

Overcoming the Impacts of Extreme Weather and Dissolved Organic Matter on the
Treatability of Water Using Ozone

by

Michelle Barry

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Graduate Supervisory Committee:

Paul Westerhoff, Chair
Peter Fox
Rolf Halden
Kiril Hristovski

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ABSTRACT

The influence of climate variability and reclaimed wastewater on the water supply necessitates improved understanding of the treatability of trace and bulk organic matter. Dissolved organic matter (DOM) mobilized during extreme weather events and in treated wastewater includes natural organic matter (NOM), contaminants of emerging concern (CECs), and microbial extracellular polymeric substances (EPS). The goal of my dissertation was to quantify the impacts of extreme weather events on DOM in surface water and downstream treatment processes, and to improve membrane filtration efficiency and CECs oxidation efficiency during water reclamation with ozone.

Surface water quality, air quality and hydrologic flow rate data were used to quantify changes in DOM and turbidity following dust storms, flooding, or runoff from wildfire burn areas in central Arizona. The subsequent impacts to treatment processes and public perception of water quality were also discussed. Findings showed a correlation between dust storm events and change in surface water turbidity ($R^2=0.6$), attenuation of increased DOM through reservoir systems, a 30-40% increase in organic carbon and a 120-600% increase in turbidity following severe flooding, and differing impacts of upland and lowland wildfires.

The use of ozone to reduce membrane fouling caused by vesicles (a subcomponent of EPS) and oxidize CECs through increased hydroxyl radical (HO^\bullet) production was investigated. An “ozone dose threshold” was observed above which addition of hydrogen peroxide increased HO^\bullet production; indicating the presence of ambient promoters in wastewater. Ozonation of CECs in secondary effluent over titanium dioxide or activated carbon did not increase radical production.

Vesicles fouled ultrafiltration membranes faster (20 times greater flux decline) than polysaccharides, fatty acids, or NOM. Based upon the estimated carbon distribution of secondary effluent, vesicles could be responsible for 20–60% of fouling during ultrafiltration and may play a vital role in other environmental processes as well. Ozone reduced vesicle-caused membrane fouling that, in conjunction with the presence of ambient promoters, helps to explain why low ozone dosages improve membrane flux during full-scale water reclamation.

For my dad, who is still the smartest man I've ever known,
my mom, whose quest for increased knowledge continues to inspire me,
my husband for his eternal support and selfless sacrifices, and
my son, who keeps it all in perspective.

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Chapter 1

INTRODUCTION

Climate change and exponential population growth impact the quality and quantity of the world's fresh water supply. By 2030, the world population is projected to reach in excess of 8 billion people (UNWater 2012). Consequently, demands on the water supply continue to rise with population growth and the corresponding increased urbanization, industrialization, standards of living (DESA 2003). By 2025, it is estimated that 1.8 billion people will live in areas with absolute water scarcity, and two-thirds of the world population could be under "water stress" conditions (UNWater 2012). These conditions of water stress are created by excessive withdrawal of surface and ground water, pollution and inefficient use (Fry 2006). Additionally, the Intergovernmental Panel on Climate Change (IPCC 2007) projects the "likely to virtually certain" changes in extreme events globally (e.g., heavy precipitations, droughts, and heat waves) between now to 2100, which will also impact the quantity and quality of the water supply (IPCC 2007).

The semi-arid region of the southwestern United States (US) including parts of Arizona, New Mexico, California, Utah and Nevada, is frequently subjected to extreme weather conditions including extended periods of drought, monsoons, and dust storms. Close examination of water quality, specifically changes in dissolved organic matter (DOM) including taste and odor (T&O) causing compounds and turbidity following extreme weather conditions will provide insight into impacts of climate change

associated weather events on water quality. The variability in supply and quality of water due to extreme weather conditions and the strain of a rapidly growing population have led to reliance upon reclaimed wastewater to augment the municipal water supply in California, Arizona, and Nevada. This reuse water is used for irrigation, industry, cooling water for thermal power generation, and aquifer recharge (Asano et al. 2007). Based on the experience of the southwestern US in meeting increasing water supply demands; the future use of reclaimed municipal wastewater to alleviate the strain of over taxed water supplies is likely in other areas. However, wastewater reuse is currently limited based on both perceived and actual water quality concerns due to the presence of contaminants of emerging concern (CECs), a component of DOM, including pharmaceuticals and endocrine disrupting compounds and the cost of additional treatment. Advanced oxidation and membrane filtration can be used to remove or destroy CECs and improve overall water quality. These processes are state-of-the-art and may be cost prohibitive; therefore optimization of these processes should increase water reuse opportunities. Relevant to these topics, surface water and treated wastewater (secondary effluent) have many similarities and several key differences that are summarized in Table 1.1.

Table 1.1. Similarities and Difference in Surface Waters and Treated Wastewater Relevant to DOM, Extreme Weather Events, and Ozonation.

Property	Surface Waters	Secondary Effluent
DOM	<ul style="list-style-type: none"> - Natural organic matter (NOM) - some CECs due to wastewater infiltration 	<ul style="list-style-type: none"> - NOM, CECs, and extracellular polymeric substances (EPS) from the activated sludge process
Impact by Extreme Weather Events	<ul style="list-style-type: none"> - Yes – but impact is not well quantified 	<ul style="list-style-type: none"> - Little to no impact on effluent quality
Effectiveness of Ozonation	<ul style="list-style-type: none"> - Capable of oxidizing some NOM, thereby reducing DBP formation potential, T&O compounds, and improving biodegradability - Improve coagulation/flocculation - Provides disinfection - Advanced treatment with H₂O₂ addition for reducing CECs 	<ul style="list-style-type: none"> - Some studies have shown reduction in membrane fouling through pre-ozonation - Some advanced treatment with H₂O₂ addition for reducing CECs

This dissertation addresses future challenges from DOM in the water supply due to climate variability and increased water reuse by first, quantifying changes in water quality following extreme weather events and second, using ozone to improve treatment efficiency and reuse water quality. Specifically, the research questions addressed in this dissertation are: (1) how do severe weather events (drought-related wildfires, dust storms, and flooding) impact quality of the surface water supply? (2) Is oxidation of CECs by hydroxyl radicals (HO[•]) during ozonation of tertiary effluent enhanced by adding hydrogen peroxide (H₂O₂) or solid-phase catalysts? (3) What are the dominant organic membrane foulants in secondary treated wastewater, and how can ozonation reduce this

fouling? Figure 1.1 illustrates the relationships among these research questions and potential water treatability implications.

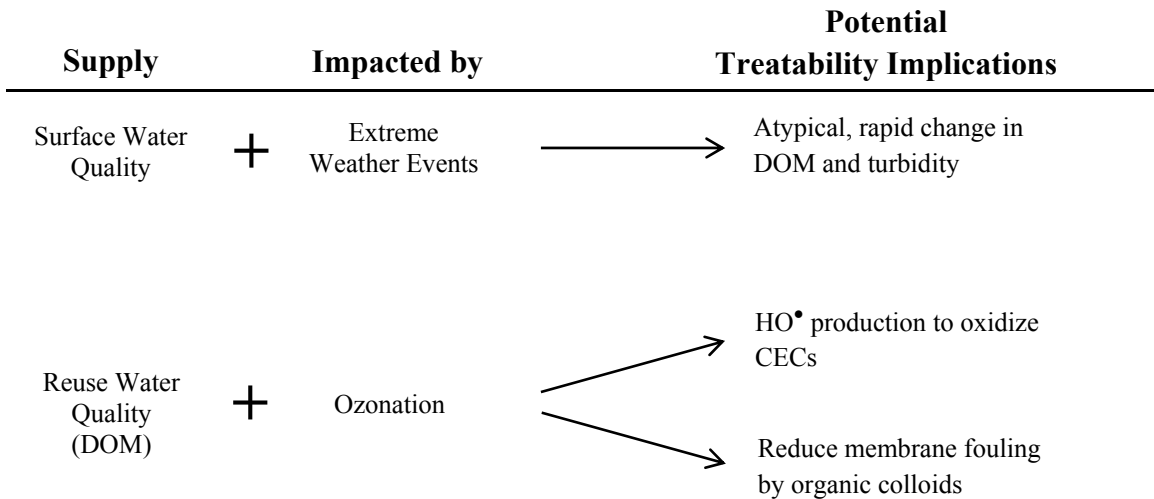


Figure 1.1 Relationship of Dissolved Organics in the Water Supply (Fresh and Reuse Water), Extreme Weather Events or Ozonation, and Potential Treatability Implications

Research Question 1 - How do drought-related wildfires, dust storms, and flooding impacted water quality of the surface water supply?

In an effort to better understand the impacts of climate change on water quality, historical weather, air quality, and hydrologic data over the past 13 years was compared with measured water quality data collected from the central Arizona water supply. Three extreme weather events over the study period were used to illustrate impacts on water quality; dust storms in 2011, drought-associated wildfires (Rodeo-Chedaski Fire, 2002), and flooding during the spring of 2005. Monthly water quality measurements of the lakes, rivers and canals from the associated watersheds were collected from 1999 to date. Measured parameters included dissolved organic carbon (DOC), T&O causing compounds [methylisoborneol (MIB) and geosmin], and turbidity. Air quality data (e.g.,

PM₁₀) from impacted national weather monitoring stations was used to identify dust storms and compare with turbidity data at nearby water treatment plants. Through examination and analysis of the collected data, the following hypothesis was established:

Hypothesis #1 - Over the past 13 years, dust storms, flooding, and wildfire in central Arizona have adversely impacted surface water quality through rapid increases in turbidity and TOC.

Research Question 2 –During ozonation of secondary effluent, is production of HO[•] enhanced by adding liquid initiators or catalytic solids?

Ozonation is used for disinfection and to oxidize organics in drinking water. Ozone/H₂O₂ is a well-established advanced oxidation process (AOP) based on the resulting significant increase in the rate of HO[•] production during ozone decay. Advanced oxidation of municipal wastewater using ozone/H₂O₂ to oxidize TOxCs is a relatively new practice. However, because this process requires continual addition of H₂O₂, it is desirable to find more sustainable alternatives. Ozonation in the presence of a solid-phase catalyst such as titanium dioxide (TiO₂) or activated carbon (AC) may provide such an alternative (Beltran 2004). By definition, catalysts are not consumed by the reaction they catalyze, and therefore, greatly limit the need for chemical addition. Published research on ozone/catalysts in model and industrial waters has demonstrated improvement of contaminant destruction (Rosal et al. 2008, 2009, Yang et al. 2009, Alvarez et al. 2009, Moussavi, Khavanin, and Alizadeh 2009, Lanao et al. 2008). However, limited research has been done on catalytic ozonation of CECs in municipal

wastewater for water reuse. In response to research question 2, the following hypotheses were established:

Hypothesis #2 - Ozonation of tertiary effluent in the presence of TiO₂ or granular activated carbon (GAC) produces similar HO[•] exposure (R_{CT}) as ozonation with the addition of H₂O₂.

Hypothesis #3 - A threshold ozone dose exists for tertiary effluent below which addition of H₂O₂ does not increase R_{CT} values.

Research Question 3 - What are the dominant organic membrane foulants in secondary treated wastewater, and how can ozonation reduce this fouling?

Membrane filtration is used during water reclamation for removal of pathogens and some CECs (Pisarenko et al. 2012, 2007). The use of membranes for advanced wastewater treatment continues to increase as regulations become more stringent and needs for higher quality water become more wide-spread (Ang et al. 2011). Membrane fouling causes a decrease in water flux and thereby treatment efficiency, (Van Geluwe, Braeken, and Van der Bruggen 2011) as well as decreases membrane life due to irreversible fouling (AWWA 1996). Recent research has been done towards reduction of fouling through anti-fouling membranes, a range of cleaning processes, and pre-treatment (Ang et al. 2011). These efforts to reduce or prevent membrane fouling have led to a better understanding of the compounds (inorganics, polysaccharides, proteins, lipid-like materials, etc.) and mechanisms (adsorption, cake formation, pore blockage and electrostatic interactions (AWWA 1996)) responsible for fouling. Ozonation is capable of

reducing membrane fouling during water reclamation, (Park et al. 2007, You, Tseng, and Hsu 2007, Zhu, Wen, and Huang 2010) but a clearer understanding of how this is accomplished is needed. Fouling of membranes by several of these compounds has been well investigated from a chemical viewpoint, but not from a physical structural perspective; that is, shape elasticity, configuration, etc. Therefore, the role physical structure plays in both membrane fouling and reduction of fouling through ozonation was explored thru investigation of the following hypotheses:

Hypothesis #4 - On a DOC-normalized basis, liposomes cause faster flux decline during UF than fatty acids, polysaccharides or bulk organics (NOM).

Hypothesis #5 - Ozonation reduces liposomal fouling of UF membranes through changes to the physical structure of the vesicle.

Dissertation Organization

This dissertation is divided into chapters and organized as follows:

- Chapter 1 – provides an introduction to the research topics and highlights the need to understand the implications of severe weather events on water quality and use of ozonation to reduce challenges of dissolved organics during water reclamation;
- Chapter 2 – provides background for the research questions and hypotheses through a literature review focusing on effluent organic matter, membrane fouling during water reclamation, and ozonation;

- Chapter 3 – addresses Research Question #1 and Hypothesis #1 related to the impact of extreme weather events on quality of the water supply;
- Chapter 4 – addresses Research Question #2 through completed work for Hypotheses #2 and #3 related to the promotion of HO[•] production during ozonation of wastewater;
- Chapter 5 – addresses Research Question #3 through completed work for Hypotheses #4, and 5 related to the occurrence of liposomal membrane fouling and prevention through ozonation;
- Chapter 6 – synthesizes research findings in the context of current literature;
- Chapter 7 – provides research conclusions and recommendations for future research work.

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Chapter 2

BACKGROUND

This chapter identifies knowledge gaps in the existing literature related to (1) impacts of extreme weather events on dissolved organics in the surface water supply, (2) organic colloids and CECs in EfOM, (3) membrane fouling during water reclamation, and (4) ozonation of dissolved organics in water, with the intent to illuminate deficiencies in the literature and provide background for the work presented in this chapter. Particular focus was placed on studies involving areas of overlap (e.g., membrane fouling by EfOM, ozonation to reduce membrane fouling, etc.).

Impacts of Extreme Weather Events on Surface Water Quality

Severe weather events including droughts, are likely to increase in the late 21st Century due to climate variability (IPCC 2013). Drought conditions also increase the likelihood of wildfires (Westerling and Swernam 2003), flash floods (Whitehead et al. 2009), and dust storms (Reheis and Urban 2011; Hahnenberger and Nicoll 2014). These extreme events will impact water quality. However, few publications are available on the impact of extreme weather on drinking water quality, regardless of geographic location. Qualitatively, potential changes in water quality due to climate variability include: changed mobility and dilution of contaminants based on amount of precipitation; potential changes in contaminant type and concentrations due to changes in chemical reaction kinetics as a result of likely changes in water temperatures; a higher sediment

load in rivers and lakes due to flooding; increased algal bloom and corresponding periods of low dissolved oxygen in reservoirs due to longer retention times during periods of drought; and short-term spikes in nutrients and contaminants as a result of storms terminating periods of drought (Whitehead et al. 2009).

Peterson et al. (2014) provides the state of knowledge relevant to air and water quality in the U.S. related to changes in weather and climate extremes. They discuss causes of changes in extreme weather events and projected changes in the future including heat waves, cold waves, droughts, floods, hurricanes, cyclones, and heavy precipitation. They note the impacts on water quality are complex and may vary over the event and acknowledge that defining an extreme event is somewhat subjective. Additionally, the occurrence of the most extreme events is rare enough that there are too few data points to establish robust trends. Thus climatologist set thresholds to define an extreme event in a manner that provides enough data points (i.e. events) to determine how extremes are changing (Peterson et al. 2014).

Due to increases in air temperatures increasing the amount of moisture in the atmosphere, changes of 20-30% in the magnitude of extreme events has been projected under “a high emissions” (carbon dioxide and other greenhouse gases) scenario (Kunkel et al. 2013). As mentioned previously, associated flooding in rivers has a complex effect on water quality where higher flows lead to dilution, they may also release pollutants trapped within typically dry sediment (Bryantmason et al. 2013) and flooding in an industrial or mining area frequently leads to release of toxic pollutants. Peterson et al. (2014) also provided a computation of a standardized precipitation index (SPI) and

calculated an increase in droughts by 6% up to 12% in some locations in the southwestern US; meaning an increase in drought frequency from 16% of the time to 22-28%. Conversely, periods of drought will decrease in the northwestern US, likely due to changes in mean precipitation and persistence resulting in unusually wet or dry periods (Peterson et al. 2014).

Available literature acknowledges the lack of quantitative evidence of specific impacts of climate variability to water quality (Restaino and Peterson 2013). Quantitative data is limited and research projects are underway to quantify the impacts of extreme weather on water quality (Michalak 2014; Stanford et al. 2014). Tang et al (2013) demonstrated impacts on DOC concentrations from simulated projected climate changes; with short-term drought events having a greater effect on DOC rather than increased temperatures (Tang et al 2013). Michalak et al. (2013) measured increased nutrient loading in Lake Erie due to agriculture and an extreme weather event. This increased nutrient load and higher detention time due to drought caused record-setting algal blooms. Turbidity data from a drinking water source in the Pacific Northwestern US was correlated with high stream flow and used in model development to demonstrate a likely increased exceedence of turbidity limits set by the USEPA at WTPs due to extreme weather events (Towler et al. 2010) and both an increase in the amount of chlorophyll A and turbidity was measured in a Nebraska reservoir as a result of drought (Olds et al. 2011).

Based on limited data, Kundzewicz et al. (2009) and Whitehead et al. (2009) suggest climate model scenarios may provide the best available information to assess

impacts of climate change on both ecology and water quality of surface water. This suggestion is based on the complex interactions of both aquatic and terrestrial systems in a watershed. They proposed a need for models that represent climate, soil, land use, lakes, rivers and coastal waters. Thus far, they further note, models to date focused more on hydrology than water quality of importance to drinking WTPs. In light of the multiple, complex interactions involved in surface water quality/weather models, there is a high overall uncertainty of these models (Kundzewicz et al. 2007; Whitehead et al. 2009).

Effluent Organic Matter - Colloids and Contaminants of Emerging Concern

Organic matter within municipal wastewater secondary effluent is referred to as effluent organic matter (EfOM). Jarusutthirak et al. (2002) isolated EfOM and characterized it through size exclusion chromatography (SEC) with on-line UVA and DOC detectors, specific UVA (SUVA), fourier transform infrared (FTIR), and analysis of total sugars. They noted the EfOM isolates showed similar characteristics of bulk effluent including NOM and soluble microbial products (SMPs) derived during biological processes in wastewater treatment (Jarusutthirak et al. 2002). Further, the colloidal fraction of the EfOM was primarily composed of polysaccharides, proteins, and/or aminosugars. Based on their findings and findings of others (Drewes and Fox 2001), EfOM is discussed in this chapter as (1) residual NOM from drinking water, (2) extracellular material produced during the activated sludge treatment process [SMPs and extracellular polymeric substances (EPS) of microbial origin] and (3) non-degraded organics from industry and other residential waste (CECs).

Natural Organic Matter

Individual natural waters have unique combinations of minerals, soils, microbes, and anthropogenic compounds from both within the body of water and its surrounding terrestrial environment. NOM is the combination of naturally synthesized organic compounds and biological byproducts within the water (Asano et al. 2007); a heterogeneous mixture including humic substances, polysaccharides, amino sugars, proteins, peptides, lipids and small hydrophilic acids (Frimmel 2001). NOM in surface water is not entirely removed during drinking water treatment and therefore has some carry over into municipal wastewater. NOM is typically quantified as dissolved organic carbon (DOC). The two major fractions of NOM are humic and non-humic. The humic fraction is more hydrophobic and includes humic and fulvic acids (Collins et al. 1986; Owen et al. 1995). The non-humic fraction is more hydrophilic and includes hydrophilic acids, amino acids, proteins, and carbohydrates. NOM is a precursor in the formation of carcinogenic, disinfection by-products (DBPs) during drinking-water treatment. These DBPs are formed when chemical disinfectants (e.g., chlorine) react with NOM (Amy et al. 1987; Reckhow et al. 1990). The amount and chemical nature of NOM influences DBP formation. Amy et al. (1987) showed specific ultraviolet absorbance [$SUVA = (UVA_{254} \times 100)/DOC$] is a good predictor of DBP formation potential (Amy et al. 1987). SUVA also correlates with aromatic content of DOC (Traina et al. 1990; Weishaar et al. 2003).

Extracellular Material

EfOM also includes SMPs and EPS primarily produced during biological wastewater treatment processes (Amy 2008). Aerobic activated sludge utilizes

heterotrophic bacteria in the conversion of organic material in wastewater into cell biomass. The heterotrophic bacteria use organic matter as an electron donor and oxygen as the electron acceptor. For aerobic activated sludge, the growth rate of heterotrophic bacteria in a well-oxygenated system is high and results in production of large quantities of biomass (Davis 1998) that includes intact cells, SMPs and EPS [5-25 mg/L total suspended solids (TSS)] (Asano et al. 2007). This EPS represents a collection of sub-organelles (e.g., virus, lipids, long linear structures, branched aggregates, spherical objects) that are also operationally measured as DOC.

The majority of the EPS may be considered as colloidal organics and are also present in other biologically impacted waters (e.g., surface water by algae and/or bacteria). The number of colloids in treated wastewater is in the range of 10⁸ to 10¹²/mL (Asano et al. 2007). In general, colloids are discrete particles that are separated by a dispersion medium (solid, liquid, or gas) and occupy a size between molecular and fine (1 nm – 10 µm) (Sawyer et al. 2003). Due to their small size, colloidal particles have properties different from coarse materials. Colloidal organics, particularly extracellular materials, are of concern in wastewater treatment because they (1) cause membrane fouling (Leppard 1997; Jarusutthirak and Amy 2006); (2) serve as precursors in the formation of DBPs, and (3) potentially sorb CECs.

SMPs and EPS include polysaccharide-like compounds that have been identified as responsible for the evolution of the irreversible fouling during membrane filtration through cohesion of colloids on membranes, thereby creating a cement like cake

(Kimura et al.; AWWA 1996). For example, Leppard (1997) focused on a fraction of EPS - polyanionic extracellular polymers, which are macromolecular aggregates of colloidal fibrils formed by polysaccharides secreted by several types of organisms (e.g., algae, bacteria, plants) to protect against environmental stresses (e.g., toxins, low nutrient levels). Leppard further explained that colloidal fibrils play a role in biofilm formation, exist in the bulk solution, or reside at the organism-water interface and that the impacts of fibrils on surface water quality are not well understood, and their abundance in surface waters has been unnoticed as a potential foulant (Leppard 1997). Therefore, the role of fibrils, and likely that of other organic colloids, in membrane fouling warrants further investigation.

Industrial and Residential Non-degraded Contaminants of Emerging Concern

Industrial and residential, non-degraded organic compounds are another component of EfOM. These organic chemicals include phenols, dyes, surfactants, pharmaceutical and personal care products, fire retardants, etc. (Shon et al. 2006). Collectively, these compounds are often referred to as CECs. CECs are of concern because they pose a potential health impacts to both animals within the aquatic environment as well as humans consuming the water, and are responsible for some limitations for water reuse applications (Westerhoff et al. 2005). Several studies have focused on the removal and/or destruction of these contaminants through advanced treatment of wastewater (Antoniou et al. 2009). AOPs using UV/H₂O₂ and ozone/H₂O₂ have been shown to oxidize a large quantity of CECs (Acero and Von Gunten 2001).

Therefore, in order to further water reuse, improved destruction and removal of CECs using ozonation is a vital component of future increased water reuse.

Membrane Fouling During Water Reclamation

Membrane Types and Characterization

Membranes used in water treatment can be categorized in several different ways including membrane structure, material composition, and separation mechanism(s). Microfiltration (MF) and UF are both pressure driven processes through membranes composed of macropores or mesopores, respectively. MF and UF both remove contaminants from a water stream typically through the mechanism of sieving (difference in pore size and compound size) (AWWA 1996; Asano et al. 2007). Due to the relatively larger pore size of UF and MF membranes, water flux is relatively high across the membrane and transmembrane pressure (TMP) is relatively low (Van Geluwe, Braeken, et al. 2011). The focus of the research presented in this dissertation is on membrane fouling by colloidal material of UF membranes based on the overlapping colloidal size range (1 nm – 10 μm) (Sawyer et al. 2003) and UF membrane pore size range (5 nm – 0.2 μm) (Asano et al. 2007).

Characteristics of UF membrane systems used for water reclamation and reuse are summarized in Table 2.1. In addition to colloidal material, UF removes the high MW fraction of NOM (Siddiqui et al. 2000; Kennedy et al. 2005; Lee, N. et al. 2005) and viruses in the size range between 9 nm – 10 μm (AWWA 1996; Van Voorthuizen

et al. 2001). Some smaller pore size UF membranes have been used to remove dissolved compounds including the high MW colloids, proteins, and carbohydrates. Asano et al. (2007) UF is used for both clarification, disinfection (based on ability to remove viruses and bacteria), and often as a pretreatment for reverse osmosis processes.

Table 2-1. Ultrafiltration membrane system characteristics in water reclamation systems (note – values are not for a specific pore size, but for the range of pore sizes that are defined as UF)

Parameter	Ultrafiltration (UF)
Permeate particle size	0.005-0.2 μm
Retained Compounds	Colloids, viruses, bacteria, organics with >1000 MW
Flux rate	400-800 $\text{L}/\text{m}^2 \cdot \text{d}$
Operating Pressure	5-500 kPa (Awwa, 1996)
Recovery	70-80 %
Membrane Material	Aromatic polyamides, ceramic (various materials), cellulose acetate, polypropylene, polysulfone, polyvinylidene fluoride (PVDF), Teflon

Source: adapted from (Asano *et al.*, 2007)

Membrane materials may broadly be categorized as organic and inorganic. The organic membrane materials include cellulose and polymers (PTFE, PVDF, PE, PC, and PP). Cellulose membranes are hydrophilic, while the polymers are hydrophobic. Both cellulose and polymeric membrane are chemically and thermally stable. Inorganic membranes are mainly ceramic membranes with oxides, nitrides or carbides of a metal (Ti, Al, Zr, etc). PVDF and ceramic membranes are the most resistant materials to ozonation, however, ceramic membranes tend to be brittle and expensive, and therefore

PVDF membranes were used for the membrane fouling experiments in this dissertation.
(AWWA 1996)

Membrane Rejection of Contaminants

The extent to which a membrane retains material is quantified as percent rejection and is often used in selecting membrane size for specific applications. Rejection may be calculated from measured parameters as follows:

(2-1)

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

Where: C_f = concentration in the feed stream, g/m³, mg/L

C_p = concentration in the permeate, g/m³, mg/L

Theoretical membrane rejection was calculated based solely on particle and pore size using an equation developed by Ferry (Ferry 1936b; MWH 2005). This equation (2-2) assumes spherical particles of equivalent diameter; uniform, cylindrical pores; and any particle that intersects the membrane will be rejected. More complex versions of this equation have subsequently been proposed and used by others; however, Ferry's basic equation is sufficient for purposes of this dissertation.

(2-2)

$$R = 1 - 2 \left(1 - \frac{d_p}{d_{EP}}\right)^2 + \left(1 - \frac{d_p}{d_{EP}}\right)^4$$

Where: R = fraction rejected

d_p = particle diameter

d_{EP} = effective pore diameter

Flux Decline and Fouling Mechanisms

As water is filtered through a membrane, there is a buildup of matter retained on the membrane surface. This buildup leads to membrane fouling, which can be caused by particles, colloidal organic and inorganic substances, and/or attachment of microorganisms (Haberkamp et al. 2008). Membrane fouling reduces plant operation by lowering flux rates, increasing reject water, increasing power consumption to overcome increased pressure, and potentially shortening the life of a membrane (Komlenic 2010; Van Geluwe, Braeken, et al. 2011). For these reasons, reduction of membrane fouling is important in the continued use of membrane filtration in water and wastewater treatment.

Table 2.2 provides a summary of the dominant mechanisms of membrane fouling. Membrane pore size plays a role in all three of these fouling mechanisms. Membrane pores are tortuous, interconnecting voids of various sizes and thus the pore sizes specified by membrane manufacturers are nominal. This distribution of pore sizes means some compounds larger than the nominal pore size will pass through the membrane filter, and some compounds smaller than the nominal pore size will be retained. Crittenden et al (2005) further explains that fouling by compounds significantly longer in one direction (rod-shaped bacteria or linear macromolecules) is dependent on the orientation of the compound as it passes through the membrane. Thus, understanding of the role compound physical structure plays in membrane filtration should provide insight into fouling mechanisms and opportunities to reduce fouling.

Table 2-2. Membrane Fouling Mechanisms

Mechanism	Description
Cake Formation	Accumulation of substances on membrane surface forming a porous mat
Attachment	Microorganisms attach to membrane surface and excrete extracellular material
Charge of membranes and foulants (important when foulant size near pore size)	Electro-static interactions (concentration polarization layer, Van der Waals forces) prevent particles from passing through like-charged membranes
Pore Sealing	Entrance to pore is sealed by substance
Internal Pore Constriction (i.e. pore blockage)	Reduction of membrane void volume due to adsorption of substance by membrane

Source: (Crittendem, *et al.*, 2005)

Membrane Fouling by Colloids

In general, inorganic colloids, NOM, polysaccharides, and proteins impact mass transfer at the membrane surface (i.e., flux). Lee, Amy and Lozier (2005) demonstrated water containing high molecular weight colloids, macromolecules and DOC led to significant membrane fouling in MF and UF dead-end cell filtrations. Using SEC-DOC/UV spectrum analysis, they further demonstrated fouling by high molecular weight compounds was likely through cake-layer formation (Lee et al., 2004). Others have also noted the significance of organic colloidal material on fouling during low-pressure membrane filtration (Te Poele 2005; Laabs et al. 2006). These dissolved organic macromolecules have been attributed as the primary foulantss contributing to membrane fouling (Jarusutthirak and Amy 2006; Rosenberger et al. 2006). In treated wastewater

(secondary effluent), these macromolecules/high molecular weight colloids are primarily EPS.

Several studies point to the role of EPS in membrane fouling (Ye et al. 2005; Garcia-Molina et al. 2006; Katsoufidou et al. 2007; Van De Ven et al. 2008). EPS are of biological origin and participate in the formation microbial aggregates. They are primarily responsible for the functional and structural integrity of biofilms (Geesey 1982) often responsible for membrane fouling. They form a gel-like biofilm matrix (Neu et al. 1999) that accounts for roughly 50-90% of the total organic matter in biofilms (Christensen and Characklis 1990). These substances include polysaccharides, proteins, nucleic acids, phospholipids, and other polymeric substances occurring in intercellular spaces of microbial aggregates (Neu et al. 1999; Wingender et al. 1999). Of these substances, fouling has been primarily attributed to polysaccharides and proteins (Amy 2008). Amy (2008) identified both polysaccharide- and protein-like NOM as the most problematic foulants during membrane filtration and, based on membrane autopsies, proposed the two primary organic matter fouling mechanisms as (i) formation of a gel layer on the membrane surface and (ii) pore blockage. In more recent studies, Ang et al. (2011) tested individual model foulants [fatty acids, polysaccharides, proteins and natural organic matter (NOM)] to determine their impacts on fouling of RO membranes. Although these are not UF membranes, the findings related to fouling are relevant to other types of membrane filtration. They found polysaccharides and polysaccharides with calcium caused greater fouling than the other model foulants tested (Ang and Elimelech, 2007; 2008). However, they did not include the EPS component of phospholipids in their

studies. In comparison with the identified organic foulants of polysaccharides, proteins, and fatty acids; phospholipids have not been well-studied.

Ozonation of Colloids and CECs

Ozone/Water Chemistry

Ozone may react directly with dissolved substances in water, or indirectly through radical species formed during ozone decomposition. The reactions and associated kinetics of ozone decomposition in pure water are provided by Staehelin, Hoigne and Buhler (1984) and in alkaline pure water by Tomiyasu, Fukutomi, and Gordon (Tomiyasu et al., 1985). These ozone decay reactions include a series of steps that are described as initiation, propagation and termination reactions. Figure 2.1 provides a simplified illustration of these steps and includes the primary steps at which NOM and CECs play a role in ozone decomposition.

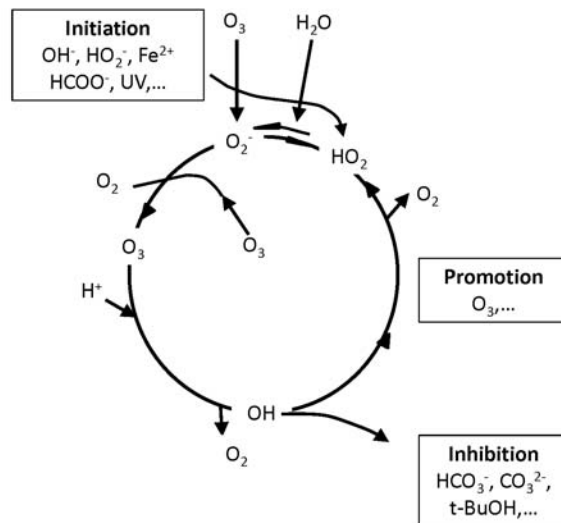


Figure 2.1 Steps in Ozone Degradation in Water [adapted from (Langlais et al. 1991)].

Initiators are substances that react directly with ozone to produce the superoxide ion radical ($O_2^{\bullet-}$) (Beltran 2004), while promoters are species that react with hydroxyl radicals (HO^{\bullet}) and thereby propagate the radical chain to yield the superoxide ion radical ($O_2^{\bullet-}$) (Staehelin J. 1985). Liquid and solid initiators/promoters include OH^- , H_2O_2/HO_2^- , Fe^{2+} , formate, humics, and total organic carbon (TOC) among others (AWWARF 1991). The stability of ozone is also impacted by pH, UV light, ozone concentration and concentration of radical scavengers.(Tomiyasu et al. 1985) (AWWA 1996) Ozone scavengers (inhibitors) include bicarbonate and carbonate ions, alkyl groups, tertiary alcohols, and humic substances (Staehelin J. 1985).

Ozone in Wastewater Treatment

Ozone can be used in various steps of the wastewater treatment train to enhance biological processes, promote micro flocculation, improve iron and manganese removal, degrade pesticides and other CECs, oxidize taste and odor causing compounds, and reduce membrane fouling. The high reactivity of ozone makes it appropriate for achieving certain objectives when applied either alone or in combination with other processes (e.g., filtration). These objectives relate to either the need to achieve higher quality standards prior to final discharge or to meeting standards for water reuse. Specifically, these objectives may include color removal, disinfection, oxidation of CECs through AOP, the conversion of "hard" chemical oxygen demand (COD), and effluent oxygenation.

Ozone as an AOP

AOPs increase the production of HO[•]. HO[•] are considered the most important radical species formed during ozone degradation because of their high standard reduction potential [2.80V vs ozone (2.07V)] (Beltran 2004) and ability to react quickly with the majority of organic and inorganic compounds in water (Von Gunten 2003). During ozonation in water, both molecular ozone and HO[•] exist. (Weiss 1935, Beltran 2004) While some compounds, react rapidly with ozone (e.g., estradiol) others react very slowly and their oxidation is controlled by exposure to HO[•] (Elovitz and Von Gunten 1999), thereby often necessitating high HO[•] concentrations. During ozonation HO[•] concentrations can be increased in a number of ways including: (1) increasing pH (Peleg 1976; Gurol and Singer, 1982; Wiesner *et al.*, 1992); (2) increasing levels of free-radical reaction initiators and promoters (H₂O₂) (AWWA 1996) and (3) addition of solid-phase catalysts. The use of model compounds to indirectly measured HO[•] concentration is briefly discussed in this section, followed by overviews of advanced oxidation by ozonation with the addition of H₂O₂ (Allemane *et al.* 1993) or in the presence of solid phase catalysts (Legube and Leitner 1999; Beltran 2004). These two AOP processes, in addition to ozone/UV, are capable of producing HO[•] to oxidize CECs in model and surface waters, industrial waste streams and, to a lesser extent, in wastewater/reclaimed water (Fujishima and Honda 1972; Glaze 1987; Buxton *et al.* 1988; Herrmann 1999; Beltran *et al.* 2012).

Model Compounds and R_{CT} Concept

The use of a model compound (t-butanol, pCBA, etc) provides a way to predict oxidation of a specific micropollutant during ozonation if rate constants for its reaction with HO^\bullet radicals are known (Acero and Von Gunten 2001). By using a model compound that reacts slowly with molecular ozone and rapidly with HO^\bullet , production of HO^\bullet can be estimated. An R_{CT} value can also be calculated to provide a means to quantify and compare production of HO^\bullet between systems. R_{CT} values are essentially the ratio of HO^\bullet formed to ozone exposure [the area under the ozone decay curve, i.e. the ct value (mg/L-min)] (Davis and Cornwell 1998) and can be calculated using a HO^\bullet probe compound (i.e. pCBA) as described elsewhere (Elovitz and Von Gunten, 1999). Higher R_{CT} values are indicative of greater HO^\bullet formation. Typical R_{CT} values in natural waters are $10^{-8} - 10^{-9}$ (M/M) (Elovitz and Von Gunten 1999).

Hydrogen Peroxide (H_2O_2)

The AOP of ozone/ H_2O_2 is broadly accepted as a viable means of increasing radical production. Briefly, H_2O_2 acts as an initiating agent of ozone degradation (Staehelin and Hoigne 1982; Tomiyasu et al. 1985) where its addition leads to the formation of HO^\bullet and superoxide. In the absence or low concentrations of other promoters, scavengers, etc., these compounds further react with ozone (Staehelin and Hoigne 1982; Von Gunten 2003), ultimately leading to faster production of HO^\bullet . In the presence of inhibitors and scavengers, production of HO^\bullet through H_2O_2 addition may be limited. For example, in drinking water treatment, addition of H_2O_2 during ozonation has been limited to lower DOC waters because of the promotion of ozone decay by DOC. In

higher DOC waters, the reaction of ozone with DOC dominates and H₂O₂ addition does not lead to increased HO[•] formation (Von Gunten 2003). Most waste streams have higher DOC concentrations than surface water, thus it is possible production of HO[•] through the addition of H₂O₂ may be superseded by DOC-promoted ozone decay (Buffle et al. 2006).

In recent years, with the testing and implementation of ozone/H₂O₂ treatment of wastewater, many individuals have been disappointed when the addition of H₂O₂ to the ozonation process produced no additional oxidation (Wert et al. 2007). Some research has confirmed the ambient promotion of HO[•] by wastewater effluent organic matter (EfOM) during ozonation without the addition of an initiator or promoter (Nothe et al. 2009; Pisarenko et al. 2012). Buffle et al (2006) observed the decomposition of ozone in wastewater was controlled by direct reactions with reactive moieties of the dissolved organic matter and introduced a kinetic model to account for ozone decomposition due to these reactions at sub-stoichiometric ozone concentrations (Buffle and Von Gunten, 2006). Pocostales et al. (2010) observed degradation of ozone-refractory micropollutants during ozonation of wastewater due to HO[•] generation by the reaction of ozone with organic matter. They observed addition of 1 mg H₂O₂/L had little effect on HO[•] yield, but high ozone doses and at a higher ozone to H₂O₂ ratio of 2, showed an increase in HO[•] production (Pocostales et al. 2010).

Catalytic Ozonation

Catalytic ozonation may provide a means to make ozonation of wastewater more commercially viable, limit bromate formation, and reduce chemical usage (i.e. replace H₂O₂ addition). Catalysts increase the rate of reaction, thereby reducing the contact time

or ozone dose required to achieve the same results when no catalyst is used. Examples of catalysts currently used in water treatment include TiO_2 , activated carbon and metal oxides. Catalytic effects of both TiO_2 and activated carbon during ozonation of a range of compounds have been demonstrated by others. Table 2.3 summarizes the key parameters and findings of the studies most relevant to the research in this dissertation (specifically Chapter 4).

Table 2.3 Summary of relevant catalytic ozonation research

Catalyst	Target Pollutant(s)	Sample Matrix/ Reaction Time	Description/Results	Ref
TiO ₂	Clofibric acid	Aqueous solution pH 3, 5 and 7 t = 10-20 min TiO ₂ = 1 g/L	No catalyst, pH 3, k=8.16x10 ⁻³ +/-3.4x10 ⁻⁴ w/catalyst, pH 3, k=2.17x10 ⁻² (3 fold increase) Theorized effect due to adsorption on catalytic sites rather than promotion of ozone decomposition	Rosal et al. 2009
TiO ₂	Carbamazepine Naproxen	Semi-continuous Temp =25 °C pH = 3-7 TiO ₂ = 1g/L	Pollutants completely consumed in first few min of reaction Mineralization during non-catalytic reached ~50% w/in 10-20 min ~75% w/catalyst in acidic and neutral solution (best in slightly acidic) Probably adsorption of reaction intermediates on Lewis acid sites Catalyst enhanced ozone decomposition in acid, inhibited in neutral	Rosal et al. 2008
TiO ₂ on silica-gel	Nitrobenzene	Investigated pH and catalyst dose	Increase of 21% removal over ozone alone Nitrobenzene degradation influenced by carbonate and t-butanol TiO ₂ /silica-gel catalyzed ozonation followed radical-type mechanism Better performance at normal to basic pH Better removal at higher catalyst dose; found independent of nitrobenzene dose	Yang et al. 2009
GAC	Gallic acid TOC	Secondary effluent WWTP (TOC = 171 mg/L, pH = 6)	No loss of catalytic activity after four times. Some GAC deactivation attributed to porosity destruction and surface oxidation produced by reaction of aqueous ozone on GAC surface Better removal of TOC than adsorption alone, or ozonation alone	Alvarez et al. 2009
GAC	Phenol	Synthetic saline wastewaters	Maximum phenol degradation at pH 8, 20 gGAC /L NaCl showed no adverse effect between 0.5-50 gGAC/L Reused 5 times	Moussavi et al. 2009

Catalyst	Target Pollutant(s)	Sample Matrix/ Reaction Time	Description/Results	Ref
TiO ₂	Clostridium perfringens	Natural water 0.9% NaCl 0.04 mM H ₂ O ₂ 1 g/L TiO ₂	4-log inactivation reached at: 3.6 mg/L ozone; 4.25 mg/L ozone-TiO ₂ ; 2.7 mg/L ozone- H ₂ O ₂ 4-log inactivation with 0.9% NaCl: 0.42 mg/L ozone; 1.15 mg/L TiO ₂ -ozone; 0.06 mg/L ozone- H ₂ O ₂	Lanao et al. 2008

Ozonation to Reduce Membrane Fouling

Ozonation of secondary effluent prior to membrane filtration reduces membrane fouling. Lehman and Liu (2009) showed that if the dissolved ozone concentration at the membrane surface is higher than 0.05 mg/L, then stable membrane fluxes of greater than 95% of the pure water flux can be maintained. That is, if the ozone dose is slightly greater than the instantaneous ozone demand of the feed water, limited flux decline was observed (Van Geluwe, Vinckier, et al. 2011). Lee et al (2005) showed something similar – optimal ozone dose for pre-oxidation of wastewater effluent was 0.1 mgO₃/L residual (Lee, S. et al. 2005).

There are several theories on how and why ozonation reduces membrane fouling. A summary of literature available on reduction of membrane fouling through ozonation is provided as Table 2.4, while additional details of the most relevant research is provided below. Ozonation is thought to reduce membrane fouling through its impact on the properties and molecular size distribution of organic matter (mineralization of small organics and breaking large molecules) (Zhu et al. 2008, 2010). Filloux et al. (2012) observed a reduction in biopolymers and increased low MW humic substances during ozonation of EfOM, but saw no impact on TOC concentration. They saw a decrease in fouling through pre-ozonation during UF when compared with untreated secondary effluent; indicating the higher molecular weight fraction of EfOM plays a significant role in low-pressure membrane fouling and ozonation reduced fouling (Filloux et al. 2012).

Table 2.4 Pre-ozonation, Organic Colloids, and/or Membrane Fouling

Water Source	Type	Colloid	Ozone Dose	General Observations	Mechanistic Insight	Ref
Seawater	MF	NOM	Varied	<p>Significant flux decline in both hydrophilic and hydrophobic membrane</p> <p>Much higher fouling in hydrophobic membranes</p> <p>Pre-ozonation reduced fouling for hydrophobic membranes but led to more severe fouling for hydrophilic membrane compare to non-ozonated seawater</p>	Hydrophobicity of membrane impacts fouling potential	Oh et al. (2009)
Model dairy wastewater (diluted skim milk powder and Chemipure CL80)	NF	Surfactant, protein, fat, others	1.0 or 0.5 dm ³ min ⁻¹ of 30 mg dm ⁻³ ozone gas	<p>Ozonation time, detergent and the gas flow rate affected flux and membrane fouling by micro-flocculation</p> <p>Micro-flocculation effect of ozone played significant role at higher gas flow rate, with a decrease in membrane fouling and an increase in gel formation</p> <p>At lower flow rate, effect of the degradation of large molecules more pronounced, causing a higher flux, and decreasing membrane resistance</p>	<p>Micro-flocculation effect of ozone impacts fouling</p> <p>Degradation of large molecules reduced fouling</p>	Laszlo et al. (2009)

Water Source	Type	Colloid	Ozone Dose	General Observations	Mechanistic Insight	Ref
Secondary Effluent	MF	EfOM	5mgO ₃ /mgSS 15 min contact time	Ozone addition broke large particles into smaller ones - leading to a narrower and smaller range particle size distribution Pre-ozonation and increased contact time reduced filtration resistance	Change PSD to a narrow range Change zeta potential of the particulates	Zhu et al. (2008)
Secondary effluent	MF	EfOM	30 mg/L	Increase in large particles following pre-ozonation and corresponding increase in fouling (possibly from lysing of bacteria)	Increased particle size improved removal	Zhu et al. (2009)
Simulated surface water	RO	Solids, turbidity COD	0.3 mg/L	Pre-ozonation showed better solid and organic removal rate and decreased flux and resistance changes over time	Major fouling mechanism identified as pore blockage	Brown et al. (2008)
Secondary effluent	MF	SMPs	varied	Hydrophilic substances have stronger fouling potential (higher macromolecular and carboxylic group content with higher SMPs or SMP-like substances) Pre-ozonation increase carboxylic and phenolic groups (could aggravate fouling)	Reduction of DOC (including mineralization) dominant criteria for reducing fouling	Zhu et al. (2010)

As discussed previously, the high molecular weight fraction of EfOM includes EPS and SMPs. These biopolymers include lipids, polysaccharides, and proteins. In regards to lipids, extensive literature is available from the medical community on the effect of ozone on the lipid bilayers of cell membranes (Pryor et al. 1995; Kafoury et al. 1999; Bridges et al. 2000; Connor et al, 2004) and from the food industry on lipid oxidation (Kubow 1992; Adegoke et al. 1998; German 1999; Morrissey et al. 2003; Soares et al. 2012). Relative to the lipid component of EPS/SMPs the processes of ozonolysis and lipid peroxidation are applicable, and are described briefly. However, the impacts of ozonation on lipid bilayers of vesicles have yet to be applied to understanding the role low-dose ozonation plays in reduction of membrane fouling during water reclamation.

Ozonolysis. Ozonolysis is the formation of organic compounds through cleavage of an alkene (at least one double bond) or alkyne (at least one triple bond) by molecular ozone in which carbon-carbon bonds are replaced with a double bond to oxygen. This reaction results in either alcohol (-OH) or carbonyl (C=O) compounds (reductive); or ketones [RC(=O)R'] or carbonic acid [OC(OH)₂] compounds (oxidative).

Lipid Peroxidation. Lipid peroxidation is the degradation of lipids through radical chain reactions produced during oxidation (Pryor et al. 1995). Figure 2.2 illustrates the radical chain reaction of lipid peroxidation. In the case of ozonation, initiation occurs when HO[•] react at carbon-carbon double bonds of polyunsaturated fatty acids, where the hydrogen ions of methylene bridges

(-CH₂-) are highly reactive, to form a water molecule and a fatty acid radical. The radical chain reaction is propagated as the fatty acid radical reacts with oxygen to produce peroxy-fatty acid radicals. This radical reacts with other fatty acids or itself, thereby producing a new fatty acid radical and lipid peroxide or cyclic peroxide, respectively. The radical chain reaction continues until termination occurs when two radical species reacted with each other and produce a non-radical species (Pryor et al. 1995).

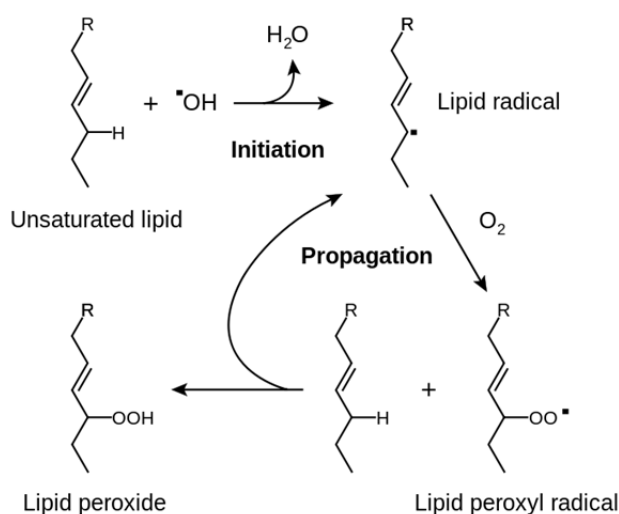


Figure 2.2 Radical Reaction Chain of Lipid Peroxidation. Image reproduced with permission. Sources: (Young and Mceneny 2001; Vickers 2007).

Deficiencies in the Literature

Through the review of a large portion of literature available on EfOM, membrane fouling, and ozonation some important gaps in the literature became apparent. There are several papers available on catalytic ozonation in industrial and model waters. This literature shows a promising trend for use of catalytic ozonation in a municipal wastewater, but limited research has been done to address this subject. Additionally,

some research has demonstrated an increase in HO[•] through ozonation of wastewater without addition of H₂O₂, but if and when the addition of H₂O₂ for advanced oxidation of wastewater is beneficial is not clear, or if the use of a solid phase catalyst would be more efficient.

In terms of membrane fouling, the impact of bulk water quality and several components of EPS have been investigated. However, membrane fouling by the phospholipid-formed components of EPS has not been explored and may play a critical role during filtration of secondary effluent. Additionally, several papers are available demonstrating a reduction in membrane fouling through ozonation. However, the associated changes of structure and composition of organic materials, specifically phospholipid-formed vesicles through ozonation to reduce membrane fouling have not been explored. Viewing these deficiencies in available literature as a whole, leads to two critical questions:

1. How do drought-related wildfires, dust storms, and flooding impacted water quality of the surface water supply?
2. During ozonation of secondary effluent, is production of HO[•] enhanced by adding liquid initiators or catalytic solids?
3. Why does ozonation prior to UF reduce membrane fouling?

Using the background information provide here in Chapter 2, hypotheses to address these research questions were made and are presented in Chapter 3.

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Chapter 3

EXTREME WEATHER IMPACTS ON WATER QUALITY IN CENTRAL ARIZONA

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Authors: Michelle Barry^{1*}, Chao-An Chiu² and Paul Westerhoff¹

1. School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287, USA

2. Carollo Engineers, 4600 E Washington Street, Suite 500, Phoenix, AZ 85034, USA

*Corresponding Author (responsible for approximately >90% of the written text, 2-3 years of DOC sample collection and analysis, 95% of all figures and data analysis)

Abstract

Extreme weather events due to climate variability are and will impact surface water supplies. Water quality measurements in central Arizona were used to quantify changes in dissolved organic carbon (DOC) and turbidity due to massive monsoon dust storms, floods, and drought-associated wildfires. First, we define “extreme events,” and explain the criticality of DOC and turbidity levels in water treatment. We describe specific extreme events, quantify subsequent changes in DOC and turbidity, and discuss their impacts water treatment processes and public perception of water quality. The findings of this study show a correlation between dust storm events [identified by average day PM_{10} (particulate matter 10 microns or less in size) values greater than 98th percentile values,] and change in surface water turbidity ($R^2=0.6$), attenuation of

increased DOC loading due to upper watershed events through the reservoir systems, 30-40% increase in TOC and a 120-600% increase in turbidity following severe flooding in 2005, and differing impacts of upland and lowland wildfires. Finally, we suggest a means to mitigate these impacts on both perceived and actual water quality by an integrated use of water information technologies.

Introduction

Extreme weather events are likely to increase in the late 21st Century due to climate variability (IPCC 2013). Extreme weather events are “any substantial change in weather type, severity, frequency, duration, or combination of events,” (Stanford et al. 2014). These events may be extreme and relatively brief, or occur over a longer period of time (e.g., drought, wildfires). The most recent IPCC report indicates a virtual certainty there will be more frequent temperature extremes on daily and seasonal timescales due to increased global mean temperatures (IPCC 2013). Drought conditions also increase the likelihood of wildfires (Westerling and Swernam 2003), flash floods (Whitehead et al. 2009), and dust storms (Hahnenberger and Nicoll 2014, Reheis and Urban 2011). Understanding extreme weather-associated impacts on the drinking water supply is important in assessing a water treatment plant’s (WTP) ability to treat the water and thereby reduce potential impacts on human health (Whitehead et al. 2009).

Among other water quality changes, severe weather events can impact DOC and turbidity levels at WTPs. DOC is a precursor in the formation of carcinogenic, disinfection by-products (DBPs) produced during drinking water treatment when

chemical disinfectants (e.g., chlorine) react with DOC (Amy, Chadik, and Chowdhury 1987, Reckhow, Singer, and Malcolm 1990). (Tang et al. 2013) demonstrated impacts on DOC concentrations from simulations of projected climate change scenarios. They found short-term drought events having a greater effect on DOC compared with increasing atmospheric temperatures, thus underscoring the importance of quantifying the changes in DOC due to extreme weather events, such as drought, to help prepare WTPs to respond to these potentially rapid changes in a manner to limit DBP production and thereby protect public health (Peterson et al. 2014).

Climate variability will likely impact water quality in several different ways. Whitehead et al. (2009) outlined several of these potential impacts including some of the following. In periods of high precipitation, there may be a dilution of contaminants due to increased volume of water, or higher sediment load in rivers and lakes due to flooding. Changing water temperatures will likely affect chemical reaction kinetics and therefore type and/or concentrations of reaction products. During periods of drought, water retention times in reservoirs will likely increase, which can contribute to increased algal blooms due to higher nutrient concentrations (less dilution) and corresponding periods of low dissolved oxygen.

Specific quantitative data on these trends is limited, but a few examples are noteworthy relevant to this study. Michalak et al (2013) hypothesized high precipitation over agriculture lands created a pulse of high concentrations of nutrients to Lake Erie. This event was then followed by “uncommonly warm and quiescent conditions in late spring and summer, and an unusually strong resuspension event” leading to a record

setting algal bloom. In the Pacific Northwestern United States (US), turbidity data from a drinking water source correlated with high stream flow and modelling predicted a likely increase in exceedences of turbidity limits set by the USEPA at WTPs due to extreme weather events (Towler et al. 2010). In a Midwestern US reservoir, an increase in the amount of chlorophyll A and turbidity was measured as a result of drought (Olds et al. 2011). Qualitative data is critical in preparing for future extreme weather events and some research projects are underway to quantify the impacts of extreme weather on water quality (Michalak 2014, Stanford et al. 2014), yet such information is lacking – especially in the southwestern US where the semi-arid climate already includes weather extremes.

Central Arizona, located in the desert southwest of the US, is already subject to extended periods of drought, wildfires, flash flooding, and dust storms. Central Arizona includes the Phoenix metropolitan area, which is home to roughly 4.3 million people (Sunnucks 2013), and a combined drinking water treatment capacity of greater than 1-billion gallons per day. High temperatures are common in Phoenix during summer months (April – September); with an average daily high temperature in August of 104⁰F (NOAA 2011). Annual precipitation is limited to an average of 10 in/yr occurring on an average of only 28 days per year (NOAA 2013). Ongoing drought conditions in Arizona over the past 10 years have led to record-setting fire seasons, declining stream flow and large-scale forest mortality (Meadow, Crimmins, and Ferguson 2013). To date, the net effects of these events on water quality, WTP operations, and public perception have not been analyzed.

The goal of this study was to demonstrate the impacts of extreme weather events on surface water quality and discuss subsequent impacts on WTP operations and public perception of water quality using long-term (2000-2013) data from the central Arizona water supply. First, we define extreme weather events using weather, hydrological and air quality data. Second, we focus on the extent to which extreme events rapidly change levels of turbidity and DOC and discuss the impacts to water treatment processes. Four specific events were used as case studies to illustrate the impact of extreme weather on water quality and treatment processes. The findings of this study quantify the changes in turbidity and DOC levels subsequent to specific dust storms, flooding, and wildfires and include a suggested approach for mitigating these impacts on both perceived and actual water quality by an integrated use of water information technologies.

Methods

Site Descriptions

The metro-Phoenix regional surface water supply consists of water from the Central Arizona Project (CAP) system and the Salt and Verde River watersheds (Figure 3.1). Samples were collected from all three sources. The CAP delivers water to metro-Phoenix from the Colorado River through approximately 150 miles of canal beginning at Lake Havasu. Canals convey water to roughly 15 WTPs, and seasonal storage is available in Lake Pleasant, an offline reservoir (not part of the waterway, i.e. water is pumped into or from). As the final reservoir upstream of WTP intakes of metro-Phoenix, Lake Pleasant is also a terminal reservoir. Natural drainage into Lake Pleasant from the Agua

Fria River typically supplies a small amount of inflow (< 10% of the reservoir inflow).

Water levels typically fluctuate considerably (> 150 ft) throughout the year. Lake Pleasant is filled with Colorado River water typically from October to April and released from Lake Pleasant into the downstream CAP canal from May to September. As a result, inflow between May to October was approximately ten times lower than the rest of the year over the study period. This mode of reservoir operation and associated range of water levels leads to biannual turbidity spike during transition periods, similar to heavy precipitation events over natural waterways, between filling or releasing water from Lake Pleasant.

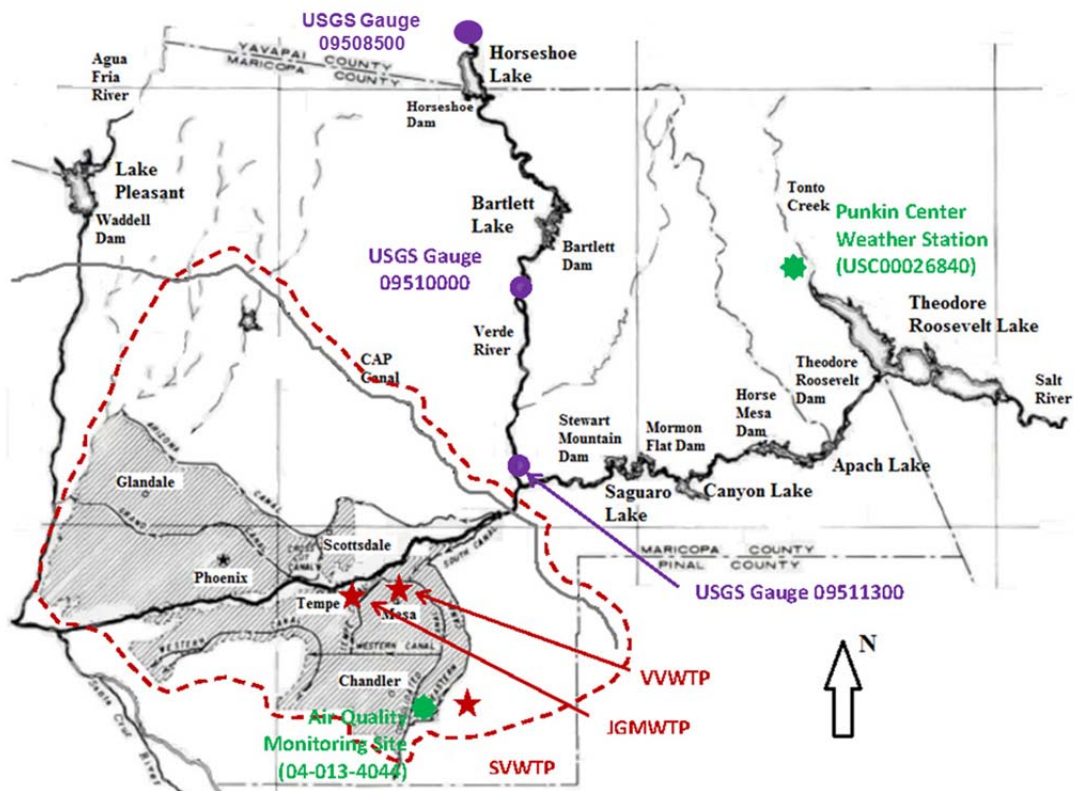


Figure 3.1 Location of the Reservoirs around Phoenix, Arizona. Concrete canals convey surface waters to water treatment plants (n ≈ 15) within the urban area. Shaded area shows the Salt River Project water service area. Dash line represents the Metro-Phoenix region served by canal system.

The Salt River watershed originates in the White Mountains and New Mexico. There are four reservoirs on the main Salt River (Roosevelt Lake, Apache Lake, Canyon Lake, and Saguaro Lake) and two on the Verde River (Horseshoe Lake and Bartlett Lake). The Verde River joins the Salt River below the lowermost reservoirs. These reservoirs store water derived mainly from snowmelt and precipitant at higher elevations with most of the fresh water (> 50%) entering the Salt River reservoir system during May to August each year (Chiu 2012). Saguaro Lake is the lowest of four reservoirs on the Salt River and is used for water storage and flood control. Three of the upstream Salt River reservoirs have hydropower generation facilities, and water is pumped back from Saguaro Lake to Canyon Lake and Apache Lake during summer months through pump-back piping to increase hydropower output. The number of reservoirs and operation of these reservoirs on the Salt River results in a hydraulic retention time of approximately 5 years.

Bartlett Lake is an inline, terminal reservoir on the Verde River located approximately two miles downstream of Horseshoe Lake. Most water enters these two reservoirs following snowmelt at higher elevations between February and May and is stored throughout the summer, with minimal release to maintain channel flow in the Verde River. Water levels typically fluctuated between 30 to 60 feet for Bartlett Lake during the study period. Although Bartlett Lake is the lower reservoir of the two reservoir system on the Verde River, the upper reservoir – Horseshoe Lake – is operated with short hydraulic residence time (~60 days) and is completely drawn down during the summer.

Field sampling

Monthly epilimnion (15 ft below the water surface) samples were collected from Saguaro Lake, Bartlett Lake, and Lake Pleasant during the study period. River and canal water samples were grab samples. The United States Geological Survey (USGS) collected samples in the upper Salt River near the inlet to Roosevelt Lake (USGS station 09498500) between 2002 and 2004 to investigate the impact of the Rodeo-Chedaski Fires (summer of 2002) on downstream water quality. All samples were stored at 4°C until analysis. Samples were filtered through ashed (550°C, minimum of 20 minutes) glass fiber filters. Filtered samples were used to measure dissolved organic carbon (DOC) of the water.

Historical data

Historical data was obtained from several different databases. Raw water turbidity values for the Johnny G. Martinez WTP (JGMWTP), Santan Vista WTP (SVWTP), and Val Vista WTP (VWVWTP) were provided by the Cities of Tempe, Chandler/Gilbert, and Phoenix, Arizona, respectively. PM₁₀ (particulate matter less than 10 microns in size) data was obtained from USEPA AirData website for the air quality monitoring station closest to the SVWTP (AQS_SITE_ID 04-013-4044). Precipitation data near the Sunflower Fire burn area was obtained from the Punkin Center Weather Station (GHCND: USC00026840). River flow data for the Verde River was obtained from USGS gauges 09508500 (Verde at Tangle Creek, located above Horseshoe Dam), 09511300 (near Scottsdale, Arizona), and 09510000 (located downstream of Bartlett Lake).

Analytical Methods

Samples were filtered through ashed glass fiber filters (Whatman GF/F) prior to DOC analysis. DOC concentrations were measured using a Shimadzu TOC-V_{CSH} analyzer (high temperature combustion at 720°C non-dispersive infrared detection with TNM-1 unit chemiluminescence detection) (Shimadzu Corp.) Blank samples (ultrapure water) and quality control (QC) samples were measured every 10 samples.

Results and Discussion

Flooding, dust storms and wildfires each impact turbidity and DOC levels in unique ways. The duration and magnitude of water quality changes were different for extreme events occurring in the upper watershed (i.e. above the reservoirs) versus extreme events occurring the in the lower watershed(s) (i.e. below the reservoirs). The impacts to water quality of dust storms, floods and wildfires are discussed and specific events are presented as case studies to illustrate the level of impact both on plant operations as well as public perception of water quality.

Dust storms

Central Arizona is annually subjected to multiple dust storms, which can be exacerbated by drought conditions as high velocity winds blow across sparsely vegetated desert lands (Figure 3.2). The National Oceanic and Atmospheric Administration (NOAA) reports more than 100 dust storms occurring across Arizona in the 10 years prior to 2012 (NOAA 2012). These storms vary in size and severity, extending more than 100 miles wide and 1.5 miles high (Raman, Arellano, and Brost 2014). Convectively-driven dust

storms are associated with cyclonic storm activity involving cold frontal passages and upper level cut-off lows (Nickling and Brazel 1984).

Dust storm dust varies in composition depending on geographic, hydrologic, ecologic, land use and climate conditions. Common components include particulate matter, industrial pollutants, soot from wildfires, specific minerals, metals and metalloids, pathogens, pesticides, etc. In semiarid environments (such as Arizona) mining operations are significant sources of metal and metalloid contaminants. (Reynolds et al. 2007)



Figure 3.2 A Dust Storm in Central Arizona during March of 2013. Photo taken looking west across south Chandler from an elevation of roughly 1000 ft. Courtesy of Jerry Ferguson Photography.

Dust storms not only contribute to PM_{10} in Arizona (Raman, Arellano, and Brost 2014), but also impact particulate matter loading in surface waters, which cause turbidity and elevated DOC. The latter, secondary effects of dust storms on water quality are less reported than PM_{10} events. The SVWTP is located on the outer southeastern edge of the Phoenix metropolitan area, where dust storms are often more extreme (Nickling and Brazel 1984). Raw water quality data for the SVWTP was compared with PM_{10} data from a nearby weather station (Figure 3.1). Raw water at the SVWTP is from the CAP canal

system, which is a very low and consistent turbidity source (average daily values ranged from 2-25 NTU from June 2010 – May 2012). Average daily PM₁₀ concentrations between June 2010 and May 2012 (695 days) ranged from 2 to 402 µg per standard cubic meter (µg/m³ SC) with an average of 34 µg/m³ SC. Of these days, 15 days had PM₁₀ values greater than 98th percentile (125 µg/m³ SC) and were considered dust storm events.

Figure 3.3a shows PM₁₀, turbidity, and total organic carbon (TOC) variation over time. From the figure there appears to be some periods of higher turbidity during periods of higher PM₁₀ values (March and September 2011, and March 2012). In order to determine this correlation raw water turbidity was plotted as a function of PM₁₀ in Figure 3.3b. A trendline through this data has an R² value of 0.004; indicating little to no correlation for all 695 days of data. However, considering only dust storm events (PM₁₀ values greater than the 98th percentile), we determined a somewhat stronger correlation (R² = 0.2). Because raw water turbidity values vary over time (<1 – 25 NTU) the correlation between dust storms and raw water turbidity may be somewhat masked. In order to eliminate the bias of the “base” turbidity concentration, a comparison of the change in turbidity and the change in PM₁₀ values was done (Figure 3.3c). Statistical analysis of PM₁₀ and San Tan WTP raw water turbidity showed a correlation (R² = 0.6) between change in raw water turbidity from the previous day and change in PM₁₀ from the previous day for days with >98th percentile PM₁₀ values, thereby establishing a correlation between dust storms and surface water turbidity.

Based on the limited TOC data available, a correlation between dust storm occurrence and TOC concentration is difficult to establish. However, Westerhoff and Anning (2010) measured DOC concentrations between 4-10 mg/L during the initial 2 minutes of rainfall following a dust storm event in central Arizona. They compared these concentrations to DOC concentration of 1-2 mg/L measured later in the rainfall event. Their findings imply the organic carbon in dust storms is soluble, thereby increasing DOC concentrations in surface waters impacted by dust storms.

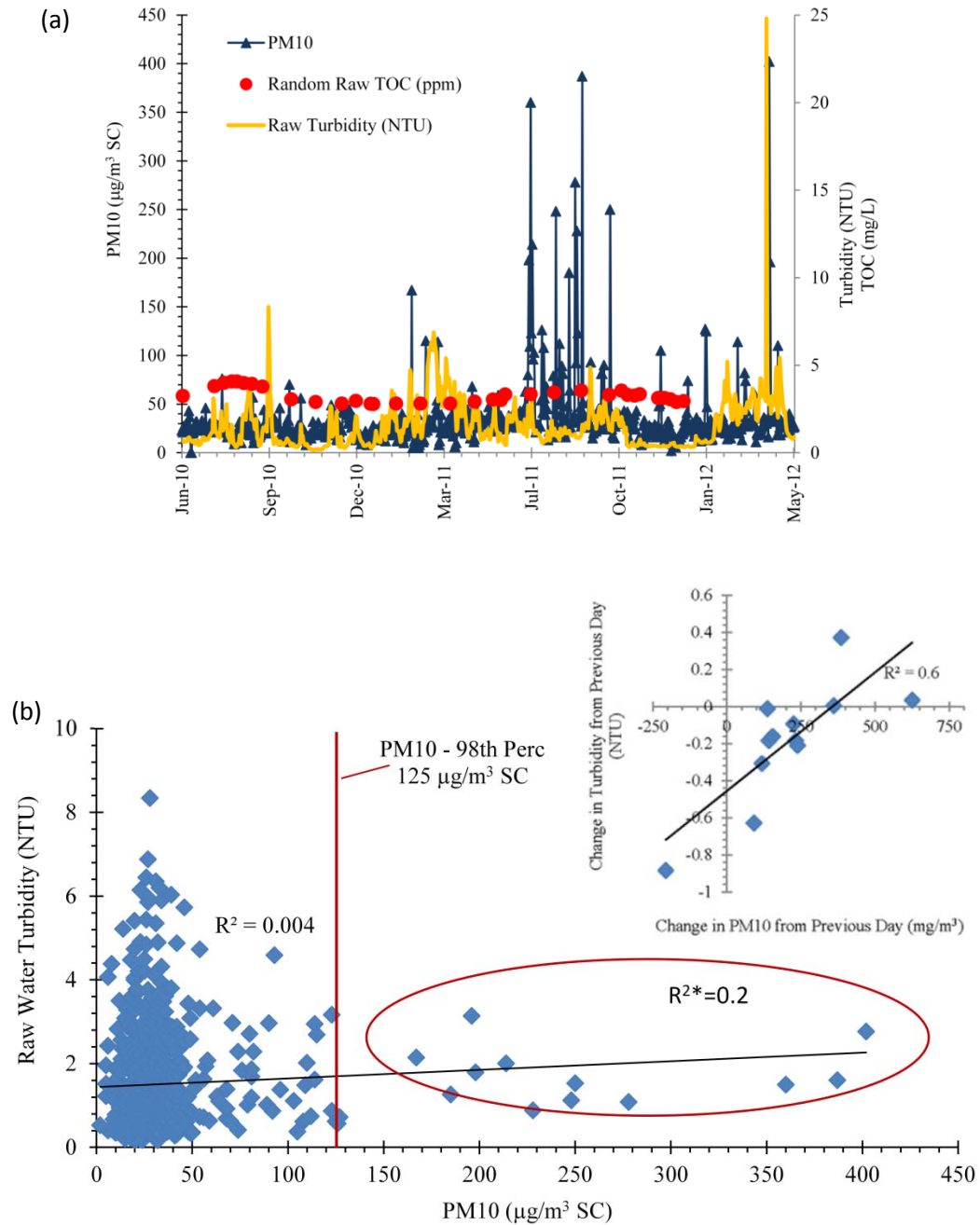


Figure 3.3 Comparison of Variations of PM₁₀ Data from Weather Station AQS_SITE_ID 04-013-4004 and SVWTP Raw Water Turbidity and (a) TOC data from (June 1, 2010 – May 2, 2012); (b) Correlation between PM₁₀ and Raw Water Turbidity; and Inset to (b) Correlation between Change in PM₁₀ and Change in Raw Water Turbidity for Days with greater than 98th Percentile PM₁₀ values.

The impact of dust storms on water quality is expected to vary depending on the location of the dust storm based on the types of soil (i.e. desert sands versus tilled soil for agriculture) and other matter entrained by high wind speeds, including pesticides. Dust storms also have the potential to influence marine microbial population densities and transport soil-associated toxins (Griffin and Kellogg 2004). The implications of changing turbidity and potentially other matter in the water supply on water treatment processes should be investigated in the future. In areas impacted by dust storms, further investigation should be done to identify what particulates and compounds are entering the water supply via dust storms.

Flooding

Flooding is of particular importance in semi-arid climates such as central Arizona, where the vast majority of waterways are ephemeral or intermittent (brief flow briefly in direct response to precipitation in the immediate vicinity or continuous flow only during certain times of the year) (Levick et al. 2008b). The USEPA estimated that 94 percent of Arizona's streams are ephemeral or intermittent (Levick et al. 2008a). Organic matter builds up in these stream/river beds due to annual vegetation cycles of spring growth and summer decay (Parks and Baker 1997). After several months with no precipitation, the spring runoff or first rains flush this accumulated material through the watershed; exporting more organic matter and particulates downstream. Approximately half of the total annual rainfall in central Arizona occurs as winter precipitation between October and March. The other half falls during monsoon season in the late summer months. These monsoon storms are typically short in duration, with periods of intense rainfall often

resulting in flash floods (CLIMAS 2012). The resulting variable stream flows in ephemeral and intermittent systems most often occurs as flash floods, lasting for minutes or persisting into weeks and that the turbulent, high velocity stream flow moves large quantities of sediment from the stream bed and overland flow into downstream channels and reservoirs (Levick et al. 2008a).

Chiu 2012 showed DOC loading significantly correlated with spring runoff and was intensified by dry-duration antecedent to first flush events. When these “first flush” events have occurred in the upper watersheds of the Verde, Salt, and Colorado Rivers, the reservoir systems typically attenuate the higher organic and turbidity loads associated with first flush events so that WTPs are not directly impacted. Monthly DOC concentrations for Bartlett Lake, Lake Pleasant and Saguaro Lake are shown in Figure 3.4. DOC concentrations fluctuated by 1-5 mg/L throughout the study period. The average measured DOC levels were 3.6, 3.8 and 4.9 mg/L with standard deviations of 0.7, 1.4, and 0.9 for Lake Pleasant, Bartlett Lake, and Saguaro Lake, respectively. Lake Pleasant DOC concentrations showed the least variation, as indicated by the lowest standard deviation and illustrated by the smaller corresponding box and whisker plot (inset Figure 3.4). The relatively stable DOC concentrations in Lake Pleasant are likely due to the relatively long hydraulic residence time (400 days) as well as its operation as off-stream reservoir (i.e. not subject to the same impact of extreme weather events on water quality of in-line reservoirs/natural lakes). The high DOC concentration in early 2005 corresponds to “first flush” through an ephemeral river located upstream of Lake Havasu on the Colorado River.

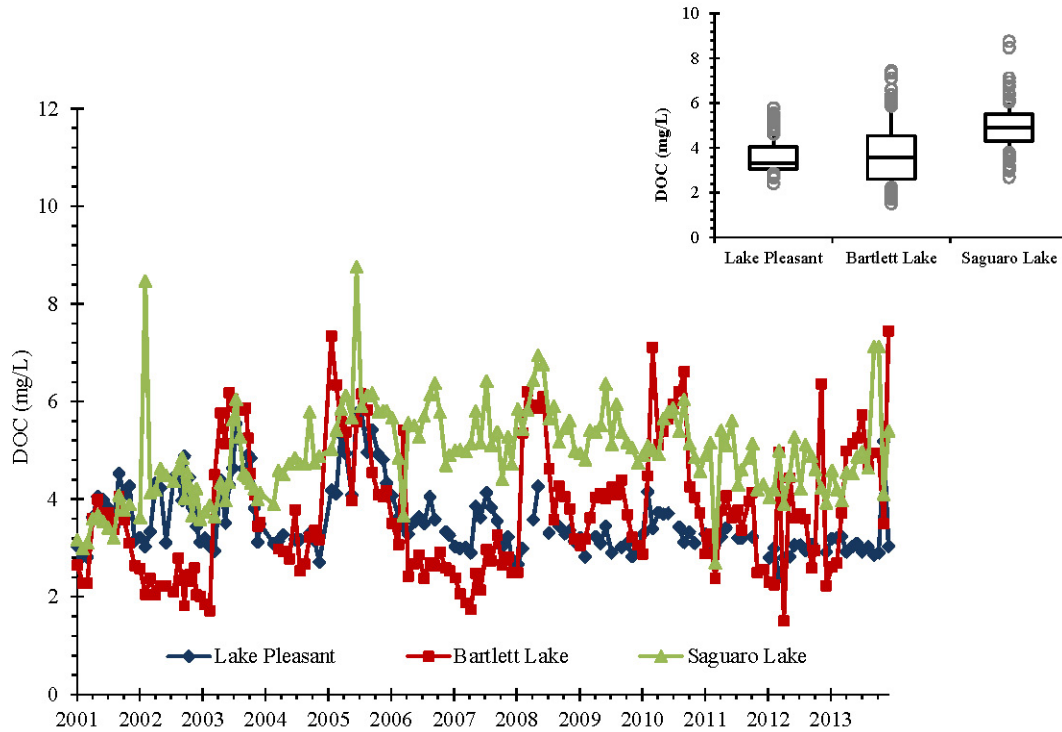


Figure 3.4 Long-term DOC Concentrations in the Terminal Reservoirs of the Drinking Water Supply for Metro-Phoenix Area from Jan 2001 – Dec 2013. Inset is a Box and Whisker Plot (whiskers at 10th and 90th percentile values and extreme events shown as grey circles).

Bartlett Lake had the most variation in monthly DOC concentration as indicated by the highest standard deviation (1.4 mg/L DOC) and illustrated by the corresponding large box and whisker plot shown in the Figure 3.4 inset. Bartlett Lake is more directly affected by spring snowmelt and precipitation in the upper Verde River watershed than either of the other reservoirs, which leads to higher variable in DOC concentrations associated with a first flush phenomenon in the spring and with precipitation events during other times of the year. The highest inflow to Bartlett Lake occurred during January to March of each year and accounted for 55% of yearly inflow. The highest DOC concentrations followed in March and June (~ 4 mg/L) most likely based on increased

algal activity during the warmer months and with the increased nutrients brought in by the previous increased flows from spring runoff.

The yearly variation of DOC in Saguaro Lake was less than observed in other reservoirs. This lower variation is attributable to the hydrological management and operational mode of multiple-lake system for Salt River resulting in longer retention times and DOC stability (i.e. impact of storm events were attenuated).

The inset in Figure 3.4 also shows “extreme” DOC events, that is, measured DOC concentrations greater than the 90th percentile value for the study period. Lake Pleasant had 16 “extreme events” with DOC concentrations greater than 4.6 mg/L (90th percentile). Bartlett Lake also had 16 extreme events with DOC concentrations greater than the 90th percentile value of 5.9 mg/L. Saguaro Lake had 14 days above a 90th percentile DOC concentration of 6.0 mg/L. Strong variation in organic carbon (measured as TOC or DOC) loading during early spring often requires timely adjustment of WTP processes to control production of DBPs. Conversely, little variation in organic carbon concentration in other months reduces the need for rapid adjustment of treatment process to maintain low DBP levels.

Typically the reservoir systems provide attenuation of high organic loading events; however, in some extreme cases high raw water turbidity and TOC concentrations have reach impacted downstream WTPs. This was the case in the early spring of 2005 when Bartlett Lake capacity was exceeded due to snow melt and heavy precipitation within the upper Verde River watershed (including flooding of Sedonna and Oak Creek Canyon), and water ran over the dam spillway. This rapid increase of flow in the Verde River

downstream of Bartlett Dam created a “first flush” type event, with a corresponding spike in TOC and turbidity levels measured at the downstream VVWTP (Figure 3.5).

Discharge flow measured below Bartlett Dam increased by 25 times. The two highest discharge flow rates occurred on January 5th (8,890 cfs) and February 10, 2005 (10,200 cfs). Correspondingly high raw water TOC and turbidity values at the VVWTP were recorded during Jan 4-5th (9.7 mg/L TOC, 240-350 NTU) and Feb 12th (10.3 mg/L TOC, 385 NTU). Roughly, in less than a day, TOC values increased between 30-40% and turbidity increased by 130-600%.

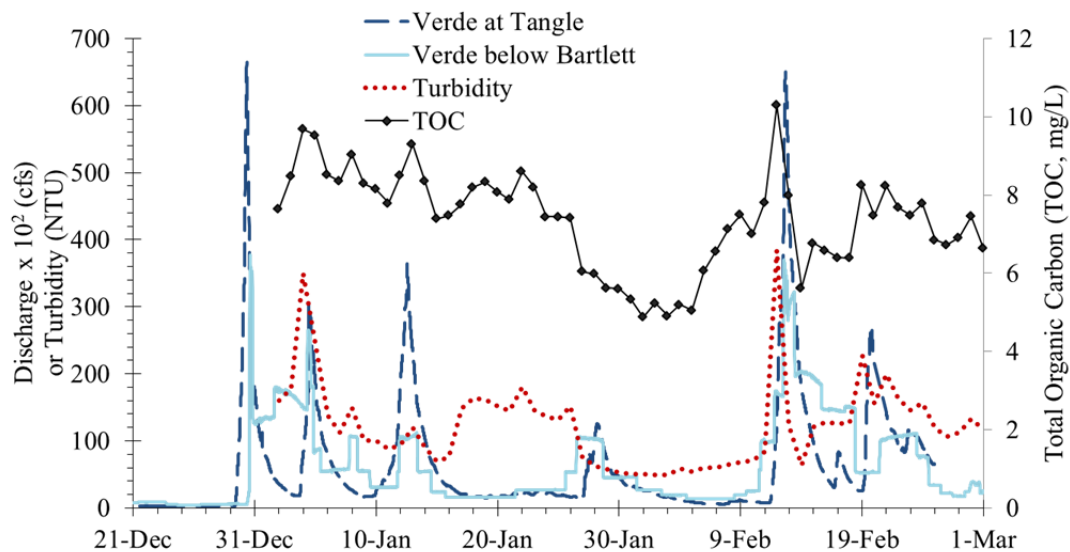


Figure 3.5 Verde River Discharge Flow at Tangle Creek (USGS 09508500) and Downstream of Bartlett Dam (USGS 09510000), and Raw Water Turbidity and TOC at the VVWTP in 2005 (turbidity and TOC data not available for 21 Dec – 31 Dec 2004).

Despite having presedimentation basins, high turbidity water reached the treatment processes, where operators worked to address the rapidly changing water quality through adjusting chemical feed for coagulation. They were unable to sufficiently

lower turbidity levels during coagulation/flocculation/sedimentation processes and high turbidity water did reach the filters, resulting in short filter run times (<12 hours). Though the turbidity was initially removed through the strained treatment processes, filter effluent eventually exceeded the EPA recommended turbidity of less than 1 NTU. Plant and city personal were concerned that higher turbidity in the finished water had the potential to contain pathogens and should not be consumed. Unfortunately, other City WTPs were offline for maintenance, and with only two of the City's five WTPs online, the VVWTP needed to keep producing water t in order to meet pressure requirements in the large distribution system.. Therefore, the City's water services department issued a "boil water advisory" to discourage drinking of tap water until the filter effluent turbidity levels were brought below the EPA recommend levels. From the Arizona Republic (Ruelas 2005), "For most Phoenix residents, the city's water scare stretched out over three days last week, beginning with an ominous plea to conserve last Monday night, escalating with a Tuesday morning order to boil water, and ending with a Wednesday afternoon all-clear from Mayor Phil Gordon, complete with a toast of tap water."

Several other WTPs in central Arizona were also operating at reduce capacity during this same time period for similar reasons (reduced filter run times, limited backwash waste storage, etc). Based on this extreme event, several changes were made in WTP operations by impacted cities in order to avoid a similar future event. These changes included: addition of multiple chemical feed systems to provide a range of coagulation options (polymers, both ferric and aluminum based coagulants, and lime to adjust alkalinity as needed), additional turbidity monitoring of recycled backwash water

with options to stop backwash return flow and release it elsewhere to avoid concentrating turbidity to untreatable levels, and an increase in groundwater wells to provide an alternate water supply. Additionally, the City of Phoenix modified city-wide drinking water system operation to have full-scale plant redundancy online when possible.

Wildfires

In the past decade, roughly 5.5 percent of the total area of Arizona has been burned by wildfires, including the two largest wildfires in Arizona history (Rodeo-Chediski Fire in 2002, and Wallow Fire in 2011) (NIFC 2012). The Rodeo-Chediski Fires left nearly 500,000 acres of total burned area with roughly 11% of the total area in the upper Salt River watershed. Record high temperatures and drought conditions in Arizona led to greater than 3,000 reported wildfires that burned more than 700,000 acres in 2002 alone. This extended period of drought has resulted in an increase in the number and size of wildfires in Arizona (Westerling and Swernam 2003). Drought and overcrowding of forests in this area had also previously led to a bark beetle outbreak that killed millions of ponderosa and pinion pine trees and therefore burned quickly, allowing the wildfire to grow quickly (USDA 2003).

Periods of droughts may be determined using the Palmer Drought Severity Index (PDSI). This index measures a balance between moisture supplied and moisture needed for a region. The index ranges from conditions of extreme drought (< -4) to extremely moist (< 4). From the years 1901-2012 the PDSI for central Arizona was mid-range (-0.04) compared with (-1.4) for the years 1999-2012; indicating a greater water deficiency in recent years.

A comparison of water quality constituents, pre- and post-fire, in the Salt River watershed was conducted in the years subsequent to the Rodeo-Chedeski Fire. Short-term effects (within one year) of this upland wildfire (i.e. upstream of terminal reservoirs), were an increase in nutrient, particulate, organic and metal concentrations in runoff water following storm-events over the burned regions of the watershed (Gill 2004).

Two years following the fire, the mass loading of all constituents decreased by one to three orders of magnitude. Pulses of various nutrients and metals observed within two years after the fires were attributed to drought conditions and post-fire concentrations returned to background levels within two years for most constituents analyzed (Gill 2004). Similar to flooding, the impact of runoff over burn areas in the upper watershed of the Salt River was attenuated through the reservoir system, thereby minimizing impacts to downstream WTPs.

In 2012 the Sunflower Wildfire burned approximately 17,500 acres within the lower Salt River basin (USFS 2014). Precipitation over both this burn area and unburned areas of the Verde River watershed rapidly increased the flow in the lower Verde River as measured at USGS gauge 09511300 (Figure 3.6). Because runoff in the lower basin enters the Verde River downstream of Bartlett Lake, there is no storage-based attenuation of increased turbidity and organic loading due. In addition to high turbidity and organic carbon levels in runoff over the burn area, runoff over the unburned regions of the Verde watershed also included significant quantities of soluble organic carbon from the terrestrial watershed due to years of dehydration, photolysis and decomposition due to drought conditions.



Figure 3.6 Illustration of the Sunflower Fire Burn Area, Sycamore Creek, Verde River USGS gauge near Scottsdale, AZ (09511300) and Neighboring Punkin Center Weather Station (GHCND: USC00026840).

Figure 3.7 shows the change in Verde River discharge corresponding to precipitation near the Sunflower Wildfire burn area and raw water turbidity measured at the downstream JGMWTP. Precipitation rates correlate with peaks in Verde River discharge that were immediately followed by turbidity spikes as high as 1400 NTU. In order to effectively treat the influx of mud and particulates caused by recent storm water

runoff in the Sunflower Fire burn area, the powdered activated carbon (PAC) feed was temporary turned off at the JGMWTP. PAC was being fed to lower DBP and THM precursors and to reduce “musty” taste and odor of the water caused by algal byproducts (MIB and geosmin). Thus, shutdown of PAC feed resulted in an increase in taste and odor in the water, and reduced DOC removal, impacting both perceived and actual water quality. To address potential public concerns, the city provided the following news release, “If you’ve noticed a “musty” taste and odor in your tap water over the last few days, it’s not your imagination – and you can rest assured that your drinking water is safe. The City of Tempe on Saturday changed the way it treats surface water for taste and odor in order to effectively treat an influx of mud and particulates caused by recent stormwater runoff in the Sunflower Fire burn area,” (2012).

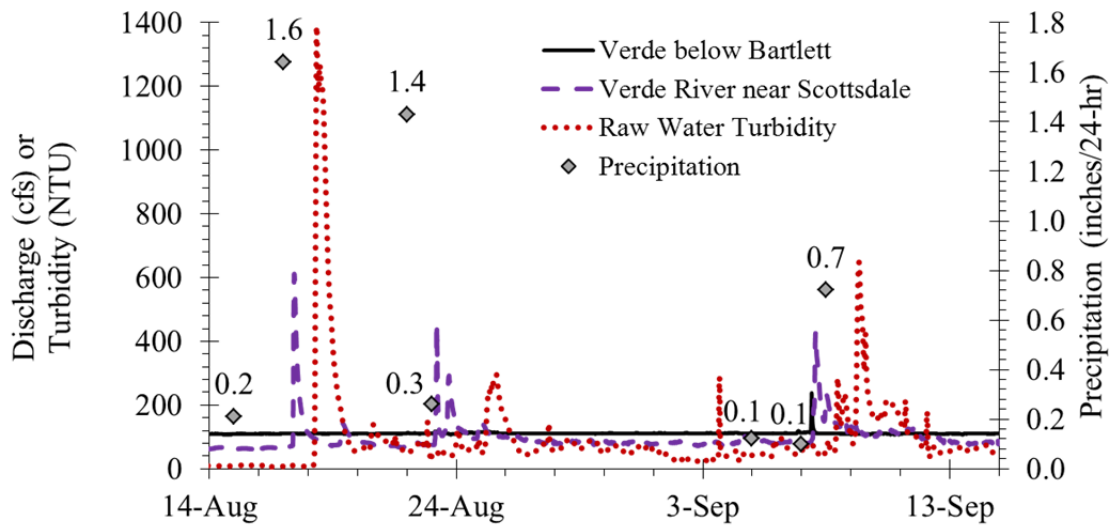


Figure 3.7 Amount of Precipitation Measured at Punkin Center Weather Station Located near the Sunflower Fire Burn Area; Verde River Discharge near Scottsdale (USGS 09511300); and Raw Water Turbidity at the JGMWTP in Tempe, AZ in 2012.

Summary

Extreme weather events increased the turbidity and organic loading in the water supply for the metro Phoenix area. Based on the experiences of central Arizona over the past 10+ years, relatively rapid increases in both DOC and turbidity are likely to occur following dust storms, flooding, and runoff over wildfire burn areas. A summary of the impacts on water quality and implications to water treatment operation of the extreme events of dust storms, flooding, and wildfire discussed in this chapter and their approximate duration is provided as Table 3.1. Each of these events resulted in an increased in organic content and turbidity of the surface water supply. When events occurred in upper watersheds, the reservoir systems were able to attenuate increases in turbidity and organic content with the exception of 2005. Events in the lower watersheds had a more immediate impact with higher turbidity/organic content waters reaching WTPs within hours or days of the event depending on the proximity of events and raw water intakes. Public perception of water quality was also influenced by the extreme events over the past decade, with impacts including fish kills in the news, taste and odor of the drinking water, and, in one case, issuance of a “boil water advisory.”

Table 3.1 Summary of impacts of extreme weather events on water quality

Extreme Event	Water Quality Impact	Water Treatment Implications	Duration of Impact
Dust Storms	Increased turbidity levels	Higher turbidity may require increased chemical feed for coagulation Varies depending on composition of particulate material deposited	days
Wet snow-rain higher elevation flooding into reservoirs	Increased turbidity, DOC and nutrient loading to reservoirs, which may lead to increased algal growth and corresponding increased DOC levels	Limited impact based on attenuation of event in reservoir system	Months to years
Thunderstorm flooding at lower elevations (below reservoirs) or atypical reservoir release	Rapid increase in turbidity and DOC	Increased chemical feed for coagulation Shorter filter run times	Days to weeks
Precipitation over wildfire burn areas in upper watershed	Increased turbidity, DOC and nutrient loading to reservoirs, which may lead to increased algal growth and corresponding increased DOC levels	Limited impact based on attenuation of event in reservoir system	Days to years
Precipitation over wildfire burn areas in lower watershed	Increased turbidity, DOC levels	Increased chemical feed for coagulation Shorter filter run times May impact effectiveness of T&O removal	days

Adjustments of water treatment plant processes were necessary to treat high turbidity water, and several system improvements have been made at WTPs within central Arizona in recent years to respond to these extreme events in a timely manner, however better integration of water information systems could be done to provide sufficient advanced notice of water quality “extreme events” to adjust operations to respond accordingly. Findings of this study demonstrate the potential benefits of an early warning system of extreme water quality events. This warning system could be developed using integrated water information systems including dopler radar systems, stream gauge readings, and online turbidity analyzers located within surface water systems (where possible), to provide water providers with advanced notification of extreme water conditions. Alert systems could include a level of severity, for instance a blue alert would indicate incoming storm events, a yellow alert would indicate measured changes in air quality or precipitation at weather/air quality monitoring stations, and a red alert would indicate rapid increase in flow measured at stream gauges, and high turbidity readings where possible. Stream gauge, weather, and air quality monitoring systems are already in place. An integration of the appropriate gauges/stations would be unique to each WTP, but should be located high enough upstream to provide sufficient warning to allow drinking water providers to adjust treatment processes or water supply (turn on groundwater wells, switch surface water sources, etc.).

Conclusions

A correlation ($R^2 = 0.6$) was determined for change in raw water turbidity at the SVWTP correlated with change in PM_{10} over the previous day during dust storm events

(daily average $PM_{10} > 98^{\text{th}}$ percentile PM_{10}). Upper watershed variation in DOC values in each reservoir range between 1-5 mg/L on average, with approximately 15 days (2% of the 13 year study period) of DOC concentrations were greater than their respective 90th percentile values. Precipitation over ephemeral or intermittent streams downstream of reservoirs were particularly problematic (rapid increases in turbidity and organic carbon) based on a “first flush” effect of high flows moving through dry or relatively empty stream or river beds. Change in turbidity levels and TOC concentrations corresponding with these floods ranged 130-600% and 30-40%, respectively. Impacts of wildfires varied with pulses of organic matter from precipitation over upper watershed burn areas being attenuated through reservoir systems, and rapid increases in turbidity and TOC following rain events over burn areas in the watershed downstream of terminal reservoirs. These rapid increases in turbidity (10 NTU to 1400 NTU over 2 days) required adjustments in treatment operations in order to meet drinking water requirements

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Chapter 4

PROMOTING HYDROXYL RADICAL PRODUCTION DURING OZONATION OF MUNICIPAL WASTEWATER

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Authors: Michelle C. Barry^{1*}, Kiril Hristovski², and Paul Westerhoff¹

Abstract

Hydroxyl radical (HO^\bullet) production during ozonation of municipal wastewater was investigated with and without liquid or solid-phase promoters. For liquid-phase promoters, an “ozone dose threshold” was observed, below which addition of H_2O_2 yielded no discernible increase in the rate of HO^\bullet production. This threshold occurs because ozonation of bulk organics in wastewater promotes HO^\bullet due to the presence of ambient promoters. Although solid-phase catalysts are reported to promote oxidation of contaminants, ozonation of effluent over TiO_2 or GAC was no more effective on trace organic removal than over inert surfaces.

Introduction

Production of high-quality reclaimed water is becoming increasingly important due to a rising world population, depletion of fresh water supplies, and concerns over water safety. In recent years, the presence of contaminants of emerging concern (CECs), including endocrine-disrupting compounds and pharmaceuticals, in reclaimed water have

led to some public reluctance toward water reuse. Public concerns over the potential adverse impacts of CECs to the environment and human health have driven research on methods for their destruction.

Ozonation oxidizes CECs in both potable and reclaimed wastewater (Westerhoff et al., 2005; Iriti and Faoro, 2008; Dodd et al., 2006; Huber et al., 2005). During ozonation in water, both molecular ozone and hydroxyl radicals (HO^\bullet) are present (Weiss, 1935; Beltran, 2004). Although some CECs (e.g., estradiol) react rapidly with ozone, others react very slowly because exposure to HO^\bullet controls their oxidation (Elovitz and von Gunten, 1999). Therefore, higher HO^\bullet concentrations improve the removal of such compounds.

Initiation of ozone decay results in the production of HO^\bullet . These HO^\bullet promote ozone decay by forming O_2^- , which then further reacts with ozone. The rate of HO^\bullet production can be increased during ozonation by increasing levels of free-radical reaction initiators and promoters (Langlais et al., 1991). This faster rate of HO^\bullet production may be achieved through H_2O_2 addition. (e.g., heavy metal oxides, activated carbon, etc.). Solid-phase catalysts (heavy metal oxides, activated carbon, etc.) provide an alternative to advanced oxidation by ozone/ H_2O_2 . Use of a solid-phase catalyst during ozonation is not a new concept (Beltran, 2004; Legube and Leitner, 1999). Excellent summaries of previous work on heterogeneous catalytic ozonation for various model and trace compounds are available for a wide range of catalysts (Beltran, 2004; Kasprzyk-Hordern et al., 2003). Among the catalysts employed during ozonation, titanium dioxide (TiO_2) and activated carbon have been used alone or in combination with other metal oxides for

oxidation of CECs including compounds common in municipal wastewater (e.g., salicylic acid, peptide and humic substances) (Cooper and Burch, 1999; Leitner et al., 1999; Fu et al., 2002; Beltran et al., 2002; Beltran et al., 2004; Rosal et al., 2008; Rosal et al., 2009; Yang et al., 2009), but not in a municipal wastewater matrix. Catalytic ozonation using TiO₂ or granular activated carbon (GAC) during municipal wastewater reclamation warrants further investigation based on the potential of replacing continuous H₂O₂ addition with a reusable catalyst.

A catalytic effect of TiO₂ during ozonation has been documented by others. Rosal et al., (2008) measured an increase from 50% of mineralization of carbamazepine and naproxen during ozonation to 75% when in the presence of TiO₂. Titanium dioxide on a silica gel improved removal of nitrobenzene by 21% when compared with ozone alone (Yang, 2009). A three-fold increase in reaction rate constants during the ozonation of chlorofibric acid when in the presence of TiO₂ has been shown (Rosal et al., 2009). Additionally, TiO₂ has been used in combination with ultraviolet (UV) radiation to increase HO[•] production as an advanced oxidation process due to its high chemical stability, optical and electronic properties, low cost, and absence of toxicity (Adamo et al., 2005; Linsebigler et al., 1995). Based on these TiO₂ properties and demonstrated improved oxidation of pollutants during ozonation, TiO₂ was selected for further testing as a catalyst during ozonation of municipal wastewater.

Activated carbon is appealing as a HO[•] promoter because of its relatively low cost, availability, and sorption capabilities of trace organics (facilitates). Several papers have demonstrated the catalytic effect of GAC in the presence of ozone. Beltran et al.

(2002) reported higher ozone decomposition rates with the addition of activated carbon, indicating a catalytic effect. With addition of activated carbon in a fluidized reactor, McKay and McAleavy (1988) improved color removal in peat water by 40% compared with ozone alone. During ozonation of acetate, methanol, and O_3 -*p*-chlorobenzoate in a natural water, Jans and Hoigne (1998) found that addition of activated carbon improved *p*-chlorobenzoate ozonation and stoichiometrically demonstrated HO^\bullet to molecular ozone ratios similar to those of other advanced oxidation processes.

Titanium dioxide and activated carbon have been tested as catalysts in batch reactors; however, very limited research has explored their effectiveness in packed-bed reactor configurations. In the case of TiO_2 , full scale implementation is limited owing to the difficulty and high cost of recovery of the fine TiO_2 particles in suspension. Solid-phase media traditionally used during water treatment (anthracite, sand, resins, and GAC) have larger particle sizes and are not subject to this limitation, thus allowing their use in a packed-bed configuration. Use of TiO_2 at full scale would be more feasible if it could also be used in a packed-bed configuration to minimize the challenges of media recovery. Hristovski et al. (2011) fabricated a TiO_2 hybrid ion-exchange media (TiO_2 sphere) that is the size of a resin with TiO_2 exhibiting formation of anatase nanoparticles. In this study we synthesized and used TiO_2 spheres to investigate catalytic ozonation using TiO_2 in a packed bed reactor configuration. In contrast to TiO_2 , activated carbon is a commonly used sorbent media. The use of powdered activated carbon as a catalyst has similar recovery challenges as TiO_2 , but the use of GAC in a packed bed reactor addresses these issues. This study includes column testing of solid phase catalysts during ozonation to

simulate the more likely full-scale configuration of a packed bed reactor, and investigate flow-through analysis of their catalytic effect during ozonation.

Recent research has confirmed the ambient promotion of HO[•] by wastewater effluent organic matter (EfOM) during ozonation without the addition of an initiator or promoter (Nothe et al., 2009; Pisarenko et al., 2012). Buffle et al (2006), observed the decomposition of ozone in wastewater was controlled by direct reactions with reactive moieties of the dissolved organic matter and introduced a kinetic model to account for ozone decomposition due to these reactions at sub-stoichiometric ozone concentrations. Pocostales et al (2010) observed degradation of ozone-refractory micropollutants during ozonation of wastewater due to HO[•] generation by the reaction of ozone with organic matter. They observed addition of 1 mg H₂O₂/L had little effect on HO[•] yield, but high ozone doses and at a higher ozone to H₂O₂ ratio of 2, showed an increase in HO[•] production. Here we further develop these findings through comparison of ambient promotion of HO[•] by effluent organic matter (EfOM) with both solid (TiO₂ and GAC) and liquid phase (H₂O₂) promoters to identify if and when addition of HO[•] promoters is beneficial during water reclamation.

The goal of this study was to compare HO[•] production using both batch and column tests of TiO₂ and GAC with that of ozone/H₂O₂ and ozone/ambient promoters. Hydroxyl radical formation was quantified using a HO[•] probe compound. Batch kinetic tests allowed comparison of HO[•] production during ozonation in the presence of ambient (EfOM), liquid (H₂O₂) and solid-phase promoters (commercial TiO₂ and nano-structured TiO₂ spheres). Column tests were used to compare catalytic effect of TiO₂ or GAC with

liquid (H_2O_2) and ambient promoters in a continuous-flow configuration by spiking tertiary effluent with a HO^\bullet probe compound at various ozone doses. Batch tests of both river and tertiary effluent showed an ozone dose threshold in tertiary effluent above which addition of H_2O_2 increases the rate of HO^\bullet production, while addition of H_2O_2 in river water increased HO^\bullet production at all ozone dosages. Production of HO^\bullet by ambient EfOM was demonstrated. Although solid-phase catalysis are reported to promote oxidation of contaminants, promotion of contaminant oxidation was not observed during ozonation of effluent over TiO_2 or GAC. Presumably because of experimental differences from others research including water quality, focus on HO^\bullet production versus surface reactions, and concentrations of ozone, catalysts, and contaminants.

Experimental Approach

Water Samples

Treated effluent samples were collected from full-scale wastewater treatment plants in Mesa, Arizona, USA (AZ WWTP) and Cranberry Township, Pennsylvania, USA (PA WWTP). For wastewater treatment, both WWTPs utilize conventional activated sludge treatment, followed by sand filtration and UV disinfection (AZ WWTP) or chlorination (PA WWTP). Samples were collected prior to UV or chlorination, respectively. In addition, surface water samples were collected from the inlet of a full-scale water treatment plant (WTP) in Mesa, Arizona, USA, which serves the same sewer shed as the AZ WWTP. Relevant water quality characteristics of samples from all three plants are provided. All water samples were filtered through 0.7- μm glass fiber filters

(Glass Microfiber filters, Whatman, Inc.) prior to ozonation. Samples were stored at 4°C and allowed to come to room temperature prior to experiments. Para-chlorobenzoic acid (pCBA) was used as a probe compound to quantify HO• production based on pCBA's low reactivity with molecular ozone (direct rate constant 0.15 M⁻¹ sec⁻¹) and high reactivity with HO• (k = 5 × 10⁹ M⁻¹ sec⁻¹) (Kasprzyk-Hordern et al., 2003; Hoigne, 1997).

Batch Experiments

Kinetic batch experiments were conducted in 500-mL glass amber bottles. Liquid ozone stock solution was prepared by continuously bubbling ozone gas produced by an oxygen-fed generator (Ozonia Triogen LAB2B) in a glass reactor filled with ultrapure water (Milipore, Inc., 18.3 mΩ), resulting in a saturated ozone stock solution of approximately 20 mg/L ozone. A stock solution of pCBA (Sigma Aldrich) was prepared in ultrapure water and stored at room temperature in an amber glass bottle. Hydrogen peroxide stock solution was prepared in ultrapure water. Aliquots of tertiary effluent or river water, ozone stock solution, H₂O₂ (when applicable), pCBA stock solution, and ultrapure water (used to account for dilution due to different volumes of ozone stock required) were combined (total volume of 500 mL), sealed, and mixed (magnetic stirrer). In select experiments, TiO₂ spheres (Hristovski et al., 2011) or solid phase TiO₂ (P25) (1 g/L) were added to the prepared solution (including pCBA) and allowed to mix for 1 hour to hydrolyze solids before addition of ozone and hydrogen peroxide stock solutions. Sample water quality characteristics and chemical concentrations were varied for each experiment. For kinetic testing, potassium indigo trisulfonate (indigo, Sigma Aldrich)

solution prepared fresh daily was used to quench and quantify the ozone residual (change in absorbance at UVvis₆₀₀). Samples were collected over time in 40-mL amber vials containing indigo (1:10 v/v sample to indigo) using a manual bottle top dispenser. The ozone residual and pCBA concentration were then measured using the analytical methods described in the subsequent section.

Column Tests

Column tests were conducted in glass columns (30 cm × 1.1 cm dia) filled with glass beads (in ozone-only and ozone-H₂O₂ experiments), GAC (Hydrodraco 4000, Norit Americas), or TiO₂ spheres (Figure 4.1). The average particle size was 0.13 mm (100 × 140 mesh) for GAC and 0.40 mm for TiO₂ spheres (Hristovski et al., 2008). Bed depths of GAC (1 cm) and TiO₂ spheres (5.4 cm) were calculated using equations for mass transfer-limited reactions in packed beds provided in Fogler (2006), including the Thoenes-Kramers correlation to calculate the mass transfer coefficient, and were based on the assumptions of 40% bed porosity and rate-limiting external diffusion. Ozone stock solution and a pCBA-spiked or pCBA/ H₂O₂-spiked sample were pumped through a combination of Teflon and stainless steel tubing and fittings and combined before entering the column. Ozone stock solution was pumped at a constant flow rate. Detention time through the reactor was adjusted by varying the speed of the sample pump, resulting in hydraulic loading rates ranging from 17 to 633 L min⁻¹ m⁻². The initial pCBA concentration was determined for each adjusted ozone dose. Initial pCBA concentrations ranged from 0.26-0.5 mg-pCBA/L. Each change in the ozone feed to adjust ozone dose was followed by equilibration for a minimum of ten bed volumes. An ozone residual was

not expected; however, to ensure its absence, nitrogen gas was bubbled into collected samples to purge any ozone residual. A column filled with glass beads was used as a control; it provided the same hydraulic loading conditions as the other media without surface reaction sites. Prior to ozonation experiments pCBA-spiked tertiary effluent was continually flowed through the GAC column until only 10% of influent pCBA remained in the effluent (approximately 40,000 bed volumes) in an effort to achieve pre-equilibration of pCBA sorption to GAC.

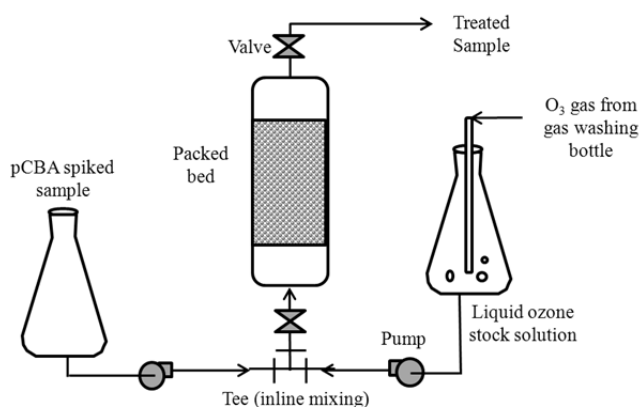
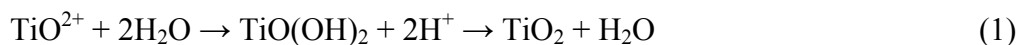


Figure 4.1 Schematic of Column Testing Apparatus used for Continuous-Flow Ozonation in the Presence of Solid-Phase Promoters.

Nanostructured TiO_2 spheres were synthesized following a protocol described in Hristovski et al. (2011 (provisional US patent 61/585,144)). Briefly, a 50-mL aliquot of ion-exchange resin (Resintech SIR-100HP) was soaked in 100 mL of ultrapure water ($< 1 \mu\text{S cm}^{-1}$) to achieve proper hydration. A 100-mL aliquot of saturated TiOSO_4 solution (ACS grade, Sigma-Aldrich) was mixed with the hydrated ion exchange resin for 6 hours. Then the TiO^{2+} precursor was converted to TiO_2 via a 24-hour hydrolysis at 80°C . The hydrolysis process is shown in Equation 1.



After the hydrolysis was completed, the TiO₂-containing resin was air dried at 104°C and ashed at 550°C in an oxygen-rich environment to remove the organic polymer and produce the nanostructured TiO₂ spheres.

Analytical Methods

The pCBA concentration was measured using high-performance liquid chromatography (HPLC) (Waters, reverse-phase RP18 analytical column, mobile phase of methanol and 10 mM phosphoric acid (55:45 v/v), UV detector wavelength of 234 nm). The DOC concentration was determined by a Shimadzu™ TOC Analyzer. UV_{vis}₆₀₀ was measured using a Hach DR 5000 spectrophotometer. The ozone stock solution concentration was determined by direct UV absorbance at 258 nm ($\epsilon_{258\text{nm}} = 3000 \text{ M}^{-1} \text{ cm}^{-1}$) and verified using the indigo method (Bader and Hoigne, 1981) (8311 AccuVac Ampul, HR using Hach DR 5000 UV spectrophotometer (range: 0.01–1.50 mg/L ozone)). Surface areas of the TiO₂ spheres were determined using the Brunauer–Emmet–Teller (BET) method (MicroMeritics Tristar-II 3020 automated gas adsorption analyzer). Material analysis employed FIB/SEM (Nova 200 NanoLab UHR FEG-SEM/FIB and FEI XL 30) for the size and shape and XRD (Bruker SMART APEX) for the chemical structure.

Quantification of Hydroxyl Radical (HO•) Production

The production of HO• was quantified through calculation of HO exposure. The HO exposure is defined by the equation for R_{CT} values often used when pCBA is used as a model compound. R_{CT} is essentially the ratio of HO• formed to ozone exposure (the area under the ozone decay curve, i.e., the CT value (mg/L-min)) were calculated as described elsewhere (Elovitz and von Gunten, 1999) and defined in Equation 2,

$$R_{CT} = \frac{\text{HO}^\bullet \text{ exposure}}{\text{O}_3 \text{ exposure}} = \frac{\int [\text{HO}^\bullet] dt}{\int [\text{O}_3] dt} \quad (2)$$

where $\int [\text{HO}^\bullet] dt$ is the HO• exposure quantified through measurement of the concentration of the probe compound (pCBA) and $\int [\text{O}_3] dt$ is calculated directly as the area beneath the ozone decay curve.

Results

Batch Experiments

Figure 4.2 compares the results of kinetic batch tests with liquid-phase and ambient promoters of HO• during ozonation of pCBA in both river water and tertiary effluent at low and high (0.5 and 2 mgO₃/mgDOC) ozone to DOC ratios. The results in Figure 4.2 are presented as the fraction of pCBA remaining as a function of ozone exposure. Paired t-tests were conducted at each ozone dose to determine if there was a statistical difference in the fraction of pCBA remaining with and without addition of H₂O₂ in both surface and wastewater. Analysis showed a statistical difference in the mean values (n=20, α= 0.05) of all paired sets, with the least difference between samples with and without H₂O₂ addition in tertiary effluent at 0.5 mgO₃/mgDOC, and the greatest

difference in the surface water sample at the highest ozone dose (2 mgO₃/mgDOC). At the lower dose of 0.5 mgO₃/mg DOC, rapid ozone consumption resulted in low ozone exposure values and the corresponding pCBA oxidation in tertiary effluent was visually indistinguishable with and without the addition of H₂O₂. In contrast, at the same ozone dose (0.5 mgO₃/mgDOC), addition of H₂O₂ to surface water resulted in faster ozone degradation (lower ozone exposure values), indicating H₂O₂ addition in surface water increased radical production, as confirmed by the higher percent difference in statistical means.

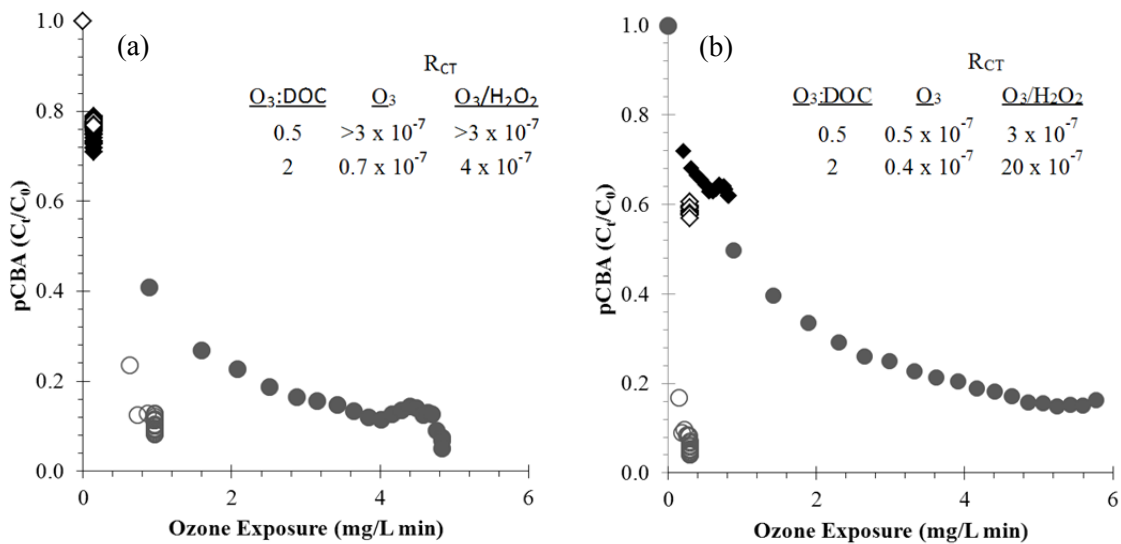


Figure 4.2 Comparison of HO[•] Promotion through pCBA Oxidation using Ozone without (closed shapes) and with (open shapes) H₂O₂ Addition (1 mgH₂O₂/mgO₃) in (a) AZ WWTP Tertiary Effluent and (b) Surface Water as a Function of Ozone Exposure. ● O₃:DOC = 2. ◆ O₃:DOC = 0.5. Parameters for both waters: DOC₀ = 2.3 mg/L, pCBA₀ = 0.75 mg/L, pH ~ 7.5.

Ozone exposure values increased when the ozone dose was increased from 0.5 to 2 mgO₃/mgDOC increased ozone exposure values. With the addition of H₂O₂ in tertiary

effluent, pCBA was almost entirely oxidized at ozone exposure values of $< 1 \text{ mg L}^{-1} \text{ min}^{-1}$. Without the addition of H_2O_2 , a higher ozone exposure was required to achieve similar levels of pCBA oxidation. This trend and the higher mean difference with and without H_2O_2 addition indicate improved production of HO^\bullet . Similarly, in surface water, near-complete pCBA oxidation occurred at ozone exposure values of $< 0.5 \text{ mg L}^{-1} \text{ min}^{-1}$. To achieve the same level of pCBA oxidation without H_2O_2 addition, a higher ozone exposure ($6\text{--}9 \text{ mg L}^{-1} \text{ min}^{-1}$) was required. There appears to be an uptick in C_t/C_0 values at the higher in the tertiary effluent sample without H_2O_2 addition at the $2 \text{ mgO}_3/\text{mgDOC}$ dose. This uptick occurs near the method detection limit of pCBA and indicates a difference of $\pm 0.02 \text{ mg/L}$.

Figure 4.3 presents calculated R_{CT} values at for ozone doses ranging from 0.5 to $2 \text{ mgO}_3/\text{mgDOC}$ for tertiary effluent samples from the AZ WWTP and PA WWTP spiked with pCBA. In PA WWTP effluent, R_{CT} values are statistically the same At an ozone doses of 0.5 and $0.75 \text{ mgO}_3/\text{mgDOC}$, R_{CT} values are statistically the same with and without H_2O_2 addition. At a higher dose of $1.0 \text{ mgO}_3/\text{mgDOC}$, R_{CT} values are statistically different, with a much higher R_{CT} value with H_2O_2 addition. In AZ WWTP effluent, differences in R_{CT} values with and without H_2O_2 addition, were statistically different at all O_3 to DOC ratios tested. However, in comparing values and standard deviations, it is apparent at ratios greater than $0.75 \text{ mgO}_3/\text{mgDOC}$, H_2O_2 addition results in higher R_{CT} values than ozone alone.

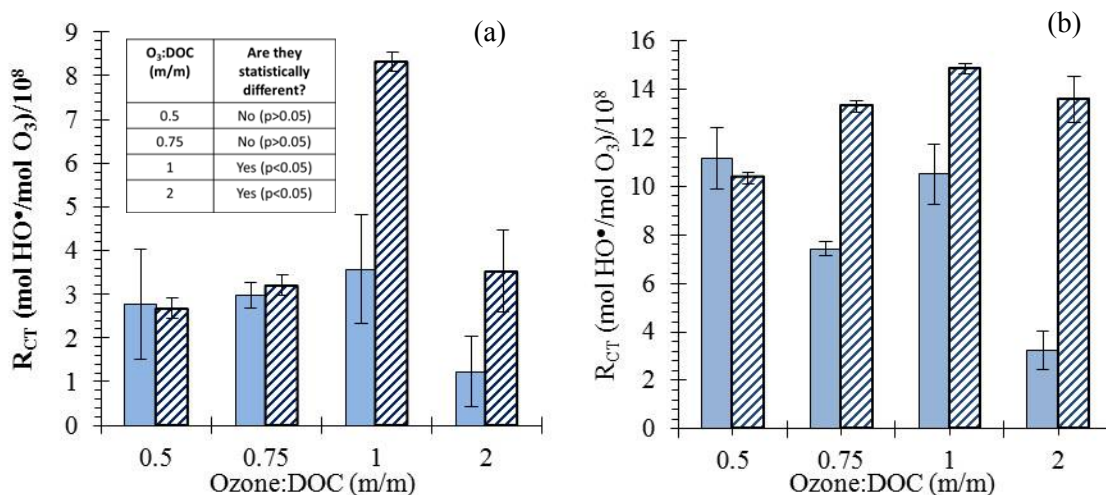


Figure 4.3 Impact of Ozone Dose ($\text{mgO}_3/\text{mgDOC}$) and H_2O_2 Addition on R_{CT} Values in (a) PA WWTP and (b) AZ WWTP pCBA-Spiked Tertiary Effluent. Solid bars are ozone only. Patterned bars are ozone/ H_2O_2 . (AZ WWTP $\text{DOC}_0 = 2.3 \text{ mg/L}$, PA WWTP $\text{DOC}_0 = 4.5 \text{ mg/L}$, $1 \text{ mgH}_2\text{O}_2/3 \text{ mgO}_3$, $\text{pCBA}_0 = 0.75 \text{ mg/L}$, $\text{pH} \sim 7.5$). Error bars indicate one standard deviation above and below (total of 2 standard deviations) on triplicate samples.

Figure 4.4(a) compares pCBA oxidation during ozonation in tertiary effluent over time using batch kinetic tests in the presence of synthesized TiO_2 spheres, powdered TiO_2 (P25), and ozone with and without H_2O_2 addition. All combinations of ozone and promoters completely oxidized pCBA within 3 minutes, with similar performance of the TiO_2 spheres and TiO_2 (P25). There appears to be a slight improvement in pCBA oxidation over ozone only with TiO_2 addition and with H_2O_2 addition, however, these differences may be within experimental error and are not conclusive. Additional comparison was conducted using column tests. Figure 4.4(b) is a SEM image of a synthesized TiO_2 sphere. Its surface area was approximately $35 \text{ m}^2/\text{g}$, compared to the bulk Degussa P25 TiO_2 surface area of approximately $50 \text{ m}^2/\text{g}$. The TiO_2 sphere particle diameter of $0.6\text{--}0.8 \text{ mm}$ is approximately five orders of magnitude larger than that of Degussa P25 TiO_2 ($25\text{--}40 \text{ nm}$). The anatase to rutile ratio of Degussa P25 is 80% to 20%,

whereas XRD analysis of the TiO₂ spheres revealed no rutile. Anatase TiO₂ is a favorable catalyst based on its crystalline structure, large surface area, availability, cost, and stability in water (Fujishima and Honda, 1972). The larger particle diameter of TiO₂ spheres allowed us to test their promoter effect in a packed bed while maintaining the advantage of a large surface area.

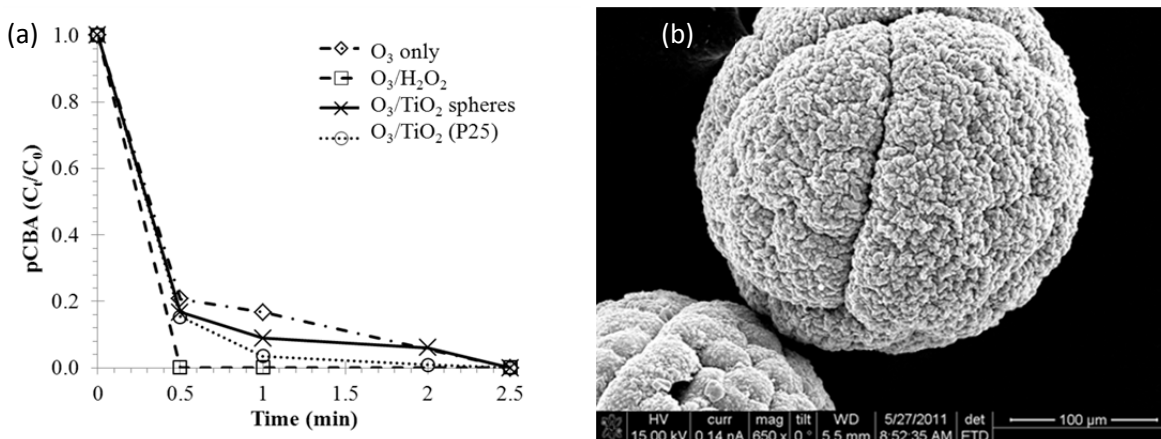


Figure 4.4 Synthesized TiO₂ Spheres' (a) Relative HO• Promotion Effect Demonstrated by pCBA Oxidation during Batch Kinetic Tests in Tertiary Effluent (2 mgO₃/mgDOC, DOC₀ = 3.5 mg/L, pH = 7.5, pCBA₀ = 0.75 mg/L, alkalinity = 78 mg/L as CaCO₃, solid catalyst concentration = 0.5 g/L, H₂O_{2,0} = 3.5 mg/L) (b) SEM Image of Synthesized TiO₂ Sphere.

Column Testing

Figure 4.5(a) presents the results of column tests to quantify the production of HO• by TiO₂, GAC, and ambient promoters (glass beads) over a range of ozone doses in AZ WWTP tertiary effluent by plotting the change in the fraction of pCBA remaining (C_t/C₀) as a function of ozone dose. The fraction of pCBA remaining is similar for all three media over the range of ozone doses tested. The fraction of pCBA remaining appears to initially increase for the O₃/GAC system. This likely indicates a desorption of

some pCBA previously sorbed during bed exhaustion. Figure 4.5(b) illustrates the production of HO[•] during ozonation of tertiary effluent in the presence of TiO₂, GAC, H₂O₂, or ambient promoters. Inclusion of H₂O₂ in column testing experiments allows for comparison of solid phase catalyst performance with a liquid promoter. At lower ozone to DOC ratios (0.2–0.3 mgO₃/mgDOC), pCBA was oxidized to a similar extent in all three systems, indicating no improvement in HO[•] production by addition of TiO₂ or H₂O₂. At higher ozone to DOC ratios (0.4–2.5 mgO₃/mgDOC), ozone/TiO₂ does not oxidize as much pCBA as ozone or ozone/H₂O₂ and is therefore not producing HO[•] to the same extent. It also appears TiO₂ may be inhibiting HO[•] production to some extent, possibly due to reduced sorption at this pH (7.5) (Kasprzyk-Hordern et al., 2003; Lanao et al., 2008). At ozone doses of 1.2 to 2.5 mgO₃/mgDOC, H₂O₂ addition increases pCBA oxidation. At the highest doses (2–2.5 mgO₃/mgDOC) pCBA oxidation is to below the detection level.

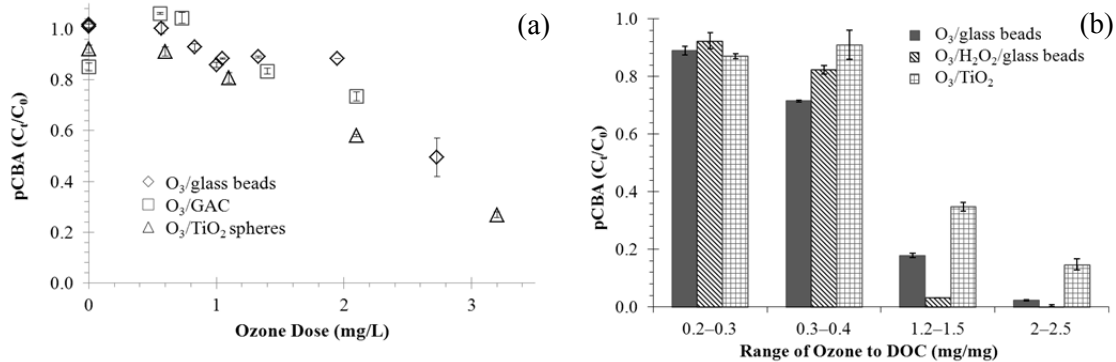


Figure 4.5 Solid-Phase Promotion of HO[•] (i.e., decrease in fraction of pCBA remaining (C_t/C_0) in Tertiary Effluent During Continuous-Flow Column Tests) (a) as a function of ozone dose (mg/L) for GAC, TiO₂, and ambient promoters (ozone/glass beads) and (b) as a function of ozone to DOC ratios for TiO₂ and ambient promoters (DOC₀ = 6.3 mg/L, pCBA₀ = 0.5 mg/L, pH = 7.5). Samples were collected in triplicate during steady-state operation. Error bars represent one standard deviation above and below the calculated average.

Discussion

Ozone Threshold in Tertiary Effluents

The difference in pCBA oxidation in tertiary effluent versus surface water with and without H₂O₂ addition (Figure 4.2) indicates the presence of ambient ozone promoters within wastewater. Municipal tertiary EfOM includes extracellular material, non-degraded industrial organics (phenols, dyes, surfactants, etc.), and other residential wastes that are not common in surface waters (Drewes and Fox, 2001). Some of these chemicals are considered fast-reacting compounds with molecular ozone (phenols and dyes (Beltran, 2004)) and are expected to react quickly, even at low ozone doses. These compounds and their ozonated by-products may act as initiators (OH[•], H₂O₂, HO₂[•] (Hoigne et al., 1985)) and/or promoters [formic acid, primary alcohols, glyoxylic acid (also an initiator), benzene, humic acid, -aryl groups, and phosphates (Stahelin, 1985; Nothe et al., 2009)], thereby increasing HO[•] production (Huber et al., 2004; Huber et al., 2005; Dodd et al., 2006; Buffle et al., 2006). For example, H₂O₂ (aqueous initiator and promoter) is produced during ozonation of aromatic hydrocarbons (Stahelin, 1985). Likewise, phenols and amines, which are commonly found in tertiary effluent, also react with molecular ozone to form O₃^{•-}, which decomposes into HO[•] and O₂ (Mvula and von Sonntag, 2003; Nothe et al., 2009). Furthermore, Buffle and von Gunten (2006) demonstrated addition of naturally occurring concentrations of primary, secondary, and tertiary amines, amino acids, and phenol produced HO[•] concentrations near, and in some cases greater than, advanced oxidation processes within the first 350 milliseconds

following ozonation in natural water. Mvula et al (2009) confirmed production of HO• during ozonation of lignin and identified final primary products (and intermediates including singlet oxygen, HO• and O₂^{-•}). Our results are consistent with this research in which an increase in HO• production generated in reactions between ozone and initiators/promoters within the wastewater matrix was observed (Ragnar et al., 1999; Nothe et al., 2009).

These initiators/promoters react with ozone until they no longer impact ozone degradation. We have termed the ozone dose that exhausts reactions with these compounds as the ozone dose threshold, above which addition of H₂O₂ increases the rate of HO• production. This phenomenon is most clearly illustrated in Figure 4.3, in which ozonation, regardless of H₂O₂ addition, has little impact on HO• exposure until doses greater than the threshold ozone dose are applied. For the AZ WWTP tertiary effluent, this threshold was between 0.5 and 0.75 mgO₃/mgDOC; for the PA WWTP, between 0.75-1.0 mgO₃/mgDOC). Buffle et al., 2006 also observed that the use of O₃/H₂O₂ in wastewater was beneficial at high ozone to DOC ratios when sufficient ozone residual was present for H₂O₂-linked mechanisms to be significant compared with reactions with ambient promoters. They noted a high HO• concentration of 0.1400 nM after 350 milliseconds during ozonation of a wastewater and noted this concentration was greater than calculated HO• concentrations during UV/H₂O₂ and O₃/H₂O₂ experiments on natural waters. After 30 seconds, the results presented in Figure 4.3 correspond to HO• concentrations ranging from 0.002– 0.026 nM; which is consistent with these aforementioned findings.

Solid-Phase Catalyst

Although solid-phase catalysts are reported to promote oxidation of CECs, this was not observed in catalytic ozonation of effluent over TiO₂ or GAC [Figure 4.5(a)], presumably because of experimental design differences including water quality characteristics (pH, DOC, alkalinity), focus on the rate of HO[•] production, and chemical concentrations. First, the impact of pH on the extent of catalysis has been confirmed for both TiO₂ (Rosal et al., 2008) and activated carbon (Akhta et al., 2012), with lower pH values showing the strongest effect and near-neutral pH values showing little to no effect. Because our focus was on municipal wastewater effluent, experiments were done at the ambient pH of the tertiary effluent (pH 7.5), likely minimizing or eliminating a catalytic effect. Additionally, differences in experimental matrices impact catalysis (Sanchez-Polo et al., 2005). For example, in a synthetic, phosphate-buffered solution of fulvic acids (DOC 2.84 mg/L), batch reactor tests with ozone/TiO₂ achieved near-complete mineralization of fulvic acids [Volk et al. (1997)]. Conversely, in the more complicated matrix of tertiary effluent (DOC 6.3 mg/L and alkalinity 65–155 mg/L as CaCO₃), we saw little to no improvement in pCBA oxidation, likely due to the increased number of compounds competing for both ozone and reactive surface sites. When compared with others' previously published work in natural water matrices at similar ozone and contaminant concentrations, the results of our tests are reasonable. For example, Gracia et al. (2000) found 11.2% TOC oxidation with ozone only and only 16.4% oxidation with ozone/TiO₂ in river water using aluminum-supported TiO₂ media.

Second, our ozonation experiments were designed to focus specifically on the impact of catalysts on the rate of HO[•] production through the use of pCBA as a probe compound. However, increased HO[•] production is not the only mechanism by which catalysis may occur. For example, Rosal et al. (2008, 2009) credited the catalytic effects they observed to sorption on the surface of the activated carbon or TiO₂; thus, the increased reaction rates were due to surface-surface interactions rather than HO[•] production. Because the focus was on increased HO[•] production, during column testing the GAC bed was exhausted prior to ozonation, thereby limiting any catalytic effect due to increased surface reactions. Others have demonstrated the catalytic effect of GAC on ozonation without first exhausting the sorption capacity of the carbon. Faria et al. (2005) observed enhanced decolorization and mineralization of three different classes of dyes (50–150 mg dye/L) through ozonation in the presence of activated carbon compared with adsorption only and ozonation only (semi-continuous batch reactor runs of up to 60 min). They further demonstrated that the activated carbon acted as both a catalyst and an adsorbent. A study on catalytic ozonation by Jans and Hoigne (1998) observed a difference in the oxidation of pCBA when ozonation occurred in the presence of activated carbon. Only 10% sorption of pCBA was reported; therefore, sorption of pCBA by activated carbon was not considered to interfere with the observed catalytic effect. This difference in both sorption of pCBA and the catalytic effect of activated carbon may be due to many reasons, including differences in carbon types and sorption testing. In particular, the catalytic behavior was observed over a “clean” bed of activated carbon. In our case, ozonation in the presence of a near-exhausted activated carbon bed likely

hindered the combined catalytic/adsorbent effect due to limited availability of reaction sites on the carbon surface.

Finally, initial contaminant and ozone concentrations can significantly impact catalysis (Akhtar et al., 2012; Shen et al., 2013). At a high ozone dose of 20 mgO₃/mgTOC in the presence of TiO₂, improved oxidation of fulvic acids, proteins, and disaccharides over ozone only in a model water (TOC 12 mg/L) was reported (Allemane et al., 1993). This ozone to TOC ratio is much higher than our observed ozone threshold ratios (0.5 and 1 mgO₃/mgDOC) at more realistic ozone dosages for municipal wastewater treatment, and is likely a significant factor in the results (Rosal et al., 2009; McKay and McAleavy, 1988). Furthermore, high pollutant concentrations would lead to increased adsorption and thereby increased catalytic oxidation at surface reaction sites (Akhtar et al., 2012; Arslan-Alaton and Caglayan, 2005). The pCBA concentration of 0.5 mg/L (3 μM) in our tests, although greater than the environmentally significant concentration of many CECs (e.g., 17β-estradiol in surface water ~27 ng/L (Khanal et al., 2006)), is 30 to 200 times less than the contaminant concentrations in the research cited previously in this chapter. Therefore, it may not have been high enough to demonstrate similar promotion effects. Oxidation of a wastewater (COD > 500 mg/L and TOC > 150 mg/L) generated by various food-processing industries was measured as 82% using ozone/GAC versus <40% using ozone only (Alvarez et al., 2011). TiO₂ (Degussa P25) addition during ozonation of clofibric acid (25–100 mg/L) in unbuffered ultrapure water (pH 3) showed a threefold increase in the reaction rate constant compared with ozone only (Rosal et al., 2009). Lower pH values, as previously mentioned, would also

increase the catalytic effect. The carbamazepine concentration ($C_0 = 15 \text{ mg/L}$) in a distilled water was reduced by 75% by ozonation in the presence of TiO_2 (Degussa P25) versus only 50% with ozone alone (Rosal et al., 2008). Additional discussion of the impacts of CEC pollutant concentration, ozone dose, and catalyst concentration during ozonation and $\text{O}_3/\text{H}_2\text{O}_2$ treatment are provided in Beltran et al. (2012) and Akhtar et al. (2012).

Summary

In summary, the key findings of this paper include the following:

- In surface water, H_2O_2 addition during ozonation immediately increased the oxidation of pCBA (production of HO^\bullet).
- In tertiary effluent, a quantifiable threshold ozone dose was identified in two different wastewaters, above which addition of H_2O_2 increased oxidation of pCBA.
- At environmentally relevant contaminant concentrations, pH and ozone dosages, packed-bed reactor tests in tertiary effluent showed HO^\bullet production was similar independent of the solid-phase media present (glass beads, TiO_2 spheres or GAC).

Conclusions

These findings led to the following important conclusions related to the use of liquid or solid-phase promoters during ozonation of treated wastewater:

- Ambient HO^\bullet promoters exist in wastewaters that are not in surface waters.

- These promoters create an “ozone threshold dose,” above which addition of H_2O_2 increases the rate of HO^\bullet formation.
- Ozonation of tertiary effluent through a packed-bed reactor of either TiO_2 spheres or GAC, does not increase the rate of HO^\bullet production at environmentally relevant contaminant and ozone concentrations and pH levels compared with ozone alone.

These conclusions indicate the potential for municipalities practicing advanced oxidation with ozone/ H_2O_2 to reduce chemical usage through elimination of H_2O_2 addition until doses greater than the ozone threshold dose are reached and future research of catalytic ozonation alternatives should include testing in a real-world matrix at concentrations and pH ranges for municipal wastewater treatment.

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Chapter 5

MEMBRANE FOULING BY PHOSPHOLIPID-FORMED VESICLES AND PREVENTION THROUGH OZONATION

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Authors: Michelle C. Barry¹, Kiril Hristovski² and Paul Westerhoff¹

Abstract

Membrane fouling is a major challenge in water and wastewater treatment. Recent observations that ozone mitigates membrane fouling during filtration of secondary effluent prompted this study into the impact of pre-ozonation on membrane fouling caused by biogenic colloids. The focus of this study was on liposomes, synthetic vesicles composed of (phospho)lipid bilayers, which are representative of the diverse cellular vesicles present in all biologically impacted waters. Although model liposomes are not exact replicates of all “soft” colloidal organic materials in wastewater, they serve as a model foulant in much the same way that alginate has been used as a model foulant of polysaccharides. Using dead-end ultrafiltration (UF) and batch ozonation tests, the key findings of this study were: (1) liposomes fouled UF membranes faster [7-20 times increase in total resistance (R_T) with volume filtered] than polysaccharides, fatty acids, and NOM on a DOC-normalized basis; (2) based on the estimated carbon distribution of secondary effluent, liposome-like biogenic nanomaterials could be responsible for 20–60% of fouling during UF; and (3) pre-ozonation reduces liposomal fouling during UF,

likely due to the disruption of the liposome structure through cleavage of the fatty acid tails at carbon-carbon double bonds.

Introduction

Use of membranes in water and wastewater treatment continues to increase in an effort to improve removal of inorganic particulates, pathogens, trace organics, and/or dissolved salts (AWWA 1996). Membrane fouling reduces production efficiency and increases operational costs and chemical usage associated with increased pressure requirements, flux decline, periodic backwashing, chemical cleaning, and membrane replacement (Van Geluwe, Braeken, and Van der Bruggen 2011, Komlenic 2010). Through identification of specific membrane foulants and their corresponding fouling mechanism(s), membrane pretreatment and chemical cleaning requirements can be tailored to maintain high flux rates. Despite significant advances in our understanding of membrane fouling, observations of reduced fouling through pre-ozonation during pilot and full-scale microfiltration (MF)/ultrafiltration (UF) tests have not been well explained. Common model membrane foulants include alginate, polysaccharides, fatty acids, and bulk organics. Extracellular polymeric substances (EPS) include these compounds. EPS, either in water or produced by organisms growing on membrane surfaces, cause membrane fouling (i.e., flux decline) (Ye et al. 2005, Garcia-Molina et al. 2006, Katsoufidou, Yiantsios, and Karabelas 2007, van de Ven et al. 2008) and are primarily responsible for the functional and structural integrity of biofilms (Geesey 1982).

Aggregates of EPS form a gel-like biofilm matrix (Neu, Flemming, and Wingender 1999) composed of polysaccharides, proteins, nucleic acids, phospholipids, and other polymeric compounds that account for roughly 50–90% of the total organic matter in biofilms (Neu, Flemming, and Wingender 1999, Wingender, Neu, and Flemming 1999, Christensen and Characklis 1990). Kennedy (2008) identified high-molecular-weight biopolymers as the most problematic natural organic matter (NOM) fraction in membrane fouling (Kennedy et al. 2008). These biopolymers include lipids, polysaccharides, and proteins found in NOM and EfOM. Amy (2008) proposed two primary fouling mechanisms for this high-molecular-weight organic matter: (1) formation of a gel layer on the membrane surface and (2) pore blockage (Amy 2008). In more recent studies, Ang et al. (2011) tested individual biopolymers to determine their impacts on membrane fouling during reverse osmosis (RO) filtration. The model protein bovine serum albumin (BSA) exhibited enhanced fouling in the presence of calcium and/or alginate (Ang and Elimelech 2007). Fatty acids (octanoic acid) did not appear to contribute to membrane fouling during RO filtration (Ang and Elimelech 2008), whereas the model polysaccharide (alginate) contributed most significantly to the fouling layer and total membrane resistance (Ang and Elimelech 2007, 2008).

Autopsies of fouled membranes revealed that the chemical composition of these model compounds is representative of most foulants. However, cellular vesicles, present in all biologically active waters, have not been investigated in the context of membrane fouling. Phospholipids comprise the lipid-bilayers that serve as plasma membranes for a range of vesicles present in, or generated by, all cells and are therefore present in all

biologically impacted waters including surface waters (e.g., algae/cyanobacteria) and wastewaters (e.g., bacteria) (Song et al. 2010). Membrane vesicles are produced by all domains of life, and are known to affect processes ranging from signaling to distribution to detoxification of bacterial products. Vesicle membranes are primarily composed of phospholipids, glycolipids and lipopolysaccharides. A single phospholipid molecule is approximately 600–800 Da (C.W and J.P. 1999) and is expected to pass unhindered through MF, UF, and nanofiltration (NF) membranes; however, as a component in the plasma membrane of a vesicle (40-1,000 nm) (Dragovic et al. 2011) they are large enough to be retained by membranes with small pore sizes. Furthermore, the relatively non-rigid (i.e., “soft”) structure of these vesicles could lead to elastic deformation during pressure filtration, resulting in passage of larger vesicles through smaller pores or blockage of large pores by smaller vesicles. Phospholipid-formed liposomes are commonly used as synthetic vesicles (Allen and Cullis 2013) and were used in this study as a model foulant. We hypothesize that these biologically produced, non-rigid or “soft” colloids (e.g., vesicles) present in wastewater, give rise to unique fouling behavior that can be mitigated by pre-ozonation.

Pre-oxidation with ozone of membrane feed waters reduces membrane flux decline (Lee et al. 2005, Park 2002, Mori et al. 1998). Lee et al. (2005) identified the two overarching mechanisms of fouling reduction by ozonation as (1) organic degradation from high- to low-molecular-weight compounds and (2) bio-fouling reduction through microbial disinfection (Lee et al. 2005). Historically, ozone has been used as a disinfectant during water treatment. Ozone inactivates bacteria by denaturing nucleic

acids, impairing enzyme function and/or protein integrity, and disrupting membrane permeability (Maier, Pepper, and Gerba 1999, Stewart and Olson 1996). Due to the similar lipid bilayer composition of vesicles and cell membranes, ozonation likely causes vesicle disruption as well. In general, ozonation of secondary EfOM transforms high-molecular-weight dissolved organic carbon (DOC) into smaller compounds (Filloux, Gallard, and Croue 2012, Zhu, Wen, and Huang 2010). More specifically, ozone reacts with carbon double bonds and the aromatic rings of organic matter (von Gunten 2003), thereby breaking down larger compounds. Ozonation of organics may also cause calcium-induced microfloculation. However, higher ozone dosages are usually required to produce significant levels of organic acids to lead to interaction with divalent metals and result in floc formation (Edwards and Benjamin 1991, Chandrakanth and Amy 1996). Furthermore, extensive literature is available from the medical community on the effect of ozone on the lipid bilayers of cell membranes (Pryor, Squadrito, and Friedman 1995, Kafoury et al. 1999, Bridges et al. 2000, Connor et al. 2004) and from the food industry on lipid oxidation (German 1999, Kubow 1992, Soares et al. 2012, Morrissey, Kerry, and Galvin 2003, Adegoke et al. 1998). However, these insights into the impacts of ozonation on lipid bilayers have yet to be applied to understanding the role low-dose ozonation plays in reduction of membrane fouling during water reclamation.

The objectives of this paper are to (1) determine the relative significance of liposomal fouling during UF through comparison with well-studied model foulants on a DOC-normalized basis, (2) demonstrate the effectiveness of pre-ozonation to reduce liposomal fouling, and (3) explore the associated reaction mechanism(s). First, total

membrane resistance (R_T) during UF of liposomes was compared with that of model organic foulants (alginate, NOM, and fatty acids), and electron microscopy was used suggest potential fouling mechanisms. Then the ability of ozone to reduce liposomal fouling was quantified and the associated mechanism(s) were investigated through measuring flux decline during UF with and without ozone, analyzing size exclusion chromatography (SEC)-DOC data before and after ozonation, and using electron microscopy to compare liposome solutions that have and have not undergone ozonation. Finally, we measured the lipid content in a representative secondary effluent stream and estimated the associated phospholipid content to demonstrate the potential contribution of liposome-like vesicles to membrane fouling during water reclamation. The model liposomes used in these experiments serve as model foulants much in the same way that alginate, octanoic acid, and bovine serum albumin have been used as model foulants for polysaccharides, fatty acids, and proteins, respectively.

Materials and Methods

Model Foulants

Liposomes were prepared in 5 mM phosphate buffer using 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC, Avanti Polar Lipids, Inc., Alabaster, AL) lipids as outlined by others (Hou et al. 2011). Briefly, a desired volume of lipid stock solution (lipids suspended in chloroform) was placed in a sterilized glass test tube. Nitrogen gas was bubbled through the solution to vaporize the chloroform. The glass test tube was then loosely covered and placed in a vacuum desiccator overnight to ensure complete vaporization of chloroform. Lipids were rehydrated in 5 mM phosphate buffer solution

(33.3 to 1 phosphate buffer solution to lipid stock solution (v/v)) and then vortexed and sonicated until no lipid film was visible on the test tube. The newly formed liposomes were then extruded through a 0.1 μm membrane using 4 to 10 passes, and liposome size was confirmed using dynamic light scattering (DLS). Prepared liposome stock was stored at 4⁰C and used within one week of initial chloroform vaporization. For SEC-DOC analysis, liposomes were prepared in a similar manner, but the initial 5mM phosphate buffer conductivity was adjusted to ~5 mS to match that of the SEC-DOC eluent in an effort to eliminate potential “popping” of liposomes due to osmotic pressure.

Octanoic acid (Sigma Aldrich), sodium alginate (Sigma Aldrich), and Suwannee River NOM (SRNOM; International Humic Substances) stock solutions were prepared following previously described methods(Ang et al. 2011). Sodium dodecyl sulfate (SDS, Sigma Aldrich) and polystyrene latex nanoparticle (Nanosphere Size Standards, Duke Scientific) stock solutions were also prepared in a similar manner. Foulant stock solutions (2 g octanoic acid/L, 2 g alginate/L, 2 g SRNOM/L, and 2 g SDS/L) were prepared by mixing each foulant with 5 mM phosphate buffered ultrapure water ((Milipore, 18.3 m Ω) a minimum of 24 hours prior to sample preparation. The octanoic acid stock solution pH was adjusted to 9.0 through gradual addition of 1 M NaOH. All stock solutions were stored in ashed glass bottles at 4⁰C. For foulant experiments without ozonation, membrane feed samples were prepared by adding foulant stock solution to phosphate buffered nanopure water in quantities to achieve the desired foulant concentration in a 2 L sample. For UF experiments, all membrane feed samples were at room temperature.

Dead-End Ultrafiltration

UF flux tests were performed with a similar setup and procedures described in Ladner, Vardon, and Clark 2010 and Ladner et al. 2012. Briefly, all tests were run at room temperature (~23°C), and samples were allowed to reach room temperature prior to testing. Polyvinylidene difluoride (PVDF) membranes (Durapore, 0.10 µm pore size) were used in UF experiments. Circular membrane coupons were used in an unstirred dead-end cell. The cell (Amicon model 8010, Millipore) had a 10-mL fluid capacity and 3.6 cm² membrane area. Pressure varied according to the experiment, but 0.9–1 bars (13–15 psi) was typical for UF. Membranes were cut to size and then, using ultrapure water, rinsed and hydrated a minimum of 24 hours; they were rinsed again before use. A mesh screen was placed under the membrane coupons to provide extra support against deformation. The membrane cell was fed sample through a 4 L feed tank pressurized by nitrogen gas. The mass of permeate collected over time was measured on a balance, and flux was determined with data acquisition software (Amiconflux4.vi). A preconditioned, clean-water UF run preceded each sample run; ultrapure water was filtered until a less than 5% change in flux was observed over a minimum 20 minute period or until accumulation of 2 L of permeate.

Reversible fouling was estimated using mass balance equations for DOC in samples collected during UF of 1 L of 3 mgC/L buffered liposome solution. UF was stopped when 850 mL of permeate were produced. Permeate (150 mL) was used to backwash the membrane coupon. The concentration of DOC was determined in

membrane feed, permeate, retentate (150 mL of sample was present in the Amicon cell when UF was stopped), and backwash samples.

Ozonation

Liquid ozone stock solution was prepared by continuously bubbling ozone gas produced by an oxygen-fed generator (Ozonix Triogen LAB2B) in a glass reactor filled with 5 mM phosphate buffered ultrapure water resulting in a saturated ozone stock solution of approximately 20 mgO₃/L. Aliquots of ultrapure water, phosphate buffer stock solution, liposomes, and ozone stock solution were combined (total volume of 1 L), sealed, and mixed (magnetic stirrer) overnight prior to membrane filtration.

Analytical Methods

The DOC concentration was determined by a ShimadzuTM TOC Analyzer. A spectrophotometer (Hach DR 5000) was used to measure absorbance at 254 nm (UV₂₅₄). The ozone stock solution concentration was determined using the indigo method (Bader and Hoigne, 1981) (8311 AccuVac Ampul, HR using a Hach DR 5000 UV spectrophotometer (range: 0.01–1.50 mgO₃/L)). Particle size was determined via DLS (ZetaPALS, Brookhaven Instrument Company). High-performance SEC coupled with inline organic carbon detection (SEC-DOC) was used to characterize changes in organic matter during ozonation and UF. A detailed description of the SEC-DOC system is provided elsewhere (Wang et al. 2013). Briefly, the system includes a high-performance liquid chromatography instrument (Waters 2695 Separation Module, Milford, MA) followed by TOC detection (Sievers 900 Portable Total Organic Carbon Analyzer) adapted to inline detection using an inorganic carbon remover (900 Sievers ICR, GE).

Prior to transmission electron microscopy (TEM) imaging, a 10 μL drop of the sample was incubated for 4-5 min on a copper mesh grid coated with formvar. The sample was then stained for 30 seconds with 2% aqueous uranyl acetate. Stained samples were imaged with a Gatan model 791 CCD camera in a Philips CM12 TEM operated at 80 kV. Scanning electron microscopy (SEM) images were acquired of a prepared sample (cut from an air dried membrane, mounted on aluminum SEM stub, and sputter-coated with approximately 10 nm gold) using a JEOL JSM6300 SEM operated at 15 kV that uses an IXRF model 500 digital processing unit to acquire the final images.

Calculations

Total resistance was calculated as outlined in AWWA 1996 with

Equation 1
$$R_T = \frac{\Delta P}{\mu J}$$

Where: R_T = total resistance

ΔP = pressure drop across the membrane, i.e., transmembrane pressure (TMP)

μ = absolute viscosity

J = membrane flux

R_T is also the sum of resistance across the clean membrane (R_M) plus the resistance of the fouling cake (R_C). The R_C value increases as a function of cake thickness and porosity (AWWA 1996) and should not be compared at the same permeate volume, but rather at the same applied carbon mass. That is, in order to compare R_C values at different initial foulant concentrations (C_0), and between foulants, a normalized R_C value can be calculated by dividing the R_C value by the applied carbon mass. That is:

Equation 2

$$R_C = \frac{R_T - R_M}{\text{mgC applied}}$$

Normalized R_C values can be calculated for each measured point during UF of one foulant ($n \approx 100$ -300 points), then averaged and compared with normalized average R_C values from other UF experiments.

Results and Discussion

Liposomes Significantly Foul Membranes

Membrane flux declined more rapidly with increasing liposome concentration (Figure 5.1). A control sample of phosphate buffer solution without liposomes was also filtered, and it exhibited a slight flux decline (<5% of clean water flux) by 800 mL permeate. At the lowest liposome concentration (0.4 mgC/L), membrane flux was 10% less than the clean water flux at 200 mL of permeate. At the highest tested liposome concentration (4.1 mg-C/L), the membrane flux was 60% less than the clean water flux after the first 200 mL of permeate. The flux decline increased with passage of more feed water containing liposomes.

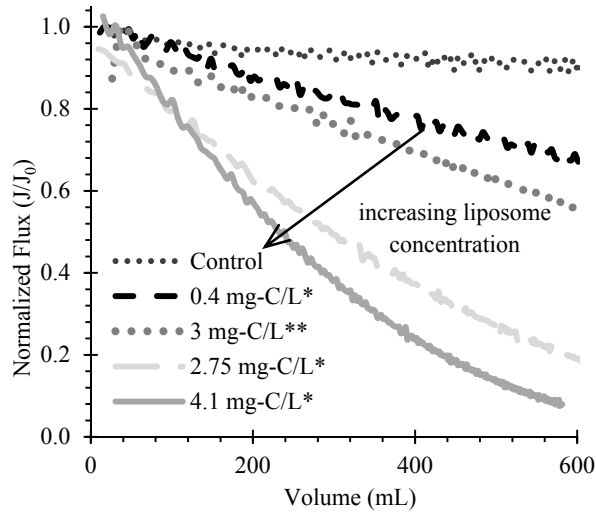


Figure 5.1 Membrane Flux Decline during UF of Different Concentrations of Liposomes with Diameters (*60-80 nm; **50 nm) Smaller than Membrane Pore size (PVDF, 0.1 μm pore size). All samples were at pH 7.5 in 5 mM phosphate buffered ultrapure water, including the control samples that had no added liposomes.

Model foulants were selected based on the repeated identification of compounds of these types in fouling cake (Amy 2008), and use as model foulants in other studies (Ang et al. 2011). Fatty acids were also selected to provide a comparison between non-polar lipid fouling and fouling by amphiphilic phospholipids, and NOM as a representation of bulk organics in natural waters. The calculated normalized averagecake resistance [R_C/mgC applied)] during UF of solutions of three common model foulants (alginate, fatty acids, and NOM) and with secondary effluent (Figure 5.2). The larger $R_C/(\text{mgC}$ applied) value of liposomes in comparison with model foulants, demonstrates a greater propensity for fouling of UF membranes..

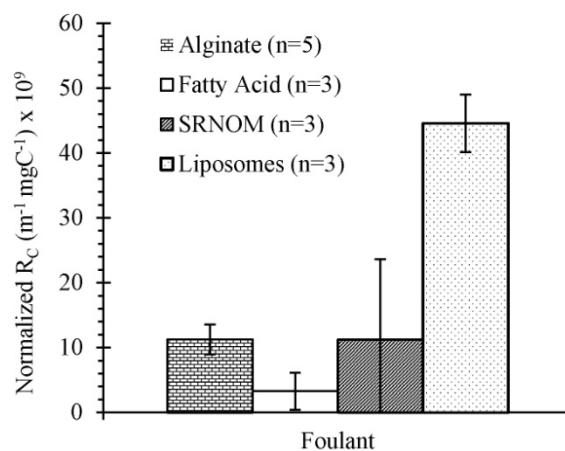


Figure 5.2 A Comparison of Calculated Average Cake Resistance (R_C) per mg Carbon during UF (where n=number of individual UF experiments), at Various Initial Concentrations. Error bars represent two standard deviations. All samples were in 5 mM phosphate buffered solution (pH 7.5).

The limited flux decline during UF is consistent with others' findings at the initial concentrations used that a large fraction of colloidal and/or soluble impurities remaining in treated effluent are able to penetrate UF membranes; that is, EfOM, including polysaccharides, fatty acids (Brinck et al. 2000), colloids, and soluble impurities, generally is small enough to pass through the pores of UF membranes (Ang et al. 2011, Zhao, Song, and Ong 2010). Additional UF experiments identified an “equivalent dose” of 50–70 mgC/L sodium alginate necessary to achieve a flux decline similar to that of 3 mgC/L of liposomes (Figure 5.3) during UF again illustrating liposome-like biogenic organic nanomaterials could be significant membrane foulants, even at low concentrations.

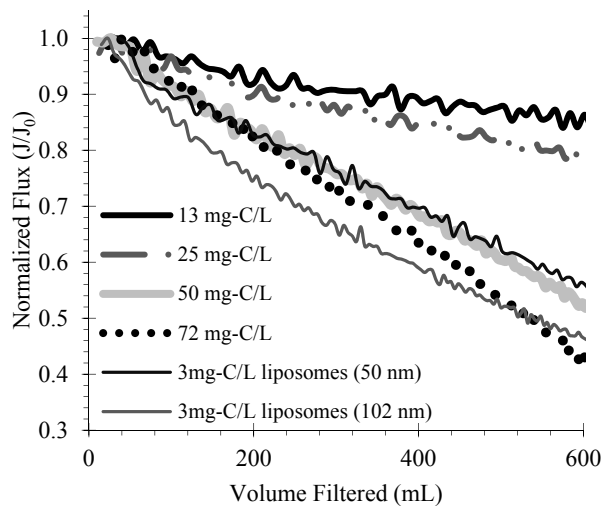


Figure 5.3 Membrane Flux Decline of Samples over a Range of Sodium Alginate Concentrations and Two Liposome Samples (3 mgC/L, nominal diameters as indicated, 5 mM phosphate buffered solution, pH 7.5, PVDF membrane, 0.1 μm pore size).

The initial permeate flux varied for each membrane and therefore each sample based on the individual membrane, initial pressure and room temperature. The baseline noise from variation in membrane resistance was minimized by using normalized flux J/J_0 . This normalization allowed for optimal comparison conditions. Considering the primary focus of these studies was to examine membrane fouling by vesicles and not to mimic full-scale UF systems, experimental initial flux values were typically between 2,400-2,800 L/hr/m^2 . Typical flux values for UF of secondary effluent range between 600-800 l/hr/m^2 (Asano et al. 2007). In theory, at a lower initial flux rate, there may be greater flux decline for the same volume of water filtered, due to a longer contact time of the foulants with the membrane surface.

Lipid Content in Secondary Effluent Indicates the Likelihood of Vesicle Fouling during Water Reclamation

To further understand the relative significance of liposomal fouling during membrane filtration, the lipid content was determined for several activated sludge samples from a wastewater treatment plant in central Arizona. The lipid content was found to be 5% of the dry weight of the total suspended solids (TSS). Assuming a concentration of 7 mg/L TSS, that all TSS in secondary effluent was biomass, that 5 to 15% of the biomass was phospholipids (Rittmann and McCarty 2001), and that all phospholipids have the same molecular weight as DOPC (786 Da), the equivalent concentration of phospholipids in secondary effluent was estimated to be between 0.24 and 0.75 mgC/L; the average concentration was approximately 0.4 mgC/L. At 500 mL of permeate, the R_T for 0.4 mgC/L of liposomes was nearly 50% of the R_T value for secondary effluent. Therefore, using the calculated range of phospholipid concentrations, liposome-like structures could account for 20-60% of fouling during UF of secondary effluent.

Figure 5.4 depicts the interactions between the liposomes and the UF membrane as observed by SEM. Figure 5.4(a) depicts agglomerations of spherical liposomes with diameters of ~ 100 nm and their ability to cause pore constriction or blockage, as well as their maintained structural integrity throughout UF. Similar trends could be observed with the larger liposomes as illustrated for the ~180 nm in Figure 5.4b. In Figure 5.4(b) it appears liposomes may cause pore blockage/cake formation as indicated by the several

dark, smooth mats of material on the membrane surface and agglomerates of spherical shapes within membrane pores not visible in a clean UF membrane (inset).

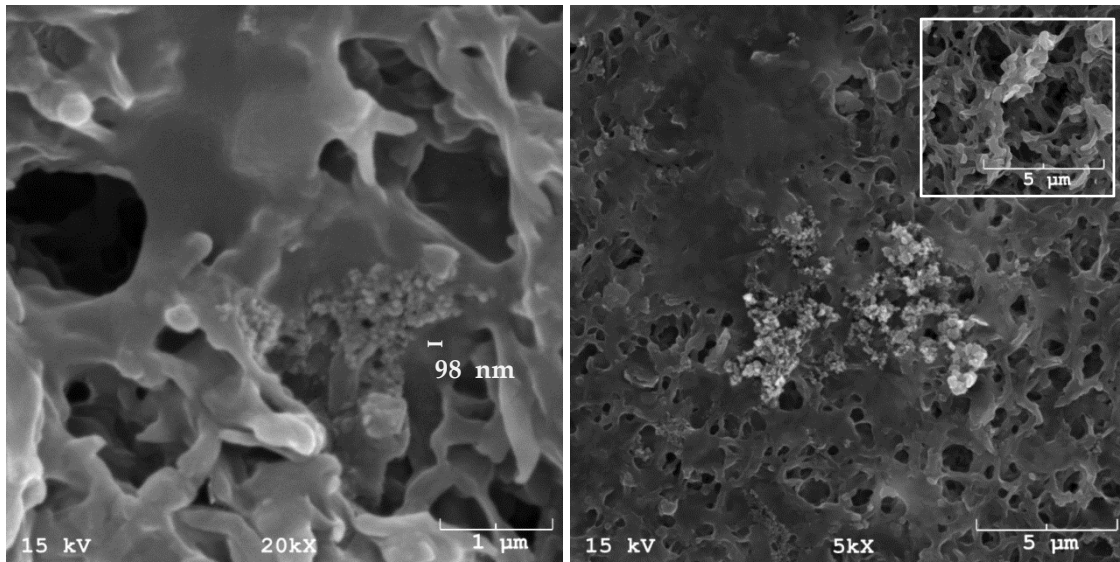


Figure 5.4 SEM Images of UF Membrane (PVDF, 0.1 μm) after Filtration of 1.5 L of 3 mgC/L Liposomes of (a) 100 nm and (b) 183 nm Nominal Diameter. Inset image is UF membrane after filtration of 1.5 L of 5 mM phosphate buffer solution at 5,000 times magnification.

Mass balance calculations using DOC concentration data collected during fouling experiments showed that liposomal fouling was partially reversible (~60%). A summary of the experimental results and formulas used to calculate percent reversible fouling is provided in Table 5.1.

Table 5.1 Summary of Data and Calculations to Determine Extent of Reversible Fouling for Liposomes in Phosphate Buffered Ultrapure Water (5 mM phosphate buffer, 54 nm mean diameter, 0.1 μm PVDF membrane).

Experimental Data for Reversible Fouling Experiments				
Replicate Number	(mgC/L)			
	Feed (F)	Permeate (P)	Retentate (R)	Backwash (BW)
1	3.17	1.36	3.17	3.10
2	3.06	1.38	3.13	4.39
3	3.31	1.33	3.21	4.73
Replicate Number	(mL)			
	Feed (F)	Permeate (P)	Retentate (R)	Backwash (BW)
1	910	850	60	150
2	910	850	60	150
3	910	850	60	150
Replicate Number	(mg-C)			
	Feed (F)	Permeate (P)	Retentate (R)	Backwash (BW)
1	2.89	1.15	0.19	0.47
2	2.78	1.17	0.19	0.66
3	3.01	1.13	0.19	0.71
Calculating % Reversible Fouling				
Replicate Number	Membrane Cake (MC, mg) = F - (P+R)	Reversible (Rv, mg) MC - BW	% reversible = Rv/MC x 100%	
1	1.54	1.08	69.8	
2	1.42	0.76	53.6	
3	1.68	0.97	57.8	
	Avg (%)		60.4	
	Std Dev (%)		8.4	

Ozonation Reduces Liposomal Fouling

Ozonation of liposomes prior to UF reduces flux decline (Figure 5.5). Even low ozone dosages (0.15 mgO₃/L; 0.05 mgO₃/mgDOC) reduced fouling to some extent. A

dosage of 0.75 mgO₃/L (0.25 mgO₃/mgDOC) nearly eliminated liposome-caused flux decline (i.e., <10% J/J₀ flux decline over 500 mL treated). The DOC concentrations were also measured, and reductions in DOC of approximately 10% following ozonation at 0.15 mgO₃/L and by roughly 20% following ozonation at 0.75 mgO₃/L were observed. These findings indicate that increased ozone concentration both reduces DOC and reduces the structural integrity of the liposomes.

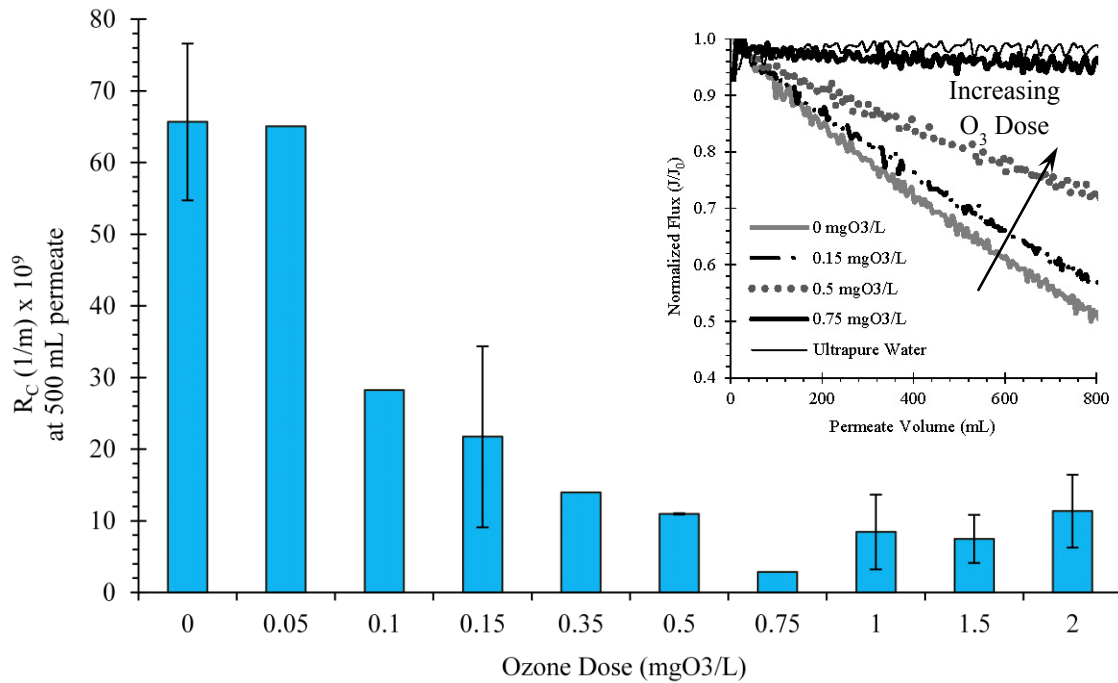


Figure 5.5 Effect of Ozonation Dose Prior to UF on Cake Resistance (R_C) at 500 mL Permeate. Inset shows impact of ozonation on liposome-caused membrane flux decline. The ultrapure water sample is the clean water flux decline curve corresponding to the membrane used for the 0.75 mgO₃/L sample. [PVDF, 0.1 μ m pore size, 3 mg-C/L liposomes (~60 nm) in 5 mM phosphate buffer].

TEM images were taken of liposome solutions pre- and post-ozonation at the 0.15 mgO₃/L dose (Figure 5.6). For the initial solution containing liposomes without ozone, Figure 5.6(a) shows intact liposomes of various sizes containing multilamellar

vesicles. Figure 5.6(b) depicts liposomes oxidized by 0.15 mg-O₃/L. This TEM image shows some remaining intact liposomes as well as considerable debris (possibly phosphate salts and glycerol) and dark globules (possibly aggregated fatty acids).

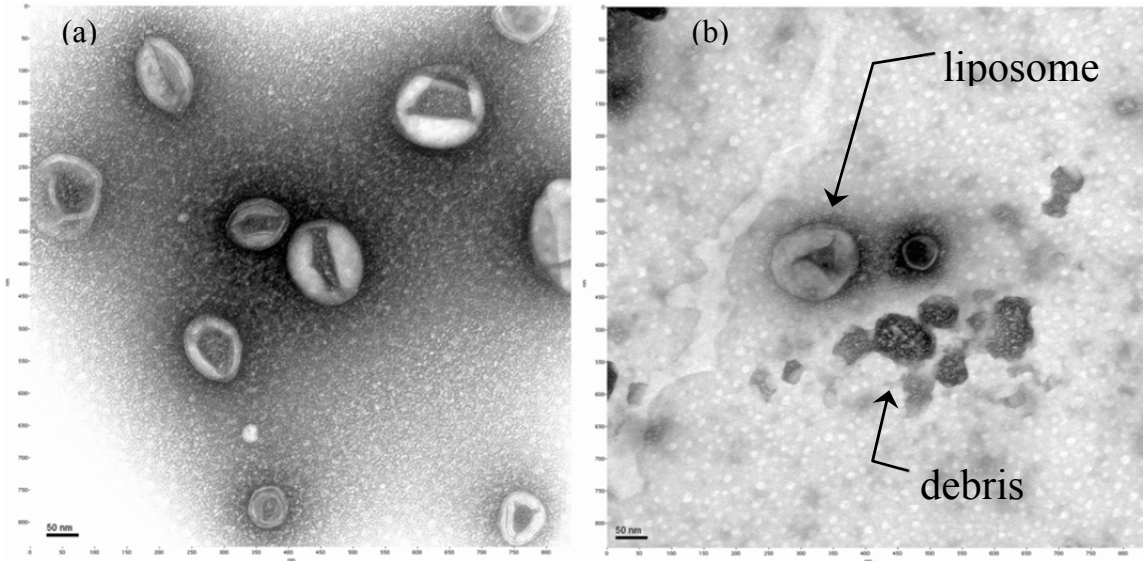


Figure 5.6 TEM Images of 3 mgC/L Liposomes (nominal diameter 183 nm) in 5 mM Phosphate Buffered Ultrapure Water (a) prior to ozonation and (b) following ozonation with 0.15 mgO₃/L.

An SEC-DOC chromatogram of liposome solutions with and without ozone is provided in supplementary Figure 5.7. The samples showed distinct peaks in a “high” molecular weight range (4,500–28,500 Da) and a “low” molecular weight range (200–2,000 Da). Sharif et al. (2012) explain the general molecular weight distribution observed in EfOM from multiple wastewater treatment plants. Substances with molecular weights >10,000 Da are considered colloidal organics (Song et al. 2010) (biopolymers), those in the 1,000–10,000 Da range are considered humic and fulvic substances, and substances in the 100–1,000 Da range are considered carbohydrates, ketones, aldehydes, and low-molecular-weight acids (Sharif, Wang, and Westerhoff 2012). In this case the samples

consisted of only DOPC and phosphate salts. Thus, the peaks corresponding to the “high” molecular weight range are most likely intact liposomes, and the peaks corresponding to the “low” molecular weight range are probably liposome fragments (DOPC) and products of lipid peroxidation. The area under the DOC response curve is proportional to DOC concentration. Initial measured DOC concentration was 2.8 mg/L and post-ozonation DOC concentration was approximately 2.8, 2.2 and 2.0 mg/L for 0, 0.15 and 0.5 mgO₃/L, respectively. Although total DOC concentration was only slightly reduced through ozonation (19-27% reduction), the change in molecular weight distribution of DOC was significant. Ozonation of the samples resulted in less area under the DOC response curve for the “high” molecular weight range [4.1, 3.5, and 0.9 (DOC response minute) for 0, 0.15, and 0.5 mgO₃/L, respectively] and increased area in the low range [0.4, 1.5, and 3.2 (DOC response minute) for 0, 0.15, and 0.5 mgO₃/L, respectively]. This change in molecular weight distribution is consistent with the general impact of ozonation of EfOM reported by others, which also showed a decrease in high-molecular-weight DOC and an increase in low-molecular-weight DOC (Sharif, Wang, and Westerhoff 2012).

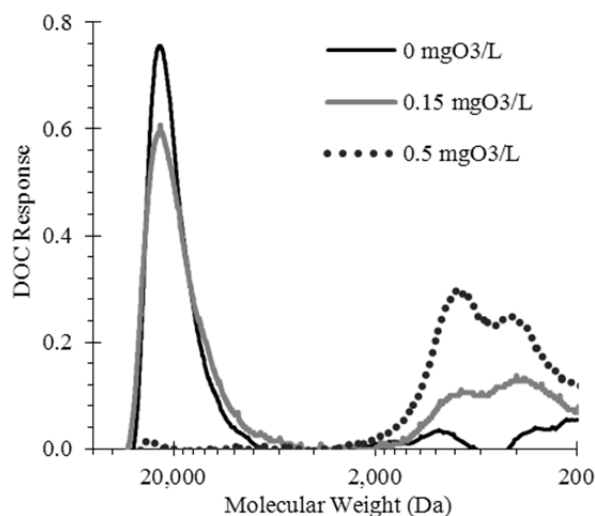


Figure 5.7 DOC Response and Molecular Weight Distribution of Ozonated Liposome Samples [3 mgC/L liposomes, 5 mM phosphate buffered solution, pH 7.5, PVDF membrane, 0.1 μm pore size, polyethylene glycol (PEG) standards used were 10,000; 8000; 4600; 3350; 1450; 1000; and 600 Da].

More specific to the liposomes, a DOPC molecule is made up of a glycerol backbone with two carbon-oxygen double bonds, two long-chain fatty acids each containing a carbon-carbon double bond, and a phosphocholine with a protonated amine group and one oxygen-phosphate double bond. Others have identified the mechanisms involved in ozonation of lipids, including the reaction chain of a similar phospholipid [1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC)] (Pryor, Squadrito, and Friedman 1995, Santrock, Gorski, and Ogara 1992); these mechanisms show that ozone reacts with unsaturated fatty acids at carbon-carbon double bonds. The net reaction in water of one mole of phospholipid and ozone yields two moles of aldehyde and one mole of hydrogen peroxide. Aldehydes are volatile and would not be measured as DOC. Salgo et al. (1995) demonstrated that direct ozonation of a POPC liposome membrane led to a change in the polarity of the phospholipid environment and in the properties of the bilayer. These ozonation products and more polarized phospholipids have a membrane

disorder-producing effect (Salgo, Cueto, and Pryor 1995) that is likely responsible for breakdown of the liposome structure. This breakdown is consistent with our SEC-DOC results, as increasing the ozone dose to 0.5 mgO₃/L yielded near-complete disintegration of the high-molecular-weight organics (i.e., liposomes) into compounds <2,000 Da.

Use of DOPC Liposomes as Model Vesicles

Liposomes have been used as the standard model of molecular vesicles based on the properties of the membrane bilayers for decades (Bangham, Hill, Miller 1974). These lipid bilayers may be composed of a range of different compounds in real waters including phospholipids, glycolipids and lipopolysaccharides (Biller et al. 2014). These compounds are all amphiphilic, thereby capable of forming bilayers. Fouling behavior by intact vesicles with membranes of different chemical composition should be similar based on vesicle size and hydrophilic surface properties. However, as Biller et al (2014) mentions, the rigidity of the vesicles is different depending on the compound makeup of the membrane (Biller et al. 2014). The rigidity or elasticity of the vesicles could impact fouling behavior as illustrated in Figure 5.8, and should be explored further.

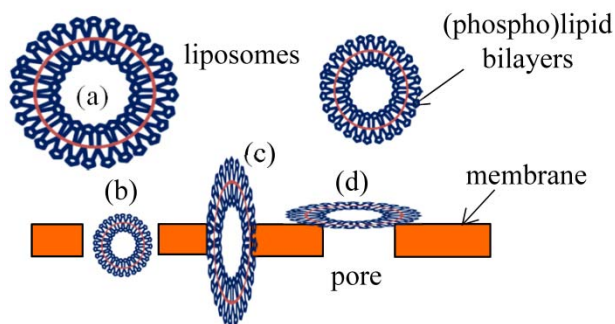


Figure 5.8 Hypothetical Cross-Section of Vesicles and a Membrane Surface to Illustrate Potential Impacts of Elasticity/Rigidity during Membrane Filtration. Where (a) vesicle is larger than membrane pore and remains in bulk solution; (b) vesicle is smaller than membrane pore and passes through; (c) vesicle is larger than membrane pore, but elastic deformation results in passage of vesicle; and (d) vesicle is either smaller or larger than membrane pore, and elastic deformation results in blockage of membrane pore.

In regards to ozonation of the vesicles, the effect of ozone should be the same; that is, disruption of the vesicle structure based on oxidation of the C=C bonds with the exception of be saturated compounds. Investigation of the effectiveness of ozonation on vesicles composed of compounds with only singular bonds, as well as those composed of glycolipids or lipopolysaccharides should be investigated in the future.

Broader Impacts

Liposomes are only one example of “soft” biogenic organic nano-sized materials (BONMs) in wastewater (Song et al. 2010). Other BONMs (e.g., fibrils, silica/organic aggregates) have unique physical properties (size, shape, elasticity, etc.) that may impact fouling potential and treatment effectiveness related to membrane fouling. A better understanding of the impact of the physical properties, in addition to the chemical composition, of organic membrane foulants will provide opportunities to better tailor membrane pretreatment processes.

Acknowledgments

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Chapter 6

SYNTHESIS OF RESULTS

The purpose of this chapter is threefold: (1) to synthesize the findings between prior chapters, (2) to discuss the implications of these findings on water and waste treatment, and (3) identify future research needs with a primary focus on the quantification, characterization and implications of vesicles in the water supply. The summary of the similarities and differences relevant to DOM between surface waters and secondary effluent presented in Chapter 1 has been updated to reflect the findings presented in this document and is provided as Table 6.1.

When viewing these findings as a whole, several advantages of integrating treated wastewater more directly in the surface water supply become apparent. First, DOM and turbidity of a treated wastewater supply are not subject to the impact of extreme weather events and could be utilized as a supplemental drinking water supply in the event of unfavorable (high DOM/TOC) surface water quality (similar to groundwater wells). Second, ambient promoters of HO^\bullet within treated wastewater would provide some advanced oxidation of surface water when combined prior to ozonation (in lieu of H_2O_2 addition). Third, the use of ozone for CEC oxidation and to reduce membrane fouling greatly increases the quality of the wastewater supply, thereby alleviating some of the concerns of more direct paths for reuse.

Table 6.1 Similarities and Differences in Surface Water and Treated Wastewater Relevant to DOM, Extreme Weather Events, and Ozonation (previously Table 1.1, revised based on the findings of Chapters 3, 4 and 5. Changes are shown in bold).

Property	Surface Waters	Secondary Effluent
DOM	<ul style="list-style-type: none"> - NOM (some CECs due to wastewater infiltration) - No ambient promoters of HO[•] production 	<ul style="list-style-type: none"> - NOM, CECs, and EPS - Ambient promoters of HO[•] are present
Impact by Extreme Weather Events	<ul style="list-style-type: none"> - Yes. Flooding, dust storms, and runoff over wildfire burn area in an arid climate resulted in rapid increase in DOM and turbidity 	<ul style="list-style-type: none"> - Little to no impact on effluent quality
Effectiveness of Ozonation	<ul style="list-style-type: none"> - Capable of oxidizing some NOM, thereby reducing DBP formation potential, T&O compounds, and improving biodegradability - Improve coagulation/flocculation - Provides disinfection - Advanced treatment with H₂O₂ addition for reducing CECs 	<ul style="list-style-type: none"> - Reduction in membrane fouling caused by liposome-like soft nanoparticles (e.g., cellular vesicles) through pre-ozonation - Identified threshold ozone dose above which advanced treatment with H₂O₂ addition for reduced CECs - Advanced treatment using TiO₂ or GAC catalyst in a continuous-flow packed bed reactor showed no improved production of HO[•] compared with ozone only

Figure 6.1 is provided to illustrate the potential advantages, based on the findings of my research, of using treated wastewater directly. A combination of extreme events is shown in this figure where a whole water system is impacted by wildfire, rain and dust

storms. In this scenario, City 1 has added ozonation and membrane filtration to provide advanced treatment at their WWTP. Based on the findings of Chapter 3, we know that rainfall over the burn area left by the wildfire will result in higher organic loading and turbidity to the lake that should be attenuated prior to reaching the downstream WTPs. The corresponding increased nutrient load to the lake would result in increased algal growth and eventual increase in DOC levels. Rainfall in the lower watershed would increase turbidity and DOM levels in the drinking water supply to a greater extent in a ephemeral or intermittent water body. The dust storm encasing City 1 would bring with it particulate matter that may be deposited into the surface water as well. Due to this combination of extreme events, as surface water quality becomes more challenging to treat, City 1 could begin to supplement their surface water supply with groundwater and treated wastewater. Without alternate supplies, City 2 would continue to be subjected to the rapid changes in water quality following these events.

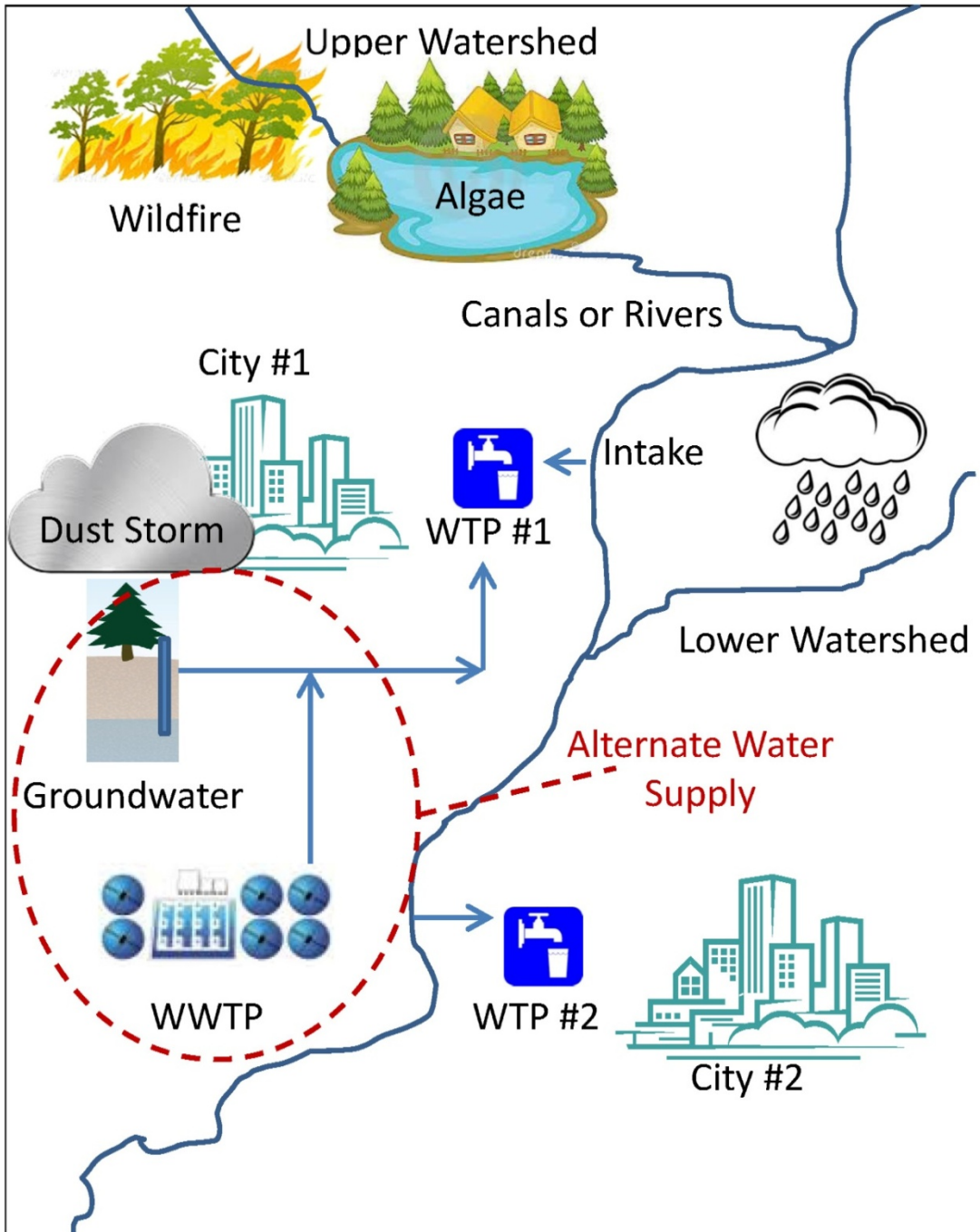


Figure 6.1 Illustration of a Whole Water System for City 1 and City 2.

A Need for Early Warning Systems for WTPs

The events outlined for Figure 6.1 are based largely on the findings presented in Chapter 3. We know that DOM is present in both surface and municipal wastewaters. It is operationally measured as DOC and represents all dissolved organics in water including NOM, organic CECs, EPS and others (Shon, Vigneswaran, and Snyder 2006). The concentration of DOM within a surface is expected to be impacted by climate change based in part on the anticipated increase in extreme weather events including dust storms, floods, drought and wildfires (IPCC 2007). The research presented in Chapter 3 focused specifically on the impact of extreme weather on turbidity and DOM in central Arizona. Historic air, weather, and water quality data for central Arizona were used to demonstrate a correlation ($R^2 = 0.6$) in raw water turbidity at the SVWTP following a dust storm event with dust storm events (daily average $PM_{10} > 98^{\text{th}}$ percentile PM_{10}). Further, DOC values in three terminal reservoirs varied between 1-5 mg/L on average, with approximately 15 days (2% of the 13 year study period) of DOC concentrations were greater than their respective 90^{th} percentile values. Precipitation over ephemeral or intermittent streams downstream of reservoirs were particularly problematic (rapid increases in turbidity and organic carbon) based on a “first flush” effect of high flows moving through dry or relatively empty stream or river beds. Change in turbidity levels and TOC concentrations corresponding with these floods ranged 130-600% and 30-40%, respectively. Table 6.2 summarizes the qualitative effects on water quality and treatment due to extreme weather.

Table 6.2 Summary of Impacts of Extreme Weather Events on Water Quality

Extreme Event	Water Quality Impact	Water Treatment Implications	Duration of Impact
Dust Storms	Increased turbidity levels	Higher turbidity may require increased chemical feed for coagulation Varies depending on composition of particulate material deposited	days
Wet snow-rain higher elevation flooding into reservoirs	Increased turbidity, DOC and nutrient loading to reservoirs, which may lead to increased algal growth and corresponding increased DOC levels	Limited impact based on attenuation of event in reservoir system	Months to years
Thunderstorm flooding at lower elevations (below reservoirs) or atypical reservoir release	Rapid increase in turbidity and DOC	Increased chemical feed for coagulation Shorter filter run times	Days to weeks
Precipitation over wildfire burn areas in upper watershed	Increased turbidity, DOC and nutrient loading to reservoirs, which may lead to increased algal growth and corresponding increased DOC levels	Limited impact based on attenuation of event in reservoir system	Days to years
Precipitation over wildfire burn areas in lower watershed	Increased turbidity, DOC levels	Increased chemical feed for coagulation Shorter filter run times May impact effectiveness of T&O removal	days

Central Arizona has been praised by others (Engle 2012) for their whole water system approach to water supply management based on “a regional collective vision of water resource management,” and co-sponsored research by cities and universities related to climate change. However, the key finding of Chapter 3 of the adverse impacts of rapid changes in both DOC and turbidity due to flooding on water treatment processes and operations, demonstrates a need for further integration of available and future water information technology (weather radar, air quality monitoring stations, stream gauges, online turbidity analyzers, etc.) to provide water treatment personnel with sufficient warning to adjust water sources and operations to respond to extreme events to continue to provide high quality water to consumers. A simplified alert system could include a level of severity, for instance a blue alert would indicate incoming storm events, a yellow alert would indicate measured changes in air quality or precipitation at weather/air quality monitoring stations, and a red alert would indicate rapid increase in flow measured at stream gauges, and high turbidity readings where possible. Stream gauge, weather, and air quality monitoring systems are already in place. An integration of the appropriate gauges/stations would be unique to each WTP, but should be located high enough upstream to provide sufficient warning to allow drinking water providers to adjust treatment processes or water supply (turn on groundwater wells, switch surface water sources, etc.).

Use of Ozonation for Advanced Treatment of Wastewater

DOM (inclusive of NOM, organic CECs and EPS) is a key water quality parameter as it has negative impacts to water quality as a precursor of DBPs and membrane fouling. Removal of DOM is a common goal of water and wastewater treatment to reduce DBP formation, color, tastes and odors, and CECs. Some DOM can be removed through enhanced coagulation, sorption to activated carbon, membrane filtration, and some limited destruction via oxidation. Specific to organic CECs, advanced oxidation processes including ozone/H₂O₂ and ozone/UV are used to oxidize these compounds through an increase in the rate of HO[•] production (Buffle et al. 2006, Acero and Von Gunten 2001, Andreozzi et al. 1999). However, a key finding of Chapter 4 was that addition of solid or liquid phase promoters of HO[•] during ozonation of secondary effluent is not necessary until ambient promoters are exhausted, and that these ambient promoters were not present in surface waters. This opportunity to achieve advanced oxidation without chemical addition indicates a distinct advantage of removal of CECs as a final step in wastewater treatment rather than during drinking water treatment when chemical addition is required.

DOM includes EPS that has been identified as being primarily responsible for irreversible fouling of membranes during filtration of water and wastewater (Zhao, Song, and Ong 2010, Haberkamp et al. 2008, Rosenberger et al. 2006). This research has focused primarily on polysaccharides, bulk organics, proteins, and fatty acids as the compounds most responsible for membrane fouling. A key finding of Chapter 5 was that vesicles within EPS/DOM cause membrane fouling at a much faster rate than previously

identified foulants of polysaccharides, fatty acids and bulk NOM. This implies that vesicles are significant contributors to membrane fouling. Physical structure of the model vesicle (liposome) played a critical role in both the fouling potential of the liposome and the ability of ozone to prevent liposomal fouling. These findings imply that the impact of shape and structure of organic colloids may also impact the effectiveness of other treatment processes. pre-ozonation could be used prior to membrane filtration to reduce fouling, and/or membrane cleaning procedures should be modified to specifically target liposome-like fouling. However, additional research is needed prior to implementation of treatment process changes as my work was conducted in buffered ultrapure water and the impacts of water quality parameters and other foulants on liposomal fouling should be thoroughly investigated prior to full scale implementation. Furthermore, our understanding of the quantity, characteristics, and implications of vesicles both in surface water and biologically treated wastewater is very limited, and also warrants further investigation.

Summary of Implications

The primary implications of my research findings are: water treatment plant design and operations should provide flexibility to respond to rapid changes in DOM and turbidity concentrations in order to ensure production of both actual and perceived high quality drinking water following extreme weather events. Additionally, water information technology should be integrated for use by water treatment personnel to provide early warning systems of atypical changes in the quality of the water supply to provide

adequate time to adjust operations (e.g., turn on groundwater wells, adjust chemical feed) to respond to the changes. Addition of solid or liquid phase promoters of HO• during ozonation of secondary effluent is not necessary until ambient promoters are exhausted. This implies individual WWTP using ozonation for advanced treatment should test their secondary effluent to determine their ozone dose threshold (dose above which addition of H₂O₂ increases HO• formation) and only add H₂O₂ when ozonating above the threshold dose. The impact of shape and structure of organic colloids may also impact the effectiveness of other treatment processes and warrants further investigation. Finally, vesicles are significant contributors to membrane fouling, pre-ozonation may be used to reduce this fouling, and/or membrane cleaning procedures should be modified to specifically target these foulants.

Summary of Research Needs

Based on the findings of this dissertation, further investigation is warranted in several different areas. The previous paragraphs included some of the research needs identified during my investigations. Specific future research needs are delineated in Chapter 7 (Conclusions and Future Research), and generally focus on the type and origins of matter in dust storms and the consequent impacts on water quality, impacts of different water quality parameters and foulants on liposomal-like fouling, the role of shape and structure on treatment process effectiveness and the implications of vesicles in treatment of all biologically active waters.

The focus of the remainder of this chapter is the implications of vesicles in treatment of all biologically active waters. The objective is to establish the need for extensive research related to the presence of vesicles in the water supply, and outline an approach to meet these needs. These needs include identification of the impacts of vesicles during water/wastewater treatment, and quantification and characterization of vesicles within secondary effluent and surface waters.

Recent breakthroughs in microbiology have centered on the role of vesicles in microbial communities. Rothman, Schekman and Sudhof received a Nobel Prize in 2013 for their discoveries related to the use of vesicles as transport system of cells (Foundation 2013). Additionally, (Biller et al. 2014) recently quantified the abundance of vesicles within the marine environment (at least one vesicle for every bacterial cell) and emphasized the role vesicles played in carbon fixation and storage. Additionally, medical research over the past 40+ years has included the use of synthetic vesicles (liposomes) as a means to transport pharmaceuticals across cell membranes for direct delivery of drugs inside the cell (Allen and Cullis 2013). In environmental engineering, the roles, uses and implications of vesicles have not been investigated. The work presented in Chapter 5 of this dissertation is only the beginning of our understanding of the potential significance of vesicles on treatment processes.

Cellular vesicles are produced by all domains of life, and are known to affect processes ranging from signaling to distribution to detoxification of bacterial products (Shifrin et al. 2013). Vesicle membranes are primarily composed of phospholipids, glycolipids and lipopolysaccharides. These compounds comprise the lipid-bilayers that

serve as plasma membranes for a range of vesicles present in, or generated by, all cells and are therefore present in all biologically impacted waters including surface waters (e.g., algae/ cyanobacteria) and wastewaters (e.g., bacteria) (Song et al. 2010). Additional research is needed to determine the significance of, quantities and characterize vesicles in the water supply.

Significance to Environmental Engineering

My research work has shown the impact of these vesicles on membrane fouling and the ability of ozone to break down the vesicle structure; however, there are likely several other treatment processes in which vesicles may play a vital role. Figure 6.2 presents a schematic of water and wastewater treatment processes with notes on the potential implications of vesicles on processes or considerations.

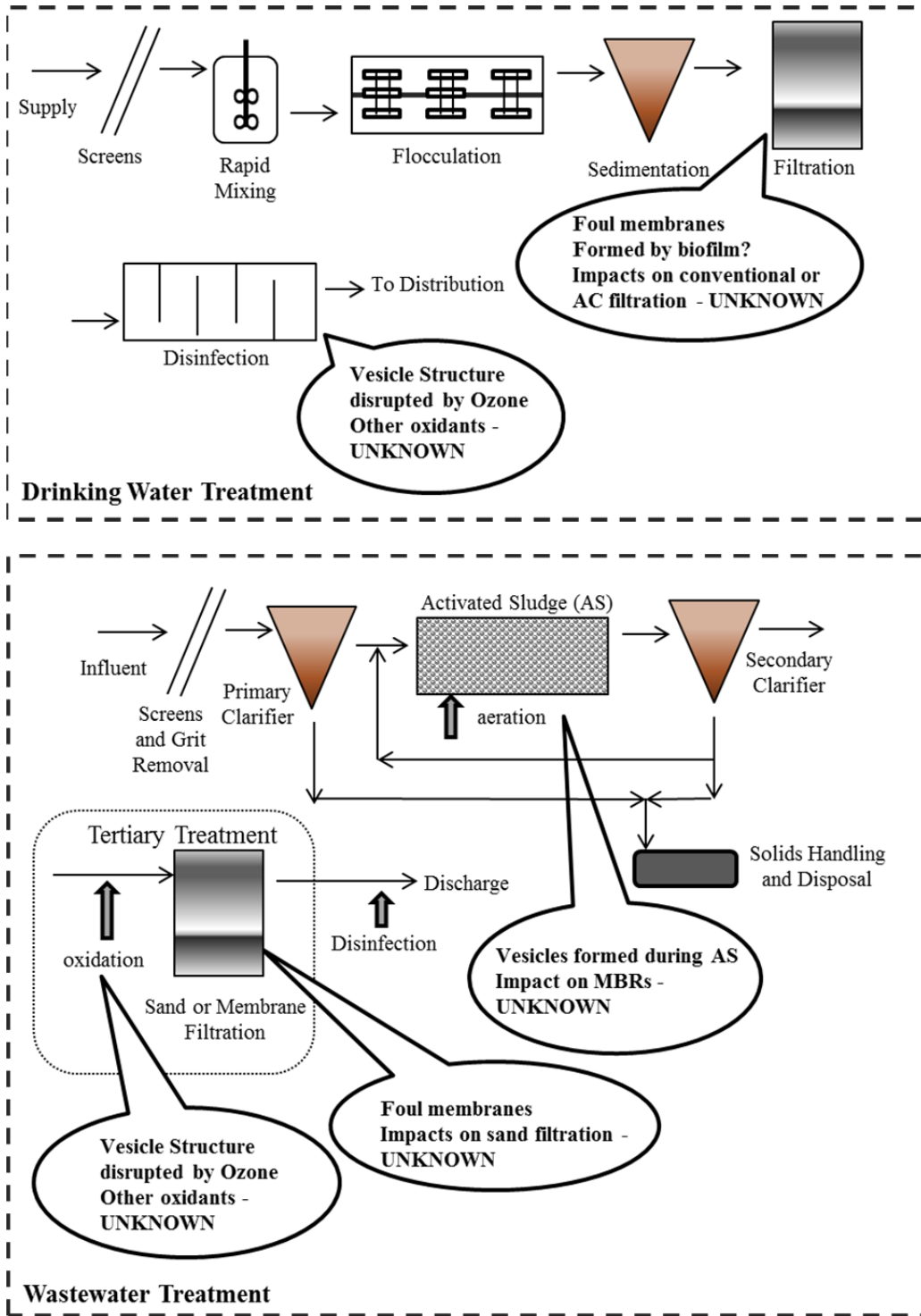


Figure 6.2 Water and Wastewater Schematics Illustrating Potential Implications of

Vesicles on Processes and Treatment

In addition to these potential treatment implications, the presence and formation of vesicles during the biological processes of wastewater treatment may also impact the potential toxicity of treated wastewater to aquatic organisms. Pharmaceuticals are present in municipal wastewater due to ubiquitous use of pharmaceuticals by the general public as well as from poorly controlled production or manufacturing facilities (WHO 2014). Wastewater treatment processes reduce the concentration of some, but not all of these CECs (Kasprzyk-Hordern, Dinsdale, and Guwy 2009). Unlike the vesicles produced by cells discussed previously, liposomes can also form through self-assembly of cell wall debris (Biller et al. 2014). When this occurs, bulk solution is encapsulated within the liposome structure and can thereby be transported across cell membranes of neighboring organisms, similar to the liposome-drug delivery system currently investigated by the medical community (Figure 6.3). This means formation of liposomes within the activated sludge or downstream processes, results in encapsulation of secondary effluent, including any pharmaceuticals present, within the liposome structure. Then, if the liposome structure is not lysed through oxidation, the liposome/pharmaceutical capsule enters the aquatic environment where it is likely capable of moving across cell membranes. In this manner, the liposome-drug delivery phenomenon would be expected to increase CEC toxicity based on delivery directly to the cell as demonstrated in the medical research community (Allen and Cullis 2013).

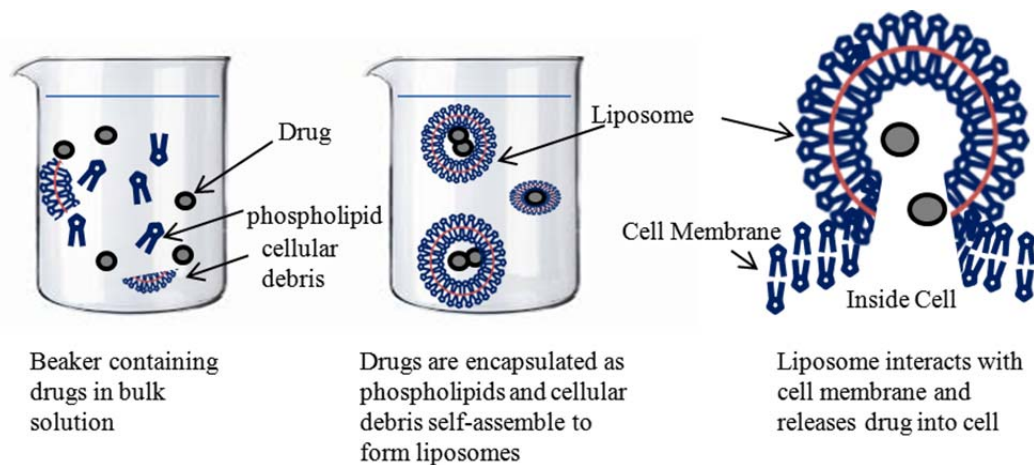


Figure 6.3 Representation of the Liposome Formation Process used to Encapsulate Pharmaceuticals

Quantification of Vesicles

Very little information is available on the quantity of vesicles within surface waters or in secondary effluent. They have not been well quantified in the environment (Biller et al. 2014) and have not been quantified in activated sludge/secondary effluent. This is in part due to the difficulty and limitations of detecting vesicles (Biller et al. 2014). Further efforts to quantify vesicles should also improve overall techniques and procedures for detecting similar soft biogenic nanoparticles.

Quantification of vesicles in biologically impacted waters is important in order to better understand the significance of their presence on water treatment processes. For example, one of the findings of Chapter 5 was an equivalent dose of 50 mgC/L of alginate (polysaccharides) was required to foul UF membranes at the same rate as 3 mgC/L of liposomes (vesicles). However, if vesicles are present in much lower concentrations than polysaccharides (<20 times) in either surface water or secondary

effluent, vesicle-caused membrane fouling may be irrelevant in comparison with polysaccharide-caused fouling. Additionally, if formation of liposomes during the activated sludge process is minimal, further investigation into increased toxicity of pharmaceuticals within treated wastewater may become irrelevant.

Characterization of Vesicles

In addition to understanding the quantities and implications of vesicles within biologically impacted waters, characterization of vesicles is important to better understand not only their effect on treatment processes, but also effectiveness of treatment processes to remove or destroy these colloids. In this regard, the importance of shape and structure of these vesicles can be further studied for a range of treatment processes and oxidants.

Research Approach

In order to determine the impacts of vesicles on water/wastewater treatment, quantify and characterize these vesicles, the research approach should include the following steps:

1. Develop a standard protocol for identifying and quantifying vesicles in solution using (Biller et al. 2014) as a guideline which includes microscopy and
2. Collect representative samples of surface water, activated sludge, secondary effluent, and biofilm (filter and/or pipe) then identify and quantify vesicles within the samples.
3. Follow approaches described in (Biller et al. 2014) and (Dotson and Westerhoff 2012) to isolate vesicles and analyze their molecular makeup using FTIR.

4. Use bench scale testing, microscopy and SEC-DOC analysis to evaluate the effect of other oxidants (chlorine, chlorine dioxide, chloramines) on the structure of model liposomes
5. Investigate membrane fouling by liposomes in surface water and secondary effluent matrix and revisit estimation of percent of fouling vesicles may be responsible for in UF of secondary effluent based on these results and quantities determined in step 2.
6. Use batch tests and rapid small scale column testing to quantify loss in activated carbon sorption of a model pollutant in the presence of liposomes
7. Collaborate with a toxicologist to evaluate the change in toxicity of selected CECs based on encapsulation within a liposome structure

Summary

The findings of this dissertation have several implications on water and advance treatment processes. Due to the limitations of this work, additional research is needed in several areas including: dust storm content, warning system using integrated water information technology, and water matrix effects on liposomal-like fouling, and the impact of the shape and structure of colloids on the effectiveness of treatment processes. Finally, I tried to make clear the need for additional research on vesicles within biologically active waters and provided an outline approach for meeting those research needs. A summary of findings, conclusions and addition future research topics are provided in Chapter 7.

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Chapter 7

CONCLUSIONS AND FUTURE RESEARCH

The goal of this research was to quantify the impacts of extreme weather events on DOM and to use ozonation to overcome challenges of DOM during water reclamation to improve membrane filtration efficiency and oxidize CECs. This chapter summarizes findings from each chapter, conclusions from the entire dissertation, and future research needs emerging from this dissertation. The key findings and conclusions of this research are summarized below and a discussion of future research is provided.

Summary

Chapter 3 is the basis for a journal paper for submission to the AWWA Journal entitled, “Severe Weather Impacts on Water Quality in Central Arizona,” which includes the following findings:

- A correlation exists between dust storms (defined as >90th percentile PM₁₀ levels) and surface water turbidity and a measured increase in surface water DOM immediately following dust storm events.
- Surface water turbidity and DOM increased as a result of flooding in intermediate and ephemeral waterways in central Arizona.
- Turbidity, taste and odor of raw water measured at a downstream WTP as runoff over wildfire burn areas entered supply waterways.

Chapter 4 of this dissertation is the basis for the journal article, “Promoting Hydroxyl Radical Production during Ozonation of Municipal Wastewater,” which has been accepted for publication in *Ozone Science & Engineering*. Key findings in Chapter 4 were:

- H₂O₂ addition during ozonation of surface water immediately increased the oxidation of pCBA (production of HO[•]).
- In tertiary effluent, a quantifiable threshold ozone dose range was identified in two different wastewaters, above which addition of H₂O₂ increased oxidation of pCBA (production of HO[•]).
- At environmentally relevant CEC concentrations, pH, and ozone dosages; packed-bed reactor tests showed HO[•] production was similar for ozonation over glass beads, ozonation over TiO₂ spheres, and ozonation over GAC in tertiary effluent.

Chapter 5 is the basis for a journal article entitled, “Membrane Fouling by Vesicles and Prevention through Ozonation,” which has been reviewed and revised for submission to *Environmental Science & Technology*. The findings of this study included:

- Model vesicles (liposomes) fouled UF membranes faster [7-20 times greater increase in total resistance (R_T) with increasing permeate volume] than model polysaccharides, fatty acids, and NOM on a DOM-normalized basis.
- An “equivalent dose” of alginate (model polysaccharide) of approximately 50 mgC/L is required to achieve a flux decline rate similar to 3 mgC/L of liposomes.
- Based on the estimated carbon distribution in secondary effluent, liposome-like materials could be responsible for 20-60% of membrane fouling during UF.

- Pre-ozonation reduces liposomal fouling during UF at relatively low doses.
- SEC-DOC results showed ozonation of liposomes reduces the amount of high molecular weight material and increases the amount of lower molecular weight carbon compounds.

Conclusions

My research led to the following important conclusions related to the impacts of extreme weather events on surface water DOM and turbidity levels, the use of liquid or solid-phase promoters during ozonation of treated wastewater, and the reduction of membrane fouling by cellular vesicles through ozonation.

- The actual and perceived quality of surface water (DOM and turbidity) are impacted by extreme weather events. With increasing turbidity during dust storms, rapid increases in turbidity and DOM due to flooding and changes in turbidity following precipitation over wildfire burn areas located within a watershed.
- DOM-based ambient promoters of HO[•] production exist in wastewaters that are not in surface waters. These promoters create an “ozone threshold dose,” above which addition of H₂O₂ increases the rate of HO[•] formation.
- Ozonation of tertiary effluent through a packed-bed reactor of either TiO₂ spheres or GAC does not increase the rate of HO[•] production at environmentally relevant contaminant and ozone concentrations and pH levels compared with ozone alone.

- Based on the estimated carbon distribution of secondary effluent, liposome-like biogenic organic nanomaterial could be responsible for 20–60% of fouling during UF of secondary effluent
- Ozonation prior to filtration reduces liposomal fouling, likely due to the disruption of the liposome structure beginning with cleavage of the fatty acid tails at the carbon-carbon double bonds.

Implications

The findings and conclusions of this dissertation have several different implications on membrane fouling research, advanced treatment for water reuse as discussed in Chapter 6. These implications include advantages of integrating treated wastewater more directly in the surface water supply based on the impact of extreme weather events on surface water quality, the presence of ambient promoters of HO[•] within treated wastewater for advanced oxidation during ozonation in lieu of H₂O₂ addition, and the use of ozone for CEC oxidation and to reduce membrane fouling greatly increases the quality of the wastewater supply, thereby alleviating some of the concerns of more direct paths for reuse.

Future Research

My research addressed critical knowledge gaps related to extreme weather events and water quality, the promotion of HO[•] during ozonation of wastewater, and the use of ozone to reduce membrane fouling by vesicles. However, this research also raises

important questions which should guide future work. These questions fall into two categories: first, immediate research questions that can be readily addressed; and second, larger-scale, over-arching research topics.

Research questions to address in the near future:

- Is coagulation/sedimentation/filtration of particulate matter deposited on surface waters by dust storms different than for particulate matter already in a surface water?
- What is the effect of dust storms at reservoirs (secchi disc depth versus PM10)? Recharge basins?
- Is ozonation effective in reducing membrane fouling by glycolipid and lipopolysaccharide vesicles?
- How is membrane fouling different between phospholipid, glycolipid and lipopolysaccharide vesicles? and how do different water matrices (multivalent cations, pH, etc.) impact fouling behavior?
- How effective are other oxidants (chlorine, chlorine dioxide, chloramines, etc.) in reducing vesicle-caused membrane fouling? and what are the associated reaction pathways?
- What other ways are vesicles ruptured mechanistically (e.g., ionic strength)?
- How does ozonation impact membrane fouling by other organic nanoparticles ((e.g., fibrils, silica/organic aggregates)?

Four critical over-arching future research topics identified through the findings and conclusions of this dissertation are briefly described below.

Future Research Topic 1 – How oxidants change the structure and shape of biogenic organic nanomaterial (BONM)

Based on the complexity of secondary effluent and economic limitations on ozone doses at a large scale, it is unlikely that organic substrates would be completely mineralized by ozone treatment. Thus the fate and toxicity of intermediate byproducts formed during ozonation of BONMs is critical. Thus research focused on the byproducts produced during ozonation of BONMs and their associated toxicity is vital, particularly because ozonation of secondary effluent has already been implemented on a large scale in some areas.

Future Research Topic 2 – The impact of BONM physical characteristics (structure, rigidity, etc.) on removal of BONMs by drinking water and water reclamation treatment processes

One of the important findings of Chapter 5 was that the disruption of the physical structure of the liposome by ozone resulted in a significant reduction of membrane fouling. Other BONMs with unique structures are present in secondary effluent (Song et al. 2010) and surface waters. These BONMs also have unique physical properties (size, shape, elasticity, etc.) that may impact not on membrane fouling potential and reduction through ozonation, but several other treatment processes in water and wastewater

treatment including coagulation-flocculation-sedimentation, filtration, oxidation/advanced oxidation and sorption. A better understanding of the impact of the physical properties, in addition to the chemical composition, of BONMs will provide opportunities to better tailor treatment processes for both improved process efficiency (e.g., reduction of fouling), and/or BONM removal.

Future Research Topic 3 – Characterization and quantification of liposomes and cellular vesicles in secondary effluent and surface waters

Based on the conclusions of Chapter 5, membrane fouling by cellular vesicles may be responsible for 20-60% of membrane fouling during UF of secondary effluent. This relatively wide percentage range is due to a lack of data for the amount and characteristics of the vesicles present in secondary effluent. Only recently has published data become available on the approximate quantities of vesicles within the marine (salt water) environment; where (Biller et al. 2014) estimated vesicle concentrations of between 1-10 times bacterial concentrations. Similar measurement methods should be employed to quantify vesicles within fresh waters and secondary effluent. Additionally, the characteristics (membrane composition, vesicle contents) of the vesicles should also be identified as they will likely be different for surface water biology and the bacteria present in activated sludge.

Future Research Topic 4 – Occurrence and toxicity implications of transport of CECs via liposomes formed in wastewaters

In medical research, liposomes are being investigated for use as a means of transport of pharmaceuticals into cells, based on their ability to cross cell membranes (Allen and Cullis 2013). Simplistically, this is done through synthesizing vesicles in a solution containing the desired drug, thereby encapsulating the pharmaceutical solution within the vesicle, rinsing off excess bulk solution, and then injecting the liposome-packaged drug into the blood stream. Due to the amphiphilic nature of the liposome membranes, they readily move across cell membranes and therefore can deliver pharmaceuticals directly to the cell. This method of drug delivery is promising based on its relatively low cost and greater effectiveness of drug delivery (stronger effect at lower dosages) (Allen and Cullis 2013). In biologically active waters, products of lysed or incompletely digested bacteria can self-assemble into liposomes (Biller et al. 2014). In secondary effluent these liposomes encapsulate secondary effluent as they form. Several pharmaceuticals and other CECs are present in secondary effluent (Kasprzyk-Hordern, Dinsdale, and Guwy 2009) and would therefore be captured within these liposome structures. If these structures are not ruptured prior to release into the environment, they are likely capable of delivering these CECs directly into cells of microbes, plants, and animals alike. Delivery of CECs in this manner may greatly increase the estimated toxicity of these compounds and potentially the overall rate of bioaccumulation of CECs within the environment. Therefore future research is needed to determine not only the increased toxicity of liposome-delivered CECs, but also to quantify to what extent

liposome formation and encapsulation of CECs is occurring in municipal wastewater treatment.

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