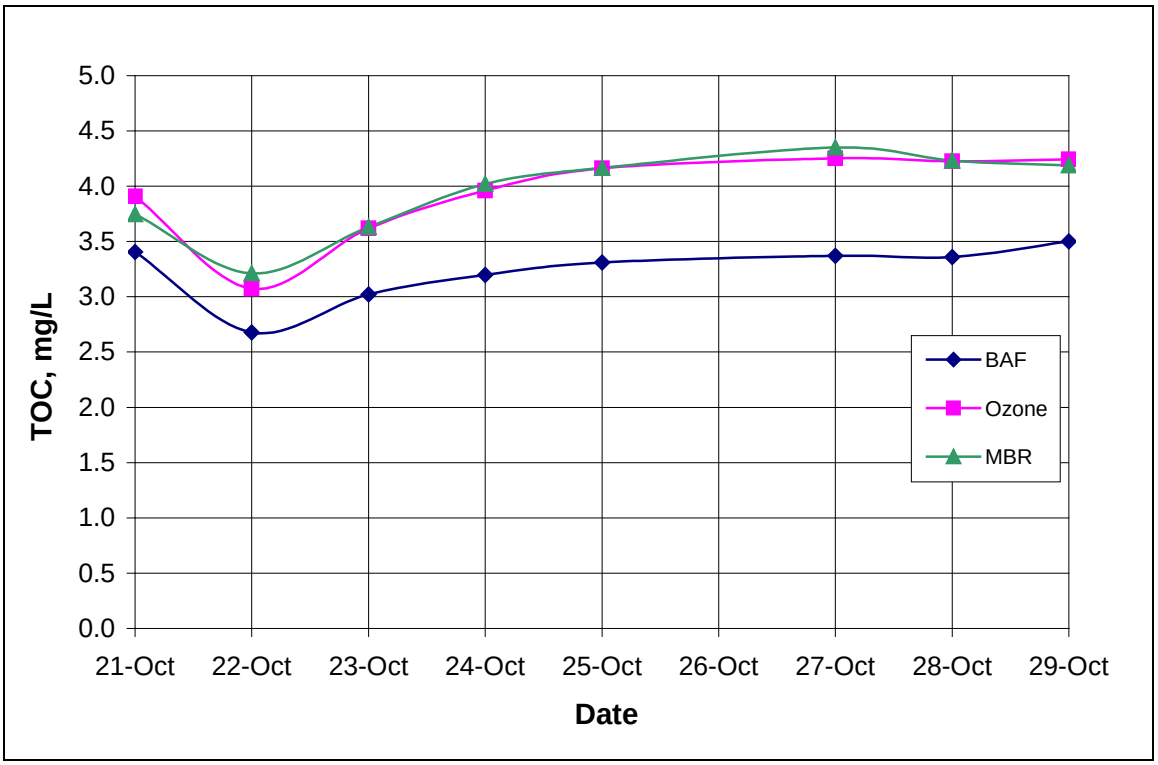

Figure 4-21: TOC values for 8 mg/L applied ozone dose during Phase 2 experiments

Unlike the TOC data, which shows no difference in TOC concentration between MBR and ozone effluents, the UV_{254} absorbance and SUVA values show a large decrease between the MBR and ozone effluents as illustrated in Figures 4-23 and 4-24. This further illustrates that recalcitrant compounds are being partially oxidized in the ozone contact chamber and then consumed in the BAF column. The UV_{254} absorbance values show that there is a significant drop in UV_{254} absorbance after the ozone contactor but that the values are almost the same after passing through the BAF column. This shows that the BAF column does not increase the biodegradable fraction of organics, but instead only consumes the newly formed biodegradable organics created in the ozone contact chamber.

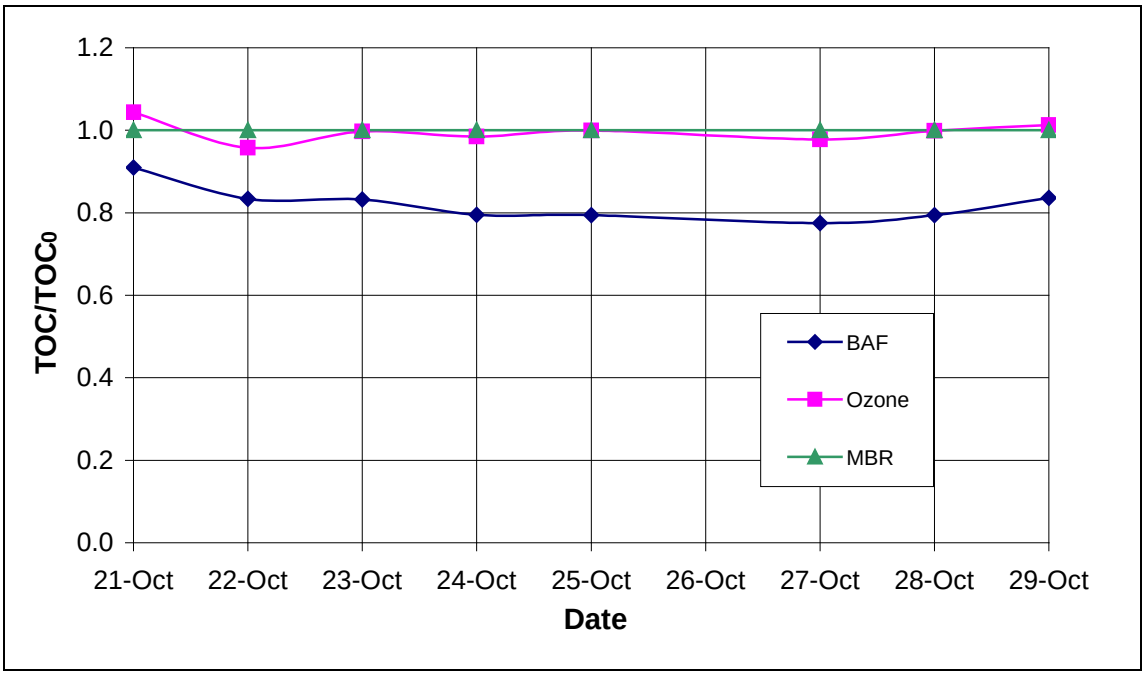

Figure 4-22: TOC/TOC$_o$ for applied ozone dose of 8 mg/L during Phase 2 experiments

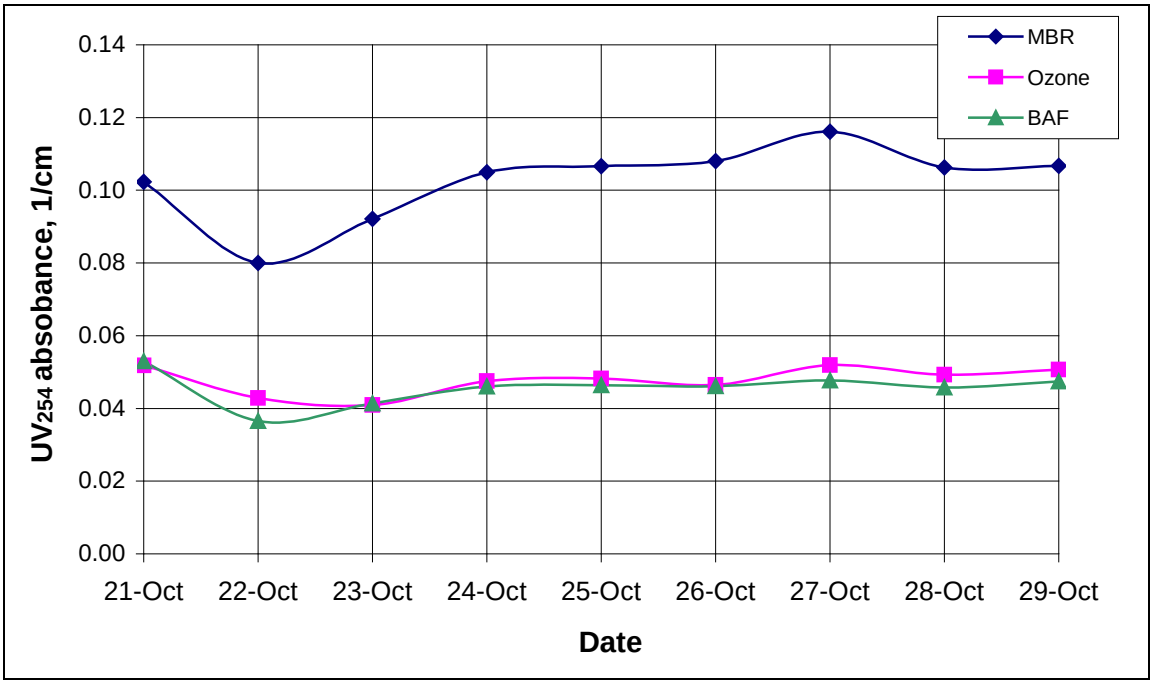

Figure 4-23: UV$_{254}$ absorption at an applied ozone dose of 8 mg/L during Phase 2 experiments

This is also seen in the SUVA values shown in Figure 4-24. The SUVA values are slightly higher for the BAF column though. This is because the TOC measured in the ozone effluent is higher than the TOC measured in the BAF effluent. SUVA is a ratio of the UV_{254} absorbance to the TOC concentration as detailed in Equation 1. Because the UV_{254} absorbance values are the same and the TOC concentration in the ozone effluent is higher than the BAF effluent, the SUVA value for the ozone effluent will be lower. The large decrease in SUVA after the MBR effluent indicates a decrease in recalcitrant compounds, especially those with a high degree of aromaticity, due to ozonation in the ozone contact chamber and biodegradation in the BAF column.

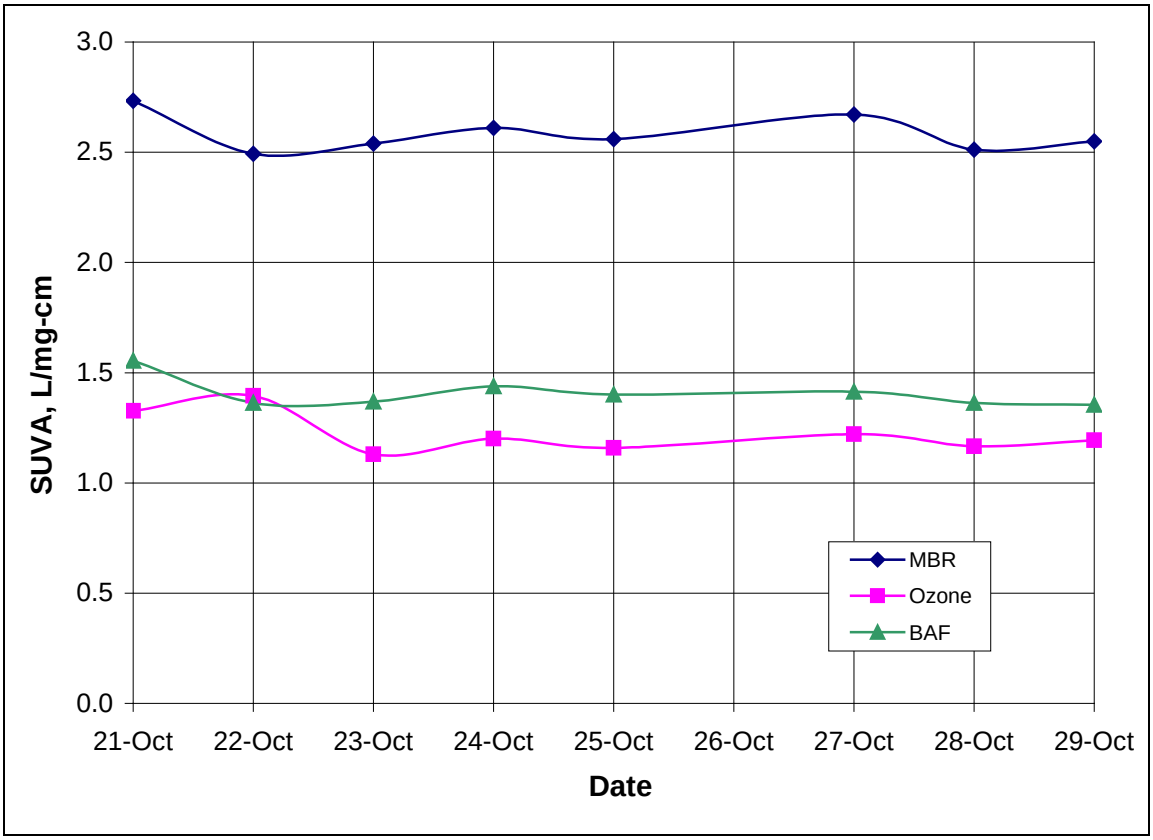

Figure 4-24: SUVA values for applied ozone dose of 8 mg/L during Phase 2 experiments

All of these parameters show consistent data for several days before the PPCP/EDC sampling date. The UV_{254} absorbance and the TOC concentration both decline on the same day that there was a large spike in conductivity and drop in pH (October 22nd). They also show that the systems quickly rebounded within a few days. The analysis for these results, as well as the results for the 4 mg/L and 2 mg/L sampling events, will be discussed in more detail in the next section.

Bulk Organic Analysis for 4 mg/L Ozone Dose

After sampling for PPCPs/EDCs, the column was backwashed and the applied ozone dose was set to 4 mg/L. As with the 8 mg/L data, there was a large change in water quality that can be seen in many of parameters measured for the 4 mg/L ozone dose. The large spike in EC and drop in pH that occurred on November 1st caused declines in TOC, UV_{254} absorbance, and SUVA values as seen in Figures 4-25, 4-27, and 4-28 respectively. The drop in SUVA values caused by the spike in conductivity and drop in pH is really only reflected in the MBR effluent values. The UV_{254} absorbance values show a clear drop in all process effluents on November 1st as do the TOC concentrations. Although the values for the individual parameters decline, the ratio of UV_{254} absorbance to TOC concentration does not decline as much. In the case of the ozone effluent, the ratio even increases although not by much. This shows that the even though there are changes in water quality, which can cause a drop in organics in the wastewater, the fraction of recalcitrant compounds being oxidized in the ozone contact chamber and consumed in the BAF column remain relatively constant.

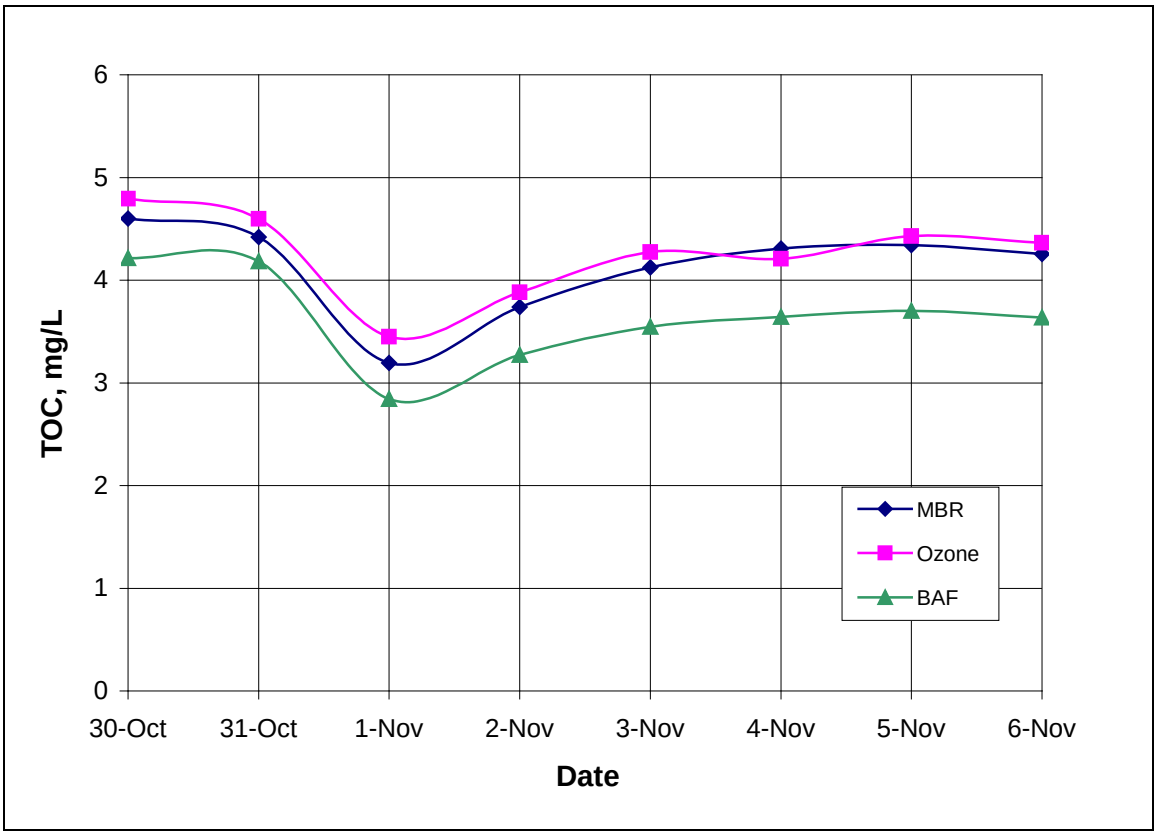

Figure 4-25: TOC at an applied ozone dose of 4 mg/L during Phase 2 experiments

As with the 8 mg/L ozone dose, there was no organic removal achieved through ozonation alone. The concentration of TOC does not really change after the ozonation as shown in Figure 4-25. This was also seen in the amount of TOC removed as illustrated in Figure 4-26. Although there was no TOC removal in the ozone contact chamber, the BAF column did show organic removal. TOC was removed by approximately 15 percent in the BAF column for the last three days before sampling for PPCPs/EDCs. As expected, this amount was smaller than what was removed at an ozone dose of 8 mg/L. The difference in removal between applied ozone doses will be further examined in the next section.

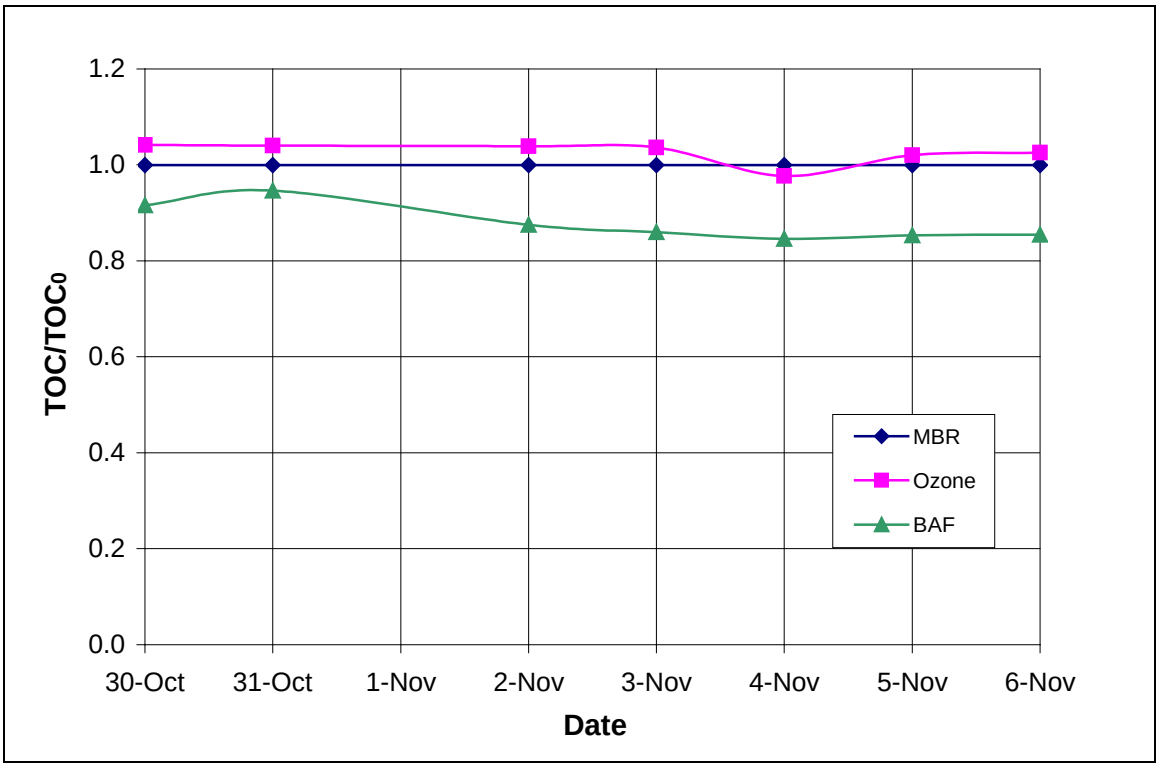

Figure 4-26: TOC/TOC$_0$ for 4 mg/L applied ozone dose during Phase 2 experiments

Like the 8 mg/L ozone dose, the UV_{254} absorbance values for the ozone and BAF effluents were much lower than the MBR effluent as illustrated in Figure 4-27. This shows that recalcitrant compounds are being oxidized into more biodegradable forms in the ozone contact chamber. The difference in UV_{254} absorbance values between the ozone and BAF effluents are larger than then 8 mg/l ozone dose. At 8 mg/L the values were almost identical, whereas the difference between most the values during the last six days of the 4 mg/L ozone dose experiments was approximately 0.1 cm^{-1}. This difference between UV_{254} absorbance between the ozone and BAF effluents will be examined further in the next section.

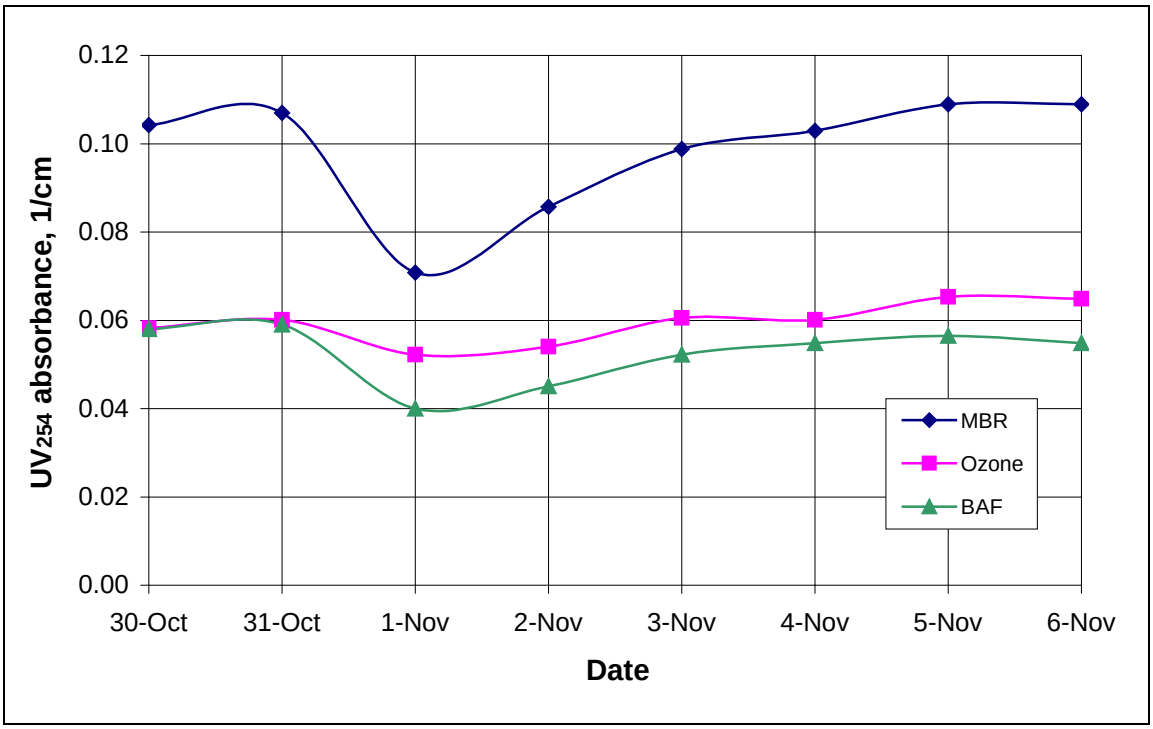

Figure 4-27: UV_{254} at an applied ozone dose of 4 mg/L during Phase 2 experiments

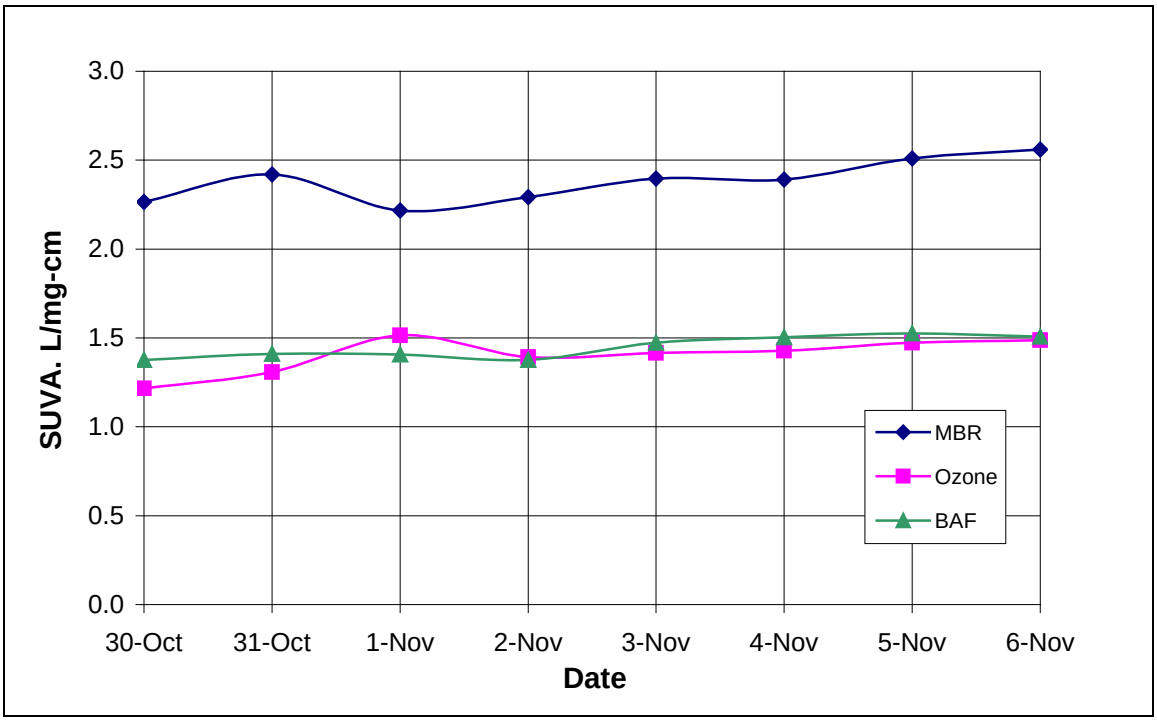

Figure 4-28: SUVA values for 4 mg/L applied ozone dose during Phase 2 experiments

As mentioned earlier, the SUVA values show little variation throughout the 4 mg/L ozone dose experiments as shown in Figure 4-28. There is the small change on November 1st which is caused by a change in the MBR feedwater quality, but the values quickly rebound within a day or two. The SUVA values are nearly identical for both the ozone and BAF effluents. They are also much lower than the MBR effluent values. This also indicates that recalcitrant compounds in the MBR effluent are being oxidized in the ozone contact chamber to more biodegradable forms. As expected, the decrease in SUVA in the ozone and BAF effluents are smaller at an ozone dose of 4 mg/L compared with the 8 mg/L ozone dose. This will be further examined in the next section.

Even with this change in water quality, the UV_{254}, TOC, SUVA, and TOC/TOC_0 parameters rebound quickly to stable conditions with little variation within a few days. Because these parameters were stable for a few days before PPCP/EDC sampling, the system was assumed to be at steady state. After steady state conditions were confirmed, sampling was done for microconstituents on November 6th. After sampling, the BAF column was backwashed and the new applied ozone dose of 2 mg/L was set.

Bulk Organic Analysis for 2 mg/L Ozone Dose

The last applied ozone dose to be examined for removing microconstituents from MBR effluent was 2 mg/L. Unlike the previous two ozone doses examined, the data showed no large spikes in EC or drops in pH. This consistency in influent quality is reflected in the TOC, TOC/TOC_0, UV_{254} absorption, and SUVA values illustrated in figures 4-29 - 4-32.

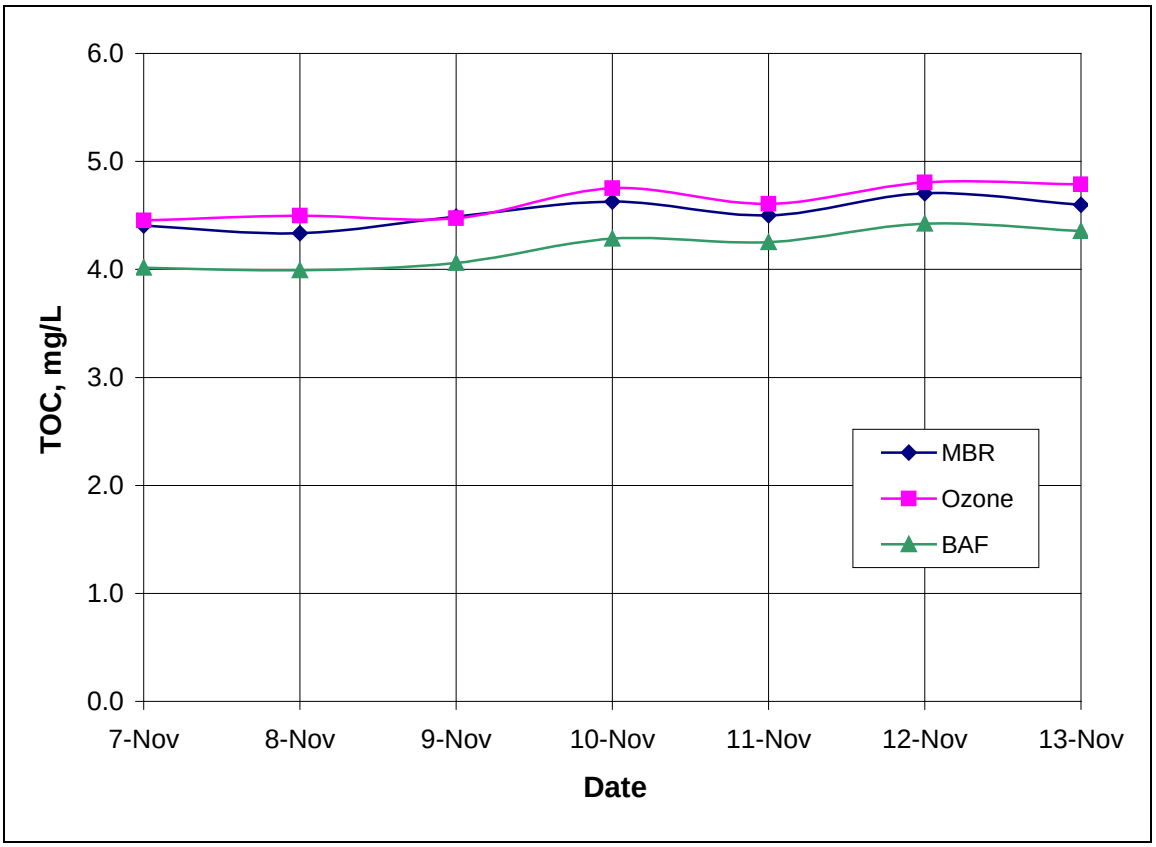

Figure 4-29: TOC for 2 mg/L applied ozone dose during Phase 2 experiments

As with the 4 and 8 mg/L ozone dose experiments, there was no decrease in TOC between the MBR and ozone effluents at an ozone dose of 2 mg/L as illustrated in Figure 4-29. This was expected because organic removal was not occurring at higher ozone doses. The TOC measured in the BAF effluent did show a decrease although the decrease was less than the 4 and 8 mg/L ozone doses. This shows that recalcitrant compounds are being oxidized to more biodegradable forms in the ozone contactor, where they are then consumed as food by the microbes in the BAF column. The TOC removal at the 2 mg/L ozone dose is only around 5 percent, as seen in Figure 4-30. This difference in organic removal at the varying ozone doses will be further examined in the next section.

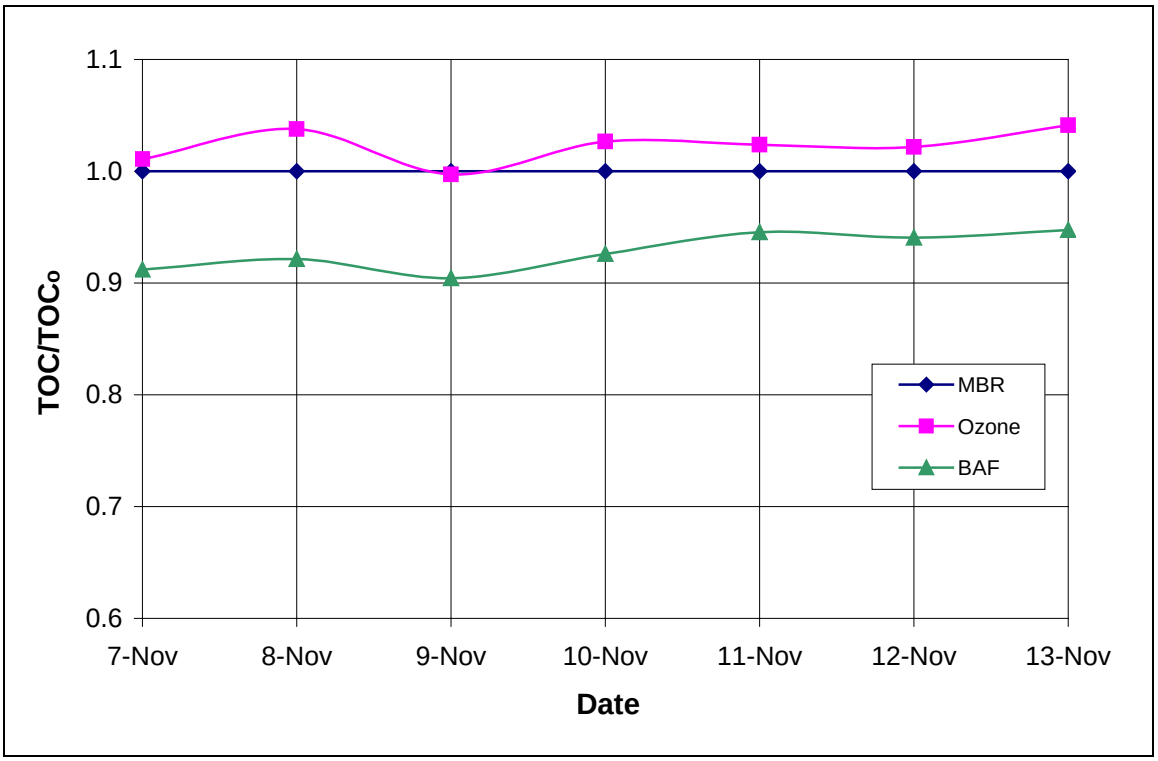

Figure 4-30: TOC/TOC_0 at an applied ozone dose of 2 mg/L during Phase 2 experiments

Like the 4 and 8 mg/L ozone doses, the UV_{254} absorbance and SUVA values are lower in the ozone and BAF effluents as illustrated in Figures 4-31 and 4-32. The UV_{254} absorbance values are slightly different for the ozone and BAF effluents though. Like the 4 mg/L ozone dose results, the ozone effluent shows larger UV_{254} absorbance values than the BAF effluent. This will be further examined in the next section. The SUVA values were nearly the same in both the ozone and BAF effluents, which was also observed in the 4 mg/L ozone dose results.

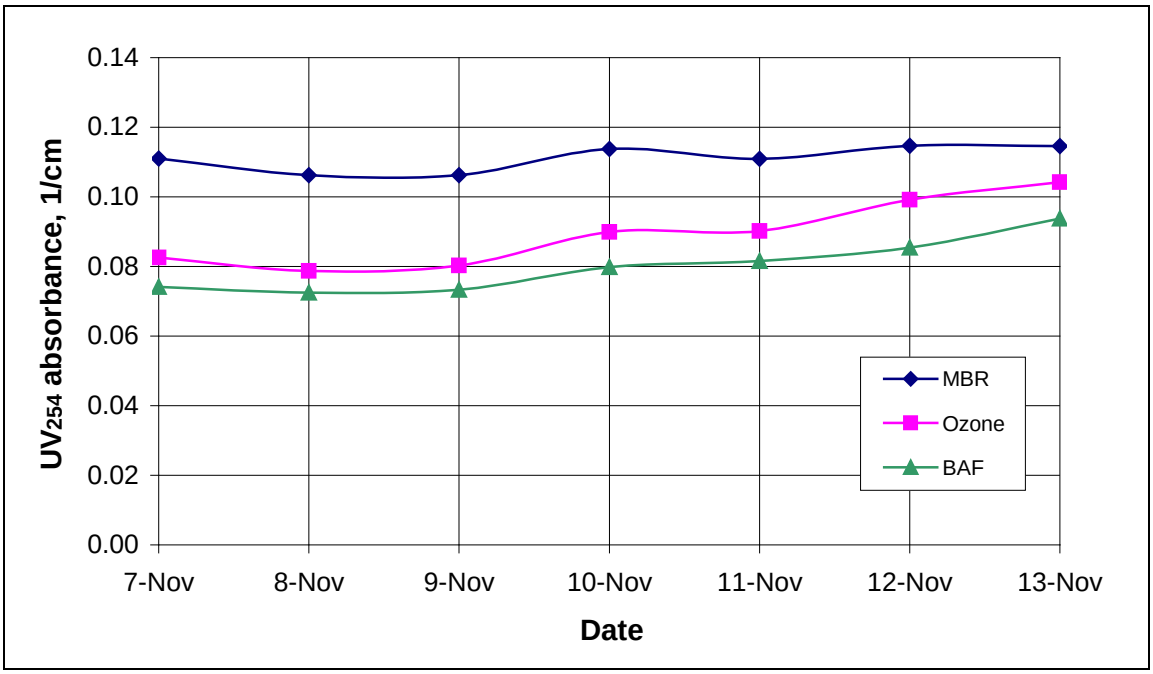

Figure 4-31: UV_{254} absorption data for 2 mg/L applied ozone dose during Phase 2 experiments

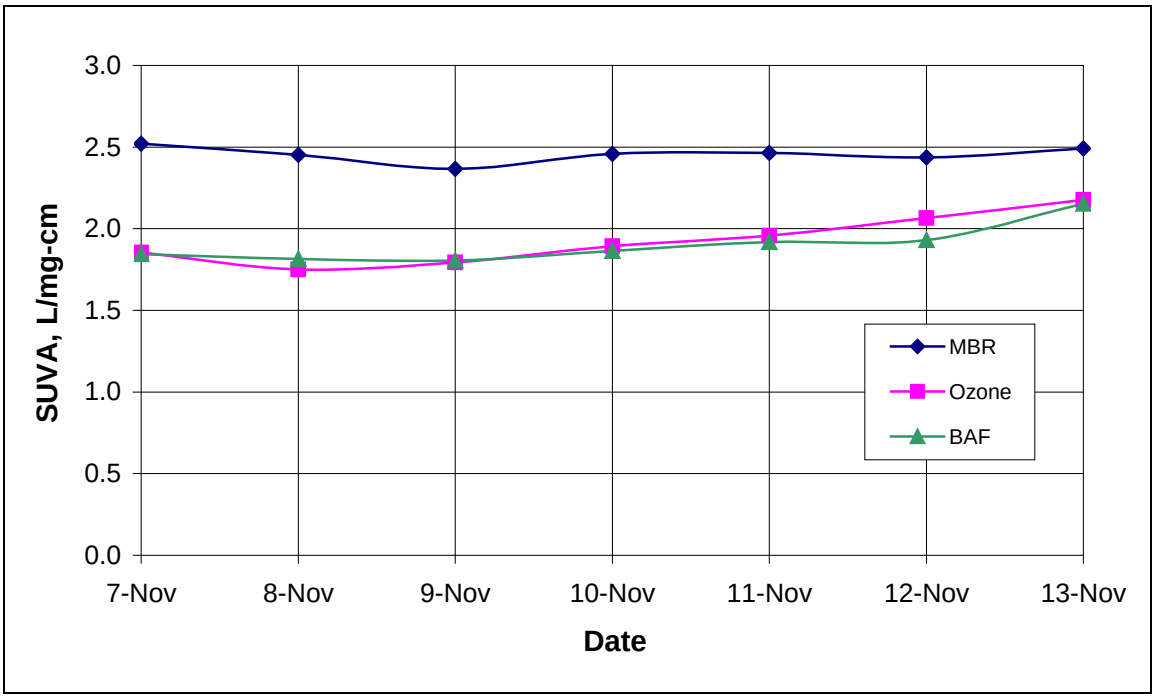

Figure 4-32: SUVA values for 2 mg/L applied ozone dose during Phase 2 experiments

Although some variation is observed in the UV_{254} absorbance and SUVA values on the day the PPCP/EDC samples were taken, the change is small. Little variation is seen in any of the measured organic parameters during the 2 mg/L ozone experiments. Because of this, the system was assumed to be at steady state for PPCP/EDC sampling. The difference in values for the organic parameters between applied ozone doses will be further examined in the next section.

Comparison of Bulk Organic Analysis for all Applied Ozone Doses

The results from the bulk organic analysis clearly show higher removal of organics by the BAF column when pre-treated by higher ozone doses. The analysis also show that although larger removal of organics is achieved with increased ozone, the 8 mg/L ozone dose only shows slight increases compared to the 2 and 4 mg/L ozone doses. This section will examine the removal of organics between applied ozone doses.

The TOC concentrations between the MBR and ozone effluents did not change at any applied ozone dose as illustrated in Figure 4-33. This leads to the conclusion that little to no organics were completely mineralized even at the highest ozone dose of 8 mg/L. Although none of the organics were mineralized by ozone alone, Figure 4-34 does show percent reductions of TOC in the BAF effluent. All values shown in Figures 4-33 - 4-38 are the averages of the last three days of samples during each sampling event.

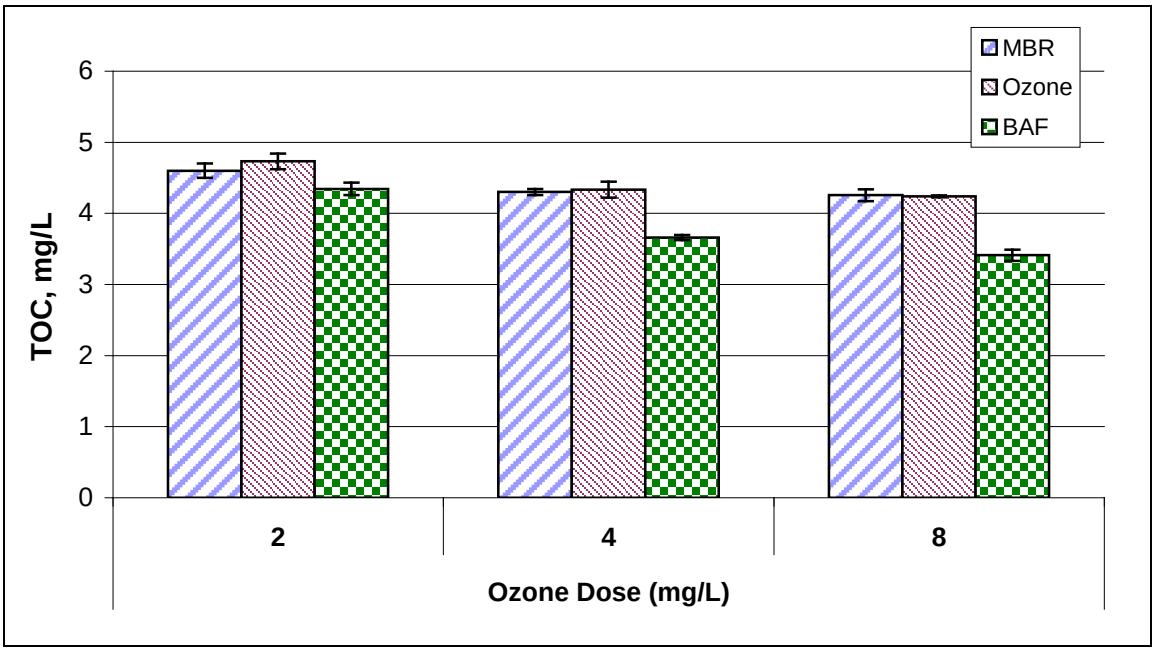

Figure 4-33: TOC concentrations for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

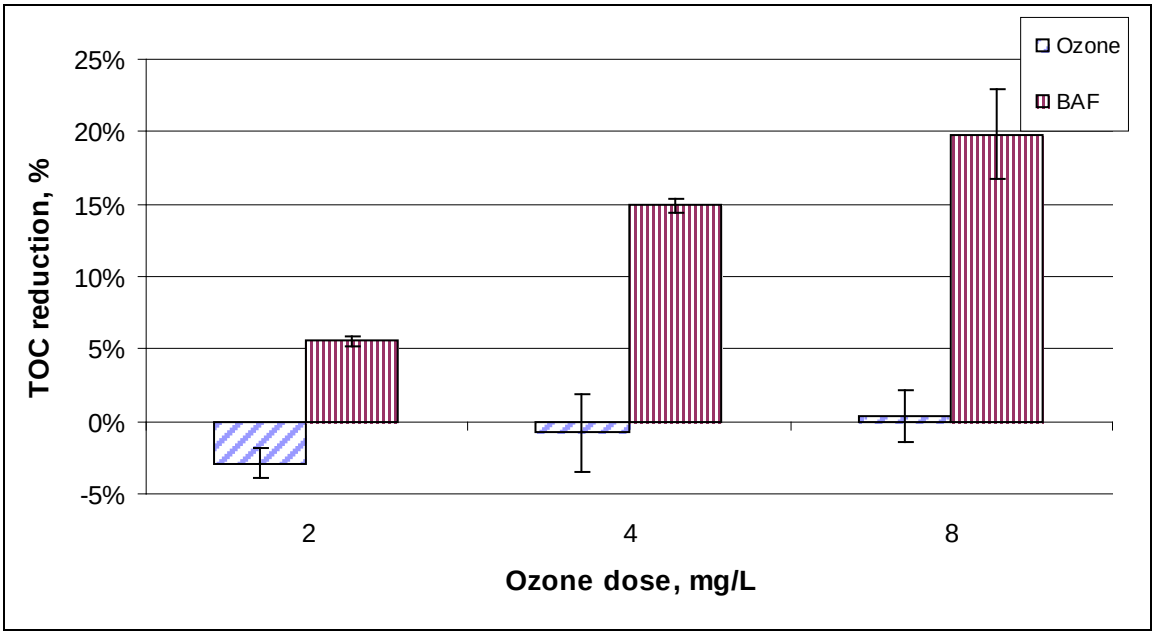

Figure 4-34: TOC percent reduction for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

As noted earlier, the change in TOC removal between ozone doses is much larger from 2 to 4 mg/L than between 4 and 8 mg/L. The percent reduction nearly triples between 2 and 4 mg/L, going from approximately 5 to 15 percent TOC reduction. Doubling the ozone dose from 4 to 8 mg/L only reduces the TOC by an additional 5%. This trend is also seen in the SUVA and UV_{254} adsorption parameters. In order to better quantify the effectiveness of ozone in removing organics at various doses, the change in organics per mg/L of ozone can be calculated for TOC, UV_{254} absorption, and SUVA, as shown in Table 4-2. These values show the removal of organics between the MBR and BAF effluents.

By examining the amount of TOC removed per mg/L of ozone added, a better picture of ozone's effectiveness in removing TOC at varying ozone doses can be established. At 2 mg/L of ozone, the removal of TOC is 0.13 mg/L per mg/L of ozone added as seen in Table 4-2. This increases to 0.16 mg/L of TOC removed per mg/L of ozone added at the 4 mg/L ozone dose. This is the peak removal efficiency. At 8 mg/L of ozone the removal of TOC drops to 0.11 mg/L per mg/L of ozone added. These values show the increasing effectiveness of ozone in removing TOC up to an ozone dose of 4 mg/L. This also shows that TOC was removed less effectively at an ozone dose of 8 mg/L. Although these values do show the overall effectiveness of ozone at various ozone doses, they do not take into account the amount of TOC already removed at lower ozone doses.

The increase in organic removal between applied ozone doses can better be understood by examining the change in organics per additional mg/L of ozone added. This is done by subtracting the amount of organics removed at lower applied ozone doses, then dividing by the amount of additional ozone added. For example, at an ozone dose of 4 mg/L there was an average of 0.39 mg/L of additional TOC removed between the ozone doses of 2 and 4 mg/L. The amount of additional ozone added between the 2 and 4 mg/L ozone doses was 2 mg/L. This gives a removal of 0.19 mg/L of TOC per additional mg/L of ozone between the applied ozone doses of 2 and 4 mg/L. The amount

of TOC removed per additional mg/L of ozone is shown in Table 4-3. These values give a better understanding of the effectiveness of ozone in removing organics at various ozone doses.

Table 4-2: Change in organic parameters per mg of ozone added

Ozone dose (mg/L)	2	4	8
ΔTOC/O3 dose	0.13	0.16	0.11
ΔUV254/O3 dose	0.013	0.013	0.008
ΔSUVA/O3 dose	0.23	0.24	0.15

The additional removal of TOC dramatically increases from 2 to 4 mg/L of ozone, going from 0.13 to 0.19 mg/L of TOC removed per additional mg/L of ozone added, as shown in Table 4-3. This is a 32 percent increase in removal efficiency. The ability of ozone to remove TOC dramatically decreases after the 4 mg/L ozone dose. The additional removal of TOC between the ozone doses of 4 and 8 mg/L is only 0.05 mg/L of TOC per additional mg/L of ozone added. This leads to the conclusion that although additional TOC removal is achieved at higher applied ozone doses, the effectiveness of ozone dramatically decreases at an ozone dose of 8 mg/L. This data also shows that the 4 mg/L ozone dose was the most efficient ozone dose examined at removing TOC.

Table 4-3: Change in organic parameters between ozone doses per additional mg/L of ozone added

Ozone dose (mg/L)	0-2 mg/L	2-4 mg/L	4-8 mg/L
ΔTOC/O3 dose	0.13	0.19	0.05
ΔUV254/O3 dose	0.013	0.013	0.003
ΔSUVA/O3 dose	0.23	0.26	0.06

Unlike the TOC values, a noticeable difference can be seen between the MBR and ozone effluents for UV_{254} absorbance as seen in Figure 4-35. This indicates that even though the total organic concentration is not decreasing with increased ozone doses, the biodegradable fraction is. As with the percent reduction in TOC, the percent reduction of UV_{254} absorbance greatly increases from 2 to 4 mg/L with much smaller increases between the applied ozone doses of 4 and 8 mg/L as illustrated in Figure 4-36. This is further illustrated by examining the change in UV_{254} absorbance per mg/L of ozone.

The decrease in UV_{254} absorbance per mg/L of ozone is quantified in Table 4-2. Similar to the TOC values, the decrease in UV_{254} absorbance is greatest at the applied ozone doses of 2 and 4 mg/L with 0.013 cm^{-1} of UV_{254} absorbance removed per mg/L of ozone. This amount decreases to 0.008 cm^{-1} of UV_{254} absorbance removed per mg/L of ozone. This shows that the lower ozone doses are more efficient in decreasing UV_{254} absorbance. The effectiveness of ozone in decreasing UV_{254} absorbance can better be quantified by examining the decrease in UV_{254} absorbance per additional mg/L of ozone added.

The additional removal of UV_{254} absorbance per additional mg/L of ozone added is the most effective at ozone doses of up to 4 mg/L. The UV_{254} absorbance decreases by 0.013 cm^{-1} for every additional mg/L of ozone for both the 0 to 2 mg/L and 2 to 4 mg/L ozone doses as shown in Table 4-3. The additional decrease of UV_{254} absorbance between the ozone doses of 4 to 8 mg/L dramatically decreases with a decrease of only 0.003 cm^{-1} of UV_{254} absorbance per additional mg/L of ozone. This is less than one-fourth the decrease in UV_{254} absorbance per mg/L of ozone added than what was observed between the 0 to 2 mg/L and 2 to 4 mg/L ozone doses.

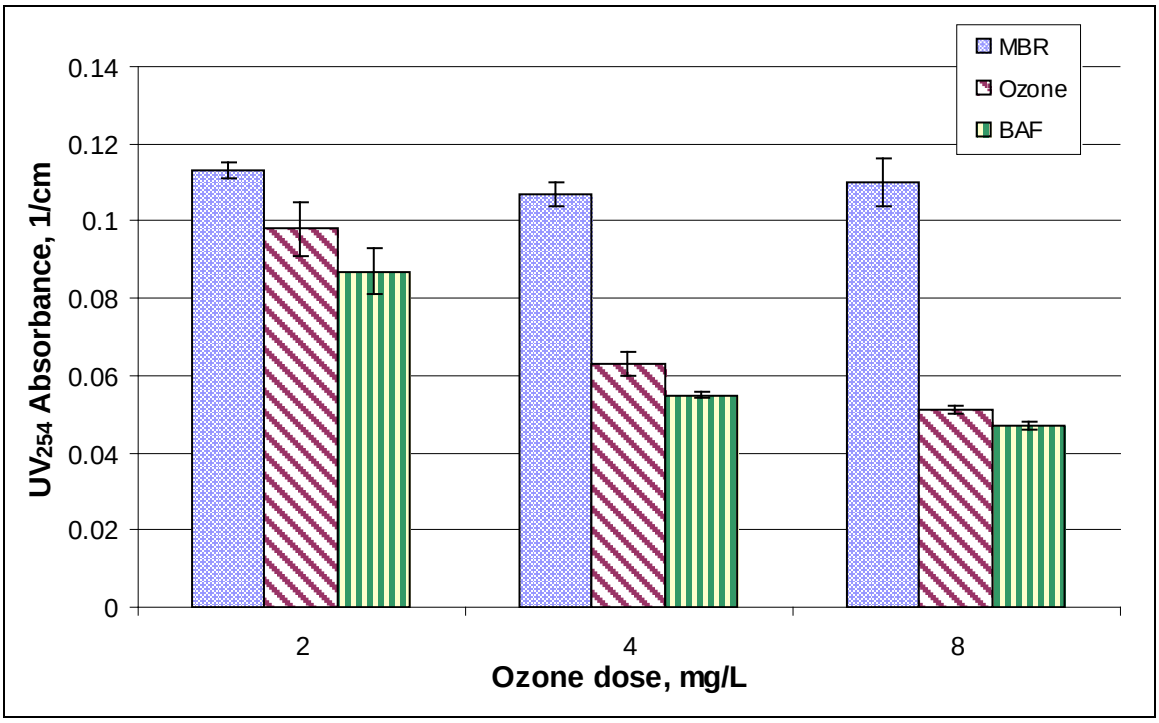

Figure 4-35: UV_{254} absorbance for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

As discussed earlier, there is a difference in UV_{254} absorbance values between the ozone and BAF effluents at the 2 and 4 mg/L ozone doses, as shown in Figure 4-35. There is a 10% difference in UV_{254} absorbance between the ozone and BAF effluents at the 2 mg/L ozone dose as shown in Figure 4-36. The difference decreases as the ozone dose increases, and at 8 mg/L the UV_{254} absorbance is nearly the same for both ozone and BAF effluents. Organics from the MBR effluent are assumed to be mostly recalcitrant. This is because effluent from the MBR has already undergone a biological process which consumes nearly all of the biodegradable organics. As shown by limited removal of TOC by the BAF in the absence of ozone pretreatment, almost all of the organics in the MBR effluent are recalcitrant, and therefore unusable as a food source for microbes in the BAF column. The organics would first have to be broken down into a more biodegradable form before they could be degraded in the BAF column. At the lower ozone doses of 2 and 4 mg/L, the recalcitrant compounds are partially oxidized in the ozone contactor and

broken down into more biodegradable forms. These compounds are broken down enough by ozone to be used as food by the microbes in the BAF column, but are still being measured in the ozone effluent due to their structure. A portion of the biodegradable compounds consumed in the BAF column still have double bonded carbon groups in unsaturated or aromatic organics that are being measured as UV_{254} absorbance. This is why the UV_{254} absorbance values are higher in the ozone effluent than the BAF effluent at ozone doses of 2 and 4 mg/L. At an ozone dose of 8 mg/L, the organics are broken down even more. As shown in Phase 1, the effectiveness of ozone to break down recalcitrant compounds peaks at an ozone dose of around 8 mg/L. At this higher dose the biodegradable fraction no longer has a chemical structure that can be measured by the UV_{254} absorbance. This is why there is little to no difference in the UV_{254} absorbance values between the ozone and BAF effluents at the 8 mg/L ozone dose.

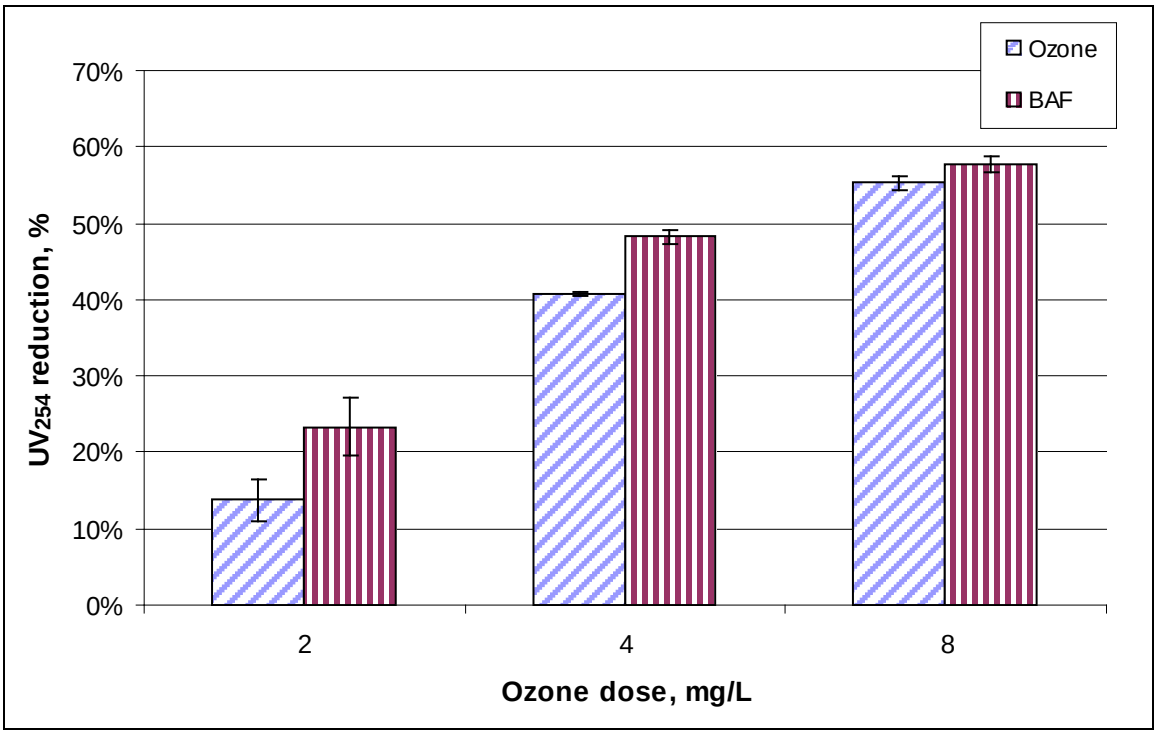

Figure 4-36: UV_{254} percent reduction for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

Similar to UV_{254} absorption, the SUVA values decrease as the applied ozone dose increases as seen in figure 4-37. Also similar to both the percent TOC and UV_{254} absorbance removal, the SUVA percent removal dramatically increases between applied ozone doses of 2 to 4 mg/L with only slight increases between 4 and 8 mg/L as illustrated in figure 4-38. What all these values seem to indicate is that although more organic degradation occurs at an ozone dose of 8 mg/L, the most efficient ozone dose used in this study for treating organics is at 4 mg/L.

This is further quantified by examining the SUVA removal per mg/L of ozone added as illustrated in Table 4-2. The amount of SUVA removed per mg/L of ozone is similar at the 2 and 4 mg/L ozone doses with 0.23 and 0.24 L/mg-cm of SUVA removed per mg/L of ozone. The amount of SUVA removed drops dramatically at 8 mg/L with only 0.15 L/mg-cm of SUVA removal per mg/L of ozone. Examining the difference in SUVA removal between applied ozone doses shows that increasing the ozone from 2 to 4 mg/L is the most effective. Going from 0 to 2 mg/L of ozone gives 0.23 L/mg-cm of SUVA removal per additional mg/L of ozone as shown in Table 4-3. This increases to 0.26 L/mg-cm of SUVA removal per additional mg/L of ozone from 2 to 4 mg/L of ozone. The removal of SUVA per additional mg/L of ozone dramatically decreases from 4 to 8 mg/L of ozone with only 0.06 L/mg-cm of SUVA removed per additional mg/L of ozone. Like the TOC and UV_{254} absorption values, the SUVA removal per additional mg/L of ozone is approximately 4 times greater going from 2 to 4 mg/L than going from 4 to 8 mg/L of ozone.

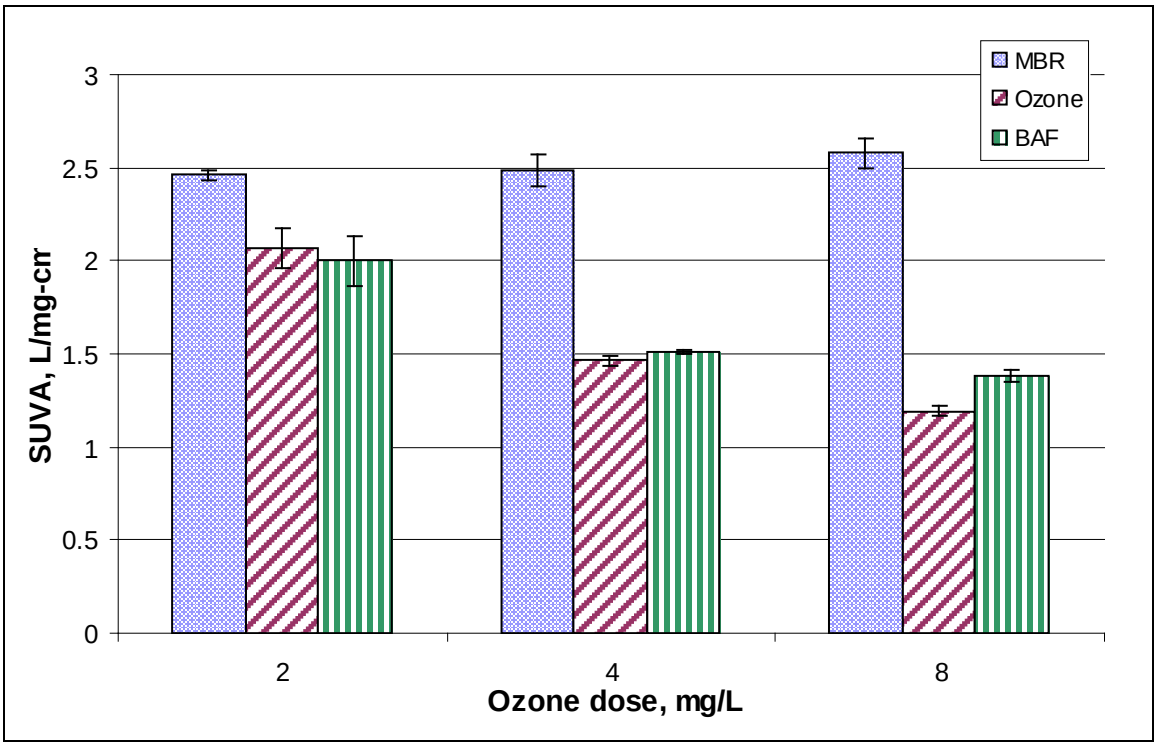

Figure 4-37: SUVA values for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

The TOC, UV_{254} absorbance, and SUVA values show that recalcitrant compounds in the MBR effluent are being partially oxidized in the ozone contact chamber. There is a trend of increasing organic removal with increasing ozone dose, although the efficiency of ozone to partially oxidize recalcitrant compounds into more biodegradable forms was not seen at the highest ozone dose examined. The most efficient ozone dose examined for removing organics was 4 mg/L.

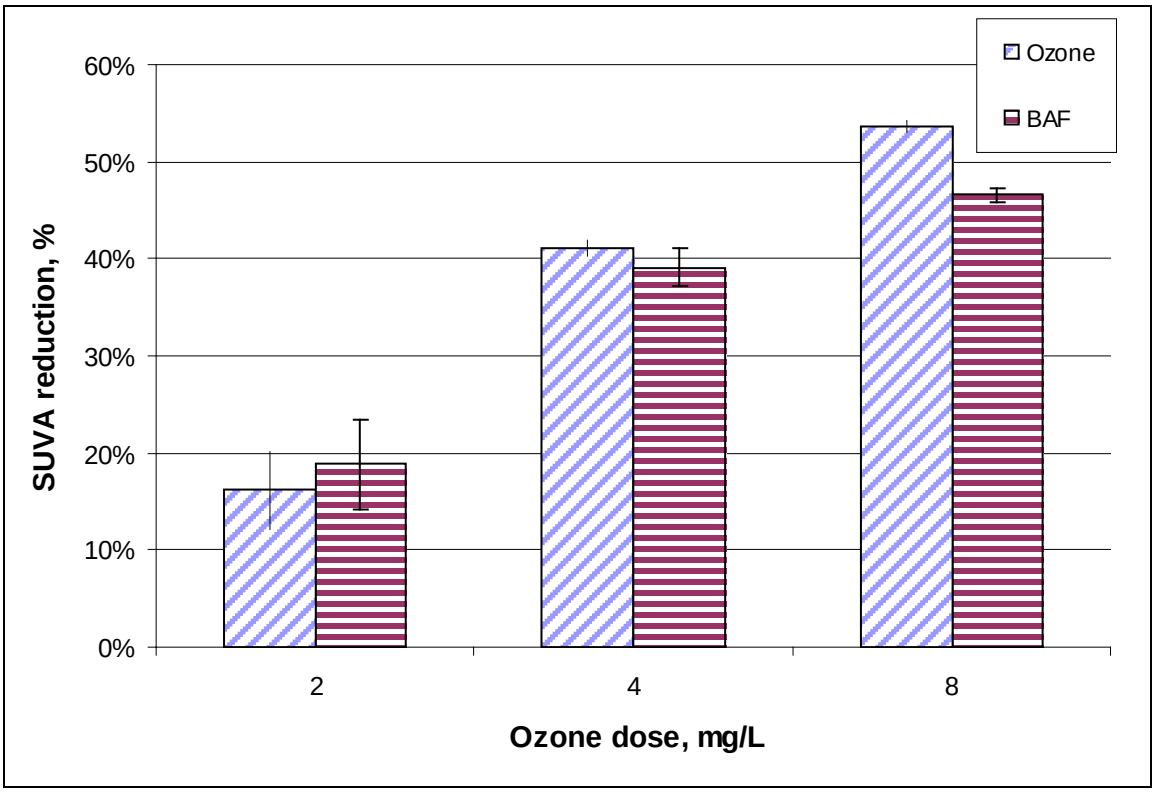

Figure 4-38: SUVA percent reduction for applied ozone doses of 2, 4, and 8 mg/L (Values are averages over the last 3 days before PPCP/EDC sampling. Error bars = ± 1 Std dev)

BDOC for Phase 2

The last of the organic analysis examined during the Phase 2 experiments was BDOC. Three BDOC sampling events were done for each applied ozone dose examined and measured the BDOC in the MBR, ozone, and BAF effluents. The October 25th BDOC results, collected during the 8 mg/L ozone dose experiments, had to be discarded due to an error with the TOC analyzer. Therefore, the 8 mg/L ozone experiments have only two sampling dates, whereas the 4 and 2 mg/L ozone experiments have three.

BDOC samples for the 8 mg/L ozone dose experiments were collected on October 21st, 23rd, and 25th. As mentioned earlier, the October 25th results had to be discarded due to an error with the TOC analyzer. The results for the 21st and 23rd, seen in Figure 4-39,

show that most of the TOC in the MBR effluent is recalcitrant and therefore non-biodegradable. The data in Table 4-4 shows that TOC is not removed in the BAF column unless it is first oxidized by ozone. This leads to the conclusion that even though a fraction of the organics in the MBR effluent is biodegradable, as shown in Figure 4-39, the microbes in the BAF column are unable to degrade this fraction. This will be discussed in more detail later.

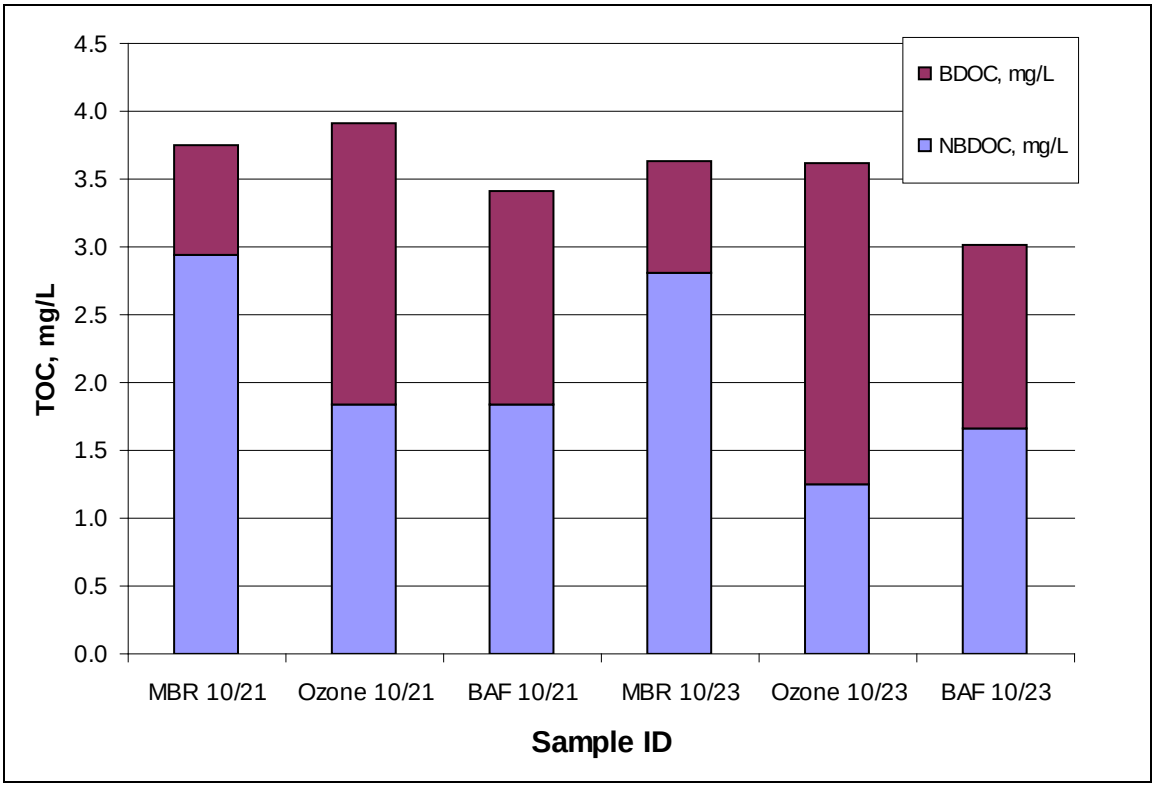

Figure 4-39: TOC, BDOC, and NBDOC measured in MBR, ozone, and BAF effluents for 8 mg/L ozone dose during Phase 2 experiments. TOC is the total column height (NBDOC+BDOC)

The results also show that a portion of the NBDOC is converted to BDOC through partial oxidation by ozone in the ozone contact chamber. The amount of BDOC significantly increases in the ozone contact chamber as illustrated in Figure 4-40. There

is an average of 1.41 mg/L of BDOC produced in the ozone contact chamber as shown in Table 4-4. A portion of the newly formed biodegradable organics are then consumed in the BAF column. An average of 0.76 mg/L of BDOC is consumed in the BAF column at an ozone dose of 8 mg/L. This gives a ratio of 0.54 mg/L of BDOC consumed in the BAF column to every 1 mg/L of BDOC created by ozone. This shows that not all of the BDOC is being consumed in the BAF column. This will be discussed in greater detail later. At the highest ozone dose examined, 8 mg/L, 58.2 percent of the initial NBDOC from the MBR effluent was converted to BDOC in the ozone contact chamber. The percent of NBDOC converted to BDOC per mg/L of ozone is 7.3 percent.

Table 4-4: BDOC statistics for 2, 4, and 8 mg/L ozone doses for Phase 2 experiments

BDOC statistics	Ozone dose		
	2 mg/L	4 mg/L	8 mg/L
Average initial TOC in MBR effluent, mg/L	4.4	4.0	3.7
Average BDOC in MBR, mg/L	1.10	0.95	0.81
Average biodegradable fraction in MBR effluent	24.9%	23.5%	22.0%
Average BDOC produced in ozone contact chamber, mg/L	0.55	1.01	1.41
Average BDOC consumed in BAF, mg/L	0.30	0.51	0.76
Ratio of BDOC consumed in the BAF to BDOC produced by ozone	0.54	0.50	0.54
Average BDOC produced in ozone contact chamber (mg/L) per mg/L of ozone	0.28	0.25	0.18
Average BDOC consumed in BAF (mg/L) per mg/L of ozone	0.15	0.13	0.09
Percent of NBDOC converted to BDOC	16.6%	33.4%	58.2%
Percent of NBDOC converted to BDOC per mg/L of ozone	8.3%	8.4%	7.3%

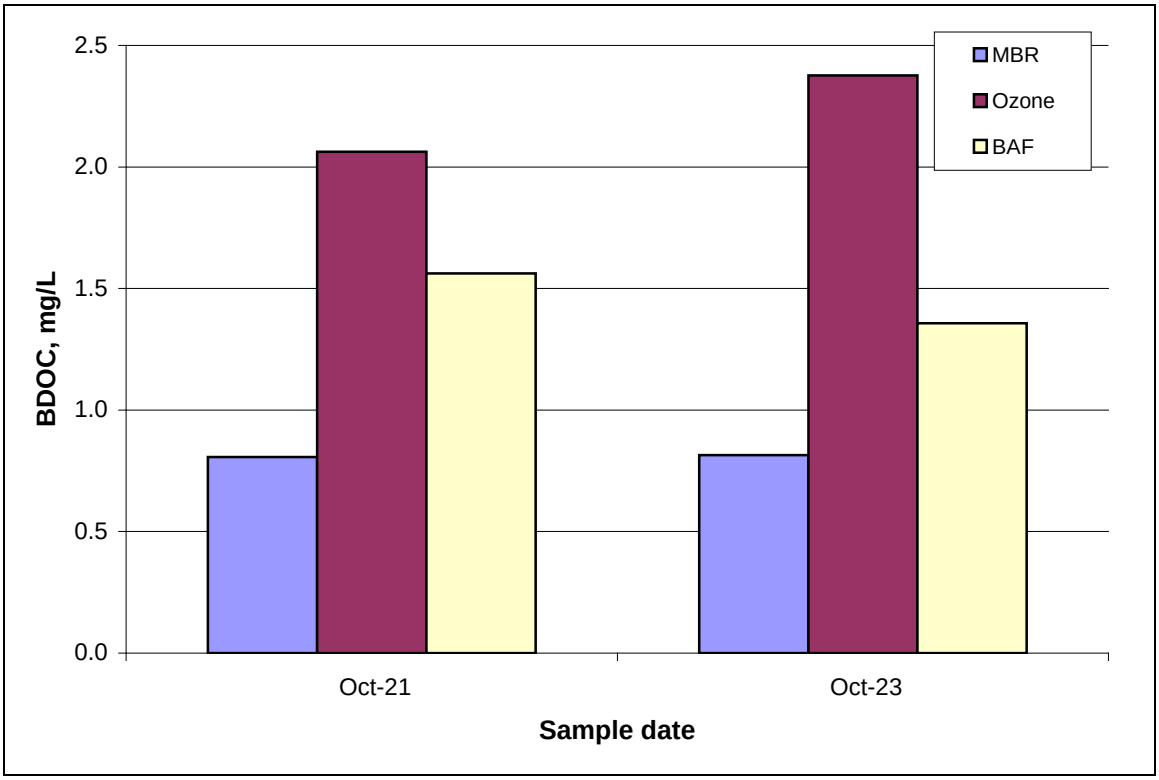

Figure 4-40: BDOC measured in MBR, ozone, and BAF effluents for 8 mg/L ozone dose during Phase 2 experiments

The first BDOC sampling date for the 4 mg/L ozone dose experiments was collected on October 30th. As discussed earlier, there is a large spike in conductivity and drop in pH on November 1st. This is reflected in the BDOC data shown in Figure 4-41, which shows a large decrease in TOC (TOC includes NBDOC and BDOC and is the total height of the column) on November 1st. The November 3rd BDOC data shows that the decrease in TOC quickly rebounds. This can also be seen in Figure 4-42, which shows the BDOC measured in all process effluents for the three sampling dates for the 4 mg/L ozone dose. The BDOC measured in all processes sharply drops on November 1st, but quickly rebounds by November 3rd. Even with these variations, the percent of NBDOC in the MBR effluent that is converted to BDOC in the ozone contact chamber shows little

variation. The October 30th results show that 32 percent of the NBDOC measured in the MBR effluent is converted to BDOC. The November 1st and 3rd results show that 34 percent of NBDOC in the MBR effluent is converted to BDOC in the ozone contact chamber. These results show that although the concentrations of organics in the MBR effluent may vary, the fraction of non-biodegradable organics that can be oxidized into more biodegradable forms is relatively constant. This consistency is also seen in the ability of the BAF column to consume the newly formed BDOC.

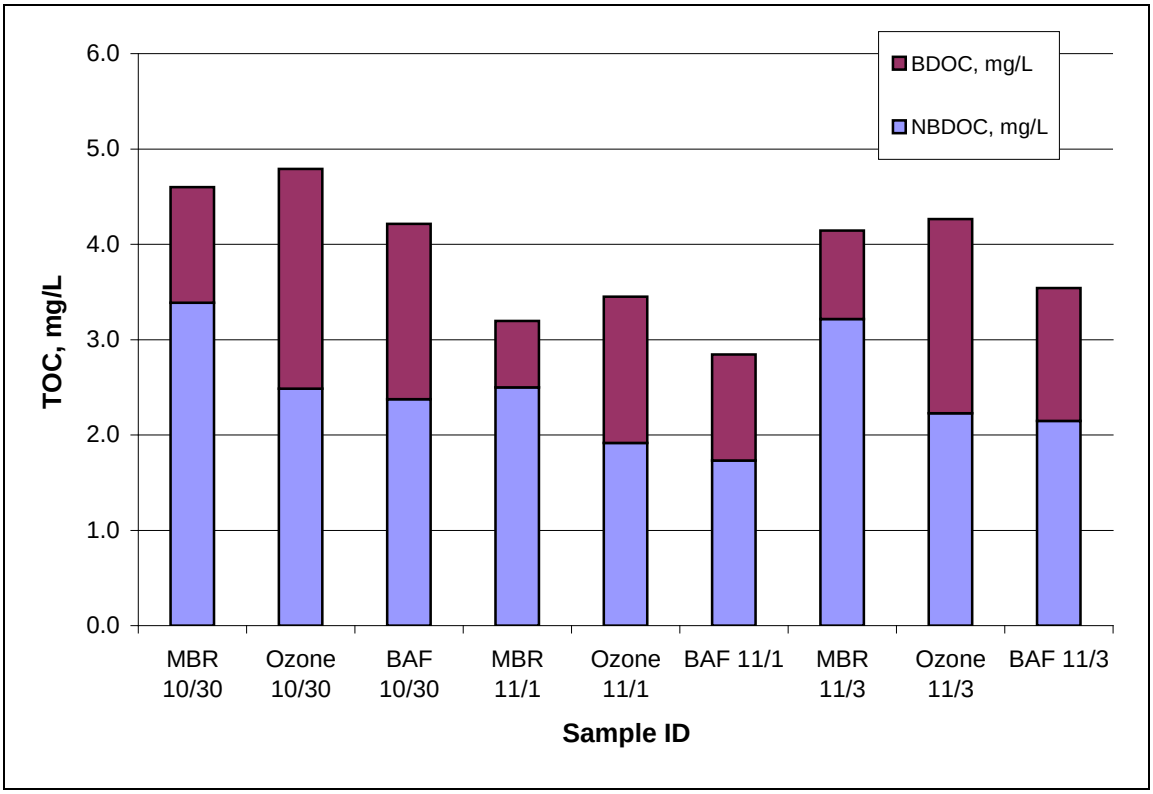

Figure 4-41: TOC, BDOC, and NBDOC measured in MBR, ozone, and BAF effluents for 4 mg/L ozone dose during Phase 2 experiments. TOC is the total column height (NBDOC+BDOC)

Similar to the 8 mg/L ozone dose, the BAF column only consumes about half of the newly created BDOC. At an ozone dose of 4 mg/L there is an average of 0.5 mg/L of BDOC consumed in the BAF column for every 1 mg/L of BDOC produced in the ozone

contact chamber. At 8 mg/L there was 0.54 mg/L of BDOC consumed in the BAF column for every 1 mg/L of BDOC produced in the ozone contact chamber. This consistent lack of further degradation of biodegradable organics in the BAF column will be discussed in more detail later.

Even though not all of the newly formed biodegradable organics were consumed in the BAF column, the 4 mg/L ozone dose shows that recalcitrant organics are being partially oxidized in the ozone contact chamber, where they are then consumed by microbes in the BAF column. The TOC data in Figure 4-41 shows that the total organics are not reduced by ozone alone.

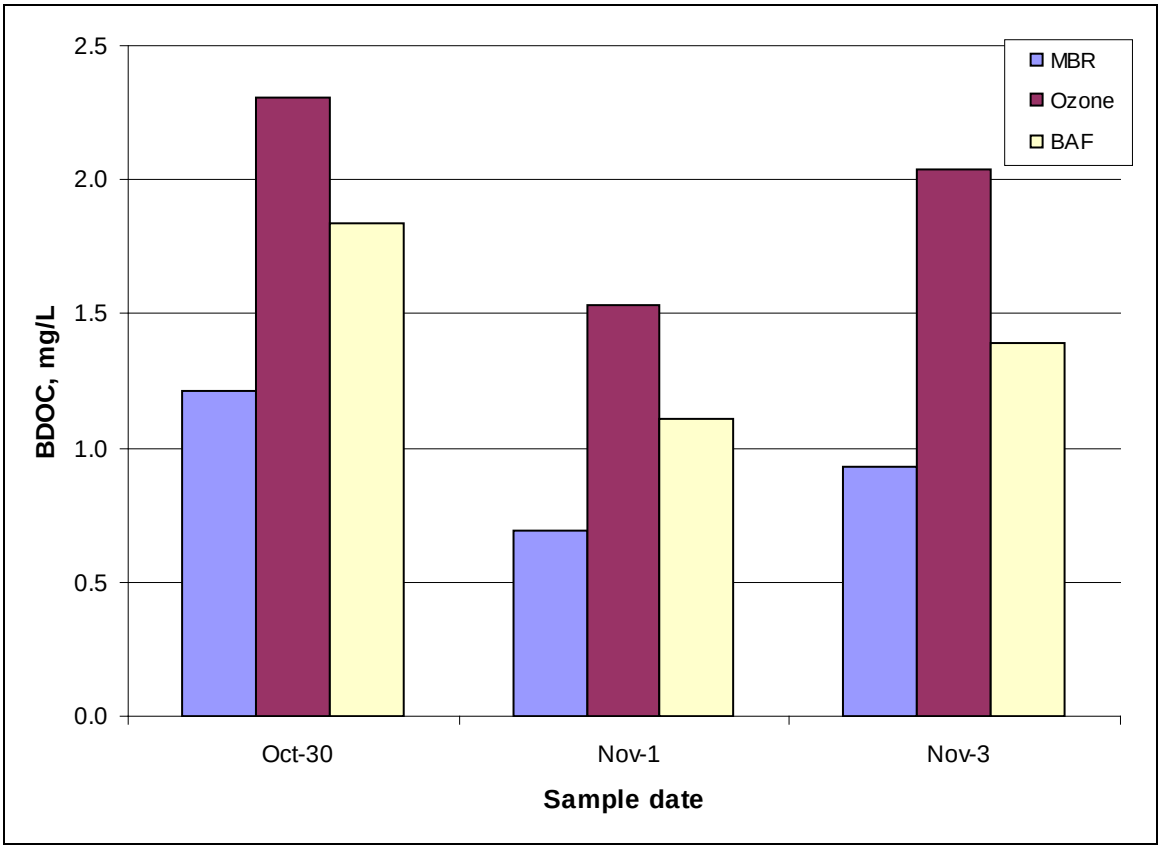

Figure 4-42: BDOC measured in MBR, ozone, and BAF effluents for 4 mg/L ozone dose during Phase 2 experiments

The BDOC results at an ozone dose of 2 mg/L show much more consistent MBR effluent values for TOC, NBDOC, and BDOC as shown in Figure 4-43. Like the 8 and 4 mg/L ozone doses, the 2 mg/L ozone dose partially oxidizes recalcitrant compounds into more biodegradable forms, which are then consumed in the BAF column. This can be seen in Figure 4-44 which shows an increase in the BDOC measured in the ozone contactor, and a decrease in the BDOC measured in the BAF column.

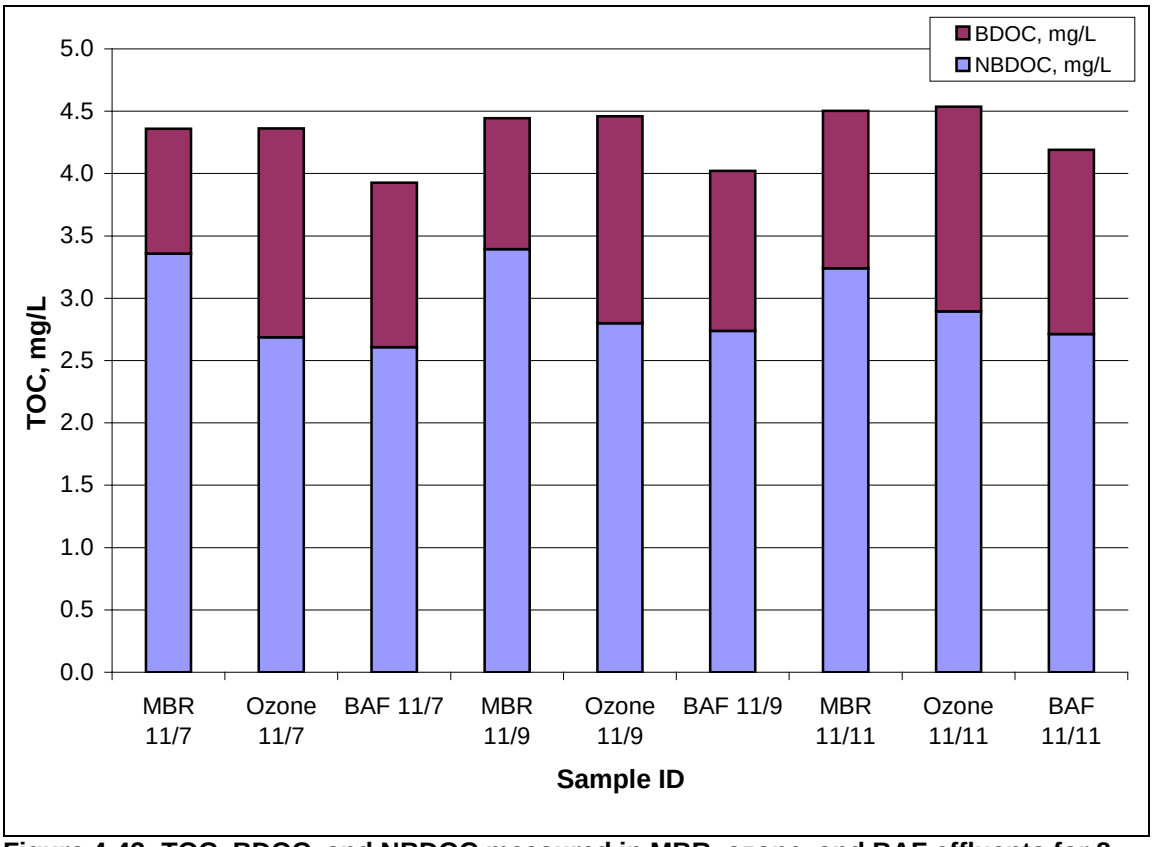

Figure 4-43: TOC, BDOC, and NBDOC measured in MBR, ozone, and BAF effluents for 8 mg/L ozone dose during Phase 2 experiments. TOC is the total column height (NBDOC+BDOC)

As expected, the amount of BDOC produced in the ozone contactor at an ozone dose of 2 mg/L is less than that produced at 4 and 8 mg/L ozone doses. The average BDOC created in the ozone contact chamber was 0.55 mg/L for the 2 mg/L ozone dose. At ozone doses of 4 and 8 mg/L the average concentration of BDOC created in the ozone contact chamber was 1.01 and 1.41 mg/L respectively. Greater oxidation is expected at higher ozone doses. This was observed in the Phase 1 BDOC results, which saw an increase in BDOC up to an ozone dose of around 8 mg/L. The ability of ozone to partially oxidize recalcitrant compounds greatly diminishes after this.

The concentration of TOC in the MBR effluent, as measured in the BDOC analysis, decreased with increasing ozone dose as shown in Table 4-4. Because this research started at an ozone dose of 8 mg/L and decreased from there, the TOC measured in the MBR effluent actually increased as the experiment proceeded. The TOC concentrations at ozone doses of 2, 4, and 8 mg/L are 4.4, 4.0, and 3.7 mg/L respectively. The concentration of BDOC in the MBR effluent also decreased with increasing ozone dose. The BDOC concentrations in the MBR effluent for ozone doses of 2, 4, and 8 mg/L are 1.10, 0.95, and 0.81 mg/L respectively. The ratio of biodegradable to non-biodegradable organics measured in the MBR effluent increased at about the same rate. The biodegradable fraction of organics initially present in the MBR effluent was almost the same at all ozone doses examined. The biodegradable fraction of organics in the three tests (ozone doses of 2, 4, and 8 mg/L) was 24.9, 23.5, and 22.0 percent respectively. This shows a slight decrease in the biodegradable fraction of organics in the 3 tests, although the increase is almost negligible. It is important to note that the increase in TOC and BDOC concentrations in the MBR effluent are likely the result of the varying quality of the MBR feedwater, as discussed earlier, and not as a result of the ozone contact chamber or BAF column. Ozone had no effect on this since this was the ozone contactor influent.

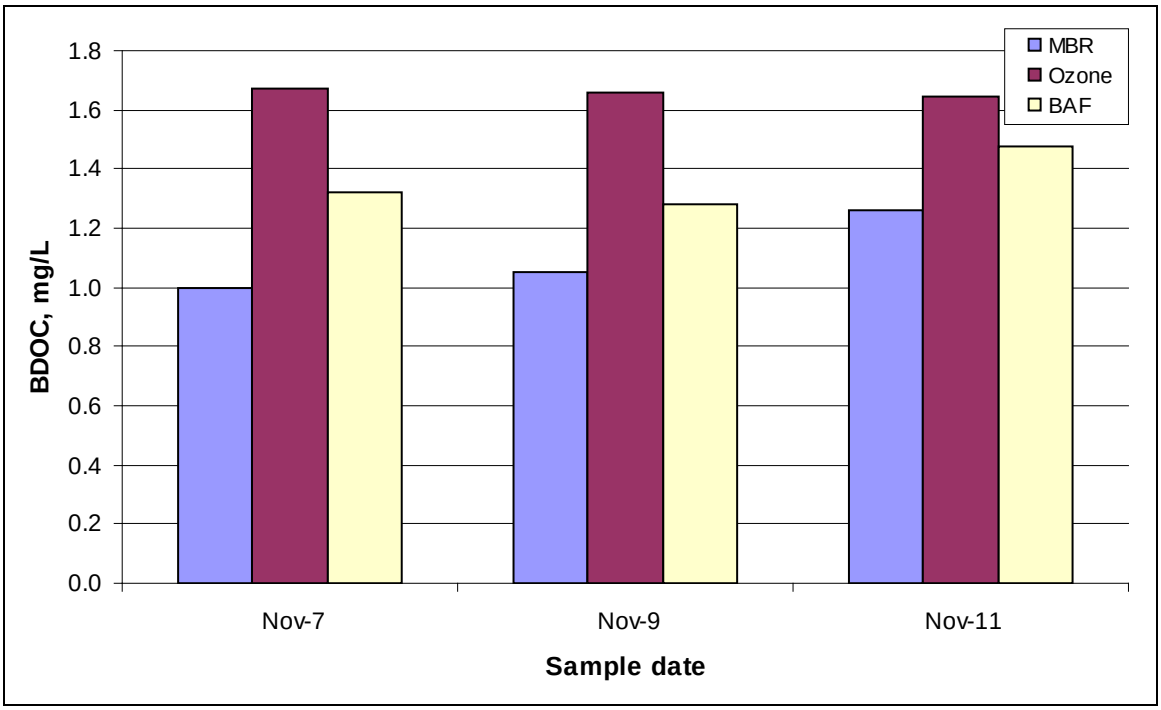

Figure 4-44: BDOC measured in MBR, ozone, and BAF effluents for 2 mg/L ozone dose during Phase 2 experiments

Even with these changes in MBR feedwater quality, the average ratio of BDOC consumed in the BAF column to BDOC produced in the ozone contact chamber was 0.54 for the 2 mg/L ozone dose. This is nearly the same ratio as what was achieved at ozone doses of 4 and 8 mg/L, which had ratios of 0.5 and 0.54 respectively. This leads to the conclusion that the BAF column is only able to consume half of the biodegradable organics produced in the ozone contact chamber regardless of the ozone dose. Half of the recalcitrant compounds that are partially oxidized to more biodegradable forms are not being consumed in the BAF column. The incomplete biodegradation of BDOC in the BAF column could be attributed to drawbacks in doing pilot scale research. Unlike a full-scale system, the pilot scale BAF column had only been operating for approximately one month. This one month of operation included all of Phase 2. This could mean the microbes in the column had not had enough time to assimilate to the type of organics being fed to them. In addition, the pilot scale BAF column was exposed to both sunlight

and changes in temperature whereas a full-scale system would be more stable in these regards. Another factor would be that in a full-scale operation, the BAF column would be subject to more control by higher experienced operators. The operators experience could allow for more optimal conditions in the BAF column. Factors such as EBCT, backwashing frequency and procedures, and better monitoring of the process could help increase the efficiency of the BAF column. This combined with the benefits of operating the system at full scale could greatly increase the biodegradation ability in the BAF column. Although drawbacks of the pilot system could be the only cause of this lack of degradation in the BAF column, further examination of the problem could be a source for a future study if this problem is also seen in full-scale operation.

Although the ratio of BDOC produced in the ozone contact chamber to BDOC consumed in the BAF column is relatively constant across all examined ozone doses, the efficiency to both produce and consume BDOC decreases with increased ozone doses. This can be quantified by examining the amount of BDOC produced and consumed per mg/L of ozone. The average BDOC produced in the ozone contact chamber is 0.28, 0.25, and 0.18 mg/L per mg/L of ozone at ozone doses of 2, 4, and 8 mg/L respectively, as shown in Table 4-4. The average BDOC consumed in the BAF column is 0.15, 0.13, and 0.09 mg/L per mg/L of ozone at ozone doses of 2, 4, and 8 mg/L respectively. These values show that although the ratio of BDOC produced to BDOC consumed remains fairly constant at all ozone doses, the ability to convert and degrade non-biodegradable organics is reduced at higher ozone doses. The effectiveness of ozone is nearly the same at the 2 and 4 mg/L ozone doses.

Although the BAF is only consuming about half of the biodegradable organics created in the ozone contact chamber at all ozone doses, the concentration of NBDOC is virtually the same between the ozone and BAF effluents at all ozone doses examined. This is seen in Figures 4-39, 4-41, and 4-43. This leads to the conclusion that further degradation of recalcitrant compounds does not occur in the BAF column. If further degradation of recalcitrant compounds were to occur in the BAF column, then the

concentration of NBDOC would decrease in the BAF column. This is not seen, although slight variations in TOC, BDOC, and NBDOC measurements are expected and do occur because of the nature of the TOC analysis. These variations are well within the range of expected errors (± 5 percent).

The fraction of non-biodegradable organics in the MBR effluent that is converted to a more biodegradable form through partial oxidation in the ozone contact chamber increases with applied ozone dose as shown in Table 4-4. The percent of NBDOC converted to BDOC in the ozone contact chamber is 16.6, 33.4, and 58.2 percent at ozone doses of 2, 4, and 8 mg/L respectively. The percent converted per mg/L of ozone is 8.3, 8.4, and 7.3 percent per mg/L of ozone at ozone doses of 2, 4, and 8 mg/L respectively. This shows that the NBDOC is converted to BDOC more effectively at the 2 and 4 mg/L ozone doses than at the ozone dose of 8 mg/L. The effectiveness of ozone to convert NBDOC to BDOC is almost the same at the 2 and 4 mg/L ozone doses with 8.3 and 8.4 percent of the NBDOC being converted to BDOC per mg/L of ozone. This drops to 7.3 percent per mg/L of ozone at an ozone dose of 8 mg/L. This follows the conclusions found in the other organic analysis previously discussed. The TOC, TOC/TOC_0, UV_{254} absorbance, and SUVA results for Phase 2, showed that increased organic removal was achieved with increasing ozone doses, although the effectiveness of ozone at 8 mg/L dramatically decreased.

Following the results of the bulk organic analysis, it is expected that PPCP/EDC removal will be achieved at all applied ozone doses examined. It is also expected that compound removal will increase with applied ozone dose. The 8 mg/L ozone dose is expected to show the highest removal of PPCPs/EDCs. The 4 mg/L ozone dose is expected to remove compounds the most efficiently while the 2 mg/L ozone dose is expected to remove some compounds well, although a majority of compounds will not be removed to below detectable limits. The PPCP/EDC results are found in the next section.

PPCP/EDC Results

The bulk organic analysis showed that organics are not completely mineralized by ozone, even at higher doses, although the biodegradable fraction is increased as the applied ozone dose is increased. The bulk organic analysis also showed that the most effective ozone dose, in terms of percent of organics treated per mg/L of ozone, occurs at an ozone dose of 4 mg/L for the ozone doses examined. The following section will examine how well microconstituents were removed at the examined ozone doses and if the removal of these compounds correlates well with what was observed in the bulk organic analysis.

Compounds Detected in MBR Effluent

The PPCP/EDC analysis performed by MWH laboratories tested for 83 different compounds with most having detection limits at 5 ng/L. A summary table of compounds and detection limits was previously presented in Table 3-8. Of these 83 compounds, 52 were detected in one or more samples in the MBR effluent. These compounds as well as average concentrations and relative standard deviation can be found in Table 4-5. Three compounds (dehydronifedipine, meclofenamic acid, and DACT) were detected in the ozone or BAF effluent, but not in the MBR effluent for at least one sample. All three of these compounds were also detected in the MBR effluent in at least one of the sampling events. The concentrations of these compounds were close to the detection limit, which leads to the conclusion that they were not detected in the MBR effluent due to the limitations of the analysis. This will be discussed in greater detail later.

Table 4-5: Summary table of concentrations, average concentrations, and relative standard deviations of compounds detected in MBR effluent (ng/L).

Analyte	Initial sample taken 8/18/2009 (ng/L)	8 mg/L sample taken 10/29/2009 (ng/L)	Average 4 mg/L sample taken 11/06/2009 (ng/L)	2 mg/L sample taken 11/13/2009 (ng/L)	Average (ng/L)	Relative std dev (%)
1,7-Dimethylxanthine	46	29	46	21	36	35.4%
4-Nonylphenol	**BDL**	330	270	280	223	64.8%
4-tert-Octylphenol	**BDL**	**BDL**	**BDL**	13	11	14.0%
Acetaminophen	59	88	62.5	18	57	50.9%
Albuterol	18	15	6.2	**BDL**	11	58.2%
Amoxicillin	470	1200	485	580	684	50.8%
Atenolol	410	490	380	240	380	27.4%
BPA	25	**BDL**	**BDL**	**BDL**	14	54.5%
Butalbital	37	80	34	25	44	55.8%
Caffeine	330	510	300	140	320	47.4%
Carbadox	13	**BDL**	6.05	27	13	79.4%
Carbamazepine	360	440	410	450	415	9.7%
Carisoprodol	150	60	48.5	46	76	65.2%
Cimetidine	240	110	100.5	100	138	49.7%
Cotinine	83	20	32.5	**BDL**	36	89.1%
DACT	6.7	**BDL**(1)	**BDL**(1)	6.8	6	17.2%
DEA	5.7	**BDL**	**BDL**	**BDL**	5	6.8%
DEET	150	33	39	13	59	105.3%
Dehydronifedipine	7.6	9.6	**BDL**(1)	6.4	7	27.3%
Dilantin	210	270	350	320	288	21.3%
Erythromycin	**BDL**	**BDL**	18.5	**BDL**	12	35.1%
Furosimide	170	230	150	87	159	37.0%
Gemfibrozil	**BDL**	85	43	9.3	36	104.2%
Iohexal	860	590	560	140	538	55.3%
Iopromide	3400	14000	5300	4100	6700	73.6%
Ketoprofen	**BDL**	**BDL**	6.9	62	20	143.0%
Lincomycin	16	**BDL**	**BDL**	**BDL**	12	26.1%
Ketorolac	**BDL**	11	7.25	**BDL**	7	40.1%
Lidocaine	**BDL**	390	335	300	258	66.9%
Lopressor	230	230	160	**BDL**	160	61.9%
Meclofenamic Acid	21	**BDL**	37.5	**BDL**(1)	17	90.7%
Meprobamate	230	380	395	390	349	22.8%
Naproxen	85	260	160	68	143	61.1%
Oxolinic acid	**BDL**	**BDL**	23	**BDL**	10	94.7%
Pentoxifylline	5.2	**BDL**	**BDL**	**BDL**	5	2.0%
Primidone	110	120	120	200	138	30.5%
Propylparaben	6.3	**BDL**	**BDL**	**BDL**	5	12.2%
Sucralose	55600	37000	43000	34000	42400	22.6%
Sulfadiazine	35	16	9.15	19	20	55.3%
Sulfamethazine	**BDL**	**BDL**	5.1	**BDL**	5	1.0%
Sulfamethoxazole	710	1600	1040	470	955	51.2%
Sulfathiazole	**BDL**	**BDL**	5.8	9.2	6	32.0%
TCEP	270	41	120	200	158	62.8%
Theobromine	150	110	62.5	36	90	56.4%
Theophylline	87	62	98	40	72	36.2%
Triclosan	73	**BDL**	14	14	28	108.9%
Trimethoprim	27	60	79.5	**BDL**	44	71.2%
Warfarin	**BDL**	7	**BDL**	**BDL**	6	18.2%
Atrazine	**BDL**	**BDL**	43	**BDL**	15	131.0%
Bromacil	20	20	**BDL**	5.6	13	67.1%
Diuron	75	23	24.5	15	34	79.7%
Linuron	**BDL**	**BDL**	5	**BDL**	5	0.0%

BDL = Below detectable limit

(1) = Compound was detected in ozone or BAF effluent and not in MBR effluent

Several compounds were not detected in all of the sampling events. To calculate the average concentrations and relative standard deviations, compounds that were not detected were assumed to have concentrations just below the detectable limits (5 ng/L for most compounds). Thirty-one of the compounds tested for by MWH laboratories were not detected in any of the 16 samples collected. A list of these compounds and their detection limits are shown in Table 4-6.

Table 4-6: List of the 31 compounds not detected and their detection limits

Analyte	Detection Limit (ng/L)	Analyte	Detection Limit (ng/L)
Andorostenedione	5	Metazachlor	5
Bendroflumethiazide	5	Methylparaben	20
Bezafibrate	5	Nifedipine	20
Butylparaben	5	Norethisterone	5
Chloramphenicol	10	Progesterone	5
Chloridazon	5	Sulfachloropyridazine	5
DIA	5	Sulfadimethoxine	5
Diazepam	5	Sulfamerazine	5
Diclofenac	5	Sulfamethizole	5
Estradiol	5	Simazine	5
Estrone	5	Propazine	5
Ethinyl Estradiol - 17 alpha	5	Chlorotoluron	5
Ethylparaben	20	Cyanazine	5
Flumeqine	10	Isoproturon	20
Ibuprofen	10	2,4-D	5
Isobutylparaben	5		

Quality Assurance

Several steps were taken to ensure the PPCP/EDC data was as accurate as possible. To ensure the results were reproducible, duplicates were collected for the MBR, ozone, and BAF effluents during the 4 mg/L ozone dose sampling event. To ensure that the sampling process was free of contamination from outside sources, a field

blank was collected during the 8 mg/L ozone dose sampling event. Both these additional analyses are used to increase the confidence in the data.

MBR, Ozone, and BAF Duplicates

The duplicates collected during the 4 mg/L ozone dose sampling event were collected in the same manner as all other PPCP/EDC samples. The duplicates for each process were collected at the same time as the primary samples. A list of the compounds detected, their concentrations, as well as the mean and difference/mean for the MBR, ozone, and BAF effluents are shown in Tables 4-7, 4-8, and 4-9 respectively.

A total of 44 compounds were detected during the 4 mg/L ozone dose sampling event. Of these compounds, only two (dehydronifedipine and DACT) were not detected in the MBR effluent. Both dehydronifedipine and DACT were detected in the ozone and BAF effluents in both the primary and duplicate samples at average concentrations of 14 and 11.5 ng/L respectively. Both compounds have a detection limit of 5 ng/L. Five other compounds (ketoprofen, sulfamethazine, sulfathiazole, atrazine, and linuron) were only detected once in either the primary or duplicate sample. Of these only atrazine was detected at a concentration greater than 6.9 ng/L with detection limits for these compounds at 5 ng/L. Because the concentrations were so close to the detection limits, the lack of detection in both samples was most likely due to concentrations of compounds being below the detection limit. Additional confidence in the data is also gained by examining the difference in the detected concentrations in the primary and duplicate samples and dividing it by the mean.

Table 4-7: Concentrations of compounds detected in primary and duplicate 4 mg/L sampling event along with mean and difference/mean

Analyte	Primary Concentration, ng/L	Duplicate Concentration, ng/L	Mean Concentration, ng/L	Difference/ Mean
1,7-Dimethylxanthine	43	49	46	13%
4-Nonylphenol	270	270	270	0%
Acetaminophen	64	61	62.5	5%
Albuterol	5.5	6.9	6.2	23%
Amoxicillin	450	520	485	14%
Atenolol	350	410	380	16%
Butalbital	38	30	34	24%
Caffeine	320	280	300	13%
Carbadox	6.3	5.8	6.05	8%
Carbamazepine	460	360	410	24%
Carisoprodol	48	49	48.5	2%
Cimetidine	110	91	100.5	19%
Cotinine	19	46	32.5	83%
DACT	**BDL**(1)	**BDL**(1)	**BDL**(1)	-
DEET	38	40	39	5%
Dehydronifedipine	**BDL**(1)	**BDL**(1)	**BDL**(1)	-
Dilantin	310	390	350	23%
Erythromycin	18	19	18.5	5%
Furosimide	150	150	150	0%
Gemfibrozil	41	45	43	9%
Iohexal	740	380	560	64%
Iopromide	5000	5600	5300	11%
Ketoprofen	6.9	**BDL**	5.95	32%
Ketorolac	7.3	7.2	7.25	1%
Lidocaine	310	360	335	15%
Lopressor	150	170	160	13%
Meclofenamic Acid	32	43	37.5	29%
Meprobamate	420	370	395	13%
Naproxen	150	170	160	13%
Oxolinic acid	21	25	23	17%
Primidone	100	140	120	33%
Sucralose	47000	39000	43000	19%
Sulfadiazine	9.1	9.2	9.15	1%
Sulfamethazine	5.1	**BDL**	5.05	1%
Sulfamethoxazole	980	1100	1040	12%
Sulfathiazole	**BDL**	5.8	5.4	15%
TCEP	110	130	120	17%
Theobromine	50	75	62.5	40%
Theophylline	98	98	98	0%
Triclosan	14	14	14	0%
Trimethoprim	76	83	79.5	9%
Atrazine	43	**BDL**	24	158%
Diuron	24	25	24.5	4%
Linuron	**BDL**	5	5	0%

BDL = Below detectable limit

(1) = Compound was detected in ozone or BAF effluent and not in MBR effluent

The difference/mean values for all compounds were low. For the MBR effluent samples, five compounds had difference/mean values of 0, 13 had ≤ 5%, 16 compounds had ≤ 10%, and 35 had a difference/mean value of < 25%. Only 7 compounds had a difference/mean value of > 25%.

Table 4-8: Ozone effluent primary and duplicate concentrations, mean, and difference/mean value for 4 mg/L sampling event

Analyte	Primary Concentration, ng/L	Duplicate Concentration, ng/L	Mean Concentration, ng/L	Difference/ Mean
4-Nonylphenol	130	150	140	14%
Atenolol	7.9	5.6	6.75	34%
Caffeine	**BDL**[(2)]	**BDL**[(2)]	**BDL**[(2)]	-
Carisoprodol	12	16	14	29%
Cotinine	**BDL**	12	11	18%
DACT	14[(1)]	9[(1)]	11.5	43%
DEET	4.9	5.5	5.2	12%
Dehydronifedipine	14[(1)]	14[(1)]	14	0%
Dilantin	79	110	94.5	33%
Iohexal	390	220	305	56%
Iopromide	1700	2900	2300	52%
Meprobamate	80	75	77.5	6%
Primidone	34	44	39	26%
Sucralose	26000	20000	23000	26%
Sulfamethoxazole	13	12	12.5	8%
TCEP	69	69	69	0%
Theobromine	**BDL**[(2)]	**BDL**[(2)]	**BDL**[(2)]	-

BDL = Below detectable limit

(1) = Compound not detected in MBR effluent

(2) = Compound detected in BAF effluent and not in ozone effluent

A total of 17 compounds detected in the effluent from the ozone contactor or BAF. As mentioned earlier, the compounds DACT and dehydronifedipine were not

detected in the MBR effluent in either the primary or duplicate samples, although they were detected in both the ozone and BAF effluents in both primary and duplicate samples. Three compounds were detected in only one sample with two, continine (12 ng/L) and theobromine (8.6 ng/L), being detected at levels close to their detection limit.

Table 4-9: BAF effluent primary and duplicate concentrations, mean, and difference/mean values for 4 mg/L sampling event

Analyte	Primary Concentration, ng/L	Duplicate Concentration, ng/L	Mean Concentration, ng/L	Difference/Mean
4-Nonylphenol	140	120	130	15%
Atenolol	10	10	10	0%
Caffeine	24	15	19.5	46%
Carisoprodol	16	14	15	13%
Cotinine	12	11	11.5	9%
DACT	8.9(1)	13(1)	10.95	37%
DEET	6.2	4.8	5.5	25%
Dehydronifedipine	20(1)	18(1)	19	11%
Dilantin	85	98	91.5	14%
Iohexal	**BDL**	160	85	176%
Iopromide	3900	2400	3150	48%
Meprobamate	78	87	82.5	11%
Primidone	48	44	46	9%
Sucralose	34000	20000	27000	52%
Sulfamethoxazole	13	12	12.5	8%
TCEP	70	51	60.5	31%
Theobromine	**BDL**	8.6	6.8	53%

BDL = Below detectable limit

(1) = Compound not detected in MBR effluent

A total of 15 compounds were detected in the ozone contactor effluent as seen in Table 4-8. Four of the compounds had a difference/mean value of ≤ 10% with two of these at 0%. Seven compounds had a difference/mean value of < 20%. A total of 17 compounds were detected in the BAF effluent as seen in Table 4-9. Nine of the

compounds had a difference/mean value of ≤ 15% with one compound having 0%. Eight compounds had a difference/mean value of greater than 20% with the highest being for iohexal at 176%. The iohexal results show inconsistency throughout the PPCP/EDC results, as will be discussed in more detail later.

Field Blank

The other test done for quality assurance purposes was collection and analysis of a field blank. The field blank was taken during the 8 mg/L sampling event. The field blank was supplied by MWH laboratories and consisted of water that was free of all compounds being tested. To sample, the water was transferred from the travel container to the sample vials. Normal sampling protocol was followed and the sample vials were the same ones used on all the other samples. The vials were packed and shipped with the other samples gathered during the 8 mg/L sampling event.

Using a field blank can ensure that contamination is not the result of the sample preparation, preservation, and shipping process. This is especially important when measuring for contaminants at ultra-low concentrations. The field blank may also explain if there are any discrepancies in the data. For example if an unexpected compound is detected at high concentrations, then the field blank might help explain why.

Two compounds, propylparaben and 4-nonylphenol, were found in the field blank at concentrations of 42 and 200 ng/L respectively. Propylparaben is an antimicrobial preservative that can be found in food, pharmaceuticals, creams, skin care products, cosmetics, and shampoos [50]. Other than the field blank, propylparaben was found in only one other sample, the 8/19/09 sample of MBR effluent. This sample was not part of the Phase 2 experiments. Based on the presence in the field blank, the detection of propylparaben in the 8/19/09 MBR effluent cannot be assumed to be valid.

4-nonylphenol was detected in all processes and in every sampling event except the 8/19/09 MBR effluent sample. This compound was even detected in the RO effluent

at concentrations of 210 and 230 ng/L for the 2 and 4 mg/L sampling events respectively. Detecting the compound in the RO effluent at these high concentrations was unexpected, but because this compound was detected at similar levels in the field blank (200 ng/L), the detection is assumed to be due to contamination.

There are several possible sources of contamination for 4-nonylphenol. The compound can be found in many different manufacturing processes as well as in pesticides [51]. The compound is also used as a plastic stabilizer and has been reported to be in the air at low levels [51]. Due to consistent levels of 4-nonylphenol being detected in all process effluents for all ozone sampling events, including the field blank, all 4-nonylphenol results were discarded. The reported concentrations for 4-nonylphenol can be found in Table 4-10.

Table 4-10: Sampling events, processes, and concentrations for 4-Nonylphenol

Sample ID	Detection of 4-Nonylphenol in all processes (ng/L)				
	8/19/2009	2 mg/L	4 mg/L primary	4 mg/L duplicate	8 mg/L
MBR effluent	**BDL**	280	270	270	330
Ozone effluent	**NS**	200	130	150	130
BAF effluent	**NS**	140	140	120	150
RO	**NS**	210	230	**NS**	**NS**
Field blank	**NS**	**NS**	**NS**	**NS**	200

NS = No sample taken

BDL = Below detectable limits

PPCP/EDC Removal

A total of 48 compounds were detected during the 2, 4, and 8 mg/L sampling events, however, propylparaben and 4-nonylphenol were not considered reliable measurements because of their appearance in the field blank. A summary of the remaining 46 compounds, as well as their percent removal for all 3 sampling events, can be found in Table 4-11.

It is important to note that even though there were a large number of PPCPs detected in the MBR effluent, the total concentration of these compounds is only a small fraction of the organic composition of the water. The average total concentration of PPCPs detected in the MBR effluent is approximately 52,000 ng/L, with almost three quarters of this total attributed to sucralose. This is approximately 1% of the total organics in the MBR effluent. The remaining 99% of the organics in the MBR effluent is material that is not well characterized, but will compete with the PPCPs for oxidation by ozone and microbial populations.

Table 4-11 tabulates the percent removal of compounds from the MBR effluent by ozonation and combined ozonation BAF processes at each applied ozone dose. For each examined ozone dose, there are two different columns of compound percent removal. The percent removal in BAF column lists the percent removal of compounds between the MBR and BAF effluents. It does not take into account compound removal in the ozone effluent and only looks at the difference in concentrations of compounds detected in the MBR and BAF effluents. The percent removal in BAF column accounts for the compounds initially detected in the MBR effluent, and then calculates the percent removal based on the concentration of compounds detected in the BAF effluent. This method looks at the total removal of compounds at the end of the treatment train. The percent removal ozone only column examines the compound percent removal between the MBR and ozone effluents. The values listed in this column do not take into account the removal of compounds by the BAF process. A third category of compound percent removal is the ozone to BAF percent removal, which examines the percent removal of compounds between the ozone and BAF effluents. This will be further examined later.

Table 4-11: Percent removal of PPCPs from MBR effluent by ozone oxidation and by combined ozone oxidation and BAF, for all compounds detected in 2, 4, and 8 mg/L sampling events

Analyte	2 mg/L results		4 mg/L results		8 mg/L results	
	Percent removal in BAF	Percent removal ozone only	Percent removal in BAF	Percent removal ozone only	Percent removal in BAF	Percent removal ozone only
1,7-Dimethylxanthine	BDL	BDL	BDL	BDL	BDL	BDL
4-tert-Octylphenol	BDL	BDL	BDL(2)	BDL(2)	BDL(2)	BDL(2)
Albuterol	BDL(2)	BDL(2)	BDL	BDL	BDL	BDL
Acetaminophen	BDL	BDL	BDL	BDL	BDL	BDL
Amoxicillin	95	94	BDL	BDL	BDL	BDL
Atenolol	42	29	97	98	BDL	BDL
Butalbital	73	70	BDL	BDL	BDL	BDL
Caffeine	42	55	94	BDL	BDL	BDL
Carbadox	19	BDL	BDL	BDL	BDL(2)	BDL(2)
Carbamazepine	95	96	BDL	BDL	BDL	BDL
Carisoprodol	22	-4	69	71	BDL	BDL
Cimetidine	BDL	BDL	BDL	BDL	BDL	BDL
Cotinine	BDL(2)	BDL(2)	65	63	BDL	BDL
DACT	9	18	BDL(1)	BDL(1)	BDL(1)	BDL(1)
DEET	8	8	86	87	BDL	BDL
Dehydronifedipine	16	-5	BDL(1)	BDL(1)	BDL	BDL
Dilantin	25	28	74	73	BDL	BDL
Erythromycin	BDL(2)	BDL(2)	BDL	BDL	BDL(2)	BDL(2)
Furosimide	BDL	BDL	BDL	BDL	BDL	BDL
Gemfibrozil	BDL	BDL	BDL	BDL	BDL	BDL
Iohexal	-64	-21	71	46	42	42
Iopromide	15	7	41	57	89	82
Ketoprofen	10	11	BDL	BDL	BDL(2)	BDL(2)
Ketorolac	BDL(2)	BDL(2)	BDL	BDL	BDL	BDL
Lidocaine	60	75	BDL	BDL	BDL	BDL
Lopressor	BDL(2)	BDL(2)	BDL	BDL	BDL	BDL
Meclofenamic Acid	BDL(1)	BDL(1)	BDL	BDL	BDL(2)	BDL(2)
Meprobamate	31	33	79	80	75	80
Naproxen	85	BDL	BDL	BDL	BDL	BDL
Oxolinic acid	BDL(2)	BDL(2)	BDL	BDL	BDL(2)	BDL(2)
Primidone	40	45	62	68	92	92
Sucralose	0	-6	37	47	57	57
Sulfadiazine	BDL	BDL	BDL	BDL	BDL	BDL
Sulfamethazine	BDL(2)	BDL(2)	BDL	BDL	BDL(2)	BDL(2)
Sulfamethoxazole	66	47	99	99	BDL	BDL
Sulfathiazole	32	BDL	BDL	BDL	BDL(2)	BDL(2)
TCEP	20	10	50	43	-BDL	-129
Theobromine	8	31	86	BDL	BDL	BDL
Theophylline	BDL	BDL	BDL	BDL	BDL	BDL
Triclosan	BDL	BDL	BDL	BDL	BDL(2)	BDL(2)
Trimethoprim	BDL(2)	BDL(2)	BDL	BDL	BDL	BDL
Warfarin	BDL(2)	BDL(2)	BDL(2)	BDL(2)	BDL	BDL
Atrazine	BDL(2)	BDL(2)	BDL	BDL	BDL(2)	BDL(2)
Bromacil	BDL	BDL	BDL(2)	BDL(2)	BDL	BDL
Diuron	27	33	BDL	BDL	BDL	BDL
Linuron	BDL(2)	BDL(2)	BDL	BDL	BDL(2)	BDL(2)

BDL = Below detectable limit

(1) = Compound not detected in MBR effluent

(2) = Compound not detected during sampling event

Because this research did not spike any compounds into the water, not all compounds were detected in every sampling event. A total of 17 compounds were not detected in any of the process effluents for at least one sampling event during Phase 2. Therefore, a few assumptions are made in order to compare the removal efficiencies for as many compounds as possible. If a compound is removed to below detectable limits (BDL) at an ozone dose of 2 or 4 mg/L, it is assumed that the compound is also removed to BDL at higher ozone doses even if the compound was not detected in the MBR sample. This assumption is based on the results for 16 compounds. These compounds were detected at all applied ozone doses and were removed to BDL at an ozone dose of 2 or 4 mg/L. All compounds that were removed to BDL at a lower ozone dose were also removed to the same level at all higher doses. Only three compounds, iohexal, meprobamate and TCEP were found to have a lower percent removal at a higher applied ozone dose. The percent removal of iohexal by the BAF varies greatly from -64%, 71%, and 42% removal at applied ozone doses of 2, 4, and 8 mg/L respectively. The ozone only percent removals were -21%, 46%, and 42% for applied ozone doses of 2, 4, and 8 mg/L respectively. The percent removal for iohexal, as well as the concentrations detected at each applied ozone dose, is shown in Table 4-12. This inconsistency for iohexal was also observed in the duplicate samples taken during the 4 mg/L ozone dose tests. The difference/mean values for iohexal were 64, 56, and 176% in the MBR, ozone, and BAF effluents respectively. These poor duplicate results show that the iohexal data may not be as reliable as the other compounds and that there might be another for the observed reverse in removal with increased applied ozone dose.

Iohexal is an iodinated X-ray contrast media (ICM). The literature has shown that ICM's are particularly resistant to oxidation degradation [46, 52, 53] although the amount of degradation varies depending on the compound. Iohexal has been shown to be particularly resilient to oxidation by ozone. A recent article by Bahr et al. (2007) reported a 35 percent removal for iohexal at an ozone dose of 1 mg O_3/mg DOC_0 [46]. This is equivalent to the 4 mg/L ozone dose used in this research which showed similar removal efficiencies for iohexal.

Table 4-12: Concentrations and percent removal for ozonation and ozonation-BAF for the compounds iohexal, meprobamate, and TCEP

Ozone dose	MBR effluent, mg/L	Ozone effluent, mg/L	BAF effluent, mg/L	Percent removal ozone only	Percent removal in BAF
Iohexal results					
2 mg/L	140	170	230	-21	-64
4 mg/L (average)	560	305	160	46	71
8 mg/L	590	340	340	42	42
Meprobamate results					
2 mg/L	390	260	270	33	31
4 mg/L (average)	395	77.5	82.5	80	79
8 mg/L	380	77	94	80	75
TCEP results					
2 mg/L	200	180	160	10	20
4 mg/L (average)	120	69	60.5	43	50
8 mg/L	41	94	82	-129	-100

Unlike iohexal, meprobamate had much more consistent data. The percent removal for meprobamate in the BAF column was 31%, 79%, and 75% for applied ozone doses of 2, 4, and 8 mg/L respectively. The ozone only results are similar with percent removals of 33%, 80%, and 80% for ozone doses of 2, 4, and 8 mg/L respectively. The percent removal for meprobamate, as well as the concentrations detected at each applied ozone dose, is shown in Table 4-12. Even though the 8 mg/L ozone dose had a slightly lower percent removal than the 4 mg/L in both the BAF and ozone only results, the difference is small enough to assume that no additional removal was achieved at an ozone dose of 8 mg/L. The reported result of decreased removal at higher ozone dose can be assumed to be due to variability in the analyzer. The removal efficiency between the ozone only and BAF column results are also close enough to assume no additional removal occurs in the BAF column.

The last compound that showed lower removal at higher applied ozone doses was TCEP. TCEP removal in the BAF column was 20%, 50%, and -100% at ozone doses of 2, 4, and 8 mg/L respectively, as shown in Table 4-12. The ozone only results were

similar with percent removals of 10%, 43%, and -129% for ozone doses of 2, 4, and 8 mg/L. At applied ozone doses of 2 and 4 mg/L, there is slightly higher removal achieved after the BAF process. There is also increased removal between the ozone doses of 2 and 4 mg/L. This follows the expected trend of increased compound removal with increasing ozone dose. At an ozone dose of 8 mg/L though, the percent in removal does not increase but drastically decreases and shows a large negative percent removal. It is noted in Table 4-12 that the TECP concentration in the MBR effluent during the 8 mg/L dose test was lower than all other results. This value may have been a bad analytical result and may have contributed to the strange results. A study done by Snyder et al. (2006) showed TCEP to be extremely resistant to oxidation even at higher ozone doses [43]. The results also showed inconsistent removal between applied ozone doses, similar to what is seen in this research.

The results have shown slight differences in PPCP removal achieved by the ozone and BAF processes. As discussed earlier in the Phase 2 bulk organic analysis, the BAF column is not expected to achieve additional removal of recalcitrant compounds beyond that achieved by ozonation. The next section will further examine the effectiveness of the BAF column in removing PPCPs/EDCs from wastewater.

Effectiveness of BAF Process in Removing Microconstituents

One of the main purposes of this research is to investigate the removal of microconstituents by both the ozone and BAF processes. The effectiveness of the BAF process can be seen by examining the percent removal of compounds by each process as illustrated in Table 4-11. Many of the compounds have similar percent removals between the ozone only and BAF processes. A majority of the compounds in all sampling events are either removed completely by the ozone and BAF processes, or have removal differences of <1%, although there are some compounds with larger differences, especially in the 2 mg/L sampling event.

The results of the previous section show that compounds are being partially oxidized in the ozone contact chamber at all ozone doses examined. To further analyze the effectiveness of the BAF process in removing microconstituents from wastewater, the percent removal of compounds from the ozone to BAF process can be examined. A summary of percent removals for 20 microconstituents between the ozone and BAF processes is presented in Table 4-13. The other 24 compounds were not listed because they were either not found, or were removed to below detectable limits in all three sampling events. The data from Table 4-13 is plotted in Figure 4-45 to further illustrate the amount of removal from the ozone to BAF process.

The data in Table 4-13 and Figure 4-45 illustrate the large range of both positive and negative compound percent removals from the ozone to BAF processes. The negative percent removal values show that the concentration of a compound is higher in the BAF effluent than the ozone effluent. Out of the 20 compounds shown in Table 4-13, 10 have a negative compound percent removal from ozone to BAF in the 2 mg/L sampling event, 8 are negative in the 4 mg/L sampling event, and only one compound has a negative percent removal in the 8 mg/L sampling event.

Table 4-13: Summary of percent compound removal from ozone to BAF processes

Analyte	2 mg/L	4 mg/L	8 mg/L
	Percent removal Ozone-BAF	**Percent removal Ozone-BAF**	**Percent removal Ozone-BAF**
Amoxicillin	12	**BDL**	**BDL**
Atenolol	18	-48	**BDL**
Butalbital	9	**BDL**	**BDL**
Caffeine	-29	**BDL**(2)	**BDL**
Carbamazepine	-35	**BDL**	**BDL**
Carisoprodol	25	-7	**BDL**
Cotinine	**BDL**(1)	4	**BDL**
DACT	-11	5(3)	**BDL**(3)
DEET	0	-6	**BDL**
Dehydronifedipine	19	-36(3)	**BDL**
Dilantin	-4	3	**BDL**
Iopromide	8	-37	36
Ketoprofen	-2	**BDL**	**BDL**(1)
Lidocaine	-62	**BDL**	**BDL**
Meprobamate	-4	-6	-22
Primidone	-9	-18	8
Sucralose	6	-17	0
Sulfamethoxazole	36	0	**BDL**
Theobromine	-32	**BDL**(2)	**BDL**
Diuron	-10	**BDL**	**BDL**

BDL = Below detectable limits

(1) = Not detected during sampling event in any process

(2) = Only detected in MBR and BAF effluent

(3) = Not detected in MBR effluent

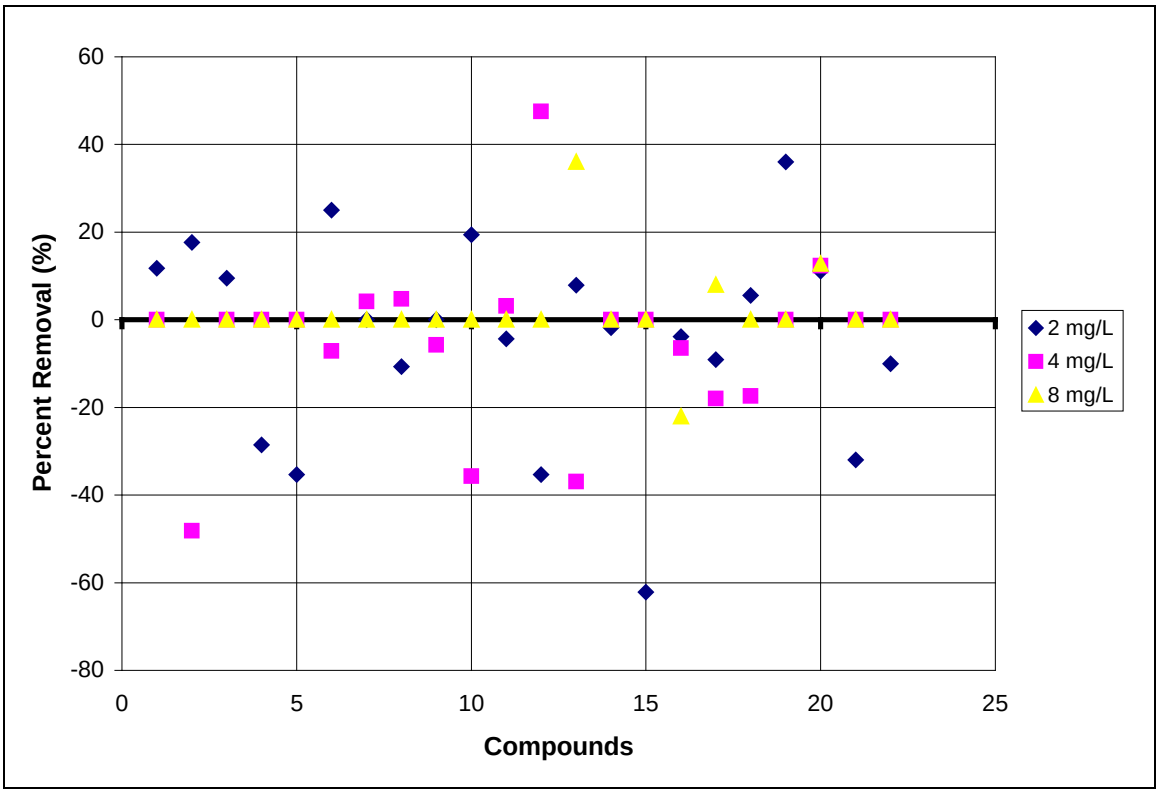

Figure 4-45: Percent removal of compounds from ozone to BAF processes for 2, 4, and 8 mg/L ozone doses

The difference in PPCP removal between the ozone only and BAF column is small, as seen in Table 4-11. As mentioned earlier, many compounds show less than a 1% difference between the two processes, although there are a few compounds with higher differences. Even though there is only a small difference in percent removals between ozone only and BAF column measurements for most of the compounds, the removal from ozone to BAF shows much larger differences, which can be misleading. A large percent removal from ozone to BAF leads to the assumption that there is a large difference in percent removals from the ozone only and BAF column. This is not the case though. For example, the percent removals for ozone only and the BAF column for the compound atenolol is 98.2% and 97.4% respectively for the 4 mg/L sampling event as shown in Table 4-14. This is a difference of 0.8%. The percent removal for this

compound from the ozone to BAF process is -48.2% for the same sampling event. The large percent removal of atenolol from the ozone to BAF is misleading because the concentration of atenolol in the ozone and BAF effluents is almost the same. Due to the small difference in compound removal between the ozone and BAF for almost all the compounds detected, the assumption is made that there is little additional removal of non-ozonated, recalcitrant compounds in the BAF column. This is also seen when examining the bulk organic analysis in Phase 2. The results of the TOC, TOC/TOC_0, UV_{254} absorbance, SUVA, and BDOC values show that there is little to no additional removal of recalcitrant organics in the BAF column.

Table 4-14: Percent removal of atenolol in BAF, ozone only, and from ozone to BAF column

Analyte	4 mg/L results		
	Percent removal in BAF	Percent removal ozone only	Percent removal Ozone-BAF
Atenolol	97.4	98.2	-48.1

Even with the wide range of both positive and negative percent removal values, the average percent removal from the ozone to BAF processes at 2, 4, and 8 mg/L was -4.3%, -7.4%, and 5.8% respectively. The average percent removal for all compounds between the ozone and BAF processes over all three sampling events was -3.9%. Because the percent removal from ozone to BAF averaged out to be close to zero, and because the actual differences in concentrations between the two processes are extremely close, and the detection levels are so small, the percent difference is assumed to be due to variability in the analysis.

It is also assumed that there is little to no removal of un-oxidized, recalcitrant compounds in the BAF process. Because the compounds have already been through a biological process in the MBR, most of the remaining organics are assumed non-

biodegradable. To make them more biodegradable, ozone is used, which breaks the compound down to a more biodegradable form. The ozonation process is essential in oxidizing recalcitrant compounds into smaller more biodegradable forms that can then be removed through biodegradation in the BAF column. Even though the initial, recalcitrant compounds are not removed by the BAF column, the bulk organic analysis shows that the compounds are not completely mineralized by ozone either. Instead, they are broken down into smaller more biodegradable compounds by the ozone, and then removed by the BAF column. It is only through a combination of both processes that removal of organics is attained.

Due to the observation that little to no additional removal of recalcitrant compounds is occurring in the BAF column, and because the concentrations of compounds detected in the ozone effluent are similar to what is being detected in the BAF effluent, the following sections will only focus on the removal of compounds between the MBR and BAF column.

PPCP/EDC Removal at 2, 4, and 8 mg/L Ozone Doses

Of the 52 compounds detected in the MBR effluents for the 4 sampling events, 11 were found in only one sampling event, as shown in Table 4-15. Four of these compounds were only detected in the 8/19/09 MBR effluent sample and not during the Phase 2 experiments. Additionally, the results for 2 compounds (4 nonylphenol and propylparaben) were discarded due to the results from the field blank. Of the remaining 46 compounds detected and examined for percent removal, 10 compounds were removed to BDL at an applied ozone dose of 2 mg/L. An additional 10 compounds, not detected in the 2 mg/L sampling event, were removed to BDL at 4 mg/L. One additional compound was removed to BDL that was not found in either the 2 or 4 mg/L samples. The removal of PPCPs/EDCs at the various ozone doses will be examined in the next section.

Table 4-15: Compounds only detected in one sampling event

Analyte	Sample ID	Result
BPA	8/19/09 MBR Effluent	25
DEA	8/19/09 MBR Effluent	5.7
Lincomycin	8/19/09 MBR Effluent	16
Pentoxifylline	8/19/09 MBR Effluent	5.2
4-tert-Octylphenol	MBR Effluent 2 mg/L	13
Erythromycin	MBR Effluent 4 mg/L	18.5
Oxolinic acid	MBR Effluent 4 mg/L	23
Sulfamethazine	MBR Effluent 4 mg/L	5.1
Atrazine	MBR Effluent 4 mg/L	43
Linuron	MBR Effluent 4 mg/L	5
Warfarin	MBR Effluent 8 mg/L	7

PPCP/EDC Removal at 2 mg/L Ozone dose

A total of 36 compounds were detected during the 2 mg/L ozone dose sampling event collected on November 13th, 2009. One of the compounds detected was 4-nonylphenol. The results for this compound were discarded because of its detection in the field blank as described earlier. The remaining 35 compounds, their concentrations in the MBR, ozone, and BAF effluents, and their percent removal in the BAF is shown in Table 4-16. Meclofenamic acid was the only compound not detected in the MBR effluent during this sampling event. The compound was only detected in the BAF effluent at a concentration of 7.4 ng/L, which is close to the detection limit of 5 ng/L. Because meclofenamic acid was not detected in the MBR effluent, the percent removal between the MBR and BAF cannot be determined for this compound.

Four compounds, meclofenamic acid, Sulfathiazole, naproxen, and carbadox, were detected in the BAF effluent and not the ozone effluent. As discussed earlier, meclofenamic acid was only detected in the BAF effluent at a concentration close to the detection limit. The other three compounds were also detected at concentrations close to their detection limit. Both sulfathiazole and carbadox have detection limits of 5 ng/L and were detected in the BAF effluent at concentrations of 6.3 and 22 ng/L respectively. The

concentration of naproxen in the BAF effluent was 10 ng/L, which is also its detection limit. This will be further examined later.

The percent removal in the BAF column of the remaining 34 compounds for the 2 mg/L ozone dose sampling event is shown in Table 4-16. A total of 10 compounds were removed to below detectable limits at an ozone dose of 2 mg/L. An additional 2 compounds had ≥ 90% removal, 2 had 70-90% removal, and 2 compounds had 50-70% removal. A chart of percent removal can better illustrate the amount of compound removal at the 2 mg/L ozone dose. The percent removal of 23 compounds is shown in Figure 4-46. The chart does not include the 10 compounds removed to below detectable limits, as well as the results for iohexal, which had a negative percent removal.

Table 4-16: Concentrations of compounds detected in MBR, ozone and BAF effluents during 2 mg/L sampling event as well as percent removal by BAF column

Analyte	MBR effluent, ng/L	Ozone effluent, ng/L	BAF effluent, ng/L	Percent removal in BAF
1,7-Dimethylxanthine	21	**BDL**	**BDL**	**BDL**
4-tert-Octylphenol	13	**BDL**	**BDL**	**BDL**
Acetaminophen	18	**BDL**	**BDL**	**BDL**
Amoxicillin	580	34	30	95%
Atenolol	240	170	140	42%
Butalbital	25	7.4	6.7	73%
Caffeine	140	63	81	42%
Carbadox	27	**BDL**	22	19%
Carbamazepine	450	17	23	95%
Carisoprodol	46	48	36	22%
Cimetidine	100	**BDL**	**BDL**	**BDL**
DACT	6.8	5.6	6.2	9%
DEET	13	12	12	8%
Dehydronifedipine	6.4	6.7	5.4	16%
Dilantin	320	230	240	25%
Furosimide	87	**BDL**	**BDL**	**BDL**
Gemfibrozil	9.3	**BDL**	**BDL**	**BDL**
Iohexal	140	170	230	-64%
Iopromide	4100	3800	3500	15%
Ketoprofen	62	55	56	10%
Lidocaine	300	74	120	60%
Meclofenamic Acid	**BDL**(1)	**BDL**(1)	7.4	**BDL**(1)
Meprobamate	390	260	270	31%
Naproxen	68	**BDL**	10	85%
Primidone	200	110	120	40%
Sucralose	34000	36000	34000	0%
Sulfadiazine	19	**BDL**	**BDL**	**BDL**
Sulfamethoxazole	470	250	160	66%
Sulfathiazole	9.2	**BDL**	6.3	32%
TCEP	200	180	160	20%
Theobromine	36	25	33	8%
Theophylline	40	**BDL**	**BDL**	**BDL**
Triclosan	14	**BDL**	**BDL**	**BDL**
Bromacil	5.6	**BDL**	**BDL**	**BDL**
Diuron	15	10	11	27%

BDL = Below detectable limits

(1) = Compound not detected in MBR effluent

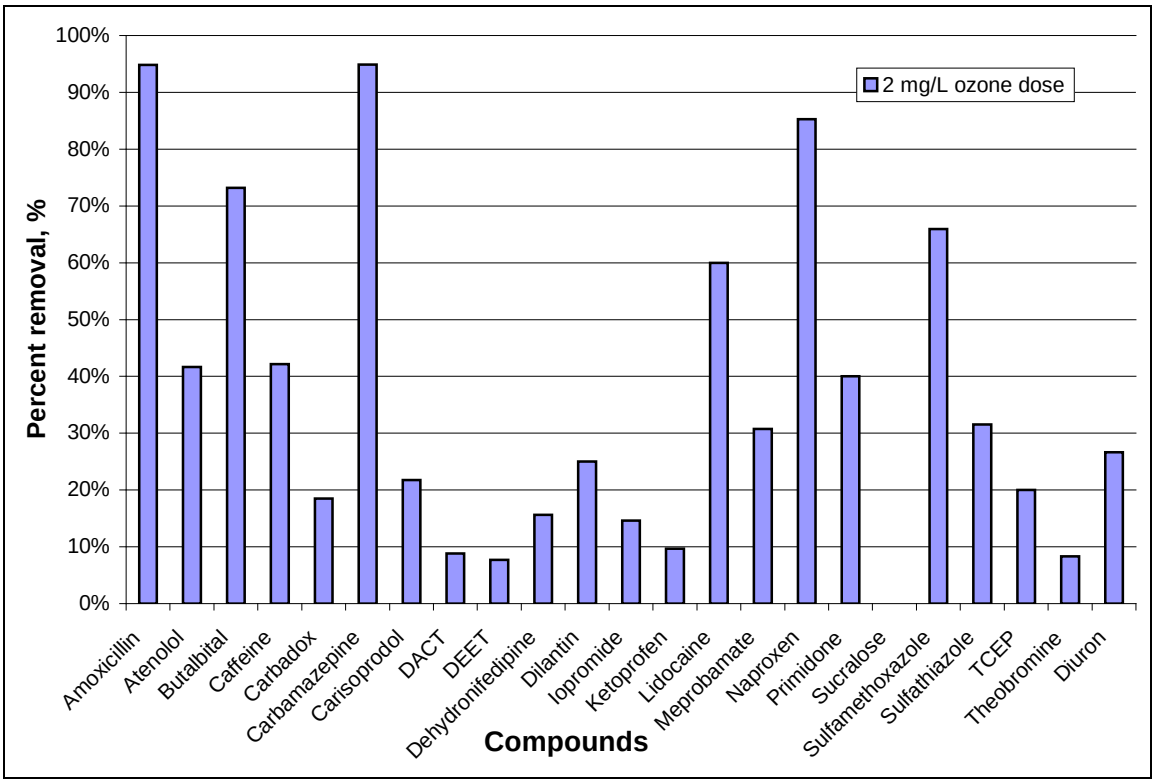

Figure 4-46: Percent removal in BAF column of selected compounds at an ozone dose of 2 mg/L

Although many compounds achieved a high level of removal at the 2 mg/L ozone dose, 18 of the 34 compounds examined did not achieve removal of ≥ 50%. The data clearly shows that most compounds are being removed or partially removed at the lowest applied ozone dose. From these results and the bulk organic analysis, it is expected that higher compound removals will be achieved with increased ozone dose. Further comparison of compound removal between applied ozone doses will be examined later.

PPCP/EDC Removal at 4 mg/L Ozone Dose

A total of 44 compounds were detected in 4 mg/L ozone dose sampling event collected on November 6th, 2009. Duplicate samples of the MBR, ozone, and BAF effluents were collected for this sampling event as described earlier. One of the compounds detected was 4-nonylphenol. The results for this compound were discarded due to their detection in the field blank as explained earlier. The remaining 43 compounds, their average concentrations detected in the MBR, ozone, and BAF effluents, and their average percent removal in the BAF is shown in Table 4-17. The compounds DACT and dehydronifedipine were not detected in the MBR effluent during this sampling event, but instead were found in both the primary and duplicate samples in both the ozone and BAF effluents. The average concentrations of these compounds were all close to the detection limits of 5 ng/L. The compound dehydronifedipine had the largest average concentration at 19 ng/L. The percent removals for these compounds could not be determined because they were not detected in the MBR effluent.

Two compounds, theobromine and caffeine, were detected in the BAF effluent and not the ozone effluent. Both compounds had average concentrations close to their detection limits. Theobromine had an average BAF concentration of 8.6 ng/L and has a detection limit of 5 ng/L. Caffeine had an average BAF concentration of 19.5 ng/L and has a detection limit of 10 ng/L. Compounds not detected in earlier processes but that are detected in low levels later in the treatment train will be discussed later.

Table 4-17: Concentrations of compounds detected in MBR, ozone and BAF effluents during 4 mg/L sampling event as well as percent removal by BAF column

Analyte	MBR effluent, ng/L	Ozone effluent, ng/L	BAF effluent, ng/L	Percent removal in BAF
1,7-Dimethylxanthine	46	**BDL**	**BDL**	**BDL**
Acetaminophen	62.5	**BDL**	**BDL**	**BDL**
Albuterol	6.2	**BDL**	**BDL**	**BDL**
Amoxicillin	485	**BDL**	**BDL**	**BDL**
Atenolol	380	6.75	10	97%
Butalbital	34	**BDL**	**BDL**	**BDL**
Caffeine	300	**BDL**	19.5	94%
Carbadox	6.05	**BDL**	**BDL**	**BDL**
Carbamazepine	410	**BDL**	**BDL**	**BDL**
Carisoprodol	48.5	14	15	69%
Cimetidine	100.5	**BDL**	**BDL**	**BDL**
Cotinine	32.5	12	11.5	65%
DACT	**BDL**(1)	11.5	10.95	**BDL**(1)
DEET	39	5.2	5.5	86%
Dehydronifedipine	**BDL**(1)	14	19	**BDL**(1)
Dilantin	350	94.5	91.5	74%
Erythromycin	18.5	**BDL**	**BDL**	**BDL**
Furosimide	150	**BDL**	**BDL**	**BDL**
Gemfibrozil	43	**BDL**	**BDL**	**BDL**
Iohexal	560	305	160	71%
Iopromide	5300	2300	3150	41%
Ketoprofen	6.9	**BDL**	**BDL**	**BDL**
Ketorolac	7.25	**BDL**	**BDL**	**BDL**
Lidocaine	335	**BDL**	**BDL**	**BDL**
Lopressor	160	**BDL**	**BDL**	**BDL**
Meclofenamic Acid	37.5	**BDL**	**BDL**	**BDL**
Meprobamate	395	77.5	82.5	79%
Naproxen	160	**BDL**	**BDL**	**BDL**
Oxolinic acid	23	**BDL**	**BDL**	**BDL**
Primidone	120	39	46	62%
Sucralose	43000	23000	27000	37%
Sulfadiazine	9.15	**BDL**	**BDL**	**BDL**
Sulfamethazine	5.1	**BDL**	**BDL**	**BDL**
Sulfamethoxazole	1040	12.5	12.5	99%
Sulfathiazole	5.8	**BDL**	**BDL**	**BDL**
TCEP	120	69	60.5	50%
Theobromine	62.5	**BDL**	8.6	86%
Theophylline	98	**BDL**	**BDL**	**BDL**
Triclosan	14	**BDL**	**BDL**	**BDL**
Trimethoprim	79.5	**BDL**	**BDL**	**BDL**
Atrazine	43	**BDL**	**BDL**	**BDL**
Diuron	24.5	**BDL**	**BDL**	**BDL**
Linuron	5	**BDL**	**BDL**	**BDL**

BDL = Below detectable limits
(1) = Compound not detected in MBR effluent

The removal in the BAF column of the remaining 41 compounds for the 4 mg/L ozone dose sampling event is shown in Table 4-17. A total of 27 compounds were removed to below detectable limits at an ozone dose of 4 mg/L. An additional 3 compounds had ≥ 90% removal, 5 had 70-90% removal, and 4 compounds had 50-70% removal. Of the 41 compounds examined, only sucralose and iopromide were found to have percent removals of < 50%. A chart of the percent removal of 18 compounds at ozone doses of 4 and 8 mg/L is seen in Figure 4-47. This will be examined further in the next section.

As expected, the removal of compounds is much higher at the 4 mg/L ozone dose than the 2 mg/L ozone dose. The data shows that most compounds were removed to below detectable limits at the 4 mg/L ozone dose. Although it is expected that removal will increase even more at the 8 mg/L ozone dose, the effectiveness of the ozone is expected to decrease at the higher dose as shown by removal of TOC, SUVA, and UV_{254} absorbance discussed earlier. This will be further examined later.

PPCP/EDC Removal at 8 mg/L Ozone dose

A total of 37 compounds were detected during the 8 mg/L ozone dose sampling event collected on October 29th, 2009. The compounds 4-nonylphenol and propylparaben were detected in this sample. The results for these compounds were discarded due to their detection in the field blank, which is explained earlier. The remaining 35 compounds, their concentrations in the MBR, ozone, and BAF effluents, and their percent removal in the BAF is shown in Table 4-18. The compound DACT was the only compound in the sampling event that was not detected in the MBR effluent. DACT was only detected in the ozone effluent sample at a concentration of 5.3 ng/L, which is slightly higher than its detection limit of 5 ng/L. Because DACT was not detected in the MBR effluent, the percent removal between the MBR and BAF effluents cannot be determined.

Table 4-18: Concentrations of compounds detected in MBR, ozone and BAF effluents during 8 mg/L sampling event as well as percent removal by BAF column

Analyte	MBR effluent, ng/L	Ozone effluent, ng/L	BAF effluent, ng/L	Percent removal in BAF
1,7-Dimethylxanthine	29	**BDL**	**BDL**	**BDL**
Acetaminophen	88	**BDL**	**BDL**	**BDL**
Albuterol	15	**BDL**	**BDL**	**BDL**
Amoxicillin	1200	**BDL**	**BDL**	**BDL**
Atenolol	490	**BDL**	**BDL**	**BDL**
Butalbital	80	**BDL**	**BDL**	**BDL**
Caffeine	510	**BDL**	**BDL**	**BDL**
Carbamazepine	440	**BDL**	**BDL**	**BDL**
Carisoprodol	60	**BDL**	**BDL**	**BDL**
Cimetidine	110	**BDL**	**BDL**	**BDL**
Cotinine	20	**BDL**	**BDL**	**BDL**
DACT	**BDL**[(1)]	5.3	**BDL**[(1)]	**BDL**[(1)]
DEET	33	**BDL**	**BDL**	**BDL**
Dehydronifedipine	9.6	**BDL**	**BDL**	**BDL**
Dilantin	270	**BDL**	**BDL**	**BDL**
Furosimide	230	**BDL**	**BDL**	**BDL**
Gemfibrozil	85	**BDL**	**BDL**	**BDL**
Iohexal	590	340	340	42%
Iopromide	14000	2500	1600	89%
Ketorolac	11	**BDL**	**BDL**	**BDL**
Lidocaine	390	**BDL**	**BDL**	**BDL**
Lopressor	230	**BDL**	**BDL**	**BDL**
Meprobamate	380	77	94	75%
Naproxen	260	**BDL**	**BDL**	**BDL**
Primidone	120	10	9.2	92%
Sucralose	37000	16000	16000	57%
Sulfadiazine	16	**BDL**	**BDL**	**BDL**
Sulfamethoxazole	1600	**BDL**	**BDL**	**BDL**
TCEP	41	94	82	**-100%**
Theobromine	110	**BDL**	**BDL**	**BDL**
Theophylline	62	**BDL**	**BDL**	**BDL**
Trimethoprim	60	**BDL**	**BDL**	**BDL**
Warfarin	7	**BDL**	**BDL**	**BDL**
Bromacil	20	**BDL**	**BDL**	**BDL**
Diuron	23	**BDL**	**BDL**	**BDL**

BDL = Below detectable limits
(1) = Compound not detected in MBR effluent

Out of the 34 compounds examined for percent removal in the BAF column, 28 were removed to below detectable limits. One additional compound achieved ≥ 90% removal, 2 had 70-90% removal, and 1 compound achieved 50-70% removal at an ozone dose of 8 mg/L. Six compounds that did not achieve 100% removal in the BAF column at an ozone dose of 8 mg/L, and only 2 compounds did not achieve greater than 50% removal. The six compounds that did not achieve 100% removal were sucralose, meprobramate, primidone, iopromide, iohexal, and TCEP. Primidone was the only compound not removed to below detectable limits that was still removed to ≥ 90%. This compound continually showed increased removal with increased ozone dose. Primidone had a percent removal of 40%, 62%, and 92% at ozone doses of 2, 4, and 8 mg/L respectively. Iopromide also had increased removal with increased ozone and was removed at 15%, 41%, and 89% for ozone doses of 2, 4, and 8 mg/L respectively. The compound sucralose also had increased percent removal with increased ozone dose. At an ozone dose of 2 mg/L there was no removal observed. The percent removal increased to 37% and 57% at ozone doses of 4 mg/L and 8 mg/L. Meprobramate had increased percent removal between the ozone doses of 4 and 8 mg/L with 31% and 79% removal respectively. The percent removal slightly drops at the 8 mg/L ozone dose with 75% removal. As discussed earlier, because the difference in removal between the 4 and 8 mg/L ozone dose is so small, the assumption is made that there is no additional removal achieved at the 8 mg/L ozone dose for the compound meprobramate and that the removal is approximately the same at both ozone doses. The only two compounds that did not achieve greater than 50% removal were TCEP and iohexal. These two compounds were also the only compounds to have negative percent removals in the BAF column. The iohexal had a -64% removal at an ozone dose of 2 mg/L. The TCEP had a -100% removal in the BAF column at an ozone dose of 8 mg/L. As discussed earlier, the literature has shown these compounds to be extremely resistant to oxidation by ozone. Similar inconsistencies for TCEP were shown in an article by Snyder et al. (2006), which showed TCEP having lower percent removals at higher ozone doses [43], similar to what was observed in this research.

All compounds not detected in the MBR effluent and detected in another process, or not detected in the ozone effluent and found in the BAF effluent were all detected at levels close to the detection limit. This was found to be true for compounds in all sampling events. This leads to the conclusion that compounds not being detected in subsequent processes but detected later on in the treatment train is likely a result of analytical variability associated with measurement of constituents at ultra-low concentrations near their detection limits. The compound is most likely at concentrations just below detectable limits. Due to slight variations in the sampling process, and that these compounds are being detected at such low concentrations, there is expected to be some slight fluctuations in the concentrations of the compounds detected.

A chart of the percent removal of 18 compounds detected in the 4 and 8 mg/L ozone dose sampling events is shown in Figure 4-47. As discussed earlier the 8 mg/L results remove 28 out of 34 compounds to below detectable limits whereas the 4 mg/L results remove 27 out of 41 compounds to below detectable limits. Most of the compounds not removed to below detectable limits for both the 4 and 8 mg/L ozone doses are still removed to a relatively high degree as seen in Figure 4-47. As expected, the 8 mg/L ozone dose achieves a higher degree of removal compared to the 4 mg/L ozone dose. The effectiveness of the ozone at the various ozone doses will be explored further in the next section.

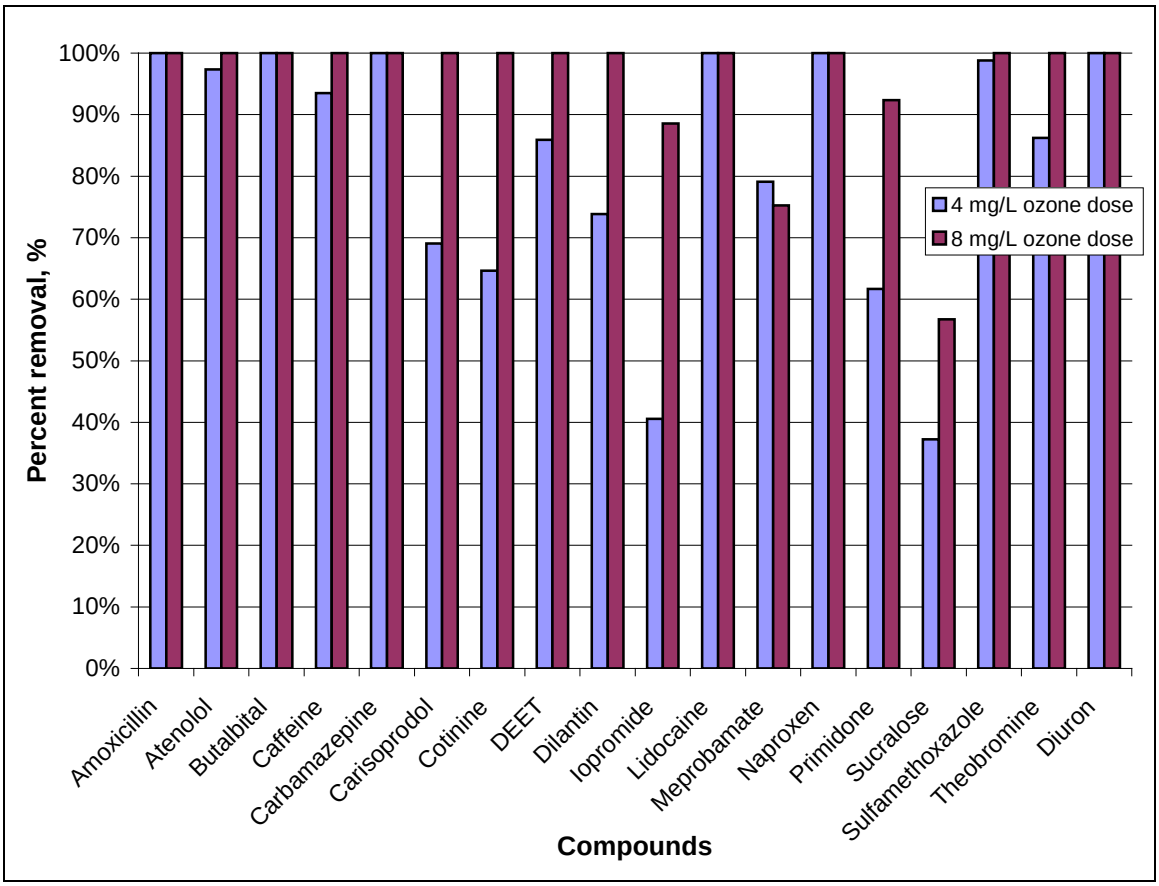

Figure 4-47: Percent removal in BAF column of selected compounds at ozone doses of 4 and 8 mg/L

Comparison of EDC/PPCP Removal Between Ozone Doses

The last section examined the removal of PPCPs/EDCs at the various ozone doses examined. This section will examine the efficiency of the ozone doses for PPCP/EDC removal. Similar to the last section, this section will only examine the compound removal in the BAF column since this is ultimately the final water produced by this combination of treatment processes.

Examination of the performance of the treatment processes at the various ozone doses examined can be done by grouping the compounds by removal efficiencies. A list of the number of compounds detected at the various ozone doses, as well as statistics for

the various degrees of compound removal are shown in Table 4-19. These statistics include compounds removed to below detectable limits, with >90%, >70%, and >50% removal.

Table 4-19: BAF column compound removal statistics at ozone doses of 2, 4, and 8 mg/L

Compound removal statistics	2 mg/L ozone dose	4 mg/L ozone dose	8 mg/L ozone dose
Number of compounds detected	36	44	37
Number of compounds compared for removal	34	41	34
Number of compounds removed to below detectable limits	10	27	28
Number of compounds with > 90% removal	12	30	29
Number of compounds with > 70% removal	14	35	31
Number of compounds with > 50% removal	16	39	32
Percent of compounds removed to below detectable limit	29%	66%	82%
Percent of compounds with ≥ 90% removal	35%	73%	85%
Percent of compounds with ≥ 70% removal	41%	85%	91%
Percent of compounds with ≥ 50% removal	47%	95%	94%

Some of the compounds detected at each ozone dose were not included in these statistics. The 2, 4, and 8 mg/L sampling events initially detected 36, 44, and 37 compounds respectively as seen in Table 4-19. As discussed earlier, the results for the compounds 4-nonylphenol and propylparaben were discarded due to their detection in the field blank. The 2, 4, and 8 mg/L sampling events all detected 4-nonylphenol in the MBR effluent. The 8 mg/L results also detected propylparaben in the field blank. As discussed earlier, each sampling event also had compounds that were detected in the BAF

or ozone effluent but not in the MBR effluent. Because these compounds were not detected in the MBR effluent, a percent removal cannot be calculated. The 2, 4, and 8 mg/L sampling events had 1, 2, and 1 compound(s) respectively that were discarded for this reason. This leaves a total of 34, 41, and 34 compounds at ozone doses of 2, 4, and 8 mg/L respectively that were used to calculate percent removal as presented in Table 4-19.

The statistics in Table 4-19 show that 29% of the compounds detected and compared for removal at the 2 mg/L ozone dose are removed to below detectable limits. The percentage of compounds removed to below detectable limits sharply increases to 66% at the 4 mg/L ozone dose. As expected, the number of compounds removed to below detectable limits increases at the 8 mg/L ozone dose to 82%. The difference in removal between the 4 and 8 mg/L ozone doses is 16%, which is much lower than the 37% difference between the 2 and 4 mg/L ozone doses.

At an ozone dose of 2 mg/L, 35% of compounds achieved ≥ 90% removal. This value more than doubles at the 4 mg/L ozone dose with 73% of compounds being removed to ≥ 90%. This is a 38% difference between the 2 and 4 mg/L ozone doses. At 8 mg/L, 85% of compounds had ≥ 90 % removal. This is an increase of only 12% over the 4 mg/L removal.

At an ozone dose of 2 mg/L, 41% of compounds achieved ≥ 70% removal. The 4 mg/L ozone dose had 85% of compounds with ≥ 70% removal, which is 44% higher than the 2 mg/L results. The 8 mg/L ozone dose results had 91% of the compounds removed to ≥ 70%, which is only a 6% difference over the 4 mg/L ozone dose. This trend continues for percentage of compounds that achieved ≥ 50% removal. The 2, 4, and 8 mg/L ozone doses had 47, 95, and 94% of their compounds achieve ≥ 50% removal. Again, the difference between the 2 and 4 mg/L ozone doses is more than double, while the 4 mg/L ozone dose actually has a higher percentage of compounds removed to ≥ 50% than the 8 mg/L ozone dose.

The removal statistics presented in Table 4-19 shows that compounds are removed to a higher degree with increasing ozone dose. These values also show that although more compound removal is achieved at higher ozone doses, the number of compounds that are completely removed doesn't linearly increase with increasing ozone dose. The amount of compounds removed greatly increases from ozone doses of 2 to 4 mg/L. At an ozone dose of 8 mg/L only slightly greater compound removal is achieved, even though the ozone dose has doubled. This was also seen in the bulk organic analysis, which saw a large increase in organic removal between the 2 and 4 mg/L ozone dose, with only slight increases at the 8 mg/L ozone dose.

Examining the change in percent removals between the ozone doses can be used to better examine how efficient the ozone doses are in removing PPCPs/EDCs. The data presented in Figure 4-48 shows the difference in percent removals between applied ozone doses for 20 compounds. The compounds examined were all detected in the 2 and 4 mg/L ozone dose sampling events. Three of the compounds (carbadox, ketoprofen, and Sulfathiazole) were not detected in the 8 mg/L sampling event but were removed to below detectable limits in the 4 mg/L sampling event. The data presented in Figure 4-48 illustrates that there is little additional removal achieved from 4 to 8 mg/L. Only two compounds, iopromide and primidone at 48.0 and 30.7 percent removal respectively, saw greater removal going from 4 to 8 mg/L than from 2 to 4 mg/L. Eight compounds saw >50% removal increases going from 2 to 4 mg/L with 5 of those achieving > 70%. This figure further illustrates the effectiveness of ozone at 4 mg/L to remove PPCPs/EDCs, and that doubling the ozone dose to 8 mg/L only slightly increase compound removal.

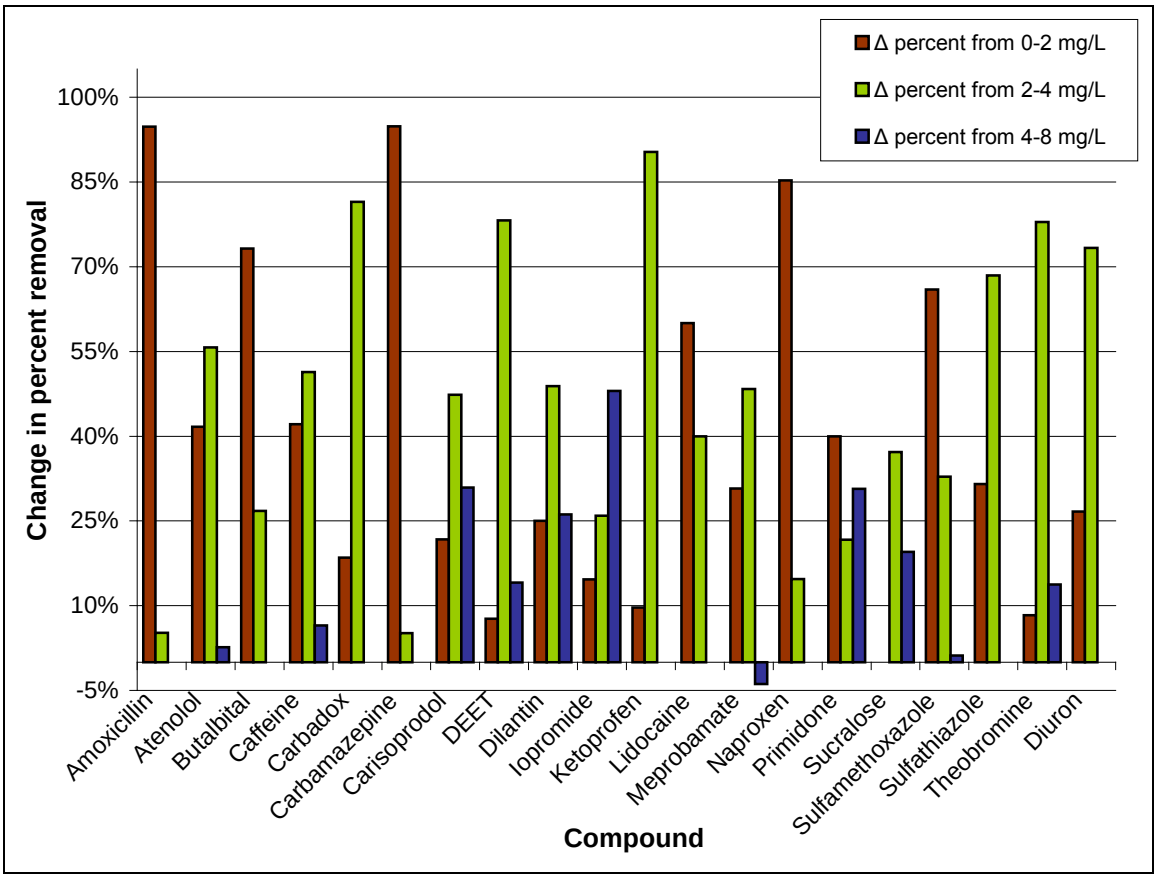

Figure 4-48: Change in compound percent removal between different applied ozone doses for MBR-BAF

The percent removal increased with applied ozone dose for almost all compounds detected and compared. As discussed earlier, only three compounds did not follow the pattern of increasing percent removal with increased ozone dose. The percent removal for the compound meprobamate was slightly lower at the 8 mg/L ozone dose than at the 4 mg/L dose. The conclusion was that the percent removal was close enough between the 4 and 8 mg/L ozone dose to assume no additional removal achieved at the 8 mg/L ozone dose.

Three compounds (meclofenamic acid, DACT, and dehydronifedipine) were detected in the ozone or BAF effluent and not the MBR effluent during one of more sampling events. These compounds were also detected in the MBR effluent for at least one of the sampling events. Meclofenamic acid was found in the BAF effluent at a concentration of 7.4 ng/L, and not the MBR or ozone effluents during the 2 mg/L sampling event. The detection limit for meclofenamic acid is 5 ng/L. It is assumed that the lack of detection of this compound in the MBR effluent is because the compound is present at levels just below the detection limit.

The compounds DACT and dehydronifedipine were detected in the ozone and BAF effluents and not in the MBR effluent during the 4 mg/L sampling event. DACT was found in the ozone and BAF effluents at concentrations of 11.5 and 10.95 ng/L respectively. Dehydronifedipine was found in the ozone and BAF effluents at concentrations of 14 and 19 ng/L respectively. DACT was also detected in the ozone effluent at a concentration of 5.3 ng/L during the 8 mg/L sampling event and not in the MBR or BAF effluents. Dehydronifedipine was only detected in the MBR effluent at a concentration of 9.6 ng/L during the 8 mg/L sampling event. Both compounds were found in all process effluents during the 2 mg/L sampling event. DACT was detected in concentrations of 6.8, 5.6, and 6.2 in the MBR, ozone, and BAF effluents respectively. Dehydronifedipine was detected in concentrations of 6.4, 6.7, and 5.4 ng/L in the MBR, ozone, and BAF effluents respectively. The compounds DACT, and dehydronifedipine were detected at levels close their detection limits (5 ng/L) in all sampling events. This leads to the conclusion that the lack of detection of these two compounds is due to the concentrations in which they are present in the wastewater. It is assumed that the concentrations at which these compounds are present in the wastewater is just below the detectable limits. The lack of detection in the MBR effluent during some of the sampling events, as well as the low levels at which these compounds are detected at, makes it hard to draw a conclusion about the effectiveness of ozone in removing these compounds.

The Phase 2 results have shown increased PPCP/EDC removal with increased applied ozone doses. The data has also shown that compound removal is not linear to ozone dose. Although more compounds are removed to a higher degree at an ozone dose of 8 mg/L, the 4 mg/L dose achieves much larger differences in percent removal. This is seen in both the PPCP/EDC data, as well as in the bulk organic analysis. The data has also shown that the BAF column achieves little to no additional removal of recalcitrant compounds.

Using lower ozone doses can be beneficial in several ways. First, creating ozone is an energy intensive process, which can be very expensive. The 8 mg/L ozone dose would actually need more than twice as much ozone than the 4 mg/L ozone dose because the transfer efficiency is lower at the 8 mg/L ozone dose. This is seen in Figure 4-19. The average transfer efficiency observed in this research was 82.3% for the 8 mg/L ozone dose compared to 88.2% 4 mg/L ozone dose. The higher the ozone dose, the larger the operating costs. Operating at an applied ozone dose of 4 mg/L instead of 8 mg/L can greatly reduce the operating costs. Another benefit of using a lower ozone dose would be that less ozonation by-products would be created. This is especially important in Bromide rich waters.

The amount of compound removal desired, as well as the type of compounds removed at the various ozone doses would better dictate the ozone dose used. For example if a compound is known to be toxic at the levels found in the BAF effluent at the 4 mg/L ozone dose, then an increased ozone dose might be desired if this increased ozone dose was shown to remove this compound to acceptable levels. Other factors, such as bromide concentrations in the feedwater, should also be considered when selecting which applied ozone dose to use.

Compounds Not Easily Oxidized by Ozone

Although a majority of PPCPs were removed to below detectable limits at applied ozone doses of 4 and 8 mg/L, there were still some compounds that were particularly

resistant to oxidation by ozone, even at the 8 mg/L ozone dose. A total of 14 compounds were detected in the BAF effluent at the 4 mg/L ozone dose and 6 compounds detected in the BAF effluent at the 8 mg/L ozone dose. The six compounds detected in the BAF effluent at an ozone dose of 8 mg/L were iohexal, iopromide, meprobamate, primidone, Sucralose, and TCEP. All of these compounds, with the exception of sucralose, have been shown to be extremely resistant to oxidation by ozone [43, 46]. Sucralose was also the most prevalent compound detected with MBR effluent concentrations in the tens of thousands of ng/L. This was an order of magnitude higher than any other compound detected and several orders of magnitude higher than most of the other compounds detected during sampling. As mentioned earlier, the fraction of organics in the MBR effluent that consisted of PPCPs was approximately 1% with most of that consisting of sucralose. Because sucralose is being detected at these high concentrations and is not easily oxidized, this might make it a good candidate as an indicator compound. If sucralose is determined to be present in wastewater at these high concentrations, then a less intensive method of determining its concentration could be developed. Current analytical techniques are able to detect this compound in wastewater in the ng/L range. This process is expensive though. If sucralose is prevalent in wastewater at concentrations in the μg/L range, then a procedure could developed that would be less intensive and costly. This research has shown that although sucralose is extremely resistant to oxidation by ozone, the compound does show increased removal with increased ozone dose. More research would be needed though to determine a correlation between ozone dose and the removal of sucralose, as well as guidelines established to determine a relationship between the amount of sucralose removed and acceptable levels of water treatment.

RO Performance for removing PPCPs/EDCs

An RO unit was used to treat MBR effluent during the 2 and 4 mg/L sampling events. The unit was run in parallel to the ozone and BAF processes. The same MBR effluent water that was used in the ozone and BAF processes was also used to feed the

RO process as described in the experimental methods section. This was done to compare the ozone and BAF treatment train with a process that the literature has shown can remove microconstituents to a very high degree.

As expected, the RO process removed all compounds well with most being removed to below detectable limits. A list of the compounds detected in the RO effluent and their percent removal is presented in Table 4-20. The 2 mg/L sampling event detected a total of 36 compounds with 34 of these being compared for removal. The results for the compounds 4-nonylphenol and propylparaben were discarded due to their detection in the field blank. Removal was not calculated for compounds not detected in the MBR effluent. The RO process removed 32 of these compounds to below detectable limits with the other two removed to greater than 98.7%. The 4 mg/L sampling event detected a total of 44 compounds and examined the percent removal of 41 compounds. The RO process removed 36 compounds to below detectable limits. The remaining 5 compounds were removed to greater than 97.6% as shown in Table 4-20.

Table 4-20: Removal efficiencies of PPCPs from MBR effluent by the RO process

Analyte	Sample during 2 mg/L ozone test	Sample during 4 mg/L ozone test
Atenolol	ND	98.2
Carbamazepine	98.7	97.6
Iopromide	ND	99.1
Meprobamate	ND	98.6
Sucralose	99.6	99.2
Sulfamethoxazole	ND	98.6

ND = Not detected during sampling event

A more effective examination of the removal of PPCPs/EDCs by the RO process can be achieved by examining the initial concentration of the detected compounds in the

MBR effluent as shown in Table 4-21. The concentration of the compounds detected in the BAF effluent during the 2 mg/L sampling event, as well as the percent removal of the detected compounds in the BAF column and RO process is also shown in Table 4-21. A total of 14 compounds had MBR effluent concentrations of greater than 100 ng/L. Two of these compounds had MBR effluent concentrations of greater than 1,000 ng/L with one of those having an initial concentration of greater than 10,000 ng/L. Iopromide had an MBR effluent concentration of 4100 ng/L and was removed to below detectable limits by the RO process. Sucralose had an MBR effluent concentration of 34,000 ng/L and the RO process achieved nearly complete removal with 99.6% removal. The BAF column only achieved removals of 15% and 0% at the 2 mg/L ozone dose, 41% and 37% at an ozone dose of 4 mg/L, and 89% and 57% at an ozone dose of 8 mg/L for iopromide and sucralose respectively. This lack of removal by the BAF column at an ozone dose of 2 mg/L is also seen in the number of compounds removed to below detectable limits. The BAF column removed 10 of the 34 compounds to below detectable limits at an ozone dose of 2 mg/L, while the RO process removed 32 of the 34 compounds.

Table 4-21: Concentrations of compounds detected in MBR, BAF, and RO effluents during 2 mg/L sampling event as well as percent removal by BAF column and RO process

Analyte	MBR effluent, ng/L	BAF effluent, ng/L	RO effluent, ng/L	Percent removal in BAF	Percent removal in RO
1,7-Dimethylxanthine	21	**BDL**	**BDL**	**BDL**	**BDL**
4-tert-Octylphenol	13	**BDL**	**BDL**	**BDL**	**BDL**
Acetaminophen	18	**BDL**	**BDL**	**BDL**	**BDL**
Amoxicillin	580	30	**BDL**	94.8%	**BDL**
Atenolol	240	140	**BDL**	41.7%	**BDL**
Butalbital	25	6.7	**BDL**	73.2%	**BDL**
Caffeine	140	81	**BDL**	42.1%	**BDL**
Carbadox	27	22	**BDL**	18.5%	**BDL**
Carbamazepine	450	23	5.9	94.9%	98.7%
Carisoprodol	46	36	**BDL**	21.7%	**BDL**
Cimetidine	100	**BDL**	**BDL**	**BDL**	**BDL**
DACT	6.8	6.2	**BDL**	8.8%	**BDL**
DEET	13	12	**BDL**	7.7%	**BDL**
Dehydronifedipine	6.4	5.4	**BDL**	15.6%	**BDL**
Dilantin	320	240	**BDL**	25.0%	**BDL**
Furosimide	87	**BDL**	**BDL**	**BDL**	**BDL**
Gemfibrozil	9.3	**BDL**	**BDL**	**BDL**	**BDL**
Iohexal	140	230	**BDL**	-64.3%	**BDL**
Iopromide	4100	3500	**BDL**	14.6%	**BDL**
Ketoprofen	62	56	**BDL**	9.7%	**BDL**
Lidocaine	300	120	**BDL**	60.0%	**BDL**
Meclofenamic Acid	**BDL**[(1)]	7.4	**BDL**	**BDL**[(1)]	**BDL**
Meprobamate	390	270	**BDL**	30.8%	**BDL**
Naproxen	68	10	**BDL**	85.3%	**BDL**
Primidone	200	120	**BDL**	40.0%	**BDL**
Sucralose	34000	34000	150	0.0%	99.6%
Sulfadiazine	19	**BDL**	**BDL**	**BDL**	**BDL**
Sulfamethoxazole	470	160	**BDL**	66.0%	**BDL**
Sulfathiazole	9.2	6.3	**BDL**	31.5%	**BDL**
TCEP	200	160	**BDL**	20.0%	**BDL**
Theobromine	36	33	**BDL**	8.3%	**BDL**
Theophylline	40	**BDL**	**BDL**	**BDL**	**BDL**
Triclosan	14	**BDL**	**BDL**	**BDL**	**BDL**
Bromacil	5.6	**BDL**	**BDL**	**BDL**	**BDL**
Diuron	15	11	**BDL**	26.7%	**BDL**

BDL = Below detectable limits

(1) = Compound not detected in MBR effluent

The concentration of the compounds detected in the BAF effluent during the 4 mg/L sampling event, as well as the percent removal of the detected compounds in the BAF column and RO process is shown in Table 4-22. The RO process removed 35 of the 41 compounds detected in the MBR effluent during this sampling event, while the BAF column removed 27 compounds to below detectable limits. A total of 17 compounds had MBR effluent concentrations of greater than 100 ng/L during the 4 mg/L ozone dose sampling event. Similar to the 2 mg/L ozone dose sampling event results, the compounds iopromide and sucralose were found in high concentrations in the MBR effluent. These are two of only 5 compounds not removed to ≥ 90% by the BAF column during the 8 mg/L ozone dose sampling event and 2 of the 11 compounds not removed to ≥ 90% during the 4 mg/L ozone dose sampling event. Two other compounds, sulfamethoxazole and carbamazepine, achieved greater percent removals in the BAF than the RO at an ozone dose of 4 mg/L. Another compound, atenolol, also achieved similar removal during the 4 mg/L ozone dose.

Table 4-22: Concentrations of compounds detected in MBR, BAF, and RO effluents during 4 mg/L sampling event as well as percent removal by BAF column and RO process

Analyte	MBR effluent, ng/L	BAF effluent, ng/L	RO effluent, ng/L	Percent removal in BAF	Percent removal in RO
1,7-Dimethylxanthine	46	**BDL**	ND	**BDL**	**BDL**
Acetaminophen	62.5	**BDL**	ND	**BDL**	**BDL**
Albuterol	6.2	**BDL**	ND	**BDL**	**BDL**
Amoxicillin	485	**BDL**	ND	**BDL**	**BDL**
Atenolol	380	10	7	97.4%	98.2%
Butalbital	34	**BDL**	ND	**BDL**	**BDL**
Caffeine	300	19.5	ND	93.5%	**BDL**
Carbadox	6.05	**BDL**	ND	**BDL**	**BDL**
Carbamazepine	410	**BDL**	10	**BDL**	97.6%
Carisoprodol	48.5	15	ND	69.1%	**BDL**
Cimetidine	100.5	**BDL**	ND	**BDL**	**BDL**
Cotinine	32.5	11.5	ND	64.6%	**BDL**
DACT	**BDL**(1)	10.95	ND	**BDL**(1)	**BDL**(1)
DEET	39	5.5	ND	85.9%	**BDL**
Dehydronifedipine	**BDL**(1)	19	ND	**BDL**(1)	**BDL**(1)
Dilantin	350	91.5	ND	73.9%	**BDL**
Erythromycin	18.5	**BDL**	ND	**BDL**	**BDL**
Furosimide	150	**BDL**	ND	**BDL**	**BDL**
Gemfibrozil	43	**BDL**	ND	**BDL**	**BDL**
Iohexal	560	160	ND	71.4%	**BDL**
Iopromide	5300	3150	47	40.6%	99.1%
Ketoprofen	6.9	**BDL**	ND	**BDL**	**BDL**
Ketorolac	7.25	**BDL**	ND	**BDL**	**BDL**
Lidocaine	335	**BDL**	ND	**BDL**	**BDL**
Lopressor	160	**BDL**	ND	**BDL**	**BDL**
Meclofenamic Acid	37.5	**BDL**	ND	**BDL**	**BDL**
Meprobamate	395	82.5	5.7	79.1%	98.6%
Naproxen	160	**BDL**	ND	**BDL**	**BDL**
Oxolinic acid	23	**BDL**	ND	**BDL**	**BDL**
Primidone	120	46	ND	61.7%	**BDL**
Sucralose	43000	27000	330	37.2%	99.2%
Sulfadiazine	9.15	**BDL**	ND	**BDL**	**BDL**
Sulfamethazine	5.1	**BDL**	ND	**BDL**	**BDL**
Sulfamethoxazole	1040	12.5	15	98.8%	98.6%
Sulfathiazole	5.8	**BDL**	ND	**BDL**	**BDL**
TCEP	120	60.5	ND	49.6%	**BDL**
Theobromine	62.5	8.6	ND	86.2%	**BDL**
Theophylline	98	**BDL**	ND	**BDL**	**BDL**
Triclosan	14	**BDL**	ND	**BDL**	**BDL**
Trimethoprim	79.5	**BDL**	ND	**BDL**	**BDL**
Atrazine	43	**BDL**	ND	**BDL**	**BDL**
Diuron	24.5	**BDL**	ND	**BDL**	**BDL**
Linuron	5	**BDL**	ND	**BDL**	**BDL**

BDL = Below detectable limit

(1) = Compound not detected in MBR effluent

These results show that although the RO process does achieve near complete removal of all detected compounds, the compound removal in the BAF column was shown to be comparable at ozone doses of 4 and especially 8 mg/L. The ozone doses required depend on the amount of removal desired and the types of compounds being detected in the wastewater. The MBR-ozone-BAF treatment train can offer an effective, lower cost approach to removing PPCPs/EDCs from wastewater without the loss of water and the production of a concentrated waste stream.

Chapter 5: Conclusions

A pilot system consisting of an MBR, ozone contactor, and BAF column was operated at the ABCWUA Southside Water Reclamation Plant (SWRP). The MBR was continually fed primary treated wastewater and operated at an SRT of approximately 10 days throughout the duration of these experiments. The MBR effluent was used to feed an ozone contactor, which then fed a BAF column. Three different ozone doses were examined. Applied ozone doses of 2, 4, and 8 mg/L, were examined, which correspond to an approximate ratio of 0.5, 1.0, and 2.0 mg ozone/mg TOC. The ozone contactor consisted of three chambers, which provided 5 minutes of contact time in each chamber for a total of 15 minutes of contact time. After ozone treatment, the water was pumped to the BAF column. The BAF column used anthracite media that was initially seeded with MLSS from the MBR and soaked in MBR feedwater for a week to establish a bio-growth prior to the Phase 2 experiments. The system was run for at least one week between sampling events to establish steady state conditions at each new ozone dose. Several organic parameters were measured daily to establish steady state conditions and to predict PPCP/EDC removal. This study also investigated the removal of PPCPs/EDCs with a reverse osmosis (RO) system that was operated concurrent to the Ozone/BAF treatment train for two of the ozone doses. The PPCP/EDC analysis tested for 83 compounds with most having detection limits of 5 ng/L. The concentrations of the examined compounds were tested in the effluents of the MBR, ozone contactor, BAF column, and RO permeate.

The project was divided into two phases. Phase 1 of the project determined the ozone doses used to examine the removal of PPCPs/EDCs. In Phase 1, a series of analysis were done to examine the effects of various ozone doses on different organic parameters. The bulk organic analysis consisted of TOC, UV_{254} absorption, SUVA, and BDOC. These parameters were measured at varying ozone doses ranging from 0 to approximately 12 mg/L. Due to the cost of each PPCP/EDC analysis and the limited budget for testing, only three applied ozone doses could be examined for PPCP/EDC

removal. It was determined that ozone doses of 2, 4, and 8 mg/L would be used which corresponds to approximately 0.5, 1.0, and 2.0 mg ozone/mg TOC. Phase 1 also showed that the effectiveness of ozone to remove organics is limited. The bulk organic analysis showed that little to no additional organic removal was achieved after an ozone dose of around 8 mg/L.

Phase 2 of this research can also be divided into two parts. Phase 2 examined both the removal of organics and the removal of microconstituents at the 3 applied ozone doses determined in Phase 1. TOC, UV_{254} absorbance, and SUVA were measured daily to establish steady state conditions and to predict PPCP/EDC removal. BDOC was measured 3 times for each applied ozone dose. The TOC analysis showed that the TOC concentrations in the MBR and ozone effluents were approximately equal at all examined ozone doses. The TOC/TOC_0 analysis also showed that there was a decrease in TOC concentrations between the ozone and BAF effluents at all examined ozone doses. In contrast to the TOC values, a decrease in UV_{254} absorbance was observed between the MBR and ozone effluents at all applied ozone doses examined. This indicates that even though the TOC is not reduced by increased ozone doses, the organics become more biodegradable and are then removed by the BAF. Similar to the UV_{254} absorbance values, the SUVA values decrease after the MBR effluent and are nearly identical for both the ozone and BAF effluents. This also indicates an increase in the biodegradable fraction of organics due to ozonation.

The TOC, UV_{254} absorbance, and SUVA values show that recalcitrant compounds in the MBR effluent are being partially oxidized in the ozone contact chamber. Although organics are not removed by ozone alone, they are broken down into more biodegradable forms that are then consumed by microbes in the BAF column. There is a trend of increasing organic removal with increasing ozone dose, although the highest efficiency of ozone to partially oxidize recalcitrant compounds into more biodegradable forms was not seen at the highest ozone dose examined. The most effective ozone dose examined for removing organics was 4 mg/L.

Examining the additional removal of organics between applied ozone doses per additional mg/L of ozone added shows a large amount of organic removal up to an ozone dose of 4 mg/L, with the largest removal achieved at the 4 mg/L ozone dose. These values were used to quantify the amount of organic removal per additional mg/L of ozone added between the ozone doses of 0-2, 2-4, and 4-8 mg/L. The TOC, UV_{254} absorbance, and SUVA values showed that the 4 mg/L ozone dose was the most effective at removing organics.

The last of the organic analysis examined during the Phase 2 experiments was BDOC. The BDOC analysis was used to examine the fraction of biodegradable and non-biodegradable organics throughout the treatment process at all ozone doses. Three BDOC sampling events were done for each applied ozone dose examined and measured the BDOC in the MBR, ozone, and BAF effluents.

Similar to the other organic analysis examined during Phase 2 of these experiments, the BDOC results showed that recalcitrant organics in the MBR effluent are partially oxidized in the ozone contact chamber where they are further degraded by microbes in the BAF column. The results also showed that although the amount of BDOC created in the ozone contact chamber increases with increasing ozone doses, ozone's effectiveness in partially oxidizing recalcitrant organics decreases after the 4 mg/L ozone dose. These results were expected based on the results of the other organic analysis.

The BDOC results did show that the average ratio of BDOC consumed in the BAF column to BDOC produced in the ozone contact chamber was approximately 0.5:1 at all examined ozone doses. The ratios were 0.54, 0.5, and 0.54 at the ozone doses of 2, 4, and 8 mg/L respectively. This leads to the conclusion that the BAF column is only able to consume half of the biodegradable organics produced in the ozone contact chamber regardless of the ozone dose. The incomplete biodegradation of BDOC in the BAF column may be the result of the short EBCT in the BAF column or incomplete maturation of the biofilm on the anthracite media. It could also be attributed to

drawbacks in doing pilot scale research and could be an issue that needs further examination in a future study.

Following the results of the bulk organic analysis, it was expected that a certain degree of compound removal would be achieved at all applied ozone doses examined. It was also expected that PPCP/EDC removal would increase with applied ozone dose with the highest removal of compounds being achieved at an ozone dose of 8 mg/L. The 4 mg/L ozone dose was expected to remove compounds the most efficiently while the 2 mg/L ozone dose was expected to remove some compounds well, although a majority of compounds would not be removed to below detectable limits.

A total of 16 samples were collected and analyzed for PPCPs/EDCs during Phase 2 experiments. The MBR, ozone, and BAF effluent were tested for PPCPs/EDCs during all three sampling events in Phase 2. Two samples from the RO effluent were tested as well as an initial MBR effluent sample collected on 8/19/09 which was used to determine what compounds were present in the wastewater. The RO effluent samples were collected during the 2 and 4 mg/L ozone dose sampling events. In addition, some samples were collected and analyzed for PPCPs/EDCs for quality assurance purposes. These include one set of duplicates for the MBR, ozone, and BAF effluent, collected during the 4 mg/L ozone dose sampling event, as well as a field blank to insure contamination was not an issue. The results from the duplicate samples showed consistency in the sampling process. The field blank detected two compounds, 4-nonylphenol and propylparaben, consequently both were not considered in evaluating process performance.

The PPCP/EDC analysis tested for 83 different compounds with most having detection limits at 5 ng/L. Of these 83 compounds, 52 were detected in one or more samples in the MBR effluent. Three compounds (dehydronifedipine, meclofenamic acid, and DACT) were detected in the ozone or BAF effluent, but not in the MBR effluent for at least one sample. All three of these compounds were also detected in the MBR effluent in at least one of the sampling events. The concentrations of these compounds

were close to the detection limit, which leads to the conclusion that they were not detected in the MBR effluent due to the limitations of the analysis.

As expected, the BAF column did not achieve any significant removal of PPCPs/EDCs. Because the compounds have already been through a biological process in the MBR, most of the remaining organics are assumed non-biodegradable or slowly degradable. To make them more biodegradable, ozone is used, which breaks the compound down to a more biodegradable form. The ozonation process is essential in oxidizing recalcitrant compounds into smaller more biodegradable forms that can then be removed through biodegradation in the BAF column. Even though the initial, recalcitrant compounds are not removed by the BAF column, the bulk organic analysis shows that the compounds are not completely mineralized by ozone either. Instead, they are broken down into smaller more biodegradable compounds by the ozone, and then removed by the BAF column. It is only through a combination of both processes that removal of organics is attained.

All compounds that were removed to BDL at a lower ozone dose were also removed at all higher doses. Only three compounds, iohexal, TCEP, and meprobamate, were found to have a lower percent removal at a higher applied ozone dose. Other studies have found both Iohexal and TCEP to be extremely resistant to oxidation by ozone. The results of one study also had inconsistent results for TCEP with increased concentrations detected at higher ozone doses. The meprobamate results showed increased removal at ozone doses of 2 and 4 mg/L. The 8 mg/L ozone dose saw a slightly lower percent removal than the 4 mg/L ozone dose. The percent differences were small enough to be ignored and the assumption was made that no additional removal of meprobamate is achieved at the 8 mg/L ozone dose.

Significant removal of most PPCPs/EDCs was observed at all applied ozone doses. As expected, greater removal was achieved as the ozone dose increased. Although the removal of PPCPs/EDCs increased with increasing ozone dose, the most efficient ozone dose examined was at 4 mg/L. The BAF column did not dramatically

decrease the concentrations of PPCPs/EDCs after the initial decrease due to ozonation, although additional TOC removal was achieved in the BAF column. The data from the bulk organic analysis was useful in predicting the effectiveness of the various ozone doses in removing PPCPs/EDCs.

As expected, the RO process achieved very high removal of all detected compounds. A total of 36 compounds were detected during the 2 mg/L sampling event with 34 of these being compared for percent removal. The RO process removed 32 of these compounds to below detectable limits with the remaining two compounds achieving > 98% removal. A total of 44 compounds were detected during the 4 mg/L sampling event with 41 of these being compared for percent removal. The RO process removed 35 of these compounds to below detectable limits with the remaining 6 compounds achieving greater than 97% removal. The 2 mg/L ozone dose was not nearly as effective at removing compounds as the RO process. At an ozone dose of 4 mg/L though, comparable results were seen although the RO process was more effective. The 8 mg/L ozone dose results had similar compound removals in both the BAF column and the RO process although some compounds were found to be particularly resistant to oxidation by ozone.

These results show that although the RO process does achieve near complete removal of all PPCPs detected, the compound removal in the BAF column was shown to be comparable at ozone doses of 4 and especially 8 mg/L. The ozone doses required depend on the amount of removal desired and the types of compounds being detected in the wastewater. The MBR-ozone-BAF treatment train can offer an effective approach to removing PPCPs/EDCs from wastewater. This process does not lose any of the treated water and has the benefit of not having a wastestream associated with it like the RO process does.

References

1. Kimura, K., H. Hara, and Y. Watanabe, *Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs).* Desalination
Membranes in Drinking and Industrial Water Production, 2005. **178**(1-3): p. 135-140.
2. Nikolaou, A., S. Meric, and D. Fatta, *Occurrence patterns of pharmaceuticals in water and wastewater environments.* Analytical and Bioanalytical Chemistry, 2007. **387**(4): p. 1225-1234.
3. Wang, S., R.M. Holzem, and C.K. Gunsch, *Effects of Pharmaceutically Active Compounds on a Mixed Microbial Community Originating from a Municipal Wastewater Treatment Plant.* Environ. Sci. Technol., 2008. **42**(4): p. 1091-1095.
4. Baumgarten, S., et al., *Evaluation of advanced treatment technologies for the elimination of pharmaceutical compounds.* Advanced Sanitation
Water Science and Technology, 2007. **56**(5): p. 1-8.
5. Kim, S.D., et al., *Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters.* Water Research, 2007. **41**(5): p. 1013-1021.
6. Snyder, S.A., et al., *Pharmaceuticals, personal care products, and endocrine disruptors in water: Implications for the water industry.* Environmental Engineering Science, 2003. **20**(5): p. 449-469.
7. Kimura, K., H. Hara, and Y. Watanabe, *Elimination of selected acidic pharmaceuticals from municipal wastewater by an activated sludge system and membrane bioreactors.* Environmental Science and Technology, 2007. **41**(10): p. 3708-3714.
8. Snyder, S.A., et al., *Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals.* Desalination, 2007. **202**(1-3): p. 156-181.
9. Vieno, N.M., et al., *Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant.* Environmental Science and Technology, 2007. **41**(14): p. 5077-5084.
10. Radjenovic, J., M. Petrovic, and D. Barcelo, *Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor.* Analytical and Bioanalytical Chemistry, 2007. **387**(4): p. 1365-1377.
11. Bernhard, M., J. Muller, and T.P. Knepper, *Biodegradation of persistent polar pollutants in wastewater: Comparison of an optimised lab-scale membrane bioreactor and activated sludge treatment.* Water Research, 2006. **40**(18): p. 3419-3428.
12. Lesjean, B., et al., *Outcome of a 2-year investigation on enhanced biological nutrients removal and trace organics elimination in membrane bioreactor (MBR).* Water Science and Technology, 2005. **52**(10-11): p. 453-460.

13. Lozier, J. and A. Fernandez, *Using a membrane bioreactor/reverse osmosis system for indirect potable reuse*. Water Science and Technology: Water Supply, 2001. **1**(5-6): p. 303-313.
14. Donn, J., M. Mendoza, and J. Pritchard, *Drugs found in drinking water*, in *USA Today*. 2008.
15. Wintgens, T., M. Gallenkemper, and T. Melin, *Removal of endocrine disrupting compounds with membrane processes in wastewater treatment and reuse.* Water Science and Technology, 2004. **50**(5): p. 1-8.
16. Yoon, Y., et al. *A Review on Removal of Endocrine-Disrupting Compounds and Pharmaceuticals by Drinking Water Treatment Processes*. in *Water Quality Technology Conference*. 2002: American Water Works Association.
17. Snyder, S.A., et al., *State of Knowledge of Endocrine Disruptors and Pharmaceuticals in Drinking Water*. 2008: American Water Works Association and Awwa research Foundation. 237.
18. Kimura, K., et al., *Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes.* Journal of Membrane Science, 2004. **245**(1-2): p. 71-78.
19. Ternes, T.A., et al., *Removal of pharmaceuticals during drinking water treatment.* Environmental Science and Technology, 2002. **36**(17): p. 3855-3863.
20. Snyder, S. *Occurrence and Relevance of Trace Pharmaceuticals in Drinking Water*. in *2009 AWWA Research Symposium: Emerging Organic Contaminants*. 2009. Austin Texas.
21. Judd, S., *The status of membrane bioreactor technology.* Trends in Biotechnology, 2008. **26**(2): p. 109-116.
22. Clara, M., et al., *Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants.* Water Research, 2005. **39**(19): p. 4797-4807.
23. Crittenden, J.C., et al., *Water Treatment: Principles and Design*. 2 ed. 2005, Hoboken, New Jersey: John Wiley & Sons, Inc. 1948.
24. Comerton, A.M., et al., *Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds.* Journal of Membrane Science, 2007. **303**(1-2): p. 267-277.
25. Clara, M., et al., *Comparison of the behaviour of selected micropollutants in a membrane bioreactor and a conventional wastewater treatment plant.* Water Science and Technology, 2004. **50**(5): p. 29-36.
26. Bellona, C., et al., *Factors affecting the rejection of organic solutes during NF/RO treatment--a literature review.* Water Research, 2004. **38**(12): p. 2795-2809.
27. Kimura, K., et al., *Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes.* Journal of Membrane Science, 2003. **227**(1-2): p. 113-121.
28. Verliefde, A.R.D., et al., *Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of*

pharmaceutically active compounds in surface water. Water Research, 2007. **41**(15): p. 3227-3240.
29. Kosutic, K., et al., *Removal of antibiotics from a model wastewater by RO/NF membranes.* Separation and Purification Technology, 2007. **53**(3): p. 244-249.
30. Muller, J.-P. and M. Jekel, *Comparison of advanced oxidation processes in flow-through pilot plants (Part I).* Water Science and Technology, 2001. **44**(5): p. 303-309.
31. Chen, P.-J., et al., *Biological assessments of a mixture of endocrine disruptors at environmentally relevant concentrations in water following UV/H2O2 oxidation.* Science of the Total Environment, 2007. **376**(1-3): p. 18-26.
32. Canonica, S., L. Meunier, and U. von Gunten, *Phototransformation of selected pharmaceuticals during UV treatment of drinking water.* Water Research, 2008. **42**(1-2): p. 121-128.
33. Okuda, T., et al., *Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan.* Water Science and Technology, 2008. **57**(1): p. 65-71.
34. Kruithof, J.C., P.C. Kamp, and B.J. Martijn, *UV/H2O2 treatment: A practical solution for organic contaminant control and primary disinfection.* Ozone: Science and Engineering, 2007. **29**(4): p. 273-280.
35. Muller, J.-P., C. Gottschalk, and M. Jekel, *Comparison of advanced oxidation processes in flow-through pilot plants (Part II).* Water Science and Technology, 2001. **44**(5): p. 311-315.
36. Vogna, D., et al., *Advanced oxidation of the pharmaceutical drug diclofenac with UV/H 2O2 and ozone.* Water Research, 2004. **38**(2): p. 414-422.
37. Andreozzi, R., et al., *Effects of advanced oxidation processes (AOPs) on the toxicity of a mixture of pharmaceuticals.* Water Science and Technology, 2004. **50**(5): p. 23-28.
38. Kim, I.H., et al., *Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H2O2.* Water Science and Technology, 2008. **57**(2): p. 195-200.
39. Pereira, V.J., et al., *UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm.* Environmental Science and Technology, 2007. **41**(5): p. 1682-1688.
40. Westerhoff, P., et al., *Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes.* Environmental Science and Technology, 2005. **39**(17): p. 6649-6663.
41. Liang, C.H., P.C. Chiang, and E.E. Chang, *Systematic Approach to Quantify Adsorption and Biodegradation Capacities on Biological Activated Carbon Following Ozonation.* Ozone: Science and Engineering, 2003. **25**(5): p. 351-361.
42. Urfer, D., et al., *Biological filtration for BOM and particle removal: A critical review.* Journal / American Water Works Association, 1997. **89**(12): p. [d]83-98.

43. Snyder, S.A., et al., *Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater.* Ozone: Science and Engineering, 2006. **28**(6): p. 445-460.
44. Huber, M.M., et al., *Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study.* Environmental Science and Technology, 2005. **39**(11): p. 4290-4299.
45. Toor, R. and M. Mohseni, *UV-H2O2 based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water.* Chemosphere, 2007. **66**(11): p. 2087-2095.
46. Bahr, C., et al., *SUVA as control parameter for the effective ozonation of organic pollutants in secondary effluent.* Oxidation Technologies for Water and Wastewater Treatment IV - Selected Papers of the 4th International Conference on Oxidation Technologies for Water and Wastewater Treatment
Water Science and Technology, 2007. **55**(12): p. 267-274.
47. Khan, E., et al., *Factors influencing biodegradable dissolved organic carbon measurement.* Journal of Environmental Engineering, 1999. **125**(6): p. 514-521.
48. Khan, E., et al., *Method development for measuring biodegradable organic carbon in reclaimed and treated wastewaters.* Water Environment Research, 1998. **70**(5): p. 1025-1032.
49. Chiou, C., Marinas BJ, Adams JQ, *Modified indigo method for gaseous and aqueous ozone analyses.* Ozone: Science & Engineering, 1995. **17**(3): p. 329-344.
50. Medicine, U.S.N.L.o., *Toxicology Data Network: propylparaben*. 2009, National Institute of Health: Rockville Pile, Bethesda, MD.
51. Commission, J.R.C.E., *4-Nonylphelol (Branched) and Nonylphenol; Summary Risk Assessment Report*. 2002, Institute for Health and Consumer Protection, European Chemicals Bureau: Ispra (VA) Italy. p. 32.
52. Ikehata, K., M.G. El-Din, and S.A. Snyder, *Ozonation and Advanced Oxidation Treatment of Emerging Organic Pollutants in Water and Wastewater.* Ozone: Science & Engineering, 2008. **30**(1): p. 21 - 26.
53. Ternes, T.A., et al., *Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?* Water Research, 2003. **37**(8): p. 1976-1982.