Initial Development of Advanced, High-Rate Treatment Process for Wet Weather Flows

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INITIAL DEVELOPMENT OF ADVANCED, HIGH-RATE TREATMENT PROCESS FOR WET WEATHER FLOWS

by

Paige E. Peters

A Thesis submitted to the Faculty of the Graduate School, Marquette University, in Partial Fulfillment of the Requirements for the Degree of Master of Science and Engineering

Milwaukee, Wisconsin
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ABSTRACT
INITIAL DEVELOPMENT OF CEPT-AOP PROCESS
FOR ADVANCED, HIGH-RATE TREATMENT
OF WET WEATHER FLOWS

Paige E. Peters

Marquette University, 2019

Billions of gallons of untreated water are discharged into lakes and rivers every year due to combined and sanitary sewer overflows during high-intensity precipitation events. Combined sewer overflows (CSOs) and sanitary sewer overflows (SSOs) pose both environmental and public health risks due to potential human contact with contaminated water. To address the overflow issue, a novel, advanced, high-rate wet weather treatment process was investigated. The high-rate treatment process combined chemically enhanced primary treatment (CEPT) with an advanced oxidation process (AOP) using ozone to rapidly remove total suspended solids (TSS) and chemical oxygen demand (COD), inactive E. coli, and oxidize the micropollutants triclosan (TCS) and triclocarban (TCC) in synthetic SSO waters.

Results demonstrated that the preferred chemicals for CEPT were ferric chloride with an anionic polymer coagulant aid, which achieved 95% turbidity removal in <5 min. For AOP treatment, ozone (O₃), ultraviolet light (UV) with hydrogen peroxide (H₂O₂), UV with O₃, and O₃ with H₂O₂ were investigated. Ozone alone was selected for further study. Initial research results also demonstrated >99% TSS removal, 90% COD removal, and at least 6-log E. coli inactivation. The micropollutant oxidation results were inconclusive. The detention time for 90% COD removal was relatively long (6 h), suggesting necessary future work to reduce this detention time (<30 min) for applicability during high-intensity precipitation events.
ACKNOWLEDGEMENTS

Paige E. Peters

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Finally, I would like to express the profound gratitude I have towards the Director of my advisory committee and thesis advisor, Dr. Dan Zitomer, for providing me with this opportunity and continuing to support me. Dr. Zitomer has mentored me throughout the many ups and downs of this project and has worked with me to help deliver a thesis of which I am very proud. Under Dr. Zitomer’s guidance, I have developed a wealth of knowledge for which I am extremely grateful and gained a deeper understanding and appreciation for the research I have been able to conduct.
DEDICATION

I am dedicating this thesis to my wife, Megan, for her patience, encouragement, and wild support throughout this effort, and to my family, for always believing in me and supporting my passions. It takes a village, and mine is one of the finest.
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1 INTRODUCTION

1.1. BACKGROUND

In many communities with municipal sewers, combined sewer overflows (CSOs) and sanitary sewer overflows (SSOs) are released without treatment to lakes and rivers during high-intensity precipitation. These overflows can contain conventional oxygen-demanding pollutants, pathogens, suspended solids and a suite of micropollutants (MPs) (Lee & Bang, 2000; Phillips et al., 2012). Contaminants released during major precipitation can be detrimental to receiving water integrity as well as to public health due to human exposure (McLellan et al., 2007; P. Phillips & Chalmers, 2009; Newton et al., 2013; Jagai et al., 2017). The minimum required combined sewer flow treatment (“minimum treatment”) in accordance with the US Environmental Protection Agency (USEPA) 1994 CSO Control Policy consists of primary treatment for solids removal followed by disinfection, typically using chlorine, and dechlorination. Minimum treatment does not address MP or conventional soluble organic pollutant removal and can result in carcinogenic disinfection byproduct formation (King County Wastewater Treatment Division, 2011; Luo et al., 2014; McFadden et al., 2017).

1.2. ADVANCED, HIGH-RATE TREATMENT

To rapidly treat the contaminants in wet weather flows and achieve high-quality effluent including soluble organic pollutant, MP, and pathogen removal, advanced oxidation processes (AOPs) can be used as high-rate technologies (Szabo et al., 2005). AOPs are characterized by the formation of hydroxyl radicals, which are the strongest known oxidants and, among other oxidants such as ozone, can oxidize MPs and remove soluble organic pollutants (Gottschalk et al., 2010; D. Gerrity & Snyder, 2011). For improved AOP performance, solids removal using chemically enhanced primary treatment (CEPT) can be implemented before AOP processes. CEPT is a technology commonly applied in wet weather treatment for rapid solids removal in which coagulants, such as alum (aluminum sulfate) or ferric chloride, and flocculant aids, such as
polymers, are added to wet weather flows either at a remote facility or a treatment plant (CH2M Hill, 2008; CDM, 2010; Exall & Marsalek, 2013).

Advanced, high-rate treatment using CEPT followed by AOPs may be a novel, appropriate method to manage sewer overflows, eliminating an important source of contaminants in lakes, river, and basements. CEPT achieves solids as well as partial nutrient and biochemical oxygen demand (BOD) removal, whereas AOPs achieve pathogen inactivation, soluble BOD removal, and MP oxidation. Using these technologies in sequence may result in a high-quality effluent that has the same or better quality than that produced by conventional secondary treatment. CEPT followed by an AOP can reduce the stress on infrastructure during intense storms, preventing CSOs, SSOs, and backups of water into building basements from occurring.

1.3. THESIS APPROACH

In this study, batch, bench-scale CEPT in sequence with various AOP treatments was evaluated as an option for advanced, high-rate treatment of a synthetic SSO water. Jar tests were conducted to determine chemical doses for rapid solids removal, which is a critical precursor to efficient, subsequent AOP treatment since particulate organics consume hydroxyl radicals (Zucker et al., 2015). AOP treatments including ozone (O$_3$) alone, O$_3$ with hydrogen peroxide (H$_2$O$_2$) (O$_3$/H$_2$O$_2$), O$_3$ with ultraviolet light (UV) (O$_3$/UV), as well as UV with H$_2$O$_2$ (UV/H$_2$O$_2$) were evaluated for chemical oxygen demand (COD) removal, E. coli inactivation, and MP removal. The overall treatment detention time to achieve 90% COD removal was determined and the treatment efficiencies for conventional wastewater constituent removal were determined using synthetic SSO after CEPT alone and after CEPT combined with AOP treatment.

1.4. THESIS STRUCTURE

The thesis is structured as two key chapters including the literature review (Chapter 2) and initial research phase (Chapter 3). Chapter 2 includes the literature review which presents public health and environmental concerns related to wet weather events (CSOs and SSOs),
provides a brief overview of relevant policies, and discusses current and future trends for wet weather treatment and management. Initial research phase (Chapter 3) includes an introduction, methods, results and discussion, and conclusions for the work conducted. Chapter 4 presents overall conclusions and suggests future work.
2 CURRENT AND FUTURE CSO/SSO CHALLENGES AND MANAGEMENT APPROACHES

2.1. INTRODUCTION

Combined and sanitary sewer overflows during wet weather events can be more detrimental to receiving lakes and rivers than conventionally treated wastewater effluent (Phillips et al., 2012). Combined sewers have both stormwater and sanitary wastewater conveyed in the same pipe. Wet weather flows, known as combined sewer overflows (CSOs) and sanitary sewer overflows (SSOs), occur when wastewater conveyance and treatment systems become overburdened during high-intensity rain events and untreated sewage is discharged into lakes and rivers. CSOs and SSOs can contain higher concentrations of contaminants including organics, nutrients, pathogens, metals, and MPs compared to treated wastewater effluent (Phillips & Chalmers, 2009; Blair et al., 2013). Some portions of wet weather flow can contain contaminant concentrations even higher than wastewater influent due to first flush and surface runoff loads combined with sanitary sewage (Lee & Bang, 2000; Even et al., 2007a).

Over 700 US cities have combined sewers that may pose both environmental and public health risks during high-intensity storm events (McLellan et al., 2007; Appel et al., 2017). For example, twenty-two billion gallons of untreated sewage was released into the Great Lakes alone in 2014 due to CSOs and SSOs (USEPA Office of Wastewater Management, 2016; ASCE Foundation, 2017). During high-intensity storm events, these systems are hydraulically overloaded due to a rapid influx of stormwater in the combined sewer conveyance system. During a storm event that surpasses sewerage system capacity, two combined sewer infrastructure failures can occur: (1) sewer overflows during which untreated sewage is released to lakes and rivers, and (2) street, outdoor area, and basement backups in which contaminated water backs up into residential and commercial basements. Both failure types pose environmental and public exposure/health risks and new methods to mitigate effects of these failures would be beneficial (Zukovs & Marsalek, 2004).
2.1.1. **CSO and SSO US Policy**

CSOs and SSOs are managed differently under US federal law described in the Clean Water Act (CWA). While CSOs are often handled under consent decrees, SSOs are illegal under the CWA and their occurrence can result in fines, fees, or lawsuits brought upon the discharging municipality or agency (USEPA, 1972). For site-specific CSO management, municipalities enter into consent decrees with regulatory agencies, government entities, and federal courts. Consent decrees are agreements, supervised by courts, that present a plan of action to reduce or eliminate overflow events typically initiated as a result of legal enforcement action brought against the non-compliant discharging entity. The guiding policy for the formation of overflow-related consent decrees is in the United States Environmental Protection Agency (USEPA) 1994 CSO Control Policy. The policy offers direction on CSO control practices for compliance with the CWA and individual National Pollution Discharge Elimination System (NPDES) permits through required minimum controls, monitoring, and development of long-term control plans (LTCPs) (USEPA, 1972, 1994, 2010; Cook, 1995). The minimum controls focus on maximizing and optimizing existing infrastructure for CSO control, while the LTCPs and consent decrees often include larger capital projects for new infrastructure construction. Both approaches are implemented to meet NPDES permit requirements.

The first consent decrees for large cities (<50,000 in population) with combined sewers involved project implementation in the late 1990s and early 2000s (e.g. Cincinnati, OH; Philadelphia, PA; Washington, D.C.). More recent consent decrees have involved Akron, OH which entered into their $0.9B consent decree in 2010 along with Chicago, IL in 2011 for their $1.8B consent decree (US District Court for the Northern District of OH, 2010; US District Court for the Northern District of IL, 2011). The decrees include a series of projects to close combined sewer outfalls, minimally treat high flows in combined sewers, and maximize use of existing infrastructure. For example, the CSO consent decree for Metropolitan Sewer District of Greater Cincinnati (MSD) includes 114 projects, with 102 completed as of 2018 and a total cost of $3.3B.
(US District Court for the Southern District of OH, 2004). These multi-decade consent decrees can be renegotiated every five years to address new challenges or accommodate updated technologies. Philadelphia and Washington D.C. were the first cities to reopen their consent decrees to introduce significant green infrastructure projects. Green infrastructure was not a common CSO control solution in the early 1990s during drafting of the initial CSO control policy; therefore its addition into consent decrees demonstrates the ability for the projects to include more updated technology (Copeland, 2014; Appel et al., 2017).

2.1.2. Current CSO Management During Wet Weather

Storage is presently a common technology used because the USEPA 1994 CSO Control Policy included the phrase “capture and treat” CSOs. “Capture” was interpreted as “store” and storage became the primary solution declared in consent decrees throughout the country (USEPA, 1994). Many current wet weather control technologies employ storage as a reliable and certain management solution; however, capital projects for storage typically come with a large footprint and cost (USEPA, 1999b; US District Court for the Northern District of IL, 2011).

Primary treatment and chlorine disinfection (with dechlorination) are commonly used and are considered the minimum treatment required to avoid classification as an unmanaged CSO or SSO in accordance with the USEPA 1994 CSO Control Policy. Minimum treatment does not fully address nutrients, biochemical oxygen demand (BOD), or MP removal nor disinfection by-product formation. Currently, however, this practice at the wastewater treatment plan (WWTP) or at a separate CSO control facility is acceptable if included in a municipality’s existing LTCP or consent decree. When conducted at a WWTP, this process is called “bypassing” or “blending” wastewater in which only minimum treatment is performed (Winter & Kreutzberger, 2017). WWTPs are still able to meet permit by dilution, but this practice is not received well by regulatory agencies, environmental groups, or other public stakeholders (Winter & Kreutzberger, 2017).
2.1.3 Developing New CSO Management Approaches

When evaluating new wet weather treatment technologies, start-up time, overall system footprint, and cost should be considered in addition to permit effluent requirements. Due to the relative infrequency of high-intensity wet weather events compared to baseline WWTP operation, a wet weather treatment technology may remain out of operation for weeks to months, and then must be able to start up quickly and effectively when needed (Szabo et al., 2005).

Conventional treatment unit operations employed at WWTPs can be used for wet weather treatment, though conventional secondary treatment is not ideal for this application. Conventional secondary treatment typically requires a biological treatment step such as activated sludge. However, biological treatment detention times are usually greater than four hours and require a large footprint to treat stormwater without storage (Metcalf & Eddy et al., 2013). A short detention time allows for a smaller footprint and subsequent flexibility with system placement, two important characteristics of wet weather treatment technologies.

Current technologies for wet weather treatment also vary based on location since constraints at municipalities vary. Some utilities are employing real-time control of sewerage systems to better regulate the amount of stormwater entering combined sewer systems. During real-time control, sensors are employed to better utilize existing infrastructure for management and storage of wet weather flows (Monteserrat et al., 2015). Sewer separation is another approach to eliminate CSO events and reduce SSO events included in LTCPs which may resolve the CSO issue, but does not offer removal of contaminants in stormwater and runoff (Lee & Bang, 2000; Birch et al., 2011; Schlaman et al., 2015).

To manage more recalcitrant contaminants that can be found in wastewater effluent as well as CSOs and SSOs, advanced oxidation processes (AOPs) are capable technologies that are becoming more widely considered for tertiary treatment at WWTPs. Such recalcitrant contaminants include pharmaceuticals, personal care products, polyaromatic hydrocarbons, and other emerging contaminants. AOPs such as ozone (O₃), ultraviolet (UV) radiation, hydrogen
peroxide (H₂O₂), or a combination of these technologies are also employed to address more difficult-to-remove pathogens such as Cryptosporidium (Mac Kenzie et al., 1994; Huber et al., 2005; Pešoutová et al., 2014). According to a study conducted by Rizvi et al. (2013) combined oxidation systems show greater (synergistic) results with pathogen removal than single systems. The use of AOPs is increasing due to their diversity in application such as water reuse, and for treating a wide variety of contaminants. Additionally, the rapid reaction rate of AOPs means the technology can be used to meet effluent goals with a short detention time (Oller et al., 2011b; Ribeiro et al., 2015). While AOPs have not been commercially applied for wet weather treatment, both the ability to remove recalcitrant contaminants and the rapid reaction rate make them an appropriate technology to be explored.

This review addresses the public health and environmental concerns related to wet weather events (CSOs and SSOs) and describes the state-of-the-art for wet weather treatment and management technologies as a preliminary guide to evaluate next steps for technology research and development.

2.2. PUBLIC HEALTH AND ENVIRONMENTAL CONCERNS

2.2.1. Public Health

The immediate public health concern related to wet weather flows is human contact with pathogens from municipal wastewater. Contact could occur during basement backups, during street flooding, or in receiving waters used for recreational activity. CSOs have been reported to contain between 10⁵-10⁶ fecal coliform colony forming units (CFUs) per 100 mL of wastewater (Passerat et al., 2011; Scheurer et al., 2015). The relatively high fecal coliform cell count implies the possible presence of pathogens which pose a risk to public health if the public is exposed. A positive correlation between rain events and increases in gastrointestinal illnesses in children was observed within urban areas due to human contact with untreated sewage during flooding, overflows, or basement backups (McLellan et al., 2007; Newton et al., 2013). Additionally, Jagai
et al. (2017) found a positive correlation between emergency room visits for gastrointestinal illnesses and SSO events in northeastern Massachusetts.

Fecal coliforms detected in surface water can originate from human or animal fecal matter and determining the origin can provide valuable information. From a public health perspective, both human and animal fecal matter can cause gastrointestinal illnesses in humans (McLellan et al., 2014; Jagai et al., 2017). However, it is important to understand the source of fecal contamination by identifying the specific bacteria present in lakes and rivers to help identify weaknesses in infrastructure. Sauer et al. (2011) sampled 45 stormwater outfalls over four years and observed average ratios of human-associated Bacteriodes to total Bacteriodes of >4.0% among Menomonee River sites in Wisconsin. They concluded that a major source of river fecal contamination was domestic sewage within storm sewers which were contaminated by nearby, leaking sanitary sewers. This conclusion was based on a correlation between increased infiltration and inflow near a stormwater outfall and elevated human Bacteriodes in the outfall effluent (Sauer et al., 2011).

Antibiotic resistance is another public health concern that may be related to human contact with wet weather flows. The complex matrix of MPs present in CSOs include antimicrobials such as triclosan that have been linked to proliferation of antibiotic resistance genes (ARGs) in bacteria as well as endocrine disrupting chemicals (EDCs) and known carcinogens including polyaromatic hydrocarbons (PAHs) (Huber et al., 2005).

2.2.2. Water Quality

2.2.2.1. Characterization

CSOs and SSOs significantly contribute to pollutant loadings in receiving waters (Diaz-Fierros et al., 2002; Szabo et al., 2005; Weyrauch et al., 2010; Madoux-Humery et al., 2013). The initial release of combined stormwater and wastewater from a CSO during a storm event contains higher contaminant concentrations due to the first flush phenomenon (Gobel et al., 2007). This initial,
concentrated first flush is defined by the presence of more concentrated contaminants during the first 50% of storm volume released or before the storm hydrograph peak flow occurs (Lee & Bang, 2000; Casadio et al., 2010). First flush is predominantly a result of the resuspension during storm flow of solids previously deposited in the sewer as well as dry atmospheric deposits on roads and roofs being removed by rainfall (Lee & Bang, 2000; Gasperi et al., 2010; P. J. Phillips et al., 2012; Luo et al., 2014). Szabo et al. (2005) and Tondera et al. (2013) concluded that capturing, storing, and then conveying the first flush volume to a WWTP may be an efficient treatment technique for pollutant removal in flow-through wet weather treatment processes. The remaining low-strength wet weather flow could be treated with technology more appropriate for dilute wastes that may be less expensive.

CSO contaminant values are summarized from the literature in Table 2.1. Refer to Suárez & Puertas (2005) for a summary of the impacts of these CSO contaminants on receiving waters.
Table 2.1 Typical Actual SSO Compositions

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Typical Values¹</th>
<th>Units</th>
<th>References</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>CH2M Hill (2008)</td>
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<td></td>
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<td>CH2M Hill &amp; CHA (2011)</td>
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<td></td>
<td>Gasperi et al. (2012)</td>
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<td></td>
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<td></td>
<td>Brown and Caldwell &amp; Black &amp; Veatch (2014)</td>
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<tr>
<td>COD</td>
<td>321 (233-395)</td>
<td>mg/L</td>
<td>Diaz-Fierros et al. (2002)</td>
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<td>Gasperi et al. (2012)</td>
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<td></td>
<td></td>
<td>Pisoieiro, Galvão, Ferreira, &amp; Matos (2016)</td>
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<tr>
<td>TSS</td>
<td>210 (100-870)</td>
<td>mg/L</td>
<td>Tetra Tech MPS (2003)</td>
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<td>Li et al. (2004)</td>
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<td>CH2M Hill (2008)</td>
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<td>El Samrani, Lartiges, &amp; Villiéras (2008)</td>
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<td>CH2M Hill &amp; CHA (2011)</td>
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<td>Madoux-Humery et al. (2013)</td>
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<td></td>
<td>Brown and Caldwell &amp; Black &amp; Veatch (2014)</td>
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<tr>
<td>NH₃-N</td>
<td>8.4 (6.8-9.9)</td>
<td>mg/L</td>
<td>Gasperi et al. (2012)</td>
</tr>
<tr>
<td>Total Kjeldahl</td>
<td>24.5 (14.4-37)</td>
<td>mg/L</td>
<td>CH2M Hill, (2008)</td>
</tr>
<tr>
<td>Nitrogen (TKN)</td>
<td></td>
<td></td>
<td>CH2M Hill &amp; CHA (2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gasperi et al. (2012)</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>2.7 (0.8-4.6)</td>
<td>mg/L</td>
<td>Tetra Tech MPS (2003)</td>
</tr>
<tr>
<td>(TP)</td>
<td></td>
<td></td>
<td>CH2M Hill (2008)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH2M Hill &amp; CHA (2011)</td>
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<td>Gasperi et al. (2012)</td>
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<td></td>
<td></td>
<td></td>
<td>Brown and Caldwell &amp; Black &amp; Veatch (2014)</td>
</tr>
<tr>
<td>Fecal Coliforms</td>
<td>10⁶ (5x10⁵-3.2x10⁶)</td>
<td>CFU/100 mL</td>
<td>CH2M Hill &amp; CHA (2011) Madoux-Humery et al. (2013)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TCS</td>
</tr>
<tr>
<td></td>
<td>1.1 (0.6-2.2)</td>
<td>µg/L</td>
<td>Halden &amp; Paull (2005)</td>
</tr>
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<td></td>
<td>Schroedel et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>1.3 (0.7-2.6)</td>
<td>µg/L</td>
<td>Halden &amp; Paull (2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Schroedel et al. (2014)</td>
</tr>
</tbody>
</table>

¹ Average value with range of values reported in parentheses

2.2.2.2. Biochemical Oxygen Demand (BOD)

Excess BOD discharged into a lake or river can be a detriment to the balance of the receiving ecosystem by providing organic content (food) for existing bacteria that will consume oxygen during the breakdown of organics, thereby starving aerobic aquatic life of dissolved...
oxygen. CSOs and SSOs can vary greatly in their BOD loading, but concentrations are typically similar to or lower than those of municipal wastewater (e.g. 30-240 mg/L) (Gasperi et al., 2012). Additionally, exertion of high BOD after storm events can cause low dissolved oxygen in rivers that can take up to a month to recover (Paul & Meyer, 2001; Suárez & Puertas, 2005; Even et al., 2007b).

2.2.2.3. Total Suspended Solids/Turbidity

Heavy TSS loading can impair surface waters in both the short-term and long-term considering the persistence of certain hydrophobic contaminants such as pesticides (Perelo, 2010). Additionally, increased turbidity caused by overflows during storm events can lead to a decrease in photosynthetic primary production (Passerat et al., 2011). High loading of TSS is associated with increased concentrations of metals, pathogens, nutrients, and MPs. This is primarily due to the contaminants’ hydrophobic characteristics and subsequent tendency to sorb to solids (Schwarzenbach et al., 2006; Gasperi et al., 2012). For this reason, many CSO and SSO treatment techniques employing only solids removal also result in reduced concentration of many contaminants, particularly BOD.

2.2.2.4. Excessive Nutrient Loadings

Phosphorous and nitrogen releases in the environment include both point and non-point sources. Wastewater treatment plant effluent is one point source, whereas agricultural runoff is the largest non-point source of nutrients (Rittmann et al., 2011). Wet weather flows have both point and non-point source components since sewer overflows occur at specific locations such as outfalls (point source), while runoff during a storm event also results in nutrient releases (non-point source). Regardless of classification, CSOs and SSOs can contribute significant nutrient loadings to the receiving waters. This type of nutrient loading can shock an ecosystem, disrupting the existing balance and requiring days to months to recover (Nie et al., 2018). With increasingly more stringent regulations on nutrient discharges, wastewater utilities are seeking or required to
manage all discharges including overflows to meet their permitted effluent loads. This process puts a greater emphasis on characterizing the nutrient content of wet weather flows and considerations for treatment (Aissa-Grouz et al., 2016).

### 2.2.2.5. Metals

CSOs and SSOs are important contributors to metals loadings in lakes and rivers (Suárez & Puertas, 2005). Numerous studies have linked heavy metal concentration to toxicity with similar results as typical dose-response curves for individual metals. However, metals can exert a greater toxicity in a complex mixture than individually, which can have synergistic results (Casadio et al., 2010).

### 2.2.3. Micropollutants

MPs including pharmaceuticals, pesticides and polyaromatic hydrocarbons (PAHs) have been found in CSOs and SSOs at environmentally relevant concentrations in microgram per liter concentrations. Wet weather flows are an important source of MPs as they typically contain both stormwater runoff that can contain PAHs, and pesticides as well as wastewater containing pharmaceuticals and estrogens (Birch et al., 2011; Musolff, Leschik, Reinstorf, Strauch, & Schirmer, 2010; Phillips et al., 2012). This results in a mixture of MPs, the public health and environmental impacts of which are not well understood. Additionally, there are numerous mechanisms that remove MPs in conventional wastewater treatment (Belgiorno et al., 2007; Le-Minh et al., 2010). During a storm event, however, runoff (non-point) and overflows (point) can rapidly release MPs into the environment. Luo et al. (2014) have summarized various wastewater treatment technologies and their efficacy in MP removal.

### 2.2.3.1. Endocrine Disrupting Chemicals

Endocrine disrupting chemicals (EDCs) represent a group of MPs including pharmaceuticals, hormones, and other compounds that exhibit influences on the endocrine system
(e.g. estrogenicity, androgenicity) and have detrimental health impacts on both aquatic life and humans. EDCs affect aquatic species including frogs, turtles, and fish with symptoms including gonadal abnormalities, vitellogenin induction, and reproductive deficiencies (Campbell et al., 2006). EDCs have also been linked to lower sperm counts in human males (Chang et al., 2009). Regulatory agencies in the US and Europe have set water quality criteria or exposure limits on select EDCs. For example, the USEPA set an Ambient Water Quality Criteria limit of 6.6 µg/L of chronic exposure to nonylphenol (Campbell et al., 2006; Chang et al., 2009). Additionally, the USEPA has added EDCs including steroid hormones to the Contaminant Candidate List (CCL), which is a list of non-regulated contaminants that are suspected of causing harm to human health (D. Gerrity & Snyder, 2011).

2.2.3.2. Antibiotic Resistance in Wastewater Flows

Antibiotic resistance is a concern involving some MPs and has recently become a global public health issue (Wuijts et al., 2017). While the antimicrobials triclosan and triclocarban were banned by the FDA in 2016 in soaps to curb antibiotic resistance proliferation, they are still employed in other chemical blends and also exist in the environment (FDA, 2016). Wastewaters are important media to develop antibiotic or antimicrobial (Ab/Am) resistance for two major reasons. First, domestic wastewater contains suspended solids to which many Ab/Ams sorb due to their hydrophobicity. Ab/Ams that sorb to solids can be removed from wastewater by settling in primary clarifiers (Le-Minh et al., 2010). Any Ab/Ams that are not removed during primary sedimentation will then typically be conveyed to an activated sludge process where a range of bacteria are exposed to the Ab/Am. Second, conventional wastewater treatment involves biological treatment where microbes have a long retention time required to break down organic matter. This treatment process facilitates a longer contact time between bacteria and Ab/Am in the wastewater stream. The average municipal wastewater treatment facility does not include tertiary treatment to remove Ab/Ams or other MPs which are, therefore, discharged into receiving waters and interact with bacteria in the environment (Phillips & Chalmers, 2009).
2.2.3.3. Micropollutant Toxicity

While concentrations of any given MP are typically very low and do not harm human or aquatic life, the abundance and diversity of MPs may pose unknown toxicity issues due to the complex mixture present in the environment (Stalter, Magdeburg, & Oehlmann, 2010). Toxicity can be measured in several ways, but laboratory experiments usually isolate one compound to test for toxicity. The effects of chemical mixtures are not often elucidated. The isolation of individual compounds is useful to determine individual effects, but does not address the possibly synergistic or antagonistic effects a combination of chemicals can have on humans or aquatic life (Schwarzenbach et al., 2006; Gerbersdorf et al., 2015). Therefore, it may be prudent to remove MPs from treated water that is discharged into the environment, including wet weather flows.

2.2.3.4. Micropollutant Removal Mechanisms

MPs can be difficult to remove and even exert more toxicity during their removal depending on the type of treatment employed. Physical removal of MPs depends on their hydrophobicity (Gasperi et al., 2012). Many MPs can be removed during clarification processes since they sorb to suspended solids or associated fats and oils (Belgiorno et al., 2007; Jung et al., 2015). Sorption was the predominant MP removal mechanism through one water resource reclamation facility (Z. hua Liu et al., 2009; Luo et al., 2014). The sorbed MPs can then be removed from suspended solids or destroyed through processes such as biosolids pyrolysis (Ross, 2014; Tong et al., 2016). However, many MPs are resistant to biodegradation or biodegrade very slowly and can persist in the environment (Al-Ahmad et al., 1999; Horakova et al., 2014; Mohapatra et al., 2014). Therefore, it is necessary to consider CSO and SSO treatment options for MP removal.
2.3. CURRENT TREATMENT TECHNOLOGIES

Most existing wet weather treatment technologies are summarized below, whereas operations adjustments, storage, and green infrastructure are not within the scope of this review. Technologies that focus on total solids removal are in Section 3.1-3.4 and all are considered potential precursors to AOPs (section 2.3.7) for high-rate wet weather treatment. Solids removal reduces oxidant demand, which results in more efficient AOP operation (in terms of treatment, energy, and cost).

2.3.1. Coagulation/Flocculation and Sedimentation

Coagulation and flocculation (C/F) rely on van der Waals and electrostatic forces to destabilize the charge on colloids in wastewater, allowing them to form large flocs capable of settling. Without destabilization, small charged particles remain suspended and are not removed without filtration. Sweep flocculation is a phenomenon in which formation of larger, positively-charged flocs facilitate, electrostatically, the attachment of negatively-charged colloids, resulting in larger flocs. After C/F processes, settling or sedimentation occurs once the flocs have formed (Exall & Marsalek, 2013). Sedimentation, or the process of settling solids, typically relies on gravitational force to proceed. High-rate sedimentation (using C/F) technologies are attractive for wet weather treatment considering their ability to rapidly remove a variety of contaminants which have sorbed to solids.

C/F technologies are also attractive due to their ability to handle large volumes with relatively low detention times and minimal maintenance. Enhanced C/F processes can support surface overflow rates of 3,600-10,600 gpd/ft², which is significantly greater than typical sedimentation rates at water resource reclamation facilities (CDM, 2010; Metcalf & Eddy, 2014; Davis et al., 2017). The main associated cost and maintenance concern involves the chemicals used. Chemicals must remain effective and be stored safely, which can be a concern for wet weather application with facilities only being used a few times per year during large storm events.
Scherrenberg (2006) offers a literature review on C/F technologies available for wet weather treatment and their application.

2.3.1.1.1. Chemically Enhanced Primary Treatment (CEPT)

CEPT has been employed by many cities with combined sewers for high-rate treatment (HRT) during wet weather events followed by chlorination/dechlorination (chlor/dechlor) for disinfection (CH2M Hill, 2008; Davis et al., 2017). CEPT is employed by utilities under consent decrees to rapidly treat wet weather flows and meet or exceed negotiated effluent requirements established in those consent decrees. CEPT systems are commonly remotely-operated facilities that ease the burden on collection systems during wet weather events. Through effective solids removal utilizing C/F processes, CEPT systems have achieved removal of both TSS and BOD, ranging from 65-90% (CH2M Hill, 2008). This contrasts with conventional primary clarification, which averages approximately 50% TSS removal and 30% BOD₅ removal (Metcalf & Eddy et al., 2013). CEPT is also employed as high-rate wet weather treatment for its ability to partially remove nutrients, particularly phosphorus when using either ferric chloride or alum as a coagulant (Omoike & Vanloon, 1999). Samrani et al. (2007) noted that the rapidly changing physiochemical properties of CSO raw water must be considered when determining the appropriate coagulant dose. The water matrix is an important consideration when determining which coagulant chemicals will be most effective. Parameters that affect coagulant performance include pH, alkalinity, temperature, TSS, and total dissolved solids (TDS) concentrations (El Samrani et al., 2008; Exall & Marsalek, 2013). Considering the rapid nature of wet weather events, real-time adjustments to wastewater parameters such as pH may be valuable but may not be feasible.

Coagulants can be added alone or in combination with coagulant aids such as polymers. The most common chemical coagulants used in high-rate clarification are ferric chloride and alum due to their lower cost, efficacy, and familiarity (El Samrani et al., 2008; Ajao, 2016). When added with coagulants, polymers can further destabilize any remaining colloids and increase the density of flocs, allowing them to settle out more rapidly (Exall & Marsalek, 2013). Additionally,
both coagulants and polymers can be either cationic or anionic, with the most effective option dependent upon the wastewater matrix. King County, WA, conducted several jar tests and pilot studies to determine the best coagulant option for their wet weather matrix. Initial jar testing was conducted using primary influent diluted with distilled water, though the pilot used secondary effluent as its dilution source. This resulted in an alkalinity difference significant enough to require repeated jar tests for improved pilot performance. After chemical optimization testing at the CEPT pilot plant, polyaluminum chloride (PAX) coagulant was ultimately chosen over ferric chloride due to lower required dose (12 mg/L vs. 40 mg/L, respectively) and the fact that ferric chloride decreased the effluent pH by 0.7 standard units (CDM, 2010).

2.3.1.2. Ballasted Flocculation

In ballasted flocculation, sand particles are used in the clarifier to enhance the formation of flocs and increase solids capture (Jacobsen & Hong, 2002). Microsand (80-100 µm) is most commonly used as a ballast agent, reducing hydraulic retention time and resulting in a smaller footprint for suspended solids removal than standard clarification (Gasperi et al., 2012). Ballasted flocculation often includes the addition of chemical coagulants, but with reduced residence time. Also similar to CEPT, this technology destabilizes colloids. Ballasted flocculation has resulted in more stable performance under influent concentration fluctuation than conventional processes that do not include ballasting agents (Young & Edwards, 2003).

Typical TSS and COD removal efficiencies in ballasted flocculation are reported by Gasperi et al. (2012) to be 70-90% and 40-60%, respectively. In addition to removal of conventional water quality parameters (COD, BOD, TSS, and nutrients), ballasted flocculation removes pollutants including pesticides, metals, PAHs, and EDCs. Removal of these contaminants is typically due to removal of particles to which the contaminants are sorbed (Casadio et al., 2010; Gasperi et al., 2012).
2.3.1.3. **High-rate Retention Treatment Basins (RTBs)**

High-rate RTBs employ high velocity gradients and chemical coagulants to achieve rapid sedimentation, quickly removing suspended solids and the contaminants adhered to them. RTBs are commonly implemented in cities with combined sewers as one solution to reduce the sediment loading entering lakes and rivers during wet weather events (Tavakol-Davani et al., 2015). Under the right conditions, RTBs can provide energy- and cost-efficient treatment during wet weather events (USEPA, 1999b). Although some RTBs have been implemented in smaller, confined footprint areas in Detroit, MI, most RTBs require large land areas which may be difficult to obtain in urban areas. A study conducted by Li et al. (2004) evaluated the relationship between coagulant concentrations and surface overflow rate (SOR) in an RTB for a given solids removal goal to determine the appropriate range of chemical doses resulting in decreased detention time. The study demonstrated that chemical addition was necessary to achieve SORs higher than conventional treatment and appropriate for wet weather treatment.

2.3.1.4. **Vortex Separators**

Vortex, or hydrodynamic, separators are widely used in the water and wastewater industry for solid-liquid separation using cyclonic flow patterns and conical reactors to achieve suspended solids removal with a high SOR compatible with wet weather treatment (43,000 gpd/ft²) (CDM, 2010). Vortex separators can be operated remotely at overflow locations with reported 25-60% and 40-60% BOD₅ and TSS removals, respectively (Szabo et al., 2005; Andoh & Egarr, 2008). One issue with remote operation is that solids accumulate and must be continuously removed or stored on-site (King County Wastewater Treatment Division, 2011). Vortex separators also can be designed with chemical coagulants or disinfectants to improve treatment (AECOM, 2006; Arnett et al., 2007).
2.3.1.5. Lamella Settlers

Lamella settlers are not a stand-alone technology like many of those described in this section, but instead are added to clarification or sedimentation tanks to provide a greater surface area upon which solids can settle (Water Environment Federation (WEF), 2014). The increased surface area reduces the clarifier footprint and can increase solids removal up to 40% (Tondera et al., 2013). Lamella settlers are more commonly found in water treatment plants instead of wastewater treatment because wastewater solids as well as fat, oil, and grease can clog lamella plates. The addition of lamella settlers to existing detention or stormwater basins may be more cost-effective than constructing new basins. For wet weather applications, the additional surface area added by lamella settlers can increase the capacity of a CEPT system by increasing the allowable SOR to achieve a more rapid treatment time (CDM, 2010).

2.3.2. High-Rate Clarification Commercial Units

There are two well-known commercially available units that apply the physical and chemical treatment attributes of C/F for high-rate treatment. This is not an exhaustive discussion of proprietary units, but instead represent the two most commonly piloted and implemented systems. Applications for both units include drinking water, industrial wastewater, and wet weather treatment.

2.3.2.1. ACTIFLO®

ACTIFLO® is patented by Veolia Water Technologies and uses microsand for ballasted flocculation in tandem with chemical coagulation to increase particle settling velocities for high-rate clarification. The microsand is cleaned and separated from the floc through hydrocyclones and is then recycled and used in the system again (Nitz et al., 2004). Veolia claims high-rate clarification with high SORs (25-80 gpm/ft²), resulting in a small, compact footprint (Veolia Water Technologies, 2014). ACTIFLO® has been installed for CSO and SSO treatment in cities across North America since 2001 including Lawrence, KS (40 MGD peak flow capacity) and
Bremerton, WA (20 MGD peak flow capacity) (WEF, 2014). The targeted parameter for removal with ACTIFLO® technology is TSS (90-95% removal), and subsequently carbonaceous BOD₅ (CBOD₅) (50-80%), fecal coliforms (85-95%), and TP (80-95%) (Tetra Tech MPS, 2003).

2.3.2.2. DenSaDeg® Clarifier/Thickener

Infilco DenSaDeg®, manufactured by Suez Environment (previously Degrémont Technologies) creates high-density sludge which is recirculated to destabilize and settle solids at a high rate. The recirculated of sludge reduces sludge volumes overall. Solids thickening, sludge recirculation, and clarification occur in conjoined vessels which, in conjunction with high-rate clarification, allows the system to maintain a small footprint (Nitz et al., 2004). The City of Toledo operates a 232 MGD peak flow capacity (5 gpm/ft²) wet weather treatment facility with six DenSaDeg® units which is capable of achieving an average removal of 74% TSS, 54% CBOD₅, and 79% TP (Yee & Hutchins, 2017).

2.3.3. Biological contact

Biological treatment techniques are not typically considered for wet weather treatment because they require longer retention times and are sensitive to rapid changes in influent flow and characteristics (Metcalf & Eddy et al., 2013). However, given their efficiency in removing organics and nutrients during conventional secondary treatment, it may be prudent to consider applying biological treatment alone or in combination with rapid treatment to manage wet weather flow (Oller et al., 2011a; WEF, 2014). Adjustments to existing infrastructure such as inclusion of biofilms or an alteration in operations can increase capacity during storm events (Schroedel et al., 2007). The ACTIFLO® unit can be modified to include biocontact (BIOACTIFLO™), though the biological aspect requires a larger surface area and slower flowrate for effective treatment (WEF, 2014).
2.3.4 Filtration

There are various contaminant removal mechanisms present in filtration processes which allows for flexibility in wet weather treatment applications. The overall governing aspect when choosing a filtration design is to ensure the filter can handle the flow rate and solids concentration of the wet weather influent (Crittenden et al., 2012). Given the high volume and large flow rate associated with wet weather flows, implemented filters should be designed for quick backwashing periods to avoid bottlenecking the system during a storm event. Filtration technologies with wet weather appropriate applications are explored in this section.

2.3.4.1. Cloth Media Filtration

Cloth media filters can be implemented as effective solids removal technologies for CSO treatment to serve as a polishing post-CEPT step ahead of disinfection or as the principal solids removal mechanism after first flush capture (Szabo et al., 2005) Proprietary units such as Aqua-Aerobic Systems Inc. AquaDisk (Loves Park, IL) have been implemented with wet weather treatment facilities in Cincinnati, OH and Rushville, IN (Hughes & Reid, 2016; Martin et al., 2017). The Rushville, IN installation was first operated as a pilot plant with a flow rate of 140-265 L/min and hydraulic loading rate (HLR) of 9-16 m/h. The plant included CEPT which was only employed during first flush to assist with solids influx. TSS removal by the Rushville pilot averaged 98% with 73% BOD$_5$ removal (Hughes & Reid, 2016). The Cincinnati, OH pilot plant installation operated with a flow rate of 265 L/min which equated to a flux rate of 6.5 gpm/ft$^2$. The average TSS removal was 77% with CBOD$_5$ removal ranging from 20-50% during testing (Martin et al., 2017). Both plants demonstrated that cloth media filtration can be used for TSS and BOD$_5$ removal at high flow rates appropriate for wet weather treatment.

2.3.4.2. Compressible Media Filters

Compressible media filtration (CMF) is a high-rate solids removal technology which is applied almost exclusively for wet weather treatment since it was designed to operate under high
HLRs (20-30 gpm/ft²). There are two proprietary media for CMF: Fuzzy Filter by Schreiber Corporation (Trussville, AL) and WWETCO FlexFilter™ by WesTech® (Salt Lake City, UT). The spherical synthetic media is compressed between two porous steel plates to form smaller interstitial pores to capture more solids during filtration periods. After a filtration period, the compression is released to open larger pore areas during a rapid backwash period. The extent of compression can be adjusted based on influent wastewater conditions. Both CMF materials were tested in Springfield, OH at a pilot plant (100 MGD, 10 gpm/ft²) for CSO treatment where average effluent concentrations were 22 mg/L TSS and 26 mg/L CBOD₅ (Fitzpatrick et al., 2011). Another CMF installation for CSO treatment in Atlanta, GA (10-27 gpm/ft²) consistently achieved 90% TSS removal (Arnett et al., 2007).

2.3.4.3. Floating Media Filtration

Floating media filters (FMFs) are still considered an emerging technology in the United States and they may provide a flexible approach to wet weather treatment capable of a high HLR and equivalent conventional primary treatment efficiency without chemical addition. FMF systems are high-rate upflow filtration units packed with various synthetic media which feature a low headloss profile (Martin et al., 2017). One pilot plant employing FMF in Seoul, South Korea used expanded polypropylene beads at a filtration flowrate of 20 m/h to achieve 35% BOD₅ and 45% TSS. The reported removals went down as the filtration flowrate increased (Yoon et al., 2012). Another FMF pilot plant was implemented in Cincinnati, OH using pinwheel-shaped floating media with a flow rate of 340 L/min and a flux rate of 17 gpm/ft². The Cincinnati FMF pilot plant achieved 30-70% TSS and 10-50% CBOD₅ removal (Martin et al., 2017).

2.3.4.4. Granular Media Filtration with Adsorption

Filtration systems where adsorption (vs. straining) is the removal mechanism are not typically applied for high-rate wet weather treatment, but can offer MP removal at targeted locations for small-scale treatment (Liu et al., 2009; Löwenberg et al., 2014). Effective adsorption
requires a lower filtration flow rate than can be afforded during storm events (Crittenden et al., 2012). Additionally, the high solids flux observed during wet weather events can cause the filter to quickly clog. Localized applications of granular media filters such modified soils under permeable pavement may ease the overall loading of MPs in waterways after storm events (Al-Anbari et al., 2008; Oller et al., 2011b).

2.3.5 Engineered Wetlands and Retention Soil Filters (RSFs)

Both engineered wetlands and RSFs are similar in that they employ natural filtration processes for solids removal and pollutant attenuation, including *E. coli*. Their design focuses on hydraulic retention time required for whichever mechanism governs specific pollutant attenuation, the three main mechanisms are adsorption (pollutants are sorbed to particles in the filter), straining (pollutants are removed based on size compared to particle size), and biodegradation (organics pollutants are broken down by microorganisms) (Bester & Schäfer, 2009; Radke et al., 2010; Christoffels et al., 2014). Sufficient surface area is required to achieve effective and efficient treatment and the required land may not be available or may be cost prohibitive. Maintenance is minimal, but necessary to ensure filter media (sand, cropped soil, engineered biosolids) remains clear ahead of a large storm event (Tondera et al., 2013). Studies have demonstrated that RSFs are effective at MP attenuation based on contaminant hydrophobicity and fate, specifically with pharmaceutical residuals (Scheurer et al., 2015). Additionally, RSFs are capable of an additional log removal of *E. coli* over wastewater treatment plant effluent due to sorption (Lefèvre et al., 2012; Christoffels et al., 2014).

2.3.6 Disinfection

Wet weather flow disinfection is conventionally achieved through chlorination, though the need to dechlorinate treated effluent and the concern for harmful disinfection byproduct formation has led to research and application of various disinfection techniques. The disinfection techniques that are typically used as, or together with, AOPs are further described in Section
2.3.7. A brief discussion on their value to disinfection in wet weather applications is included herein.

2.3.6.1. Conventional Chlorination

Chlorine is the most commonly-used disinfectant in wastewater treatment due to its ability to inactivate numerous pathogens and its relatively low cost; however, the use of chlorine may result in the formation of carcinogenic disinfection by-products (DBPs) (USEPA, 1999c; Tondera et al., 2016). While most DBPs have so far only shown carcinogenic impacts based on human consumption, there remains concern about aquatic life or within semi-closed water/wastewater systems (Wojtenko et al., 2001). Semi-closed water infrastructure systems could pull drinking water from the same source of water accounting only for the environmental buffer of a surface water. Concerns over carcinogenic DBPs has led some regions such as Quebec, Canada to ban the use of chlorine (Gehr et al., 2003).

For wet weather flows, the potential formation concern for DBPs is higher as the precursor to DBPs is natural organic matter (NOM) that is typically present in wet weather flows (Mayer et al., 2014). Wet weather flows receiving minimal treatment only undergo solids removal followed by (chlor/dechlor) and these minimally treated flows could have a larger concentration of NOM for two main reasons. First, the first flush phenomenon carries a high volume of solids through systems that may not be designed to handle such an influx (J. H. Lee et al., 2002; El Samrani et al., 2008). In this scenario, more solids would be passed onto the chlor/dechlor phase where they might contribute to DBP formation (McFadden et al., 2017). Second, in the absence of secondary or chemically enhanced primary treatment, minimally treated wet weather flows will still have colloidal and dissolved material which may include NOM (Chiemchaisri et al., 2008). Additionally, the requirements of chlorine contact time and two chemical feeds (chlor/dechlor) can be difficult to manage during a storm event. While chlorine is effective in meeting effluent requirements for pathogens, there are logistical concerns with its use, especially...
during wet weather treatment. One such concern is the proper dosing during variable influxes and water characteristics for both chlorination and dechlorination chemicals (Chhetri et al., 2014).

2.3.6.2. Ozone

Ozone is broadly known for its strength as an oxidant and is applied for disinfection in drinking water systems or in water reuse treatment trains. For example, an ozonation step was added to Milwaukee’s drinking water treatment plant after an outbreak of Cryptosporidium in 1993 (Ruffell et al., 2000). The application of ozone for municipal wastewater disinfection or tertiary treatment is more commonly considered in recent years due to its MP oxidation abilities; however, the ozone demand of municipal wastewater effluent and the related costs of operation have kept ozone from broad implementation (Gehr et al., 2003; Stalter et al., 2010). Ozone may be valuable in a wet weather treatment scenario because of its high reaction rate, but can be limited, similar to chlorine, in the high demand of the wastewater matrix. Unlike chlorine, ozone disinfection is not solely based on the “Ct” approach where only chemical concentration and time are considered. Because the delivery mechanism of ozone is gas diffusion into liquid, the ozone mass transfer rate is the limiting factor. Therefore, to make ozone a viable option for wet weather flow disinfection, the treatment system must be designed to optimize diffusion into the water and the subsequent reaction with pathogens (Xu et al., 2002). An additional concern with ozone related to the wastewater matrix is that ozone can react with bromide-containing waters and create bromate, a carcinogenic byproduct (von Gunten & Hoigné, 1994).

2.3.6.3. UV

Technology has advanced greatly since the beginning of UV disinfection, making the lamps more powerful and more efficient, both energy- and cost-wise (Bell & Silva, 2013). Of the three categories of lamps (low-pressure low-intensity, low-pressure high-intensity, and medium-pressure high-intensity), medium-pressure lamps produce the most UV output and, generally, low-pressure mercury lamps are the most common. Concerns of fragility and potential toxicity
due to mercury have led to increased research in the use of UV light-emitting diodes (UV-LEDs) (Chevremont et al., 2013). While UV-LEDs can be more environmentally friendly, more energy-efficient, and more durable, their novelty translates into a lack of research and data compared to UV mercury lamps in terms of disinfection effectiveness (Song et al., 2016). In general, UV mercury and UV-LED lamps are effective at inactivating bacteria, viruses, and protozoa (Crittenden et al., 2012; Song et al., 2016).

The most important design factor to address for UV disinfection remains the turbidity and particle size of the wastewater to be treated. High levels of TSS, turbidity, and organic matter inhibit performance by preventing the light from penetrating through the wastewater effectively through refraction, reflection, or scattering (Crittenden et al., 2012; Uslu et al., 2015). For this reason, UV couples well with CEPT for high-rate solids removal to increase UV transmittance (Gehr et al., 2003). A pilot study conducted in King County, WA for a high-rate CSO treatment facility using UV disinfection found that UV mercury lamps (254 nm) were able to completely inactivate Enterococcus at doses between 10-15 mJ/cm² in filtered wastewater samples, whereas 40 mJ/cm² was required to meet effluent limits in unfiltered samples (36 mg/L TSS) (Mysore et al., 2017). Additionally, UV radiation is one of the only disinfection techniques that is not known to form DBPs nor leave a residual (Crittenden et al., 2012).

2.3.6.4. Peracetic acid (PAA)

The use of PAA as an alternative disinfectant to chlorine is more common in recent years among utilities for wastewater disinfection and is under consideration for wet weather treatment. PAA is an attractive option because, unlike chlorination, there is no need to remove the PAA residual nor are there any known harmful byproducts (Rizvi et al., 2013). However, similar to chlorine, any organics in the wastewater matrix will exert a PAA demand and require a higher dose (Gehr et al., 2003). PAA can be a cost-effective solution, but it may not be the best fit for wet weather treatment as it has shown slower reaction times on the order of hours for effective disinfection (Chhetri et al., 2014). While few pilot studies have demonstrated PAA’s ability to
disinfect water, the EPA has only recently approved its use and any implementation is likely on a site-by-site basis (Bell & Silva, 2013).

2.3.6.5. Performic acid (PFA)

PFA can also be applied in lieu of chlorine, but the major challenge is that it must be generated on-site and requires a contact time of at least ten minutes (Tondera et al., 2013). The additional value to utilities is that, like PAA, PFA does not require a second chemical step to remove the chemical residual. Full-scale implementations using PFA are limited, making it more difficult to build support with the EPA for widespread implementation. PFA has been demonstrated to inactivate *E. coli* with a rapid rate of reaction, making it a valuable candidate for wet weather treatment application (Chhetri et al., 2015). Additionally, there are no known harmful by-products or toxicity formed after treatment (Chhetri et al., 2014).

2.3.7. Advanced Oxidation Processes (AOPs)

AOPs are applied to water and wastewater treatment for their high rates of reaction and ability to disinfect and oxidize a wide range of contaminants. Specifically, AOPs could be used as high-rate technologies to rapidly treat the unique index of contaminants in wet weather flows to the same or higher quality as conventionally secondary treated effluent during high-intensity rain events. Rapid, real-time treatment of wet weather flows can reduce the stress on infrastructure during intense storms and can prevent CSOs, SSOs, and basement backups from occurring. In addition to a high rate of reaction, AOPs are capable of oxidizing MPs, achieving disinfection, and reducing BOD, making them attractive technologies to consider for CSO and SSO treatment (Esplugas et al., 2007; Ikehata et al., 2008; Ribeiro et al., 2015). However, to date, no one has implemented a pilot- or full-scale wet weather treatment system using AOPs.

AOPs are characterized by the enhanced formation of hydroxyl radicals capable of a high rate of reaction (*k* = 10⁸-10¹⁰ M⁻¹ s⁻¹) with target compounds (Gottschalk et al., 2010). Hydroxyl radicals are the strongest known oxidant and, among other oxidants such as ozone, are capable of
MP oxidation (Esplugas et al., 2007). Radicals have an unpaired electron on the outer orbital of the molecule, making them extremely and rapidly reactive. They react non-selectively by either adding to or removing a hydrogen atom from an organic compound. This produces a radical organic compound that is also highly reactive, continuing the chain reaction. The radical reaction stops at a stable end product or when two radicals react, ending the chain reaction (Gottschalk et al., 2010).

Unlike other advanced treatment options, AOPs degrade organic compounds instead of concentrating or transferring them into a different phase (Metcalf & Eddy, 2013). A result of increasing wastewater biodegradability is the removal of BOD/COD and particularly, the recalcitrant components of a wastewater COD makeup. The ability for AOPs to reduce organic strength could provide value in terms of wet weather treatment and the impact CSOs have on receiving waters. AOPs are typically applied to municipal wastewater in tertiary treatment for disinfection or MP oxidation in which any COD or BOD removal is auxiliary and not the intended treatment goal. For industrial wastewater, AOPs are often employed as pretreatment to reduce COD before discharge to a municipal sewer. This is common in the dye industry since AOPs, particularly ozone-based, are capable of color removal (Miodrag Belosevic, 2014).

AOPs are able to treat a wide range of MPs (Huber et al., 2005; Klavarioti et al., 2009). Instead of complete mineralization, however, MP oxidation can yield degradation or transformation products (DTPs). DTPs can be more toxic than their parent compounds, as is the case for ibuprofen (Quero-Pastor et al., 2014) and bisphenol A (Chen et al., 2006). Accordingly, more studies are considering the toxicity of AOP-treated effluent to ensure complete mineralization of harmful MPs as opposed to incomplete mineralization resulting in a toxic DTP (D. Gerrity & Snyder, 2011; Magdeburg et al., 2012). Additionally, complex mixtures of MPs can create a synergistic effect during advanced treatment, in which the target compound behaves differently in a mixture than it does when treated alone (Campbell et al., 2006; Jasim et al., 2006; Rosenfeldt et al., 2007). The possibility of complex mixtures impacting reaction kinetics and
outcomes emphasizes the importance of looking at toxicity in real wastewater samples, as in Miralles-Cuevas et al. (2016).

Klavarioti et al. (2009) provides a comprehensive review of AOP treatment studies for pharmaceutical removal in various water matrices. Esplugas et al. (2007) provides an overview of AOP treatments for EDC and pharmaceuticals and personal care products (PPCPs) removals and the study outcomes.

2.3.7.1. Toxicity

One concern in the use of AOPs is the possible increase in toxicity during treatment as more toxic DTPs are formed. Various studies discuss the toxicological effects of AOPs on MPs, drawing similar conclusions: toxicity may increase during treatment, but generally the treated effluent is less toxic than before oxidation (Oturan et al., 2008; Hollender et al., 2009; Qiang et al., 2010; Stalter et al., 2010; Karci, 2014; Garcia-Galán et al., 2016). These studies have only been conducted for a selection of MPs though all have the capability to display novel behavior. Each study referenced here concludes that further work needs to be done to understand the different forms of toxicity after advanced treatment of wastewater, including wet weather flows.

2.3.7.2. Factors for Design and Cost

AOP effectiveness is dependent on the water matrix, pH, presence of NOM, and target MP characteristics (Wojtenko et al., 2001; Mohapatra et al., 2014). pH impacts the concentration of carbonate and bicarbonate, the concentrations of which vary based on water source, but both are radical scavengers. pH adjustment can increase the efficacy of certain AOPs as different AOPs are more effective at different pH values. However, rapid treatment can be time- and cost-prohibitive for pH adjustment of the wet weather flow. NOM is also a known radical scavenger. Scavengers exert a greater oxidant demand by competing with target compounds for hydroxyl radicals; therefore, removal of NOM and control of carbonate/bicarbonate prior to AOP treatment increases the treatment efficiency (Ikehata & Gamal El-Din, 2005). High carbonate/bicarbonate
concentrations also affect ozone stability, increasing the half-life and decreasing the decay rate (Gottschalk et al., 2010). In contrast, Barry et al. (2014) demonstrated the presence of hydroxyl radical promoters in effluent organic matter from municipal wastewater which were not present in surface waters. This emphasizes the importance of understanding AOP performance specifically for CSO discharges due to their unique contaminant matrix which yields a different scavenging capacity compared to other waters (Huber et al., 2003).

AOPs are most commonly known for their high-level treatment capabilities, but they are often limited by their cost. Part of the consideration for AOPs in a wet weather application is that the systems will not be used consistently, and the relatively easy start-up and infrequency of use may justify the cost of operations during storm events. However, no singular wet weather treatment solution will work for every wastewater utility; therefore, cost estimations for energy consumption are still factored into the value of each technology. There are three typical ways to address the cost-benefit analysis for AOPs: determine the (1) cost per unit of hydroxyl radical formation; (2) cost per specific contaminant removed; and/or (3) unit of hydroxyl radical required to remove target contaminant. Katsoyiannis et al. (2011) and Rosenfeldt et al (2006) provide examples of specific AOP costs for removal of certain contaminants. Additionally, Miklos et al. (2018) published electrical energy per reaction order values ($E_{EO}$, kWh/m³/order) for different AOPs, which is a normalized value to compare energy efficiency among processes (Bolton & Stefan, 2002). Miklos et al. (2018) demonstrated that ozone alone is the most energy efficient AOP, followed closely by O$_3$/H$_2$O$_2$, and that the UV-based AOPs are the least energy efficient.

2.3.7.3. Ozone Alone

Ozone reaction pathways can be either direct or indirect, where the indirect pathway involves the formation of hydroxyl radicals and is considered an AOP. Indirect reactions involve radicals driven by the initiation of ozone decay in water and are nonselective (Barry et al., 2014). Direct ozone reactions are selective and slower, reacting first with organic constituents that offer high electron density. Both mechanisms are present in ozone alone and UV/O$_3$, while H$_2$O$_2$/O$_3$
reactions proceed through the formation of the hydroxyl radical (Gottschalk et al., 2010).

Similarly, catalytic ozonation using metal oxides for the promotion of hydroxyl radical production can increase reaction efficiency (Beltrán et al., 2005; Nawrocki & Kasprzyk-Hordern, 2010; Barry et al., 2014; Vittenet et al., 2015). For wet weather treatment seeking a fast rate of reaction, it is more desirable to enhance ozone reactions for increased hydroxyl radical production than using direct ozone reactions.

Wastewater composition, pH, and temperature are three of the most important influencers on ozonation success, and are also three of the most difficult parameters to control during wet weather events (Xu et al., 2002; Tondera et al., 2013). Scavengers such as carbonate/bicarbonate and NOM in wastewater can consume ozone, requiring a higher dose for target contaminant oxidation and efficient ozone mass transfer (Ikehata & Gamal El-Din, 2005; Tizaoui et al., 2009; Miklos et al., 2018). Similar to UV, the presence of solids diminishes the treatment capacity as the ozone demand would focus on particulate matter until it is oxidized. However, ozone alone is able to generate hydroxyl radicals through reactions with certain compounds present in wastewater such as phenols and amines (D. Gerrity & Snyder, 2011). Additionally, pH influences ozone reactions by affecting ozone solubility and dictating whether the direct or indirect reaction will dominate. At low or neutral pH, direct ozonation occurs because molecular ozone is present. As pH increases, ozone decomposition increases, favoring the indirect reaction pathway through the formation of hydroxyl radicals and other reactive oxidants (Quero-Pastor et al., 2014; Miklos et al., 2018). Finally, water temperature impacts the solubility of ozone gas, similar to pH in that as temperature increases, ozone decomposition into hydroxyl radicals also increases (Flores-Payán et al., 2015).

Ozonation is known as an effective method to treat a variety of organic compounds including recalcitrant MPs and COD. Studies have demonstrated >95% removal of ibuprofen (12 mg O₃/L), carbamazepine (0.3-5.0 mg O₃/L), estrogens (4.4 mg O₃/L), among others through direct and indirect ozonation processes (Pešoutová et al., 2014; Quero-Pastor et al., 2014; Mohapatra et al., 2014). Certain MPs can be oxidized by slower molecular ozone reactions (e.g.
atrazine and meprobamate) while other MPs are oxidized by the faster hydroxyl radical reaction (e.g. naproxen and carbamazepine) (D. Gerrity & Snyder, 2011). While treatment times for MPs are typically within the range of 5-30 min, ozonation treatment time for COD removal in industrial wastes requires hours. At an ozone production rate of 2 g O$_3$/h (pH = 9), Azbar et al. (2004) achieved 90% COD removal in acetate fiber dyeing effluent in 120 min. In contrast, Lucas et al. (2010) achieved only 12% COD removal in winery wastewater after 180 min of ozonation at production rate of 6 g O$_3$/h due to the low pH of 4, which prohibited the formation of reactive radical species.

2.3.7.4. O$_3$/H$_2$O$_2$

Ozone with H$_2$O$_2$ can treat a wide array of wastewater contaminants through enhanced hydroxyl radical production that fills in gaps left by ozone alone. Both O$_3$/H$_2$O$_2$ and ozone alone can oxidize compounds that the other is unable to, so understanding the wastewater matrix before treatment design is imperative for effective treatment (Beltrán, Encinar, et al., 1997). As an example of varying treatment results, river waters subject to AOPs responded to H$_2$O$_2$ addition better than high COD wastewaters (Guedes Maniero et al., 2008; Barry et al., 2014). Additionally, Beltran et al. (1997) discovered that distillery wastewaters were more effectively oxidized by molecular ozone than the hydroxyl radicals formed from the O$_3$/H$_2$O$_2$ AOP.

H$_2$O$_2$ can promote hydroxyl radical formation but can also act as a radical scavenger, slowing the COD or MP degradation rate and decreasing the process efficiency (Ikehata & El-din, 2006). One of the major difficulties with the O$_3$/H$_2$O$_2$ AOP is the determination of proper H$_2$O$_2$ dosing as excess H$_2$O$_2$ will quench the ozone and inhibit either the oxidation reaction or disinfection. Depending on the presence of hydroxyl radical promoters or scavengers, the appropriate dose ratio for H$_2$O$_2$ to O$_3$ is within a molar range of 1:2 or 1:1 (Rosenfeldt et al., 2006; Gottschalk et al., 2010). By optimizing the dose ratio, the ozone mass transfer should improve compared to ozone alone (Rosenfeldt et al., 2006; Gottschalk et al., 2010).
2.3.7.5. UV/H$_2$O$_2$

The AOP UV in combination with H$_2$O$_2$ results in a faster reaction rate (than UV alone) through enhanced hydroxyl radical production (Beltrán, 2004; Rosenfeldt et al., 2006). The addition of H$_2$O$_2$ increases hydroxyl radical production as direct UV photolysis splits the H$_2$O$_2$ into two hydroxyl radicals. Rosenfeldt & Linden (2004) observed greater estrogen removals in river water using direct photolysis with the addition of H$_2$O$_2$ than without. However, H$_2$O$_2$ has poor UV absorption where $<$10% of the chemical is converted to hydroxyl radicals (Miklos et al., 2018). This inefficiency results in excess H$_2$O$_2$ additions in order to meet oxidant demand and, subsequently, high H$_2$O$_2$ residual which must be quenched before being discharged into waterways. The study conducted by Rosario-Ortiz et al. (2010) demonstrated the inverse relationship between UV absorption of wastewater and UV/H$_2$O$_2$ treatment efficiency by linearly correlating the reduction in UV absorption to the increase in MP removal.

Similar to the other AOPs discussed, UV/H$_2$O$_2$ process efficiency is dependent upon pH and influent wastewater matrix. The UV/H$_2$O$_2$ AOP operates best at low pH values (2.5-3.5) (Stasinakis, 2008). pH adjustment to such low values would not be practical for rapid treatment during wet weather events. The wastewater matrix influences UV/H$_2$O$_2$ efficiency based on the UV absorption of the wastewater. H$_2$O$_2$ requires UV energy to cleave into hydroxyl radicals and a high UV demand by the wastewater would inhibit the H$_2$O$_2$ reaction (Beltrán, 2004; Stasinakis, 2008; Crittenden et al., 2012). Katsoyiannis et al. (2011) evaluated the energy demand of the UV/H$_2$O$_2$ for the oxidation of four MPs from surface water and wastewater effluent. They concluded that the energy demand was greatest in the wastewater effluent, which also had the highest carbonate (alkalinity) concentration and scavenging rate. UV/H$_2$O$_2$ achieved 90% degradation of pCBA in wastewater effluent, but at a much higher energy demand (0.70 kWh/m$^3$, 10 cm path length) than ozone alone (0.25 kWh/m$^3$) and O$_3$/H$_2$O$_2$ (0.2 kWh/m$^3$) (Katsoyiannis et al., 2011).
In addition to MP oxidation, UV/H$_2$O$_2$ is capable of COD removal, which is valuable for wet weather treatment and common practice as pretreatment for industrial wastewaters. Beltrán et al. (1997) evaluated COD removals during UV/H$_2$O$_2$ treatment of industry wastewaters and concluded that the high COD concentrations made UV/H$_2$O$_2$ oxidation inefficient as only 38% COD removal was observed. Considering a wastewater effluent with a lower initial COD, Giannakis et al. (2015) observed 100% COD removal with UV/H$_2$O$_2$ after 30 min of treatment time. Acetate fiber dyeing effluent was treated with UV/H$_2$O$_2$ where 90% COD removal was observed after 90 min of treatment at an optimum pH of 3 (Azbar et al., 2004). The same study by Azbar et al. (2004) also demonstrated the design challenge that excess H$_2$O$_2$ can become a hydroxyl radical scavenger where COD removal decreased between 300 mg H$_2$O$_2$/L and 400 mg H$_2$O$_2$/L due to the increased H$_2$O$_2$ concentration. The longer treatment times for COD removal compared to those for MP removal pose a challenge for wet weather applications, which should be addressed with proper wastewater characterization during the design process.

2.3.7.6. UV/O$_3$

The mechanisms for treatment in the UV/O$_3$ AOP involve those present in ozone alone, O$_3$/H$_2$O$_2$, and UV/H$_2$O$_2$, making it one of the most complex AOPs to study (Beltrán, Encinar, et al., 1997). Ozone gas is dissolved in water to form H$_2$O$_2$, which is then cleaved by UV to form hydroxyl radicals. At pH >8, ozone decomposes into hydroxyl radicals. Ozone has a significantly higher extinction coefficient of UV at 254 nm (3,300 mol/L-cm) than H$_2$O$_2$ (19 mol/L-cm), which means that ozone absorbs light more readily (Gottschalk et al., 2010). However, the energy demand to produce hydroxyl radicals via ozone conversion to H$_2$O$_2$ is limiting (Beltrán, Encinar, et al., 1997; Azbar et al., 2004; Miklos et al., 2018). Both UV and ozone have low radical generation energy efficiency (high demand for minimal output) making this AOP difficult to implement and scale.

Studies using UV/O$_3$ for treatment of MPs and COD have demonstrated high reactivity. UV/O$_3$ was used to treat the herbicide alachor and its degradation was improved when compared
to ozone alone treatment (Beltrán et al., 2000). Carbamazepine was 100% removed using UV/O₃ in a study conducted by Ternes et al. (2003). Studies measuring COD removal by UV/O₃ have reported successes. Beltrán, Encinar, et al. (1997) reported 90% COD removal in tomato wastewaters treated with UV/O₃ compared to 30-50% with ozone alone (Beltrán, Encinar, et al., 1997). Ozone mass transfer efficiency also increased from ozone alone to UV/O₃ during the same study, which was confirmed by Lucas et al. (2010). Lucas et al. (2010) observed that UV/O₃ was more effective at COD removal of winery wastewater than ozone alone, but not as efficient as UV/H₂O₂/O₃.

2.4. FUTURE CONSIDERATIONS FOR CSO AND SSO TREATMENT

CSOs and SSOs are high-volume flows that contain a mix of contaminants requiring rapid treatment. High-rate treatment technologies exist, such as CEPT and AOPs, which may produce effluent quality as high or higher than CWA wastewater effluent permit requirements. With increasing knowledge of CSO and SSO characterization, at or above permit-level effluent requirements can be factored into wet weather management. Additionally, CSOs and SSOs can release harmful pathogens such as viruses into bodies of water that may also be used as a drinking water source and that receive insufficient treatment to prevent transmission. New technologies for rapid, high-rate disinfection should also consider viruses now as they may be regulated in the future to protect public health. Moreover, MP removal and the formation of ARGs in wet weather flows should be further investigated as CSOs and SSOs continue to occur. Few studies have addressed MP removal using existing wet weather treatment technologies, or the application of AOPs for wet weather treatment. Finally, as new advanced, high-rate technologies are considered for wet weather treatment, startup time and operating cost must be analyzed.

2.5. CONCLUSIONS

CSOs and SSOs pose both environmental and public health concerns since untreated water is discharged into lakes and rivers during high-intensity rain events. The presence of
pathogens and the potential public health implications of MPs in untreated discharges can possibly be addressed by implementation of advanced, high-rate technologies appropriate for rapid treatment during wet weather events. The industry trends in wet weather management focus mostly on storage or rapid solids removal followed by disinfection with chlorine then dechlorination. Therefore, most of the currently implemented technologies such as CEPT, vortex separation, and cloth and compressible media filtration address only solids and particulate COD/BOD removal. Chlorine disinfection remains common, although emerging disinfectants for commercial use such as PAA and PFA offer similar results without the formation of harmful DBPs.

AOPs can also achieve high-rate disinfection, as well as MP oxidation and COD removal. Wastewater characteristics heavily influence the performance of AOPs and should be well-analyzed before choosing and designing an appropriate AOP to avoid excessive energy and chemical costs. Current literature results demonstrate efficient removal of solids during CSO and SSO treatment using various technologies, primarily CEPT. Additionally, there is sufficient data to demonstrate the effectiveness of AOPs in MP oxidation and disinfection of surface waters and wastewater effluents. However, there are no studies that combine high-rate solids removal with subsequent AOPs. More research is necessary regarding AOPs to treat wet weather flows. Future research involving high-rate wet weather treatment should include a more comprehensive assessment of wastewater parameters beyond TSS, COD, and fecal coliforms to include more recalcitrant pathogens and MPs present in CSOs and SSOs.
3 BENCH-SCALE EVALUATION OF CEPT-AOP TO DETERMINE PREFERRED PROCESSES

3.1. INTRODUCTION

In many communities with municipal sewers, combined sewer overflows (CSOs) and sanitary sewer overflows (SSOs) are released without treatment to lakes and rivers during high-intensity precipitation. These overflows can contain conventional oxygen-demanding pollutants, pathogens, suspended solids and a suite of MPs (Lee & Bang, 2000; Phillips et al., 2012). Contaminants released during major precipitation can be detrimental to receiving water integrity as well as to public health due to human exposure (Jagai, DeFlorio-Barker, Lin, Hilborn, & Wade, 2017; McLellan et al., 2007; Newton, Bootsma, Morrison, Sogin, & McLellan, 2013; Phillips & Chalmers, 2009). The minimum required combined sewer flow treatment in accordance with the US Environmental Protection Agency (USEPA) 1994 CSO Control Policy consists of primary treatment for solids removal and disinfection, typically chlorine, followed by dechlorination (“minimum treatment”) (USEPA, 1994; WDNR, 2013). This minimum treatment does not address MP or conventional soluble organic pollutant removal and can result in carcinogenic disinfection byproduct formation (King County Wastewater Treatment Division, 2011; Luo et al., 2014; McFadden et al., 2017).

Studies conducted in the U.S. and Europe have shown the detrimental impacts wet weather flows (CSOs and SSOs) can have on receiving waters, further emphasizing the need to address untreated flows discharged into lakes and rivers (Diaz-Fierros et al., 2002; USEPA, 2004; Passerat et al., 2011; ASCE Foundation, 2017). Many U.S. cities whose sewer systems were built before 1950 have combined sewers since combining sanitary wastewater and stormwater was a more common practice when conveyance systems were first established across the country in the late 1880s. Combined sewer infrastructure was recommended for larger, more dense cities with large volumes of household wastewater and where stormwater runoff was a prevalent concern (Tarr, 1979; USEPA, 2004). The majority of U.S. cities, however, have separate sewer systems where the sanitary sewers are conveyed to a treatment plant or reclamation facility, and the storm
sewers are regulated under a municipal separate storm sewer system (MS4) permit. SSOs are also a pressing concern due to increased infiltration and inflow (I&I) of stormwater during rain events into cracked and leaking sanitary sewer pipes or through connected downspouts (Sauer et al., 2011). While CSOs are often handled under consent decrees, SSOs are illegal under the CWA and their occurrence can result in fines, fees, or lawsuits brought upon the discharging municipality or agency (USEPA, 1972).

For site-specific CSO management, municipalities enter into consent decrees with regulatory agencies, government entities, and federal courts. Consent decrees are agreements, supervised by courts, which present a plan of action to reduce or eliminate overflow events typically initiated as a result of enforcement action brought against the non-compliant discharging entity. The guiding policy for the formation of overflow-related consent decrees is the USEPA 1994 CSO Control Policy. The policy offers direction on CSO control practices for compliance with the CWA and individual National Pollution Discharge Elimination System (NPDES) permits through required minimum controls, monitoring, and the development of long-term control plans (LTCPs) (USEPA, 1972, 1994, 2010; Cook, 1995). The minimum controls are directed at maximizing and optimizing use of existing infrastructure for CSO control, while the LTCPs and consent decrees often include larger capital projects. Both approaches are implemented to meet NPDES permit requirements.

The first consent decrees with large combined sewer cities began project implementation in the late 1990s to the early 2000s (e.g. Cincinnati, OH; Philadelphia, PA; Washington, D.C.). More recent agreements include Akron, OH, which entered into their $0.9B consent decree in 2010, and Chicago, IL entered into their $1.8B consent decree in 2011 (US District Court for the Northern District of OH, 2010; US District Court for the Northern District of IL, 2011). The agreements include a series of projects to close combined sewer outfalls, minimally treat combined sewer flows, and maximize use of existing infrastructure. For example, the CSO consent decree for Metropolitan Sewer District of Greater Cincinnati (MSD) includes 114 projects with 102 completed as of 2018 and a total cost of $3.3B (US District Court for the
Southern District of OH, 2004). These multi-decade consent decrees can be renegotiated every five years to address new challenges or accommodate updated technologies. Philadelphia and Washington D.C. were the first two cities to reopen their consent decrees for the introduction of significant green infrastructure projects. Green infrastructure was not as common a CSO control solution in the early 1990s during drafting of the CSO control policy, and therefore its acceptance into consent decrees demonstrates the ability for agreements to be more current and responsive (Copeland, 2014; Appel et al., 2017).

There are numerous methods for CSO control including storage (tunnels, equalization tanks), pollution prevention (reduction of pollutants entering waterways), sewer separation, real-time control (use of sensors throughout conveyance area), and Low Impact Development ([LID], typically green infrastructure or other best management practices) (Monteserrat et al., 2015; Schlaman et al., 2015; Tavakol-Davani et al., 2015; Martin et al., 2017; Hopkins et al., 2018). Many municipalities interpreted the “capture and treat” directive of the CSO control policy to mean construction of large storage infrastructure, such as underground tunnels, which then became a focus of LTCPs and consent decree projects (USEPA, 1994). Storage helps alleviate CSOs and SSOs by capturing large flows during a storm event, then pumping and treating them once treatment plant capacity allows. Another approach to wet weather management is high-rate treatment. Effective wet weather treatment technologies must be capable of long-term stagnation since they are planned to be used less than 50 times per year, able to start up rapidly, and feature a low detention time resulting in a small footprint considering the high flowrate typically handled. Additionally, the technology must be able to address and respond to large fluctuations in influent characteristics (Szabo et al., 2005).

High-rate technologies must include solids removal (measured as total suspended solids [TSS]) since solids are a significant cause of receiving water impairment after storm events, as runoff (non-point source pollution) or overflows (point source pollution), as well as a major source of other contaminants which sorb to solids. For example, MPs are found in higher concentrations in sediment in combined and separate sewer systems and downstream of CSO and...
SSO outfalls during and after storm events than in conventionally treated secondary effluent (Gasperi et al., 2010; Phillips et al., 2012). The higher, initial sediment concentrations are typically released due to the first flush phenomenon in which sewer deposits are mobilized during the initial period of a storm event, particularly hydrophobic compounds characterized by high logK_{ow} values (Phillips et al., 2012). First flush is characterized by a significantly higher pollutant mass within the first 50% of stormwater volume released (Lee et al., 2002). A higher concentration of contaminants at the onset of a storm event is also attributed to runoff from impervious surfaces (Jasim et al., 2006). Solids removal is typically followed by disinfection, the efficiency of which is dramatically impacted by turbidity.

One technology commonly applied in wet weather treatment for rapid solids removal is chemically enhanced primary treatment (CEPT) in which coagulants, such as alum (aluminum sulfate) or ferric chloride, and flocculant aids, such as polymers, are added to wet weather flows either at a remote facility or a treatment plant (CH2M Hill, 2008; CDM, 2010; Exall & Marsalek, 2013). Wet weather flows contain a diverse matrix of contaminants due to the combination of both domestic wastewater (pathogens, organics, pharmaceuticals) and stormwater (high TSS, polycyclic aromatic hydrocarbons, pesticides) (Cook, 1995; Hwang & Foster, 2006; Passerat et al., 2011; Al Aukidy & Verlicchi, 2017). Some fraction of hydrophobic contaminants is sorbed to suspended solids and removed by primary treatment (i.e., CEPT), whereas some are carried over to disinfection. While CEPT is capable of removing TSS, insoluble chemical and biochemical oxygen demand (COD and BOD), and a fraction of nutrients, other harmful contaminants including pathogens present in CSOs and SSOs are not addressed (Schroedel et al., 2007; CDM, 2010; Davis et al., 2017).

To rapidly treat the contaminants in wet weather flows and achieve high-quality effluent, including removal of soluble organic pollutants, MPs, and pathogens, during high-intensity rain events, advanced oxidation processes (AOPs) can be used as high-rate technologies (Szabo et al., 2005). AOPs are characterized by the formation of hydroxyl radicals capable of a high rate of reaction \( k = 10^8-10^{10} \text{ M}^{-1} \text{ s}^{-1} \) with target compounds (Gottschalk et al., 2010). Hydroxyl radicals
are the strongest known oxidant and, among other oxidants such as ozone, can oxidize MPs and remove soluble organic pollutants (Gottschalk et al., 2010; D. Gerrity & Snyder, 2011). Rapid, real-time treatment of wet weather flows could reduce the stress on infrastructure during intense storms and prevent CSOs and SSOs from occurring. AOPs are capable of oxidizing MPs, achieving disinfection, and reducing both COD and BOD, making them attractive technologies to consider for CSO and SSO treatment (Esplugas et al., 2007).

The main objective of this study was to use CEPT with various AOPs for high-rate treatment of a synthetic SSO water. The tasks included determining the preferred chemical doses for CEPT to achieve >95% solids removal in <5 min, determining the preferred AOP based on time to achieve 90% COD removal, *E. coli* inactivation, and MP removal/oxidation, and conducting a cost analysis of the preferred system in comparison to current practices for wet weather treatment. The overall hypothesis was that the preferred CEPT-AOP process could treat a synthetic SSO water to the same or higher quality as conventionally treated wastewater effluent in a cost- and energy-efficient manner. Additionally, it was hypothesized that effective solids removal would improve AOP efficiency. Jar tests were conducted to determine operating conditions and chemical doses for rapid solids removal, which is a necessary precursor to effective AOP treatment as particulate organics consume hydroxyl radicals (Zucker et al., 2015). AOP treatments including ozone alone, O$_3$/H$_2$O$_2$, O$_3$/UV, and UV/H$_2$O$_2$ were conducted and analyzed over time for COD removal, *E. coli* inactivation, and MP removal. The overall treatment detention time was determined for 90% COD removal, and the treatment efficiencies for conventional wastewater parameters were measured in the synthetic SSO influent, after CEPT, and after CEPT-AOP.

3.2. METHODS AND MATERIALS

Laboratory batch reactors were used with a synthetic SSO water to find the best-performing treatment combination.
3.2.1. Synthetic SSO Water Characterization

A synthetic SSO was developed considering published, actual SSO constituent concentrations (see Table 2.1 in Chapter 2). Synthetic rather than real SSO water was employed to maintain consistency while testing the effectiveness of CEPT and the various AOPs. The synthetic SSO used in this study (Table 3.1) was created by modifying a synthetic primary effluent developed and employed by Seib et al. (2016) to mimic primary effluent at a municipal water resource recovery facility (South Shore Water Reclamation Facility (SSWRF), Oak Creek, WI). Modifications to the synthetic primary effluent were made to mimic SSO water. Bentonite (10 mg/L) was added to model the inert solids present in wet weather flows. Humic acid (3.5 mg/L) was added since it is present in wet weather flows and may influence AOP performance. Additionally, the acetic acid concentration was reduced to more accurately mimic actual SSO water (Gasperi et al., 2012; Exall & Marsalek, 2013). Concentrations of Escherichia coli (E. coli) of 10^7 colony forming units (CFU)/100 mL were added to the synthetic SSO (Passerat et al., 2011; Scheurer et al., 2015).

Triclosan (TCS) and triclocarban (TCC) concentrations in primary influent at the SSWRF were previously determined to be approximately 2 µg/L (Schroedel et al., 2014). TCS (as Irgasan, Sigma-Aldrich, Saint Louis, MO) and TCC (as 3,4,4’-Trichlorocarbanilide, Sigma-Aldrich, Saint Louis, MO) were added at higher concentrations (50 µg/L each) to observe their removal given the instrument detection limit of 0.5 µg/L. TCS and TCC were chosen based on their presence in wet weather flows and wastewater treatment plant effluent, and as representatives of other common hydrophobic compounds (Halden & Paull, 2005; Schroedel et al., 2014). Stock solutions for TCS and TCC were prepared by pre-dissolving the compounds through sonication in HPLC-grade methanol (Sigma-Aldrich, Saint Louis, MO). Control tests were conducted to determine any loss throughout the treatment system due to sorption to glass or plastic surfaces. Glassware and reactors were silanized to reduce TCS and TCC sorption.
Table 3.1. Synthetic SSO Ingredients

<table>
<thead>
<tr>
<th>Constituent Name</th>
<th>Concentration (mg/L, unless otherwise specified)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solids Solution (organic and inert)</strong></td>
<td></td>
</tr>
<tr>
<td>Powdered Milk</td>
<td>133</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>133</td>
</tr>
<tr>
<td>Yeast Extract</td>
<td>67</td>
</tr>
<tr>
<td>Casein Peptone</td>
<td>67</td>
</tr>
<tr>
<td>Cysteine</td>
<td>10</td>
</tr>
<tr>
<td>Bentonite</td>
<td>10</td>
</tr>
<tr>
<td>Dog Food at 149-297 µm (Nutro Natural Choice, Franklin, TN)</td>
<td>15</td>
</tr>
<tr>
<td><strong>Humic acid</strong></td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Metals Solution</strong></td>
<td></td>
</tr>
<tr>
<td>CoCl₂*6H₂O</td>
<td>1</td>
</tr>
<tr>
<td>NiCl₂*6H₂O</td>
<td>1</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1</td>
</tr>
<tr>
<td>MnCl₂*4H₂O</td>
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</tr>
<tr>
<td>NH₄VO₃</td>
<td>0.5</td>
</tr>
<tr>
<td>CuCl₂*2H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>AlCl₃*6H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>NaMoO₄*2H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>0.5</td>
</tr>
<tr>
<td>NaWO₄*2H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>Ferric Sulfate (FeSO₄*7H₂O)</td>
<td>23.5</td>
</tr>
<tr>
<td>Sodium Bicarb (NaHCO₃)</td>
<td>510</td>
</tr>
<tr>
<td>Magnesium Sulfate (MgSO₄)</td>
<td>36</td>
</tr>
<tr>
<td>Potassium Chloride (KCl)</td>
<td>12</td>
</tr>
<tr>
<td>Potassium Iodide (KI)</td>
<td>10</td>
</tr>
<tr>
<td>MgCl₂*6H₂O</td>
<td>260</td>
</tr>
<tr>
<td>(NaPO₃)₆</td>
<td>4</td>
</tr>
<tr>
<td>MgHPO₄*3H₂O</td>
<td>7</td>
</tr>
<tr>
<td>CaCl₂*2H₂O</td>
<td>275</td>
</tr>
<tr>
<td>NaCl</td>
<td>140</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>64</td>
</tr>
<tr>
<td>Triclosan (ug/L)</td>
<td>50</td>
</tr>
<tr>
<td>Triclocarban (ug/L)</td>
<td>50</td>
</tr>
<tr>
<td><em>E. coli</em> (CFU/100 mL)</td>
<td>10⁷</td>
</tr>
</tbody>
</table>
3.2.2. Synthetic SSO Particle Size Distribution

Particle size distribution was determined using 0.1 µm, 3.0 µm, and 8.0 µm Whatman polycarbonate filters (GE Healthcare Life Sciences, Issaquah, WA) based on the method described by Tiehm, et al. (1991).

3.2.3. Experimental Setups

3.2.3.1. CEPT Jar Tests

Jar testing was conducted to determine the influence of coagulant chemical and dose on particle removal from the synthetic SSO. Particle concentration was quantified using turbidity since TSS concentrations were low and difficult to accurately measure. Chemical coagulants tested included alum (Al₂(SO₄)₃•18H₂O) (Spectrum Chemical, Gardena, CA) and ferric chloride (FeCl₃) (VWR International, Radnor, PA), with and without an anionic polymer flocculant aid (Praestol A4060, Solenis, Wilmington, DE). A gang mixer (Jar Tester, Phipps and Bird, Richmond, VA) was used for batch coagulation, flocculation, and sedimentation jar testing. The gang mixer had six square, 2-liter beakers each stirred with a speed-controlled, flat paddle.

Initial jar testing parameters were based on values used in previous SSO jar testing studies (CH2M Hill, 2006; King County Wastewater Treatment Division, 2011). Rapid mix duration for all jar tests was 1 min at 100 rpm (velocity gradient, G = 120 s⁻¹). Flocculation mix (30 rpm) duration ranged from 2 min to 30 min at 30 rpm (G = 20 s⁻¹). Settling duration ranged from 2 min to 35 min. Floc formation and settling was observed during each run and times were reduced to achieve rapid solids removal in 5 min.

3.2.3.2. Advanced Oxidation

The various AOP test systems included UV/O₃, UV/H₂O₂, H₂O₂/O₃, and ozone alone.

A collimated UV beam apparatus was used to provide 254 nm low-pressure UV light for treatment alone or in combination with ozone or H₂O₂. The apparatus was designed based on
specifications from Gerrity (2008) and noted in Kuo et al. (2003). For each UV treatment, a 45-mm diameter glass Petri dish with a 2-mm magnetic stir bar was filled with 14 mL of sample (CEPT supernatant) water and the surface of the water was set 10 mm from the bottom of the collimated beam. All dishes and stir bars were autoclaved before use. A UV intensity of 0.065 mW/cm² was measured using a radiometer (ILT1700, International Light Technologies, Peabody, MA) and the average adjusted UV intensity was 0.13 mW/cm² (Bolton & Linden, 2003). The O₃/UV AOP was performed by adding 0.5 mL of ozonated water to the 14 mL sample.

![Ozone generator and batch reactor configuration](image)

**Figure 3.1.** Ozone generator and batch reactor configuration

The ozone gas was produced using a corona discharge generator (LAB2B, Ozonia, Leonia, NJ). The unit could produce up to 4 g O₃ per hour using air. The feed gas to the generator was compressed air, conveyed through a desiccator before entering the generator (Figure 3.1). The compressed air flow rate was 4 LPM at 10 psi, per manufacturer recommendations. During the ozone AOPs, the ozone generator was set to output 8 mg O₃/L (2 g O₃/hr) and the post-treatment ozone residual averaged 0.3 mg O₃/L. Ozone residual was not quenched after treatment. All ozone experiments were conducted under a ventilation hood.

A 30% volume/volume H₂O₂ concentration solution (Fisher Scientific (Fair Lawn, NJ) was used. Stock solutions were prepared fresh each day and discarded after use. Sodium thiosulfate (Mallinckrodt Baker, Inc., Phillipsburg, NJ) or manganese oxide (Alfa Aesar, Ward
Hill, MA) was added to quench residual H$_2$O$_2$ prior to COD testing; others have observed residual H$_2$O$_2$ interferes with standard COD tests (Liu et al., 2003; Ertugay & Acar, 2017). Chlorine disinfection was performed using sodium hypochlorite (8.25% NaOCl, Walgreens, Deerfield, IL) and sodium thiosulfate was used for dechlorination.

### 3.2.3.3. H$_2$O$_2$ Interference

H$_2$O$_2$ was discovered to interfere with Standard Method 4500 colorimetric testing for COD by creating artificial COD. Two methods were developed for quenching H$_2$O$_2$ residual from the sample prior to COD testing. The first was referenced from a study completed by Liu et al. (2003), wherein the molar equivalents between sodium thiosulfate and H$_2$O$_2$ were determined. The residual H$_2$O$_2$ concentration was measured after each treatment. This value was converted to molar equivalents of sodium thiosulfate, which was then added to the sample at a strong concentration to limit dilution. After the required quenching reaction time according to the method, the H$_2$O$_2$ residual was measured again to ensure complete removal before COD testing.

The second method for H$_2$O$_2$ quenching was using manganese oxide (MnO), a solid in powder form. The protocol established for quenching with MnO, adapted from Azbar et al. (2004), only required testing of H$_2$O$_2$ residual after quenching. The quenching process involved 50 mg of MnO added to approximately 30 mL of sample, which was then mixed for 20 minutes for the reaction to occur. After mixing, the MnO powder was filtered out of the sample. The MnO method proved to be more reliable as it was determined that sodium thiosulfate can also interfere with COD testing if added in excess of H$_2$O$_2$ molar equivalents.

### 3.2.4. Analyses

Standard methods were used to determine synthetic SSO, CEPT supernatant, and AOP effluent concentrations of BOD$_5$, COD, NH$_3$–N, organic nitrogen (N$_{org}$), TKN, TP, TSS, volatile suspended solids (VSS), *E. coli*, and metals (APHA et al., 2012).
E. coli 15597 stock solutions were prepared using the overnight culture method. Difco™ modified tryptic soy broth (TSB) (Becton, Dickinson and Company, Sparks, MD) was prepared and autoclaved for use during overnight culture and log phase preparation. A frozen aliquot of E. coli was thawed at 37°C, added to an aliquot of TSB in a sterile centrifuge, and incubated at 37°C overnight. Log phase cultures were prepared by adding an aliquot of the incubated overnight stock to an aliquot of TSB in a sterile centrifuge (aliquot volumes based on E. coli concentration requirements) and placing the centrifuge on a shaker table for approximately 3 h. Prior to plating and enumeration, 1:10 sample to phosphate buffer solution dilutions were made. The E. coli concentration was enumerated using the membrane filtration method (APHA et al., 2012) with Difco™ m Endo Broth MFT™ (Becton, Dickinson and Company, Sparks, MD).

Analysis for any test involving UV was limited by the sample size available (total sample size = 14 mL). Aqueous ozone concentrations were measured using a commercial test kit with a range up to 1.5 mg/L O₃ (AccuVac ampules, HACH, Loveland, CO). The aqueous H₂O₂ concentration was measured using a commercial test kit (K-5513 vacuum sealed ampules, CHEMetrics, Inc., Midland, VA). Free and total chlorine concentrations were measured using commercial kits (Model CH-66, HACH, Loveland, CO).

TCS and TCC were quantified using liquid chromatography-massspectrometry (LC-MS) (LC-MS 2020, Shimadzu Corporation, MD, USA). Details of methods for sample preparation and compound quantification can be found elsewhere (Ross, 2014; Tong et al., 2016). Briefly, LC-MS samples were analyzed in 1.5-mL amber vials in a solution of 1:1 methanol (99.9% HPLC grade, Fischer Scientific, Pittsburgh, PA) to Milli-Q water. Compounds were separated with a stainless-steel column (Luna C18, Phenomenex, Torrance, CA) and quantified by analyzing the sample peak area in comparison to a standard curve.

Microsoft Excel (Microsoft Corporation, Redmond, WA) was used to conduct Student t tests to demonstrate significance between various treatments or chemical doses. Significance was demonstrated with a p-value less than 0.05.
3.3. RESULTS AND DISCUSSION

3.3.1. Synthetic SSO Particle Size Distribution

An important aspect of synthetic SSO development was achieving the proper particle size distribution for effective solids removal by CEPT. The particle size distribution reported by others for four municipal wastewaters in Germany was targeted (Tiehm et al., 1991). Figure 3.2 shows the particle size distribution determined using 0.1 µm, 3.0 µm, and 8.0 µm Whatman polycarbonate filters (GE Healthcare Life Sciences, Issaquah, WA) based on the method described in Tiehm, et al. (1991).

![Graph of synthetic SSO and Tiehm et al. raw particle size distribution](image)

Figure 3.2. Wastewater and synthetic SSO particle size distribution

3.3.2. CEPT Jar Tests

The influence of chemical identity and dose on turbidity removal in short-duration CEPT (<5 min) was determined. Once the lowest chemical doses (coagulant and polymer) to achieve 95% turbidity removal were determined, triplicate jar tests were conducted at those doses to determine the removal achieved for conventional wastewater parameters.
3.3.3. Turbidity Removal

Figure 3.3 shows turbidity removal over a chemical concentration range of 0 to 100 mg/L ferric chloride or alum. The initial operating conditions for Figure 3.3 were 1 min rapid mix (100 rpm, \( G = 120 \text{ s}^{-1} \)), 30 min floculation mix (30 rpm, \( G = 20 \text{ s}^{-1} \)), and 10 min settling. Ferric chloride resulted in larger flocs and more rapid settling at lower doses compared to alum.

![Figure 3.3](image-url)

**Figure 3.3.** Ferric chloride vs. alum for turbidity removal (41 min). Chemical doses are as ferric chloride and as alum. \( n = 3 \) for each data set and the error bars represent standard error. Alum performed similar to ferric chloride at doses (average \( p = 0.6 \)) at 41 min.

Operating conditions for ferric chloride were then changed to be more rapid and, therefore, appropriate for wet weather treatment (28 min total: 1 min rapid mix (130 rpm, \( G = 150 \text{ s}^{-1} \)), 17 min floculation mix (30 rpm, \( G = 20 \text{ s}^{-1} \)), and 10 min settling). Under these conditions, ferric chloride achieved 99% turbidity removal at 80 mg/L, while alum required extended settling time and achieved only 87% at 80 mg/L after 41 min. These tests demonstrated that ferric chloride could achieve better turbidity removal at lower doses and shorter treatment times than alum. The test also demonstrated that 20 mg/L ferric chloride achieved 96% turbidity removal in 28 min (Figure 3.4); however, the higher concentration at 80 mg/L was shown to work better with polymer for a shorter treatment time. The residual iron concentration was 5.3 mg Fe/L, which was actually a 37% iron reduction from the synthetic SSO influent.
Ferric chloride doses for turbidity removal with influent turbidity at 64 NTU. Chemical doses are as ferric chloride \( (n = 1) \). Total treatment time was 28 min: 1 min rapid mix \( (G = 150 \text{ s}^{-1}) \), 17 min flocculation mix \( (G = 20 \text{ s}^{-1}) \), and 10 min settling.

Ferric chloride was then used with flocculant aid polymer. Based on initial jar test observations for ferric chloride floc settling behavior, the treatment time was reduced to five minutes including 1 min for rapid mix, 2 min for flocculation mix, and 2 min for settling. This time also accommodates the research goals of rapid solids removal for wet weather events. As suggested in literature and verified in testing, the polymer flocculant aid was more effective for turbidity removal when added 30 sec after the ferric chloride was added compared to when both chemicals were added simultaneously (Young & Edwards, 2003; Krill et al., 2014). Turbidity removal was 15% higher when the addition of polymer flocculant aid was delayed by 30 sec. While 80 mg/L ferric chloride achieved 99% turbidity removal alone in 28 min, the addition of 0.8 mg/L polymer flocculant aid to 80 mg/L ferric chloride achieved 95% turbidity removal in 5 min.

### 3.3.4 Advanced Oxidation

Supernatant from the jar test with the highest turbidity removal was transferred to each AOP reactor. Each AOP was then evaluated for effectiveness of disinfection, COD removal, and MP oxidation in batch tests. \( \text{H}_2\text{O}_2 \) doses were derived from literature for the specific AOP (Beltrán, Encinar, et al., 1997; Ksibi, 2006; Rizvi et al., 2013)
3.3.4.1. Disinfection

The ability for each AOP to disinfect the CEPT supernatant was measured by *E. coli* log inactivation with a maximum log removal of 7 given the starting value of $10^7$ CFU/100 mL. On average, turbidity removal during CEPT achieved an average of one log removal of *E. coli*, ostensibly due to sorption to and removal of solids, with $10^6$ CFU/100 mL remaining in the sample at the onset of AOP treatment. Each AOP tested was capable of achieving 5-log inactivation of *E. coli* within 20 minutes of treatment, as shown in Figure 3.5, with ozone-based AOPs achieving 5-log inactivation in less than 10 min. Many of the analyzed samples were below detection (<30 CFU/100 mL). This was expected considering the high-strength oxidants and disinfectants used during treatment (Xu et al., 2002; Gehr et al., 2003). While the ozone residual from the treated sample was not quenched before plating, the sample was diluted 1:10 in a buffer solution to where the ozone residual was 0.03 mg O$_3$/L. This is assumed to be too low to continue disinfecting and is considered negligible.

![Figure 3.5](image_url)

*Figure 3.5.* *E. coli* log inactivation in CEPT supernatant for various AOPs. $n = 3$ for UV alone and UV/H$_2$O$_2$ and $n = 1$ for ozone alone and O$_3$/H$_2$O$_2$. UV alone and UV/H$_2$O$_2$ error bars represent standard error on triplicate values. Log values are log($C_o/C$) where $C_o$ is the initial concentration of *E. coli* in CFU/mL. The H$_2$O$_2$ dose for UV/H$_2$O$_2$ was 3.0 mM, while the H$_2$O$_2$ dose for O$_3$/H$_2$O$_2$ was 10 mM. Applied O$_3$ dose was 8 mg/L for both ozone-based AOPs. UV fluence was 2,800 mJ/cm$^2$ for UV-based systems.
There was a significant difference in the *E. coli* log inactivation between the UV-based and ozone-based AOPs before 10 min (at 5 min, \( p = 0.0003 \); at 10 min, \( p = 0.01 \)). This could be due to the ability of ozone-based AOPs to break down recalcitrant complex substrates in wastewaters more efficiently than UV-based AOPs, allowing disinfection to happen faster.

3.3.4.2. Soluble COD Removal

Considering 95% turbidity removal during CEPT, the insoluble COD fraction was largely removed before entering the AOP step. On average, CEPT achieved 47% COD removal. This is an important treatment consideration because while hydroxyl radicals react non-selectively overall, they sequentially break down particulate matter first (Gottschalk et al., 2010). The removal of solids allows for the reactions present in AOPs to focus on the removal of soluble COD primarily, resulting in a decreased detention time. Solids removal during CEPT was consistent when testing the different AOPs and therefore turbidity at time = 0 was constant for each AOP treatment.

Due to sample size limitations with UV/H\(_2\)O\(_2\) testing and the methods required to quench H\(_2\)O\(_2\), only ozone alone, O\(_3\)/H\(_2\)O\(_2\), and O\(_3\)/UV were tested for COD removal. All AOP reactions for COD removal were modeled as first-order (Figure 3.6).
The y-intercept was forced through $C/C_0 = 1$. The trendlines shown are first order degradation models. The first-order reaction rate constants and doses for the AOPs tested are shown in Table 3.2. $n = 3$ for ozone alone; $n = 3$ for O$_3$/H$_2$O$_2$; $n = 1$ for O$_3$/UV. Error bars for O$_3$/H$_2$O$_2$ are not visible. Error bars represented standard error.

O$_3$/UV resulted in the lowest rate constant (Table 3.2), likely due to reactor limitations causing inefficient ozone transfer and, therefore, poor hydroxyl radical formation (Rosenfeldt et al., 2006; Katsoyiannis et al., 2011). The small sample size of 14 mL with the collimated UV beam prevented direct ozonation of the sample and required dosing stock solutions of ozone; however, this method for batch AOP tests with ozone has been reported by others (von Gunten & Hoigné, 1994; Huber et al., 2005; Zucker et al., 2015).

Table 3.2. Summary of AOP First Order Reactions for 90% COD Removal. The AOPs were sampled continuously until 90% COD removal for the respective treatment was met. COD removal at 90% in the AOP corresponds to a higher % COD removal across the entire CEPT-AOP system, but corresponded to an acceptable effluent COD concentration around 30 mg/L.

<table>
<thead>
<tr>
<th>Applied $[O_3]$ (mg/L)</th>
<th>Applied $[H_2O_2]$ (mg/L)</th>
<th>UV dose (mJ/cm$^2$)</th>
<th>AOP First Order Reaction Rate Constant (min$^{-1}$)</th>
<th>Time to 90% COD Removal during AOP (min)</th>
<th>Final COD Concentration at 90% COD removal during AOP (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>-0.006±0.003</td>
<td>360</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>340</td>
<td>0</td>
<td>-0.005±0.0</td>
<td>360</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>2,800</td>
<td>-0.004±0.001</td>
<td>360</td>
<td>45</td>
</tr>
</tbody>
</table>
The $\text{O}_3/\text{H}_2\text{O}_2$ AOP proceeded slightly faster than $\text{O}_3/\text{UV}$. The $\text{H}_2\text{O}_2$ dose was 10 mM (340 mg/L) all added at once at the beginning. The $\text{H}_2\text{O}_2$ concentration was based on literature using AOPs to remove COD from wastewater. Due to the more complex substrate (COD) to oxidize, $\text{H}_2\text{O}_2$ concentration is higher in this study than many other AOP studies which typically focus on organic compound and MP oxidation, and disinfection. For example, Azbar et al. (2004) applied 200 mg/L $\text{H}_2\text{O}_2$ concentration to 2 g $\text{O}_3$/h. Both $\text{H}_2\text{O}_2$ and $\text{O}_3$ may have been more efficiently used with a periodic dosing of $\text{H}_2\text{O}_2$ during treatment instead of $\text{H}_2\text{O}_2$ addition. However, based on system pH at the time of dosing, the $\text{H}_2\text{O}_2$ might instantaneously quench the $\text{O}_3$ present and slow the overall reaction rate (Katsoyiannis et al., 2011).

The $\text{H}_2\text{O}_2$ residual decreased over time as it reacted with ozone and the contaminants present in the synthetic SSO (Figure 3.7). $\text{H}_2\text{O}_2$ consumption was modeled as first order where a plot of ln($[\text{H}_2\text{O}_2]$) vs. time yielded a rate constant of -0.023 min$^{-1}$. Adding the full $\text{H}_2\text{O}_2$ dose in increments over the treatment time might have resulted in a lower detention time for COD removal than ozone alone as $\text{H}_2\text{O}_2$ is an ozone scavenger and can limit the reaction rate when present in excess (Katsoyiannis et al., 2011).

![Figure 3.7. $\text{H}_2\text{O}_2$ C/Co vs. time during $\text{O}_3/\text{H}_2\text{O}_2$ AOP demonstrating $\text{H}_2\text{O}_2$ consumption where $C_o = 340$ mg/L.](image-url)
Of the three AOPs tested for COD removal, ozone alone proceeded at the fastest rate. The average detention time to achieve 90% COD removal across the CEPT-AOP (ozone alone) system was 6 hours. While the other AOPs had limitations in either design or due to scavenging, ozone alone was most efficient for COD removal. Additionally, wastewater composition plays an important role in AOP efficiency because other wastewater components such as alkalinity are hydroxyl radical scavengers (Gottschalk et al., 2010; Jekel et al., 2015). Other studies have demonstrated that ozone alone is more effective than other AOPs in similar wastewaters (Rosenfeld et al., 2006).

3.3.4.3. Micropollutant Removal

MP removal through this system would be achieved through two mechanisms: sorption to solids during CEPT and oxidation during the various AOPs. Both TCS and TCC are hydrophobic and therefore sorb to solids where they are physically removed, which is a mechanism similar to other contaminant removal (Jasim et al., 2006). Any contaminant remaining in the system would then be removed during AOP treatment.

Though MP removal was observed after CEPT and during AOP treatment, the results were inconclusive. The mechanism for removal could not be confidently discerned. Control experiments would have demonstrated, with more confidence, the MP fate observed. Future work will address the inconclusive-ness through spike and recovery and glassware sorption control testing.

3.3.5. Preferred AOP: Ozone alone

Considering the comparable treatment efficiencies among ozone alone, O₃/UV, and O₃/H₂O₂, ozone alone was selected as the optimal choice to reduce chemical, operations, and maintenance costs for a full-scale system. Additionally, ozone alone had a higher first order rate constant for COD removal than the other AOPs tested, which will further decrease operating costs. Based on wastewater matrix, ozone alone is more energy-efficient in the production of
hydroxyl radicals than UV/H₂O₂ and O₃/H₂O₂ when comparing the electrical energy per order values (Rosenfeldt et al., 2006; Miklos et al., 2018). Conventional wastewater parameters and E. coli were analyzed with the preferred CEPT-AOP system and compared to minimum treatment of CEPT followed by chlorine disinfection then dechlorination (Chlor/Dechlor).

3.3.5.1. Preferred CEPT-AOP System Treatment Efficiency

Removal of solids typically includes removal of various other wastewater parameters due to sorption to solids (Gasperi et al., 2012). Table 3.3 demonstrates the percent removals for conventional wastewater parameters using the optimal chemical dose of 80 mg/L ferric chloride with 0.8 mg/L polymer. Ferric chloride (in CEPT) is known to enhance phosphorous removal (Zhang et al., 2015) to which the 67% TP removal during CEPT can likely be attributed. Additionally, the CEPT process efficiently removed solids and turbidity, allowing the AOP to remove the soluble COD and BOD.

Table 3.3. CEPT-AOP (Ozone alone) Treatment Efficiency and Comparison with CEPT+Chlor/Dechlor. n = 3 for all tests for which a standard deviation is provided, except for TP where n = 2.

<table>
<thead>
<tr>
<th>Parameter (mg/L, unless otherwise stated)</th>
<th>Synthetic SSO</th>
<th>CEPT Supernatant</th>
<th>% Removal</th>
<th>CEPT-AOP Effluent</th>
<th>% Removal</th>
<th>CEPT+ Chlor/Dechlor Effluent (n = 1)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>485 ± 50</td>
<td>288 ± 34</td>
<td>39</td>
<td>51 ± 15</td>
<td>90</td>
<td>249</td>
<td>49</td>
</tr>
<tr>
<td>BODs</td>
<td>172 ± 20</td>
<td>166 ± 53</td>
<td>4</td>
<td>5 ± 0.9</td>
<td>97</td>
<td>168</td>
<td>2</td>
</tr>
<tr>
<td>TSS</td>
<td>251 ± 27</td>
<td>ND</td>
<td>&gt;99</td>
<td>ND</td>
<td>&gt;99</td>
<td>10</td>
<td>96</td>
</tr>
<tr>
<td>Fecal Coliforms (CFU/100 mL)</td>
<td>10⁷</td>
<td>10⁶</td>
<td>90</td>
<td>ND</td>
<td>99.9999</td>
<td>ND</td>
<td>99.9999</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>17 ± 1.2</td>
<td>16 ± 0.8</td>
<td>11</td>
<td>16 ± 0.0</td>
<td>11</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Organic N</td>
<td>21 ± 2.4</td>
<td>13 ± 2.3</td>
<td>37</td>
<td>8.4 ± 1.0</td>
<td>60</td>
<td>11</td>
<td>42</td>
</tr>
<tr>
<td>TKN</td>
<td>38 ± 2.6</td>
<td>29 ± 1.8</td>
<td>24</td>
<td>25 ± 1.0</td>
<td>37</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>TP</td>
<td>5.8 ± 0.1</td>
<td>1.9 ± 0.1</td>
<td>68</td>
<td>1.6 ± 0.1</td>
<td>73</td>
<td>1.2</td>
<td>80</td>
</tr>
</tbody>
</table>
3.3.5.2. Comparison with Chlor/Dechlor

During high-intensity rain events when the wastewater treatment plant (WWTP) is taking in more wastewater than it can handle under maximum operations, there is an option to “bypass” or “blend” wastewater where only minimum treatment is performed (primary clarification and chlorine disinfection). WWTPs are still able to meet permit by dilution, but this practice is not received well by regulatory agencies, environmental groups, or public stakeholders. Another discouragement for the use of chlorine during wet weather treatment is the formation of possibly carcinogenic disinfection byproducts (DBPs) (Bell & Silva, 2013). Chlorinated DBPs such as total trihalomethanes (TTHM) and halocetic acids (HAA5) are formed when natural organic matter (NOM) reacts with chlorine (Mayer et al., 2014). Their formation can only be avoided by complete removal of NOM prior to chlorination, which is a concern with the bypassing or blending approach. The minimum treatment combination is also practiced in modular wet weather treatment systems using physical or chemical treatment for solids removal (such as vortex separation, ballasted flocculation, or CEPT) followed by chlorine disinfection (USEPA, 1999b; CDM, 2010).

Considering the frequent use of chlorination for wet weather treatment, treatment efficiency of CEPT-Chlor/Dechlor was tested and compared to the CEPT-AOP. Table 3.3 shows the treatment comparison using the same CEPT process followed by chlorine or ozone alone (the chosen AOP). The chlorine treatment detention time was 30 minutes, which is the industry standard contact time required for minimum treatment (USEPA, 1999c). The AOP treatment time was six hours considering this is the treatment time required to achieve 90% COD removal. The detention times were not set equal for this comparison because chlorine alone would not remove COD as ozone does, meaning no further treatment would be observed. This is confirmed in Table 3.3 where CEPT with Chlor/Dechlor only achieved 47% COD removal in comparison to the 90% removal by CEPT-AOP. As discussed in Section 3.2.2, the overall 47% COD removal can be attributed to the CEPT process before Chlor/Dechlor. Additionally, the MP removal likely
occurred during solids removal due to their hydrophobicity and concentrations were below the detection limit in the effluent. Finally, the chlorine worked efficiently at complete disinfection of *E. coli*.

### 3.3.5.3. Operating Cost Estimates

AOPs are capable of high-level treatment including organics removal, MP oxidation, and rapid disinfection, though the current practice of providing minimum treatment to wet weather flows is more cost effective (Szabo et al., 2005). Generally, the practice of preliminary treatment with chlorine disinfection with dechlorination makes it possible for municipalities to meet NPDES permit effluent requirements (CH2M Hill, 2008; Davis et al., 2017; Martin et al., 2017). AOPs can be cost-competitive for their benefits considering these wet weather treatment systems would only go online a few times per year. Another benefit of the system is that if it operates remotely, the maintenance needs would be infrequent, reducing associated labor costs.

Operating cost estimates were performed to evaluate two different scenarios during which the wet weather treatment systems may be used. The first scenario treats 750 MG annually at a remote SSO or CSO location, which covers the 95th percentile annual overflow total based on historic Milwaukee Metropolitan Sewerage District (MMSD) overflow data from 2003-2016 (MMSD, 2017a, 2017b). The second scenario covers a storm event of 340 MGD, which is the average peak flow for the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). This peak flow occurs annually for 350 hours resulting in a total treatment volume of 4,958 MG (AECOM, 2006). Ozone energy requirement was 35 kW-hr/kg O₃ including 22 kW-hr/kg O₃ for ozone production power requirements and 13 kW-hr/kg O₃ for air feed system requirements. These values are derived from Table 3.3 in USEPA (1999a) based on characteristics of ozone generators. Table 3.4 compares the operating costs of the CEPT-AOP (ozone) system to minimum treatment using CEPT with Chlor/Dechlor.

Not surprisingly, the minimum treatment system was extremely more cost effective at $422/MG treated than 6-hr CEPT-AOP at $107,500/MG treated during the first scenario treating
750 MG annually. These cost estimates only represent the operating costs during a storm event. The ozone production costs were calculated by multiplying the power requirements per kg O₃ by the applied ozone dose and the treatment volume. Given the large detention time of 6 h, the applied ozone dose was 10,000 mg O₃/L. This translates to 2.83x10⁷ kg O₃ and over $80M and $531M in operating costs for the two scenarios, respectively. This calculation is only considering the direct scaling of the batch system tested in this study and is not adjusted for scaling factors. Efficiency should increase with scaling; however, at 6 h detention time, the ozone alone AOP for wet weather treatment is extremely cost-prohibitive. Therefore, reducing the detention time is imperative and should be the sole focus of future work.
### Table 3.4. Operating Costs Comparing CEPT-AOP to Minimum Treatment during Wet Weather Events

<table>
<thead>
<tr>
<th>Annual O&amp;M Item</th>
<th>Conc. Applied (mg/L)</th>
<th>Bulk Cost</th>
<th>CEPT-AOP Cost</th>
<th>Min. Treatment Cost</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>750 MG Annual</td>
<td>340 MGD (4,956 MG Annual)</td>
<td></td>
</tr>
<tr>
<td>Ferric chloride (FeCl₃), 40%</td>
<td>80</td>
<td>$1.40/gal</td>
<td>$147,177</td>
<td>$972,939</td>
<td>$164,177</td>
</tr>
<tr>
<td>Anionic polymer flocculant aid, 100%</td>
<td>0.8</td>
<td>$1.91/lb</td>
<td>$9,558</td>
<td>$63,184</td>
<td>$63,184</td>
</tr>
<tr>
<td>Sodium hypochlorite (NaOCl), 12.5% solution</td>
<td>10</td>
<td>$1.45/gal</td>
<td>$0</td>
<td>$0</td>
<td>$69,768</td>
</tr>
<tr>
<td>Sodium bisulfite (NaHSO₃), 38% solution</td>
<td>4</td>
<td>$3.18/gal</td>
<td>$0</td>
<td>$0</td>
<td>$19,034</td>
</tr>
<tr>
<td>Applied ozone dose</td>
<td>10,000</td>
<td>$0.081/kW-hr</td>
<td>$80.3M</td>
<td>$531.1M</td>
<td>$0</td>
</tr>
<tr>
<td>Solids handling</td>
<td>180</td>
<td>$55/ton</td>
<td>$30,962</td>
<td>$204,681</td>
<td>$204,681</td>
</tr>
<tr>
<td>Chemical feed pumping</td>
<td>5 hp/chemical</td>
<td>$0.081/kW-hr</td>
<td>$108</td>
<td>$211</td>
<td>$216</td>
</tr>
<tr>
<td>Effluent pumping</td>
<td>731 hp/150 MGD</td>
<td>$0.081/kW-hr</td>
<td>$40,016</td>
<td>$51,237</td>
<td>$51,237</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td>$80.6M</td>
<td>$532.4M</td>
<td>$316,731</td>
</tr>
</tbody>
</table>

1Brown and Caldwell & Black & Veatch (2014)  
2Rosenfeldt et al. (2006)  
3USEPA (1999a)  
4CH2M Hill (2008)
3.4. CONCLUSIONS

The results of this study demonstrate that CEPT can be combined with AOPs to treat synthetic SSO water to a higher effluent quality than minimum treatment typically applied during storm events (CEPT with Chlor/Dechlor). Ozone alone was chosen as the preferred AOP based on the first order rate constant \( k = -0.006 \pm 0.0003 \text{ min}^{-1} \) achieved during COD removal. Both the faster rate of reaction and singular treatment component would keep capital and operating costs lower than the other AOPs tested. The CEPT-AOP process showed greater removals of COD and BOD\(_5\) (90 and 97%, respectively) over minimum treatment (49% and 2%, respectively) but required a greater detention time (35 min vs. 365 min). CEPT-AOP performed similar to minimum treatment for E. coli inactivation with both systems achieving at least 6 log removals in less than 30 minutes. CEPT performed with ferric chloride (80 mg/L) and a polymer flocculant aid (0.8 mg/L) also achieved TSS removal to below detection in less than 5 min. Considering the large solids loadings during storm events, the impact of 100% solids removal in wet weather flows receiving waters could greatly improve impaired waters.

Future work should focus on improving the treatment detention time from 6 hours to less than 30 minutes for 90% COD removal. In addition to reducing operating costs, this will limit the need for storage capacity and reduce capital costs for system implementation. The key element to accelerate ozone reactions will be improved ozone mass transfer and increased concentration of hydroxyl radicals, possibly through catalytic ozonation. The CEPT-AOP system should also be evaluated for effluent toxicity to ensure that the degradation of MPs in wet weather flows does not produce toxicity. Future studies should further the understanding of various organic compounds present in wet weather flows during treatment and characterization tests.
4 OVERALL CONCLUSIONS

The goal of the research was to evaluate chemically enhanced primary treatment (CEPT) and advanced oxidation processes (AOP) to establish a sequential, advanced, high-rate treatment process for use during wet weather events. The initial phase of the research involved batch-scale testing of both processes to determine the treatment scheme with the lowest detention time to treat a synthetic sanitary sewer overflow (SSO) water.

Based on the initial results, CEPT can be combined with AOPs to treat synthetic SSO water to a higher effluent quality than that achieved by the minimum treatment typically applied during storm events (primary treatment followed by chlorination and dechlorination). Ozone alone was chosen as the preferred AOP because of the relatively rapid rate of reaction with COD and the simplicity of using ozone alone without ultraviolet (UV) light or hydrogen peroxide ($\text{H}_2\text{O}_2$). Not using UV light or $\text{H}_2\text{O}_2$ was expected to keep capital and operating costs lower. The CEPT-AOP process achieved higher removal of COD and BOD$_5$ (90 and 97%, respectively) than minimum treatment (49% and 2%, respectively), but required a greater detention time (356 min vs. 35 min). CEPT-AOP performance was similar to that of minimum treatment for $E.\ coli$ inactivation; both systems achieved 6 log removal in less than 30 min. CEPT with ferric chloride (80 mg/L) and a polymer flocculant aid (0.8 mg/L) also achieved TSS removal to below detection in less than 5 min in bench scale. Considering the large solids loadings that could occur during storm events, the impact of nearly 100% solids removal for wet weather flows could improve impaired receiving water quality.

In conclusion, advanced high-rate treatment of synthetic SSO water can be achieved using the CEPT followed by AOP treatment process evaluated during this research. Further work on this wet weather treatment approach must consider reducing the detention time for 90% COD removal to less than 30 min, a much more appropriate detention time for wet weather applications. Decreasing the detention time involves increasing ozone reaction rates which includes two topics for further research: improved ozone mass transfer and increased production.
of hydroxyl radicals, which may include metal oxides for catalytic ozonation. Additionally, the batch system should be tested in a bench-scale continuous flow reactor to better understand how the two treatment processes (CEPT and AOP) function together.
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