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DEVELOPMENT OF NANOMATERIAL-ENABLED ADVANCED OXIDATION TECHNIQUES FOR TREATMENT OF ORGANIC MICROPOLLUTANTS

by

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CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph. D. thesis of

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has been approved by the Examining Committee
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To my family,
with deep appreciation for their unending love and support

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CHAPTER 1: INTRODUCTION

1.1 Need for Fresh Water Alternatives

Sufficient availability of fresh water is considered by some to be the greatest challenge of the 21st century [5]. As populations continue to increase, this challenge will only continue to worsen [6]. Already, in arid regions of the U.S., accessing a sufficient and reliable supply of water to meet the needs of urban centers, agriculture, and the natural environment creates significant areas of conflict [7]. California, for example, relies on water from the San Joaquin River Delta, which is at risk of saltwater encroachment, declining fish habitats, and damage from aging and under-designed levees [8, 9]. Low precipitation has left groundwater basins overdrawn, and the Colorado River Basin is in the midst of a crippling year drought [8]. Climate change represents an emerging threat that could reduce the Sierra snowpack by 40% by 2050 [10]. Meanwhile, California's population continues to grow, anticipated to increase from 36.7 million in 2005 to 59.5 million by 2050 [11].

This problem is not limited to California or the Western United States, however. Even in areas with high annual rainfall, anticipated population growth poses a threat to adequate fresh water resource capacity all over the United States. As shown in Figure 1-1, even areas of the country with traditionally abundant rainfall, such as the East Coast and the Midwest, show areas of extreme water shortages [2]. Climate change may further exacerbate this problem as well. For instance, here in Iowa, many farmers rely solely on natural rainfall to irrigate their crops and do not have irrigation systems in place for their fields. The drought in the summer of 2012 left many farmers facing extraordinarily low yields [12, 13]. Such challenges will likely get worse and more wide-spread if climate change continues as expected.

1.1.1. Waste Water Reuse Presents an Opportunity to Reduce Reliance on Fresh Water Resources. In response to such challenges, municipalities in arid regions of the U.S. are becoming increasingly reliant on alternative, typically impaired (i.e., lower quality) sources to bridge the ever-widening divide between supply and demand. One such alternate source includes the reclamation and reuse of municipal wastewater, with applications including agricultural irrigation and aquifer recharge for indirect potable reuse. Several states are already dependent on sources historically viewed as ill-suited for domestic use in their current and future water management plans. For example, as shown in Figure 1-2, almost 1.5 million acre-feet of treated municipal wastewater are reused annually in California and Florida combined [14]. Projections suggest that another 1.4-1.7 million acre-feet per year could be utilized by 2030 in California alone [15].

1.2 Emerging Organic Contaminants Present a Challenge for Waste Water Reuse

1.2.1. Ubiquity of Organic Micropollutants One of the problems with placing a greater reliance on impaired water supplies such as wastewater is the higher level of pollution inherent in those impaired sources. Compared to most freshwater sources, impaired sources require a higher level of treatment in order to address public concerns and meet regulatory requirements, such as removal of pathogens [16]. Another issue of rising public concern is the ubiquity of pharmaceutically active compounds (PhACs) and other emerging micropollutants in those impaired sources [17]. PhACs include pharmaceuticals and their active metabolites and breakdown products. Typically present in waters at concentrations of μg/L or less, PhACs are considered “micropollutants” or “microcontaminants.” PhACs and other micropollutants have been found in surface waters and even drinking water systems throughout the county [18]. The primary entry route for these pollutants into water systems is via discharge from wastewater treatment plants (WWTPs) [19]. Pharmaceuticals enter the wastewater system as metabolic waste, through disposal of excess medication down the drain, as hospital waste, or other similar means [19]. Once in the wastewater system, a number of pharmaceuticals pass through

WWTPs into the environment, many believe largely unaffected by traditional (e.g., primary and secondary) treatment methods [20].

There are currently no regulations in place to limit WWTP effluent concentrations of organic micropollutants [21]. Further, the potential impact of these pharmaceuticals in drinking water on human health remains open to debate [21]. A study comparing the measured concentration in tap water to an acceptable daily intake, based on established risk levels, determined that a person would have to drink upwards of several thousand 8 oz. glasses of water each day to exceed that risk level [22]. However, other studies question the potential synergistic health effects found in mixtures of PhACs [21, 23-25]. Further, while presence of some pharmaceuticals can be measured, the presence and potential health effects of uncharacterized transformation products of these PhACs remains largely unknown [26-28]. It is largely due to these unknown effects that there is increasing public concern over the presence of PhACs in drinking water sources [17].

While genuine impacts of these contaminants on human health are still in question, there is little debate that such organic contaminants have significant potential to impact ecological health. Numerous studies have shown direct causation between organic pollutants in wastewater effluent, such as pharmaceuticals and endocrine-disrupting compounds, and declining populations of microbial communities, benthic organisms, and numerous species of fish [21, 23, 29, 30]. Further, recent ecotoxicology studies suggest that chronic exposure to a mixture of pharmaceuticals may have additive or even multiplicative levels of impact above that of a single drug [24, 25], even in mixtures where the effects of individual components are negligible and where each compound exhibits different modes of action [31, 32]. As WWTP effluents are complex mixtures of generally low concentrations of PhACs, these studies suggest that the impact of WWTP discharges on ecosystem health may be significantly greater than presently understood. Further, the contaminants which are most likely found in the environment are those which are most persistent. They are resistant to the biodegradation and sorption treatment processes which occur during waste water treatment, suggesting that they are likely resistant to most natural degradation processes as well [28].

1.2.2. Treatment Challenge Traditional water and wastewater treatment focuses on removal of conventional constituents of concern. Primary wastewater treatment removes solids, secondary biological treatment reduces biological oxygen demand (BOD) and nutrient levels, and finally disinfection removes pathogens prior to discharge. Conventional treatment technologies were not designed to address microcontaminants, and studies suggest that many such contaminants are essentially unaffected by these methods [18].

Current tertiary treatment options offer some improvement. Typical tertiary treatment measures include use of sand filtration, granular activated carbon or other filtration mechanisms, which rely primarily on sorption for constituent removal. In general, sorption shows only minimal improvement in removal of microconstituents, compared to conventional treatment alone [33-38]. Advanced biological treatment processes, such as membrane bioreactors or biological activated carbon, show greater contaminant removal as they allow for biodegradation of the organic pollutants though that process seems too selective and only effective for certain pollutants [37, 39]. Chemical oxidation, such as ozone treatment, shows the greatest removal [40]. However, studies show that several pharmaceuticals still exhibit resistance to oxidative treatment [41]. In fact, ozone is known to be a fairly specific oxidant that will only react with select functional groups on organic pollutants [42]. However, current knowledge of microcontaminant removal during wastewater treatment is not nearly as complete as that for drinking water treatment. A more comprehensive understanding of how microcontaminants are affected during wastewater treatment processes is warranted.

Given the growing number of water shortages across the US, an increased dependence on using treated wastewater as a drinking water source via direct or indirect reuse systems is likely. The most effective way to keep microcontaminants such as

PhACs out of drinking water is to prevent them from entering drinking water sources in the first place. Improved means of emerging contaminant removal during wastewater treatment must be developed.

1.3 Advanced Treatment Technologies are Necessary to Ensure Sustainable Water Supplies

In an effort to address the challenge of effective removal of emerging contaminants, a number of more advanced treatment technologies have been or are under development. Membrane separation technologies, such as reverse osmosis (RO) and nanofiltration (NF), are primarily used for production of very high quality drinking water or industrial process water, rather than wastewater treatment. In that context, they are known to be effective for removal of micropollutants [36, 43]. RO and NF involve forcing water through a semi permeable membrane, using pressure to fight the concentration gradient. The benefit of RO is that it produces water with very little to no measurable pollutants, but this comes with the associated cost of a large volume of highly concentrated brine, which often poses disposal challenges [36]. Another concern with RO is the high energy demand associated with the process. While RO technology is capable of removing micropollutants, the sustainability of this technology remains in question for widespread use in wastewater streams, due to the high energy demands and the brine disposal challenges [44].

An alternative to membranes are advanced oxidation processes (AOPs). AOPs generate highly reactive and non-selective hydroxyl radical ($^{\bullet}OH$) through the combination of reagents such as ultraviolet light (UV) with hydrogen peroxide (H_2O_2), UV with ozone (O_3), and O_3 with H_2O_2. Considered the most powerful oxidant in water, $^{\bullet}OH$ will readily degrade most organic compounds at near diffusion-limited rates [42]. AOPs have proven effective for treatment of organic micropollutants in drinking water [42, 45-47] and in a limited number of investigations have shown great promise for pollutant removal in more complex wastewater matrices [48, 49].

Current AOPs, however, have several potential shortcomings, including high cost of operation, development of hazardous oxidation byproducts such as bromate and N-nitrosodimethylamine (NDMA), and efficacy that is highly variable depending on the water quality, which is particularly problematic for wastewater treatment [45, 50]. These shortcomings suggest that new treatment technologies are needed, or that existing AOP technologies need further optimization before they can mature into a viable means of treating emerging organic microcontaminants.

1.3.1 "Catalytic" Ozonation Presents an Alternative Approach to Current AOPs Research into a new technique, catalytic ozonation, suggests that it has the potential to overcome traditional limitations associated with AOPs [51]. In water, ozone naturally breaks down, forming ${}^{\bullet}OH$ as a transient product, as described in the following reaction mechanism [51]:

$$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2 \qquad (1\text{-}1)$$

$$O_3 + OH^{-} \rightarrow O_2^{\bullet-} + HO_2^{\bullet} \qquad (1\text{-}2)$$

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^{+} \qquad (1\text{-}3)$$

$$O_3 + HO_2^{\bullet} \leftrightarrow 2O_2 + HO^{\bullet} \qquad (1\text{-}4)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \qquad (1\text{-}5)$$

While ${}^{\bullet}OH$ is a product of natural reactions of O_3 in water, it is not typically generated in sufficient quantities to be effective for treatment during standard ozonation, due to the presence of ${}^{\bullet}OH$ scavengers [16]. The addition of H_2O_2 during ozonation results in an effective AOP because it significantly increases ${}^{\bullet}OH$ production in sufficient quantity to overcome the background matrix scavenging effect [45].

Catalytic ozonation utilizes metal oxide or activated carbon (AC) surfaces to enhance ${}^{\bullet}OH$ production via O_3 decomposition, resulting in increased ${}^{\bullet}OH$ yields and greater contaminant removal compared with ozonation alone [51]. Research suggests that although the reaction between ozone and AC takes place on the AC surface, ${}^{\bullet}OH$ is present in the bulk aqueous phase, leaving it free to react with other dissolved species

[51]. While current studies are limited, research also suggests that AC high in surface area and exhibiting basic surface functionalities (such as -OH and $-NH_2$) are most effective [3] or that reaction takes place between O_3 and the unpaired π electrons of the AC's grapheme plains [52]. A proposed mechanism for catalytic ozonation of GAC is shown in Figure 1-3 [3]. Further, as AC is already in common usage in water and wastewater treatment as an adsorbent, it is a very logical first choice substrate to use in catalytic ozonation [53].

It should be noted that there is currently debate over whether AC surfaces truly behave as catalysts for $^{\bullet}$OH production during ozonation. This term was adopted during early research into the phenomena, and more recent research suggests AC does not behave as a catalyst (i.e., it is consumed during the reaction) because of reports that it loses functionality over time and repeated reactions [46, 52].

1.4 Can Carbon Nanotubes Offer Unique Advantages Over other Substrates in O_3-AOPs?

Based on the promising initial reports utilizing AC as an ozonation catalyst, we propose that carbon nanotubes (CNTs) are ideally suited for this use in advanced water and wastewater treatment. CNTs are one-dimensional (1-D) carbon nanostructures consisting of one or more graphene sheets rolled into a cylinder several microns in length with a nanoscale diameter [54]. Similar to their bulk counterparts [55], CNTs have recently shown promise as highly stable and selective gas phase oxidation catalysts [56-65]. Although CNTs share some attributes with bulk carbon, they also exhibit unique differences owing to their nanoscale dimensions [66]. Many of these features, including high external surface area, tremendous mechanical strength and thermal stability [67], make them far superior for engineered application relative to activated carbon. Thus the aforementioned benefits associated with activated carbon during ozonation will likely be accentuated in the presence of CNTs.

CNTs also make ideal catalytic materials because their physical, chemical and electrical properties are tunable through manipulation of their bulk and surface composition, which may allow their catalytic activity toward O_3 to be optimized. The conductivity of CNTs, for example, varies in response to the number of graphene sheets incorporated into their structure; single-walled carbon nanotubes (SWCNTs) consisting of a single rolled graphene sheet can exhibit metallic or semi-metallic properties, whereas dual-walled (DWCNTs; two graphene sheets) and multi-walled (MWCNTs; > two graphene sheets) CNTs behave as semiconducting materials similar to graphite [68]. Accordingly, SWCNTs exhibit redox reactivity [69, 70], which should improve their catalytic function because oxidizable centers promote $^{\bullet}OH$ yields during ozonation [71]. Surface functionalization represents another route by which CNT activity can be manipulated [72, 73]. This is particularly advantageous for CNT application as ozonation catalysts because the existing body of work in this area provides a starting point for the rational synthesis of functionalized CNT with optimal $^{\bullet}OH$ yields. Figure 1-4 shows potential surface moieties present on functionalized CNTs, based on existing research [74, 75]. More recently, considerable progress has been made in the ability to decorate CNT surfaces with a range of nanostructures of well-defined composition, size, crystallinity, and morphology [76-78]. These hybrid nanomaterials display unique properties unlike the building blocks from which they are constructed, and their development has led to significant advances in the fields of sensing, optics, electronics, media storage and catalysis [76-78].

In the field of water research specifically, CNTs have been explored for the use as selective filters, antimicrobial agents, and powerful sorbents [4]. We propose that their potential as tools for pollution control is just beginning to be understood. This study explores another avenue: the potential for CNTs to enhance $^{\bullet}OH$ production during ozonation.

1.5 Study Goals and Approach

The overall objective of this research is to evaluate the potential and limitations for microconstituent removal during waste water treatment and investigate the feasibility of a CNT-enabled AOP for treatment of recalcitrant organic micropollutants. Despite the extensive use of CNTs in current environmental research, no studies to date have systematically examined the potential for CNTs to positively impact $^{\bullet}$OH production during ozonation. This study proposes to fill that gap.

We hypothesize that due to their analogy to AC, CNTs will promote $^{\bullet}$OH during ozonation. Further, because of their high external surface area and tunable surface chemistry, we anticipate CNTs will be superior substrates for $^{\bullet}$OH generation relative to AC. Specifically, CNT functionalization to incorporate oxygen-containing moieties onto the CNT sidewalls and end caps will enhance their activity toward O_3 by generating electron-rich sites for reaction with ozone. In turn, this increased $^{\bullet}$OH production will allow for improved removal of emerging organic contaminants.

Specifically, this study aims to address the following research objectives:

- Research Objective 1: Evaluate whether current advanced treatment technologies provide adequate removal of emerging organic micropollutants, specifically in regard to wastewater treatment, which represents the primary mechanism for introduction of those pollutants into the environment.
- Research Objective 2: Determine whether CNTs are viable materials to enhance effectiveness of ozone-based AOPs via increased production of $^{\bullet}$OH compared to ozone-only systems, and determine how CNT-enhanced ozonation compares to other current AOPs.
- Research Objective 3: Identify the key surface chemistry and structural characteristics of CNTs that may be controlled to optimize their reactivity and increase $^{\bullet}$OH production during ozonation.

- Research Objective 4: Explore the practical considerations that may influence lifetime, performance, and overall viability of CNT-enhanced ozonation techniques during simulated water treatment.

1.6 Thesis Organization

This work contains four chapters of original research. Each chapter specifically addresses one of the research questions above while also testing the overarching research hypothesis motivating this work.

Chapter 2 explores the need for advanced treatment of pharmaceuticals and, by extension, other personal care products and emerging organic contaminants, during tertiary waste water treatment. Using published material from over 40 different journal articles covering over 100 different full- or pilot-scale wastewater treatment plants, we performed a comprehensive evaluation of available data to compare the relative removal of pharmaceuticals during conventional treatment to several tertiary-treatment operations, including ozonation, filtration, granular activated carbon, engineered wetlands, and membrane technologies. Our goal was to establish general trends in PhAC removal as a function of treatment technology, and to identify the optimal treatment mechanisms for PhAC removal. Chapter 2 also reviews AOP treatment options that are on the horizon, although data for full- or pilot-scale implementation of AOPs during wastewater treatment were not available for inclusion in our data analysis. While AOPs are in use for wastewater treatment at some advanced treatment facilities, those plants tend to perform their own monitoring and that information is not publically available. Also, those facilities tend to be in the more affluent communities, and technologies in use in those areas may not necessarily be appropriate for widespread use. Current AOPs are known to exhibit high cost and resource use, and they are energy intensive [79]. For these reasons alone, they require their further optimization before they can be considered viable for large-scale use.

The remainder of this work explores the opportunity for engineered nanomaterials, specifically CNTs, to play a role in development of next-generation advanced oxidation treatment systems. Based on their analogy to AC, Chapter 3 explores whether CNTs are effective substrates to enhance $^{\bullet}OH$ production during ozonation. Using MWCNTs from multiple vendors, we compare $^{\bullet}OH$ production during ozonation for both as-received CNTs and CNTs that have been functionalized via oxidation with various strengths of nitric acid (HNO_3). Further, using the convention of R_{ct} values, which is a metric commonly used to compare efficacy of different ozone-based treatment approaches, we quantitatively compare the reactivity of systematically varied CNT systems to that of O_3 used in combination with AC and that of a more traditional ozone-based AOP (i.e., H_2O_2:O_3 which was used a reference standard AOP for this study). In addition to reactive studies measuring the extent of $^{\bullet}OH$ formation, we also performed complementary characterization of the CNT surface chemistry (e.g., extent of surface oxidation via X-ray photoelectron spectroscopy) to glean insight into the structure-activity relationship between CNT surface chemistry and reactivity.

Results of the initial demonstration study conducted in Chapter 3 illustrated the need for further study into the relationship between $^{\bullet}OH$ production and both CNT surface chemistry and CNT structure. Accordingly, Chapter 4 explores these relationships in greater depth. We examine the relationship between R_{ct} values and surface chemistry via a variety of CNT functionalization methods beyond simply HNO_3, with these new methods not only producing varying degrees of surface oxygen concentration but also unique distributions of oxygen-containing surface functional groups on the CNT surface. Through collaboration with Dr. Howard Fairbrother of Johns Hopkins University, we utilized XPS with chemical derivitization to determine the specific breakdown of carboxyl, hydroxyl, carbonyl, and additional oxygen groups on the CNT surfaces. We also explore the contribution that surface-bound amorphous carbon, generated during the most aggressive of functionalization processes involving mixtures of sulfuric and nitric acid, may play in influencing ozone decay and $^{\bullet}$OH production. Finally, we explore how our findings for MWCNTs compare to those for SWCNTs, DWCNTs, as well as lower purity (i.e., so-called industrial grade (IG)) CNTs, to understand the influence of CNT structure and purity on $^{\bullet}$OH production. This study of IG CNTs is important since industrial-grade production of CNTs will be necessary for this technology to eventually become financially viable.

Chapter 5 explores additional practical aspects that must be considered for nanomaterial enhanced ozonation to achieve viability. We moved beyond model water systems and consider systems with varying levels of alkalinity and dissolved organic matter. We also utilized Iowa River water from Sediment Basin A at the University of Iowa Water Treatment Plant. Minimally treated, Sediment Basin A water represents a similar level of quality as might be expected during application of ozone-based AOPs during drinking water treatment, or even for a relatively high quality secondary wastewater effluent. We also explored the potential lifespan of the nanomaterials via extended exposure (up to 36 hours) to concentrated ozone streams prior to use in experimental reactors. We conducted accelerated aging on as-received and MWCNTs treated with concentrated (70%) HNO_3, as-received SWCNTs, and as-received IGCNTs. Finally, we examined the efficacy of the optimal CNT system on a specific ozone-recalcitrant contaminant, the herbicide atrazine [80]. This final study provides encouraging results that nanomaterial-enabled advanced oxidative processes may indeed provide a viable means of treating structurally diverse, emerging organic micropollutants over a range of water chemistries.

1.7 Expected Outcomes

One key outcome of this work is an improved understanding of the ability of current water and wastewater treatment technologies to address the challenge of organic micropollutants. This understanding will provide guidelines for development of future technologies most likely to be effective. It will also provide perspective on the grasp the water and wastewater treatment community has on the challenge of treating organic micropollutants. Currently there are no regulations in place regarding wastewater effluent levels for such contaminants. However, the EPA is in the early stages of developing such regulations [21] and some communities such as CA and FL which rely on wastewater reuse are also developing regulations regarding allowable levels of contaminants in such reclaimed water [8, 9, 10]. From a human and ecological health standpoint [21], a public relations standpoint [17], and a regulatory standpoint, the need to control levels of organic micropollutants is on the horizon.

Another key outcome of this work is to further development of new technologies to improve removal of organic micropollutants and promote sustainable water reuse. I expect that CNT-enhanced ozonation may play a key role in development of these technologies.

As more and more communities search for ways to make better use of their resources to meet drinking water needs, effective treatment of wastewater will become increasingly important. Reuse of treated wastewater will help to alleviate the growing number of drinking water shortages nationwide. Nonpotable uses of treated wastewater, such as municipal and agricultural irrigation and industrial uses, are gaining wide acceptance; indirect potable uses are the next step. Wastewater effluent can be used for groundwater recharge and to supplement drinking water reservoirs, if it is adequately treated to provide necessary protection for human and environmental health [81].

Results presented herein will show that CNTs in combination with ozone can be a valuable tool in reducing organic micropollutants from wastewater effluent. Current research in the field of membrane filtration suggests an application for this technology. Recent membrane research has focused on composite membrane materials that incorporate CNTs into their structure to increase membrane structural integrity and to exploit the antimicrobial properties of CNTs to slow membrane fouling [82]. Figure 1-5 shows a conceptualization of such a composite membrane consisting of a CNT coating on a ceramic filter [4]. I propose that these hybrid filters, when used in contact with an ozonated feed solution, can simultaneously disinfect the wastewater, chemical break-down organic micropollutants, and minimize or sequester ozonation byproducts. Similar filters with metal oxide-coated ceramic membranes have been previously proposed [83]. However, the potential for refinement of CNT surfaces suggests that they offer even better potential for $^{\bullet}$OH production during ozonation, and therefore offer even greater promise for protection of human health and the environment.

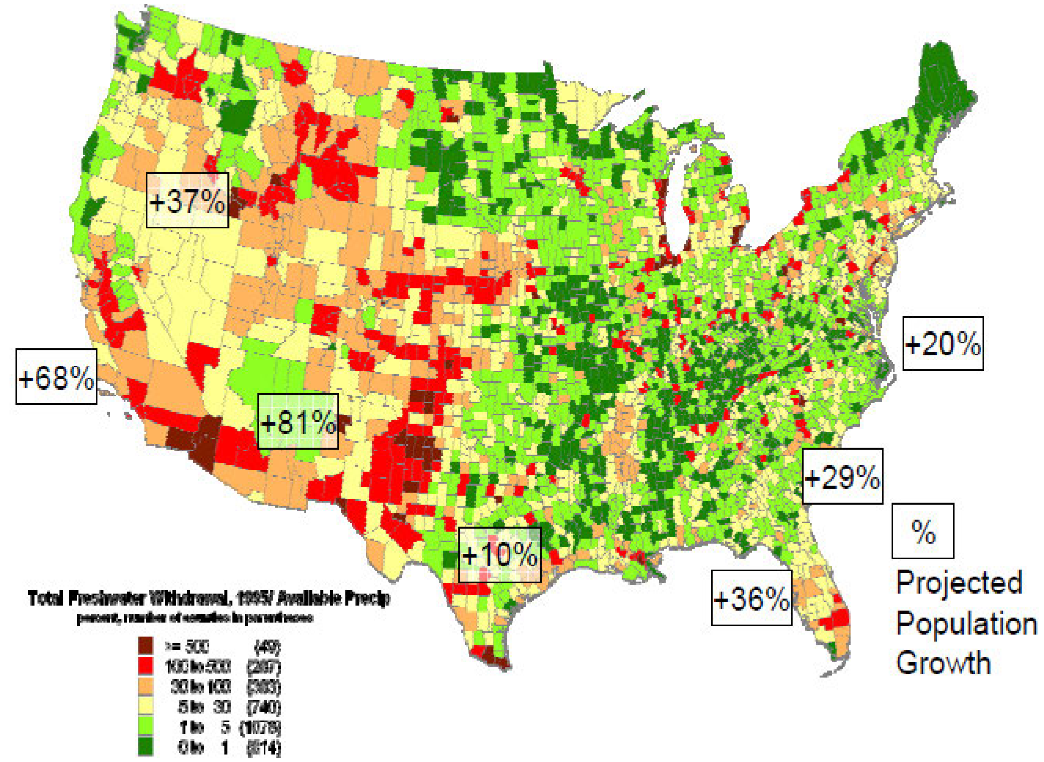

Figure 1-1. Water Shortages and Population Growth. Water shortage areas, marked with shades of red, indicate that annual withdrawal significantly exceeds annual precipitation. [2]

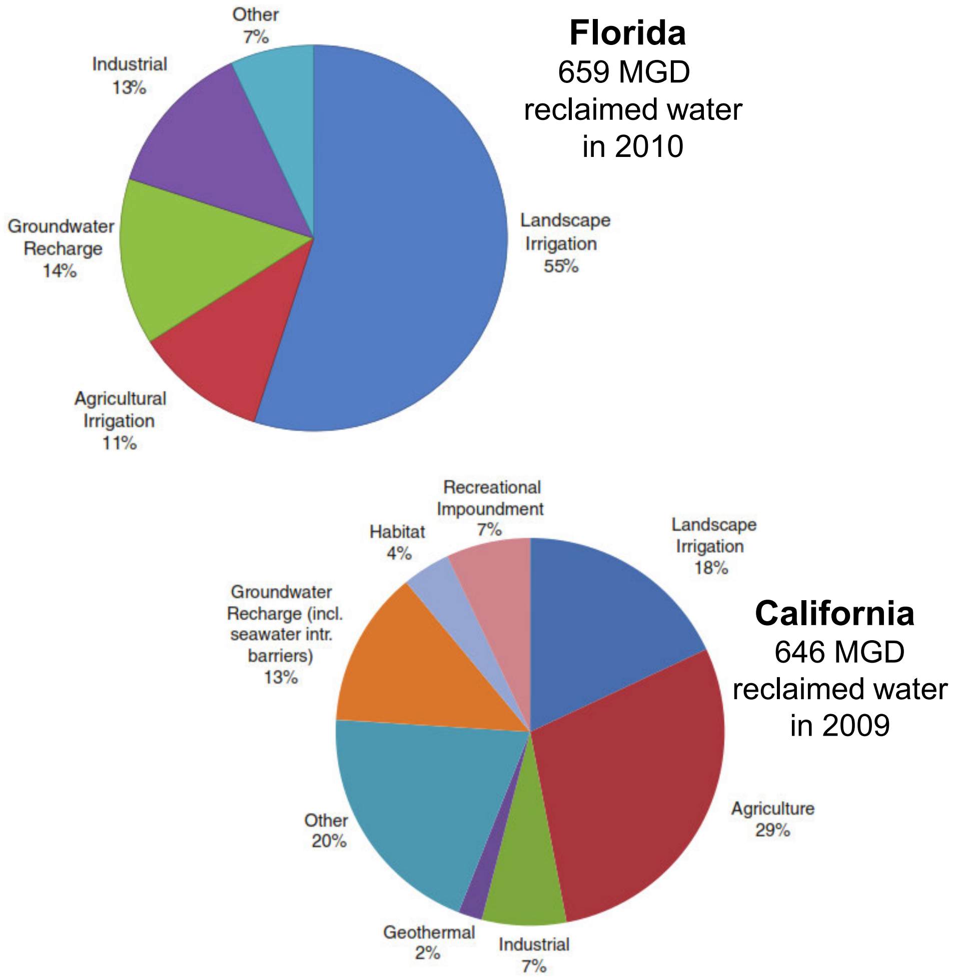

Figure 1-2. Quantity and uses of reclaimed water in Florida and California [1]

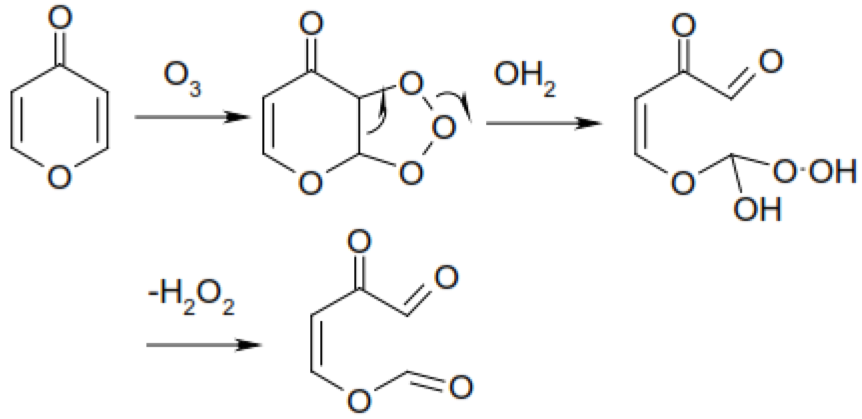

Figure 1-3. Proposed reaction pathway for ozonation of Granular Activated Carbon [3]

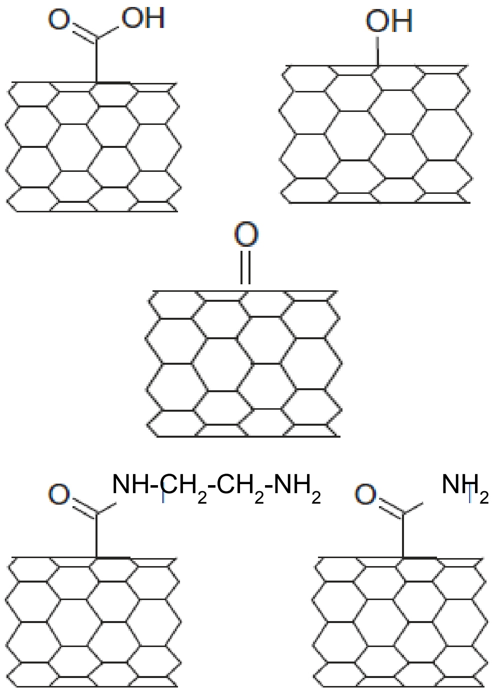

Figure 1-4. CNT Surface Moieties Potential CNT surface groups include carboxyl (-COOH), hydroxyl (-OH), carbonyl (=O), and –N containing groups.

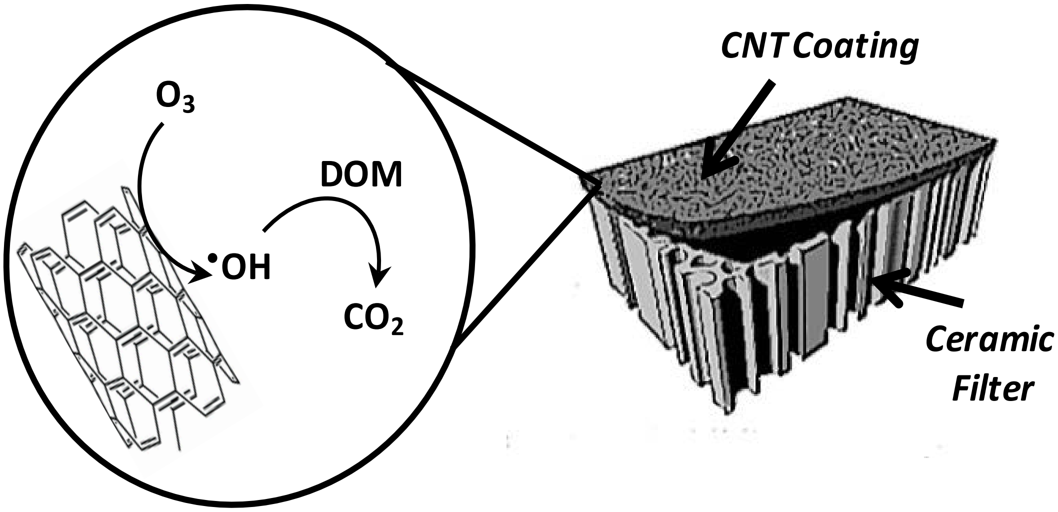

Figure 1-5. Conceptualization of Multi-purpose CNT-composite Membrane (adapted from [4])

CHAPTER 2: PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN EFFLUENT MATRICES

2.1 Abstract [1]

Pharmaceuticals and personal care products (PPCPs) represent a pollutant class of emerging concern, originating in surface and drinking waters largely as a result of their persistence in wastewater effluent. Accordingly, a wealth of recent investigations has examined PPCP fate during wastewater treatment, focusing on their degree of removal during traditional (e.g., conventional activated sludge) and advanced (e.g., membrane filtration) treatment technologies. In this critical review, we compile existing data from over 40 published sources regarding the occurrence of PPCPs in wastewater effluent to evaluate the extent of their removal in unit operations applied at sewage treatment works. Specifically, we compare influent and effluent PPCP concentrations measured at full-scale and pilot-scale wastewater treatment facilities utilizing a range of treatment technologies in hopes of identifying the series of operations (i.e., treatment train) most effective at minimizing effluent PPCP concentrations. Published data suggest that at most 1-$\log_{10}$ concentration unit of PPCP removal can be achieved at plants employing traditional wastewater treatment operations (i.e., preliminary, primary and secondary unit operations). Indeed, only a relatively small subset of compounds (e.g., ibuprofen, acetaminophen, aspirin, 17β-estradiol and estrone) is consistently removed beyond this treatment threshold using conventional activated sludge (CAS) after primary treatment. Furthermore, although some variability in removal efficiencies is observed for specific PPCPs at different treatment plants utilizing CAS, increases in hydraulic retention time (HRT) or sludge retention time (SRT) do not appear to appreciably increase PPCP

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[1] A version of this chapter has been published: Oulton, R.L., T. Kohn, and D.M. Cwiertny, *Pharmaceuticals and personal care products in effluent matrices: A survey of transformation and removal during wastewater treatment and implications for wastewater management.* Journal of Environmental Monitoring, 2010. **12**(11): p. 1956-1978.

removal beyond 1-$\log_{10}$ concentration unit. Available data suggest, therefore, that 1-$\log_{10}$ concentration unit should be viewed as an upper limit to the efficacy of traditional wastewater treatment practices for PPCPs. Notably, this removal threshold for traditional wastewater treatment is maintained over the entire range of reported PPCP influent concentrations, the highest of which (on the order of 10^5 ng/L) can produce effluent concentrations on the order of 1-10 μg/L. In contrast, the existing literature suggests that plants employing advanced treatment methodologies, particularly chemical oxidation via ozone and/or membrane processes, result in the vast majority of PPCPs being removed beyond this 1-$\log_{10}$ concentration unit threshold and often times to levels below existing analytical limits of detection in effluent. Based upon growing evidence that ozone can be applied cost-effectively to secondary effluent, we recommend ozonation in tandem with some form of biological filtration (i.e., sand filtration or biological activated carbon) as a viable option for significantly lowering PPCP effluent levels in the event that toxicological data ultimately support that such degree of removal is warranted. Alternatively, data also suggest passive approaches for tertiary treatment (e.g., engineered wetlands and treatment lagoons) represent promising options for reducing PPCP loads in final effluent. We conclude by addressing future challenges in wastewater management posed by PPCPs including the need for improved analytical methodologies for real-time measurement of these compounds, energy demands associated with advanced technologies, and the next generation of treatment byproducts arising from the chemical and biological transformation of PPCPs during wastewater treatment.

2.2 Introduction

Over the past decade, overwhelming evidence has shown that pharmaceuticals and personal care products (PPCPs) are ubiquitous in surface water, groundwater, and even some drinking waters [18, 84, 85]. Improved analytical methodologies have lowered detection limits for these compounds to parts per trillion (ppt) levels even in the most complex of environmental matrices, leaving little doubt as to their occurrence in water supplies around the globe. What remains, however, is a growing list of questions pertaining to the environmental fate of PPCPs, the ecotoxicological and human health risks associated with their occurrence, and the ability of current water and wastewater treatment infrastructure to remove effectively these compounds.

Although agricultural operations and other non-point sources serve as entry routes for PPCPs into the environment, the dominant pathway responsible for their occurrence is effluent from domestic wastewater treatment [86]. Accordingly, PPCPs and their metabolites are often referred to as “effluent-derived” contaminants, present in wastewater from their use in medicinal and personal care products that are ultimately discharged into municipal sewer systems as human waste products. The tendency of these compounds to persist or be only partially degraded during treatment or to bypass treatment altogether via sewage overflows will, therefore, contribute to their load in receiving waters, many of which serve as recreational and drinking water sources.

Concerns over the biological activity of PPCPs, specifically their potential to act as endocrine disruptors [87], have motivated laboratory, pilot- and full-scale investigations exploring their occurrence in treatment plant influent, their removal during unit operations and processes commonly utilized in water and wastewater treatment, and the concentrations that persist in treated effluent. Despite over a decade of study, however, consensus on many of these issues remains limited. This is due in part to the large number of PPCPs available commercially and through prescription, the diverse chemical structure and physicochemical properties common PPCPs display, the range of unit operations, as well as operating conditions, employed in wastewater treatment, and analytical challenges associated with their reliable quantification in wastewater matrices.

The goal of this review is to use published data pertaining to the occurrence of PPCPs in wastewater influent and effluent to evaluate the performance of conventional wastewater treatment plants in removing this emerging contaminant class. Furthermore, using published data we aim to identify those compounds most likely to persist through wastewater treatment and thus pose the greatest probability of exposure after effluent discharge. Removal efficiencies implied from differences in influent and effluent concentration data are then rationalized on the basis of results from laboratory, pilot-scale and full-scale studies examining PPCP removal in specific unit operations and processes employed in wastewater treatment, including traditional (e.g., solids removal and biological wastewater treatment), advanced (e.g., membranes and advanced oxidation processes), and passive or natural (e.g., lagoons, wetlands) treatment techniques. Whenever possible, fundamental insights into PPCP removal will be linked to physical and chemical properties of the compound or compound class.

Although PPCPs are not routinely monitored in wastewater treatment, nor is their occurrence in wastewater effluent regulated, public perception and concerns over possible adverse health effects associated with exposure to PPCPs and PPCP mixtures have resulted in increased scrutiny of PPCP fate during wastewater treatment. It can be argued, therefore, that wastewater engineers should strive to implement treatment approaches that not only focus on traditional targets such as suspended solids, biochemical oxygen demand (BOD) and nutrients, but also efficiently and cost-effectively reduce PPCPs levels in treated effluent. Accordingly, we also draw upon the available literature on advanced or alternative treatment strategies to develop recommendations for optimal technologies for lowering PPCP loads in effluent. Finally, we conclude our review by identifying future frontiers and challenges associated with PPCPs in wastewater, while also addressing the implications and potential hurdles that PPCPs pose to wastewater management.

2.3 PPCP Occurrence and Removal during Wastewater Treatment: An Analysis of the Current Literature

To better predict the occurrence and concentrations of PPCPs in wastewater effluent, a thorough understanding of their removal during wastewater treatment is warranted. Wastewater treatment involves a series of physical, chemical and biological unit operations and processes that are broadly designated as preliminary, primary, secondary or tertiary treatment. Briefly, preliminary operations are initial stages of treatment implemented to improve the overall performance of subsequent treatment steps. Of preliminary treatment processes, perhaps the most relevant for PPCP transformation is pre-disinfection or pre-oxidation, which entails the use of a chemical oxidant (e.g., free chlorine, ozone, permanganate) at the front of the treatment train to prevent biological fouling of subsequent steps. It is possible that these oxidants could also react with PPCPs in raw effluent, although the complex influent matrix at this point exerts a large oxidant demand that will tend to competitively protect PPCPs. Primary treatment encompasses solids removal through the sequential processes of coagulation, flocculation and sedimentation. Here, the degree of PPCP association with the destabilized particles is an important consideration; particle-associated PPCPs will be removed from the treatment stream with sludge and their fate will then be tied to the solids handling and disposal processes occurring subsequent to clarification. Secondary or biological treatment is intended to reduce the organic load or biochemical oxygen demand (BOD) of the influent. Common approaches include activated sludge, trickling filters and membrane bioreactors (MBRs), in which biodegradable PPCPs will undergo biologically mediated transformation. For the purpose of this review, tertiary treatment will be applied to all additional treatments beyond conventional preliminary, primary and secondary operations. These encompass operations that are physical (e.g., filtration, adsorption), chemical (e.g., chemical oxidation, disinfection) or biological (e.g., nutrient removal, wetlands and lagoons) in nature.

Although several laboratory investigations have considered PPCP removal in model systems representative of wastewater treatment, studies considering the performance of full-scale wastewater treatment facilities are perhaps the most appropriate starting point for evaluating PPCP occurrence in wastewater effluent. Thus, to facilitate our discussion, we have conducted a survey of recent literature to establish the compounds most frequently investigated in occurrence and treatability studies, those most commonly detected in wastewater influent, species largely removed during both traditional (i.e., primary and secondary) and more advanced (i.e., primary, secondary and tertiary) treatment operations, and the identity and amount of persistent PPCPs likely to be discharged into receiving waters.

For our analysis, we compiled PPCP influent and effluent concentration data from over 40 sources, which surveyed the performance of more than 100 pilot- and full-scale wastewater treatment facilities or treatment configurations from around the globe. These sources produced a database of nearly 140 compounds and 1500 data points related to site-specific PPCP concentrations in the influents of treatment plants and effluents of specific unit operations. Analysis was limited primarily to pharmaceuticals, and to a lesser degree, some personal care products. Pesticides and other classes of emerging organic micropollutants (e.g., nitrosamine disinfection byproducts) were not considered, as their entry routes into wastewater differ significantly from that of PPCPs. The treatment plants surveyed from the literature utilized a range of approaches, including traditional wastewater treatment (i.e., solids removal with biological treatment via activated sludge) as well as more advanced methodologies including MBRs, granular media depth filtration, membrane processes including ultra-, micro-, and nanofiltration and reverse osmosis, granular activated carbon packed beds, and chemical oxidation via ozonation.

This survey is not meant to be an exhaustive review of all occurrence studies for PPCPs during wastewater treatment. Rather, it is intended to serve as a representative database of typical influent and effluent concentration data that can be used to assess current performance of wastewater treatment plants (WWTPs) with respect to PPCP removal. Unlike a similar recent analysis of PPCP concentrations in wastewater [88], our analysis is limited almost entirely to studies reporting corresponding influent and effluent concentrations for the same treatment facility. Unless otherwise noted, studies reporting only influent or effluent concentrations or studies that only provide inlet and outlet concentrations for a specific unit operation were not included because they provide no insight as to the total degree of PPCP removal over the course of treatment (i.e., differences in concentration between raw influent and final treated effluent).

We readily acknowledge that there are some limitations to this approach, which draws data from a broad range of independent sources. First, we only report compounds quantifiable in both the influent and effluent at the same treatment facility. As limits of detection tend to be lower in an effluent matrix, several instances exist where only effluent concentration data are available. We reiterate that these data were not included in our survey. Similarly, limits of detection can be sufficiently high such that non-detects in effluent do not rule out that the PPCP is present at appreciable concentrations. When values below the effluent detection limit were reported, the method detect limit (MDL) was used for comparison to the influent concentration. In our subsequent analysis, these data have been noted accordingly. Second, we make no attempt to differentiate between various sampling approaches employed in occurrence studies (e.g., grab versus 24 h composite samples), nor do we do rigorously account for variations in the operational parameters of treatment processes (e.g., hydraulic residence time, sludge loading, etc.) at each facility. We note that in studies reporting replicate concentrations from one sampling event or concentrations from multiple sampling events temporally close to one another, the mean concentration was used in our analysis. However, for studies in which multiple sampling events occurred at a single facility over an extended time period (e.g., over a one year duration), individual data from each sampling event were used rather than the mean of all events to account for the possibility of seasonal variations in PPCP loads.

2.3.1. PPCP Removal During Conventional (Primary and Secondary) Wastewater Treatment Conventional wastewater treatment typically involves preliminary unit operations, solids removal (primary treatment) and reduction of biochemical oxygen demand (BOD) through biological (secondary) treatment. Studies focusing on PPCP removal during primary wastewater treatment via coagulation, flocculation and sedimentation are generally limited [89-93], as based on findings from drinking water treatment it is widely assumed that removal during these stages is relatively insignificant. In contrast, the biggest contribution to PPCP removal during conventional wastewater treatment occurs during secondary treatment [19]; secondary treatment is therefore the most thoroughly studied process in wastewater treatment with respect to PPCP removal and a multitude of data exists pertaining to treatment efficiency. We note that the term “removal” is used herein to describe both processes that result in true removal of PPCPs from the treatment stream (e.g., adsorption onto sludge or solids) and for processes that lead to PPCP transformation rather than complete removal (e.g., biodegradation or chemical transformation). We acknowledge that the latter processes do not constitute true removal, as metabolites and transformation products derived from PPCPs will remain in the system. For ease of comprehension, however, we will use “removal” to describe all processes resulting in PPCP loss.

The most detailed work on PPCP removal during primary treatment to date has been conducted by Carbella and co-workers [89, 90]. They examined the fate of several PPCPs during primary treatment in a WWTP in Spain [89], and in a subsequent work, conducted laboratory scale experiments with WWTP influent to examine the impact of several operational variables including coagulant identity, coagulant loading, temperature, and mixing time on PPCP removal [90]. As expected, their findings suggest that PPCP removal via primary treatment is generally limited, only occurring to a significant extent (> 20%) for very hydrophobic compounds; the largest degree of removal was observed for musks (i.e., galaxolide and tonalide) with high octanol-water partitioning coefficients ($\log K_{ow}$ values on the order of 5.5-6.0).

Consistent with these results, it is widely believed the predominant mechanism for PPCP removal during primary treatment is sorption to suspended organic matter, which is then subsequently removed from the treatment stream via sedimentation after destabilization of the suspension through coagulation and flocculation. Accordingly, descriptors of PPCP organic partitioning such as K_{ow} values or solid-water distribution coefficients (K_d values) are often suggested as possible predictors of PPCP removal. However, based on the limited number of published data currently available from full-scale evaluations of primary treatment operations [36, 38, 94, 95], little, if any, correlation is observed between reported K_{ow} values for PPCPs and PPCP removal during coagulation, flocculation and sedimentation (data not shown). More data is certainly needed to validate if such a correlation does indeed apply to full-scale wastewater treatment.

Conventional activated sludge (CAS) is the most common secondary treatment system used in wastewater treatment. PPCP removal during CAS treatment can be attributed to both biodegradation, as well as to adsorption of the compounds to the sludge. Adsorption to sludge in CAS treatment is particularly important for compounds with a sorption coefficient $K_d > 300$ kg/L [34]. Many acidic PPCP have low sorption coefficients, therefore removal can be ascribed to biodegradation [34]; in contrast, similar to what was described for primary treatment, fragrances such as galaxolide and tonalide are predominantly removed by adsorption on sludge [96].

Figure 2-1 shows the degree of PPCP removal in conventional wastewater treatment facilities (i.e., those employing primary and CAS), for which we assume that the majority of PPCP loss is attributable to removal during CAS treatment. The data, which pertains to concentrations in the treatment plant influent and CAS effluents, were obtained from published sources [33, 38, 89, 94, 95, 97-125] and are presented on a log-log scale. While this scale might at first seem unorthodox, we contend it is necessary given the broad range of PPCP concentrations typically encountered in wastewater treatment, which spans nearly six orders of magnitude (from ~0.1 to 10^5 ng/L) in the published literature. Thus, a log-log plot allows all concentration data to be compared on the same scale, while also allowing possible trends in removal efficiency as a function of PPCP influent concentration to be discerned.

Even though some scatter in the data certainly exists, likely due to variability in the operating conditions associated with treatment and sample collection, a number of species are essentially resistant to conventional treatment (data located along the "no removal" line). A useful point of comparison is effluent levels corresponding to the removal of one-$\log_{10}$ concentration unit of PPCP. In the U.S., national standards for secondary treatment require an average removal of BOD_5 over a 30-day interval of no less than 85% [126], or roughly, one-$\log_{10}$ equivalent of removal. Thus, juxtaposition of the influent-effluent data to this unit-$\log_{10}$ removal line (indicated in Figure 2-1) allows the performance of conventional WWTPs for removal of an emerging organic pollutant class (i.e., PPCPs) to be compared to the classical goal in biological treatment for organic removal (i.e., lowering biochemical oxygen demand).

As shown in Figure 2-1, wastewater treatment plants utilizing solids removal and CAS treatment typically achieve less than a1-$\log_{10}$ concentration unit of PPCP removal. Of the 818 (n_{total}) available data points pertaining to concentration data for conventional treatment plant influent, only 25% ($n_{\text{1-log}} = 202$) exceeded 1-$\log_{10}$ removal in the corresponding effluent concentration, a trend that holds over the entire range of PPCP concentrations typically found in wastewater influent (~0.1-10^5 ng/L). It can be generally assumed, therefore, that conventional facilities not employing some form of tertiary treatment generally remove at best 90% of the PPCPs present in all influents.

Although toxicological data is lacking to determine whether this removal threshold is sufficient for PPCPs, there are certainly instances where only 1-$\log_{10}$ removal may not be sufficient. For example, influent concentrations of 10^5 ng/L (or 100 μg/L) would be expected to produce at best an effluent concentration 10 μg/L; concentration levels on this order have been shown in laboratory studies to induce adverse ecotoxicological effects toward aquatic organisms likely to be encountered at effluent discharge sites. For example, both triclosan and ciprofloxacin concentrations as low as 0.012-1.5 μg/L were found to induce a strong, concentration-dependent decline in genus diversity of algal communities sampled upstream and downstream of a WWTP in Kansas [127].

As highlighted in a recent review of PPCP biodegradation during wastewater treatment [128], the available literature currently does not allow generalizations to be made regarding the removal of different compound classes or even individual compounds. Indeed, a closer examination of the data presented in Figure 2-1 reveals that PPCP removal via conventional wastewater treatment is heavily compound specific. Figure 2-2 presents the $\log_{10}$ removal efficiencies for select compounds in WWTPs employing solids removal and biological treatment with CAS. Rather than reporting average removal efficiencies with appropriate statistical analysis, individual removal data from published reports are shown to illustrate differences not only between PPCPs, but also among WWTPs. This type of presentation also allows insights into those compounds most frequently the subject of WWTP occurrence studies.

Figure 2-2 reveals that one of the most highly researched PPCPs is ibuprofen, an over-the-counter anti-inflammatory. Our database contains 65 reports of influent and effluent concentrations from conventional treatment facilities for ibuprofen, with roughly 70% ($n_{\text{1-log}} = 44$) reporting treatment efficiencies greater than 1-$\log_{10}$ removal. In contrast, certain species such as the antiepileptic carbamazepine are recalcitrant; effluent concentrations from conventional treatment facilities are essentially equal to influent concentrations for all 48 reported instances of carbamazepine detection. Other compounds with particularly high susceptibility to conventional treatment are shown in Table 2-1. These include acetaminophen (or paracetamol), thymol, aspirin, salicylic acid, estriol, 17β-estradiol, estrone, fenoprofen, bezafibrate, bisphenol A, cortisol, cortisone, dexamethasone, and prednisone. This relatively small subset of compounds, including ibuprofen, comprise 160 of the 202 (~80%) instances in the entire dataset exceeding 1-$\log_{10}$ removal. Accordingly, conventional wastewater treatment may be sufficient for their removal, particularly at low influent concentrations. It is also worth noting that these compounds most susceptible to biological treatment display the broadest range of removal efficiencies in Figure 2-2. This is not surprising, as those compounds most amenable to this treatment should also be those species most responsive to changes in the CAS operating conditions.

Relative to CAS, PPCP removal by trickling filters has received less scrutiny and there are fewer reports of field-scale occurrence studies at plants using trickling filters. Findings to date generally agree that trickling filters exhibit lower PPCP removal than CAS systems [93, 118, 129]. Similarly, several non-PPCP wastewater-derived compounds were found to be removed to a lesser extent by trickling filters than by CAS [130]. Exceptions to these trends are endocrine disruptors, sunscreen agents and disinfectants, all of which have been found to be more effectively removed via trickling filters than CAS [99]. This was attributed to the ability of trickling filters to produce immobilized, stable bacterial populations which are capable of degrading rather recalcitrant compounds. In CAS systems, in contrast, these bacteria are likely to get washed out before stable populations can be established.

Despite the multitude of studies and available data, PPCP removal by secondary treatment systems still faces several challenges. First, open questions remain regarding the influence of operational parameters such as hydraulic retention time (HRT) and solids retention time (SRT) on removal efficiency. For example, Maurer et al. [111] reported that the elimination of beta-blockers in WWTP depended on the HRT of the plant. In contrast, Joss et al [34] found no impact of either SRT or HRT on the removal of seven pharmaceuticals and fragrances in full-scale WWTPs. Similarly, Göbel et al. [131] found no difference in the removal efficiencies of various antibiotics in two WWTPs with SRTs of 21-25 and 10-12 days, respectively. We note that for Figures 1 and 2, data correspond to CAS systems with HRT values ranging from 1 h to as much as 10 days and SRT values spanning 5 h to over 100 days. Clear trends in PPCP removal as a function of these variables could not be discerned in our analysis of published data.

Second, PPCP removal has mainly focused on the presence and fate of the original PPCPs, whereas much less scrutiny has been devoted to the fate of their metabolites. This applies both to human PPCP metabolites present in treatment plant influent and to metabolites produced by biodegradation during secondary treatment. Göbel et al. [131] included a human metabolite of the antibiotic sulfamethoxazole, N4-acetylsulfamethoxazole, in their analysis of antibiotic occurrence and fate during secondary treatment. They found that the human metabolite accounted for the majority of the total sulfamethoxazole load in untreated wastewater. Similarly, Leclercq et al. [132], who studied the occurrence and removal of carbamazepine, oxcarbazepine and seven of their human metabolites, reported that at least two human metabolites were present at significantly higher concentrations than the parent substances. Pérez and Barceló [133] reported similar or higher concentrations of hydroxylated human metabolites of diclofenac and aceclofenac compared to their parent compounds in wastewater. These data clearly indicate the need to include human metabolites in future studies.

The occurrence and characteristics of metabolites produced by PPCP biodegradation have also not been adequately addressed to date. While some PPCPs can be completely mineralized during biodegradation (e.g., ibuprofen), others (e.g., ketoprofen, benzafibrate) form stable metabolites or are not biodegraded at all (e.g., diclofenac) [134]. Even though biodegradation metabolites are often considered less environmentally problematic than their parent compounds, examples of enhanced toxicity have been observed. For example, the biodegradation product of clofibric acid, 4-chlorophenol, exhibits higher toxicity than the parent substrate [135]. It has also been suggested that biological treatment can lead to an increase in PPCP concentrations. This is due to the ability of microorganisms to convert human metabolites of PPCPs, in particular glucuronide conjugates, back to the original PPCP [115, 133, 136]. These examples highlight the need for a better understanding of the biodegradation pathways of PPCPs and their human metabolites.

Finally, it has not been possible to date to predict the propensity of micropollutants to undergo biodegradation based on their physical-chemical properties (e.g., see studies conducted by Joss et al. [34], Onesios et al. [128], and Radjenovic et al. [137]). This lack of fundamental insight presents one of the biggest challenges in optimizing PPCP removal during secondary wastewater treatment. In particular, it is difficult to assess the biodegradation efficiency for new and untested compounds in the absence of analytical measurements. Yu et al. [106] compared biodegradation efficiencies predicted using the software package BIOWIN to PPCP removal measured in full-scale treatment plants and laboratory experiments and found great discrepancies between predictions and measurements. Instead of *ab initio* predictions, we thus currently rely on empirical data, such as that presented here, to predict biodegradation efficiency during wastewater treatment. For example, Joss et al. [138] proposed a simple classification scheme for the biodegradability of pharmaceuticals based on their biodegradation rate constants obtained in batch experiments. Compounds were divided into three classes according to their extent of removal. Based on this classification scheme they concluded that current practices in municipal wastewater treatment do not remove micropollutants efficiently.

Table 2-1 also provides some empirical insights into those compounds most susceptible to removal. Noticeable for this subset of PPCPs are similarities based on compound class, with most being steroids and hormones (e.g., estrogens and glucocorticoids) or low molecular weight analgesics and anti-inflammatory drugs. Likely, similarities in the degree of compound removal have less to do with their therapeutic function than the shared presence of bioavailable moieties, including phenols or carboxylic acids. For some examples, however, trends in therapeutic class do not hold. Notable exceptions of hormones relatively resistant to treatment include the 17α-ethinyl estradiol and prednisolone, suggesting that subtle changes in compound structure can have great impact on removal efficiencies, thus illustrating the challenge of trying to generalize biodegradability based upon simple physical and chemical compound characteristics.

2.3.2 PPCP Removal During Advanced Wastewater Treatment Operations We now compare the efficiency of PPCP removal in conventional wastewater treatment to removal efficiencies reported at facilities employing alternative approaches for secondary treatment (e.g., MBRs) and tertiary treatment operations for secondary effluent (e.g., depth and membrane filtration, chemical oxidation with ozone or AOPs, and activated carbon sorption). When available, influent-effluent data for each treatment technology are compared to trends observed for conventional wastewater treatment (see Figure 2-1). For such analysis, reported effluent concentrations from each treatment technology are compared to concentrations measured in the plant influent (rather than the influent for the specific unit operation). This allows the maximum achievable removal of PPCPs via a treatment train incorporating each technology to be clearly identified. As an additional source of discussion, we also present influent-effluent data comparing the removal efficiencies of select PPCPs and compound classes reported for each technology, thereby helping to identify those treatment approaches most suitable for a particular compound or compound class.

2.3.2.1. Membrane bioreactors (MBRs). To enhance biodegradation of PPCPs, MBRs have emerged as an alternative approach to CAS. Like CAS, MBRs rely on biodegradation as the dominant removal mechanism, but their operational parameters, such as HRT, SRT and sludge concentration differ greatly. MBRs operate at higher sludge concentrations that yield higher biological activity compared to CAS. It has therefore been assumed that they will lead to greater PPCP removal, yet studies have reported contradictory findings. Enhanced removal in MBRs has been observed in several studies [110, 137, 139, 140], albeit not for all compounds investigated. In contrast, several authors have reported no benefit of MBRs relative to CAS [34, 103, 131]. A generalization for these contrasting findings was offered by Weiss et al. [39]. They concluded that MBRs were only superior in the case of compounds with an intermediate biodegradation potential, whereas no benefit was apparent for easily biodegradable or recalcitrant compounds. The authors therefore questioned whether the use of MBRs was justified because of its limited benefits. Alternatively, De Wever et al. [141] argued that while MBRs do not necessarily yield higher removal efficiencies, they are nevertheless beneficial because they exhibit a more consistent performance and shorter lag times, indicating a superior response to fluctuating influent concentrations. The resistance of MBRs to large fluctuations in PPCP loads is particularly important for single household MBRs; due to the lack of equilibration with other wastewater streams, PPCP occurrence in single household MBRs is irregular, with concentrations 500-1000-fold higher than in centralized wastewater systems [142].

Our survey of the available literature suggests that MBRs result in modest improvements in PPCP removal efficiency relative to CAS systems. Figure 2-3 compares treatment plant influent concentrations to concentrations measured in effluents of MBRs utilized for wastewater treatment [36, 43, 100, 102, 103, 110, 111, 134]. Also included are the data previously presented in Figure 2-1 for conventional wastewater treatment. Using the threshold of 1-$\log_{10}$ removal as a reference for treatment efficiency comparison, 49% (63 out of 129) of MBR effluent concentrations achieve this degree of removal compared to 25% meeting this threshold for CAS.

An alternative means of comparing treatment technologies for PPCPs is through percentiles analysis of their treatment efficiencies. The results of this analysis are shown in Figure 2-4, where the box plot illustrates the distribution of reported removal efficiencies, expressed as the fraction of PPCP remaining in the treated effluent, for CAS, MBRs and additional technologies to be discussed subsequently. Maxima and minima in this plot correspond to the 90th and 10th percentile for effluent fractions, respectively, whereas the boxes span the 25th to the 75th percentile. The horizontal line within the box indicates the median value (or 50th percentile). From this analysis, half of all PPCPs treated by MBR fall within the range of treatment efficiencies between 41-98% (indicated by the box in Figure 2-4). For comparison, the range is broader for CAS, with half of all PPCPs falling between removal efficiencies of 23% and 91%. Available data therefore suggest that MBRs will yield moderate improvements in the extent of PPCP removal relative to biological treatment via CAS.

When comparing literature values of PPCP removal by MBR and CAS on a compound-specific basis, it becomes evident that many of the same species known to be susceptible to CAS are removed to an equal (e.g., ibuprofen) or greater (e.g., acetaminophen) extent by MBRs (see corresponding data in Figure 2-5a and 2-5b, respectively). However, PPCP removal seems to be highly variable between different MBR systems. One example is carbamazepine, for which some MBRs have little to no impact on removal, whereas other reports indicate far better performance that yields effluent levels below detection limits (see corresponding data in Figure 2-6). These differences may stem from differences in the operating parameters of MBRs. As for CAS systems, there is little agreement regarding the effects of SRT and HRT on PPCP removal. Kimura et al. [110] reported that an MBR with a SRT of 65 days displayed greater removal of six acidic PPCPs compared to another MBR with a SRT of 15 days. In contrast, Joss et al. [34] found that neither SRT nor HRT affected the removal of seven pharmaceuticals in MBRs. A more nuanced result obtained by other researchers suggests that the dependence of compound removal on SRT differs between compounds. For example, Göbel et al. [131] found that the removal of sulfonamides in a MBR was independent of SRT, whereas the removal of trimethoprim and several macrolide antibiotics increased with increasing SRT. Indeed, this behavior is generally observed in the influent-effluent data for these compounds (Figure 2-7). The removal of sulfonamides in treatment plants utilizing MBRs is relatively constant for instances reported in the literature, whereas a wider degree of scatter exists for the removal of trimethoprim and macrolide antibiotics in MBRs. Göbel et al. [131] suggest that these differences in degradation behavior arise from different substrate dependencies. Sulfonamide degradation appeared to correlate with the ratio of substrate to sulfonamide concentrations in the influent. Trimethoprim and macrolide removal, however, depended on the ratio of substrate to sludge concentration. As the latter ratio decreases with increasing SRT, the resulting increase in the biodiversity of the active biomass leads to more effective transformation of these substances.

2.3.2.2. Sand Filtration. One tertiary treatment approach for secondary effluent is the use of granular media depth filters, which typically employ sand as the filtration medium. The application of this technology to secondary effluent aims to remove suspended solids and turbidity that persist after clarification. For these wastewater constituents, removal mechanisms are primarily physical in nature (e.g., straining). In addition to solids removal, PPCP decay can also occur in these systems through additional biological degradation that takes place within biofilms present on the filter media [143]. It is also possible for incidental removal of PPCPs via their association with solids that are retained during filtration, although this contribution is generally considered insignificant relative to biodegradation within the filter.

A handful of studies report influent concentrations of PPCPs, as well as the concentrations present in the tertiary effluent of sand filters [33, 36-38, 112]. Similar to observations with MBRs, examination of available data shows a slight increase in removal when sand filtration is used post-secondary treatment (Figure 2-8). Roughly 31% of all data from sand filters demonstrated PPCP removals greater than 1-$\log_{10}$ concentration unit (32 out of the 104 data points), only slightly greater than the value of 25% observed for conventional treatment. Furthermore, based upon percentile analysis (see Figure 2-4), half of all substances exhibit removal efficiencies greater than 69% when sand filtration is employed, compared to a median removal of 61% for CAS.

As PPCP removal by sand filters is largely, if not entirely, attributable to biological activity, it is difficult to predict from structural and physical properties those PPCPs most amenable to treatment during filtration. Furthermore, there is no consensus as to the influence of operational variables such as hydraulic residence time, hydraulic loading rate, as well as bulk water quality characteristics, on the removal of PPCPs during filtration. For example, Göbel et al. [131] observed considerable differences in the extent of trimethoprim removal (15% versus 74%) in two sand filters despite comparable hydraulic retention times and hydraulic loading rates per biofilm surface area in each case. They attributed this behavior to differences in the BOD loads to each unit (i.e., higher removal occurred with lower background BOD levels). However, evidence suggests that trends in the relative treatability of PPCPs during sand filtration can likely be predicted from the larger body of empirical results available for alternative forms of biological treatment. For example, Nakada et al. [112] considered the removal of 24 different PPCPs during sand filtration. Although they attempted to rationalize their observed removal efficiencies based solely upon sorption tendencies (i.e., correlation to K_{ow} values), a closer analysis reveals that the highest removal efficiencies were obtained for compounds we previously identified (see Table 2-1) as highly susceptible to degradation during CAS (e.g., ibuprofen, estrone, thymol and bisphenol A). Similarly, Göbel et al. [131] noted that the subset of PPCPs eliminated to the greatest extent during sand filtration in their study agreed well with those compounds demonstrating increased elimination within MBRs. A noteworthy example from their study was trimethoprim;

available literature suggests it is only modestly transformed during traditional biological treatment, but its extent of removal can be enhanced not only using MBRs, but also via sand filtration (see appropriate data in Figure 2-7a).

2.3.2.3. Activated Carbon. Activated carbon (AC) in either powdered (PAC) or granular (GAC) form represents the most widely used sorbent in water treatment, traditionally used for the removal of taste and odor causing organic compounds in drinking water [144]. In this capacity, AC is also a recognized route for the sequestration of organic micropollutants, and growing evidence suggests it is effective at removing PPCPs in drinking water. Ternes et al. [145] were among the first to demonstrate that GAC exhibits high affinity for several commonly encountered PPCPs in drinking water including bezafibrate, clofibric acid, carbamazepine, and diclofenac, while the majority of subsequent work has focused on identifying additional compounds or compound classes likely to be removed by GAC during water treatment (e.g., Westerhoff et al. [47]).

Removal of PPCPs by AC is driven by sorption, which encompasses the uptake of a compound onto the surface (i.e., adsorption) or into the porous bulk matrix (i.e., absorption) of activated carbon. Accordingly, PPCP removal with AC depends on properties both of the sorbent (i.e., AC) and the target solute (i.e., the PPCP). Characteristics of the AC believed important for performance include surface area, porosity and pore size distribution, and surface acidity or basicity, which will affect the slurry pH and surface charge [47, 146]. For PPCPs, sorption on AC is driven by hydrophobic, or organic-organic, interactions. Thus, compound hydrophobicity, typically quantified in terms of octanol-water partitioning coefficients ($\log K_{\mathrm{ow}}$ values), is often looked to as a predictor of PPCP removal via AC, although other solute characteristics including molecular size (e.g., molar volume), hydrophobic surface area, charge and polarity are also believed to influence sorption to some extent [47, 146].

Based largely upon promising results from drinking water treatment, it is assumed that the use of AC will yield significant benefits in wastewater effluent quality [36].

However, there are few, if any, available data regarding PPCP removal at pilot or full-scale wastewater treatment facilities incorporating AC. Furthermore, given the greater complexity of the wastewater matrix, it is difficult to predict PPCP removal efficiencies from the results of studies focused on drinking water treatment. Specifically, high levels of effluent organic matter (EfOM) in wastewater can be expected to limit AC performance. EfOM will compete for sorption sites on the AC surface and block access to pores within the bulk sorbent structure [36], behavior that has been shown to diminish AC performance toward PPCPs during drinking water treatment [145].

Because influent-effluent data for wastewater treatment facilities using AC do not yet exist, we cannot compare PPCP removal with AC to other treatment technologies. However, to provide some measure of full-scale AC performance, Figure 2-9 presents recent results from a full-scale GAC test facility treating drinking water with relatively high levels of total organic carbon (TOC) [36]. Although obtained at a water treatment facility, PPCP removals from this high TOC facility may provide a reasonable estimate of AC performance during wastewater treatment.

PPCP removal with GAC at this full-scale facility was generally weak, as effluent concentrations largely scaled with plant influent concentrations. Only acetaminophen exhibited greater than 1-$\log_{10}$ removal, although a few others (e.g., hydrocodone, diclofenac and pentoxifylline) were removed to levels below the effluent MDL. Notably, the authors reported considerably better PPCP removal at another full-scale facility in which the source water exhibited lower levels of TOC and the GAC was more frequently regenerated and replaced. For wastewater treatment, therefore, pretreatment to lower TOC and the rate of AC regeneration or replacement will likely be key design criteria [36]. In particular, fresh AC is known to outperform aged material due to the accumulation of TOC and other non-target species on the sorbent surface [145, 147]. Such considerations may make PAC a more attractive option for wastewater treatment. Fresh PAC can be added continuously to the process stream, is not recycled during the treatment process, and its dose can be controlled to account for variations in influent quality [36].

Finally, a potentially useful variation on AC treatment is biological activated carbon (BAC). In addition to PPCP removal via sorption on activated carbon, BAC also allows for biodegradation of organic pollutants due to biofilm formation on the sorbent material. The potential benefits of BAC are great, including biological regeneration of the AC as sorbed organic matter is degraded over the operating life of the reactor, biodegradation of less biodegradable organics, which can be initially sequestered on the AC and then degraded by microbes in the biofilm, and enhanced biological activity due to the concentration of organic substrate on the AC surface [148]. There are multiple instances of BAC application during wastewater treatment [37, 149, 150], and it is viewed by some as a "core process" for water reuse and reclamation [149, 150]. Data also in Figure 2-9 show that full-scale treatment of wastewater incorporating BAC as tertiary treatment [37] displayed good removal for several PPCPs including atenolol, carbamazepine, diclofenac, fluoxetine, naproxen, triclosan and trimethoprim, all of which exhibited removal efficiencies greater than 97%. Other PPCPs including bisphenol A, meprobamate, dilantin, sulfamethoxazole were only partially removed by BAC, and more work is needed to understand the design and application factors governing PPCP removal in these systems. Nevertheless, early indications suggest that this approach is an improvement over simple GAC and PAC treatment due to the additional biotransformation reactions that can occur.

2.3.2.4. PPCP Transformation by Chlorine-based Disinfectants. PPCPs will be subject to various, oftentimes unintended, transformation reactions during disinfection of wastewater. Due to its relatively low cost, chlorine based disinfectants such as chlorine gas (Cl_2) and hypochlorous acid (HOCl) are among the most widely utilized disinfectants in wastewater treatment [151]. These are strong oxidizers, and thus, have the potential to react with electron rich (or reduced) functionalities present on PPCPs. Chlorine-based disinfectants should not be viewed as reagents of choice for chemical oxidation of PPCPs; ozonation or advanced oxidation processes are better suited for this purpose. However, the inevitable formation of unintended byproducts during disinfection of PPCP-containing waters mandates that their reaction with chlorine-based oxidants be understood. Here, we touch upon general principles governing PPCP transformation via reaction with common chlorine-based disinfectants. Because chlorine should not be viewed as a viable treatment option for PPCPs, no influent-effluent data or analysis of removal efficiencies are presented.

The reaction of PPCPs with free chlorine is dictated in large part by the acid-base character of hypochlorous acid (HOCl), which is estimated to be 40-80 times more potent as a disinfectant than its deprotonated form, hypochlorite ($^{-}$OCl) [126]. The acid dissociation constant for HOCl (or pK_a value) is 7.54 at 25 °C, which falls within the pH range relevant for wastewater. Thus, for most PPCPs, pH dependent reactivity toward free chlorine is observed, with faster rates and greater extents of PPCP transformation observed at pH values where HOCl is the dominant chemical form (e.g., Dodd and Huang [152], Pinkston and Sedlak [153]). The chemical nature of the PPCP also dictates its propensity to undergo reaction with free chlorine. In a recent review of chlorine reactivity toward organic compounds of relevance to water and wastewater treatment, second order rate constants for reactions with PPCP ranged over 10 orders of magnitude (from <0.1-10^9 $M^{-1}s^{-1}$) [151]. Common structural moieties most prone to HOCl attack include phenols [154-158], secondary amines [159-162], reduced sulfur functionalities, and activated aromatic systems [151], many of which are found on common PPCPs.

Pinkston and Sedlak [153] investigated the reaction of free chlorine with several PPCPs containing such functional groups. These included five analgesics (acetaminophen, ibuprofen, indometacine, ketoprofen, and naproxen), four blockers (atenolol, metoprolol, nadolol, and propranolol) and one cholesterol lowering compound (gemfibrozil). All compounds except ibuprofen and ketoprofen reacted readily with free chlorine in a manner consistent with established trends in chlorine chemistry. For example, HOCl reacted more readily with the deprotonated, phenolate anion of acetaminophen because of the increased electron density present on the aromatic ring. For PPCPs with aromatic ether moieties (e.g., gemfibrozil, indometacine, and naproxen), not only did the electron density from the ether group promote chlorine attack on the aromatic ring, but the rate of reaction was also impacted by the ability of additional ring substituents to donate (or withdraw) electron density. A more unique result was observed for beta blockers with secondary amine substituents (e.g., atenolol, metoprolol, and propranolol), which reacted rapidly with free chlorine to produce chlorinated amines. However, these chlorinated amines could be reversibly transformed back into the parent beta blocker in the presence of common dechlorinating agents in water and wastewater treatment (e.g., thiosulfate), illustrating some of the complex chemical processes impacting PPCP fate that can occur in the strongly oxidizing and reducing environments encountered during treatment.

When chlorine is used as a disinfectant for wastewater with nitrogen containing organics or ammonia, free chlorine will be transformed to chloramines (e.g., monochloramine (NH_2Cl) and dichloramine ($NHCl_2$)), which are commonly referred to as combined chlorine. As a disinfectant, chloramines possess less oxidizing power than free chlorine [144]. Thus, in studies comparing their activity toward PPCPs, chloramines have been found to be less reactive than corresponding doses of free chlorine [153, 163]. This leads to slower rates of PPCP transformation and thus, a lesser degree of transformation product formation. However, one would also anticipate that products of reaction with combined chlorine would exhibit a lower degree of structural transformation, potentially allowing some biochemical activity of the PPCP to be retained after reaction with combine chlorine.

2.3.2.5. PPCP Transformation during Chemical Oxidation. There is rapidly growing interest in the application of chemical oxidation processes for the treatment of organic micropollutants in water and wastewater. This approach utilizes strong oxidants or oxidizing conditions to chemically transform PPCPs ideally into species lacking biological activity that pose no risk to the quality of effluent-receiving waters. Oxidants typically used for this purpose include ozone (O_3) as well as advanced oxidation processes (AOPs), which utilize hydroxyl radical ($^{\bullet}$OH).

Ozone has been used previously in water treatment as an alternative disinfectant to free chlorine. As with free chlorine, ozone reactivity toward PPCPs is dictated by its chemical character; it is a selective oxidant with electrophilic character that targets □ bond systems, non-protonated secondary and tertiary amines, and reduced sulfur moieties [164, 165]. Ozone, therefore, can be considered a relatively specific oxidant, preferentially reacting at functional groups on PPCPs with high electron density. In addition to the direct reactions between PPCPs and ozone, indirect oxidation can also occur during ozonation due to transient oxidants generated from ozone decomposition. In water, ozone decays through a series of radical chain reactions that ultimately yield $^{\bullet}$OH, one of the most powerful oxidants in water [164]. Unlike ozone, $^{\bullet}$OH is a non-specific oxidant capable of degrading a broader range of PPCPs and other organic micropollutants via radical addition, hydrogen abstraction or electron transfer mechanisms [126]. The non-specific nature of $^{\bullet}$OH is problematic for wastewater treatment, however, as EfOM and other non-target reductants present at much higher concentrations than PPCPs can scavenge most, if not all, $^{\bullet}$OH generated from ozone.

Encouraged by early results demonstrating PPCP transformation by ozone under conditions representative of water treatment [47, 166-168], attention has focused more recently on the treatment efficiency of ozone for PPCPs in wastewater [37, 40, 49, 112, 117]. Huber et al. [40] conducted a pilot scale investigation in which ozone was applied to secondary effluents from a CAS system and a MBR that they spiked with a range of PPCPs. Their results showed nearly complete degradation of macrolides, estrogens, and sulfonamides due to transformation of their tertiary amino groups, phenolic moieties and aniline moieties, respectively. Diclofenac, naproxen and indomethacin were also nearly entirely transformed at ozone doses (≥ 2 mg O_3/L) that the authors deemed cost-effective for wastewater treatment. Although they found very little variability in ozone performance among the different secondary effluents and total suspended solids (TSS) loadings tested, certain PPCPs were found to be relatively resistant to ozonation. Iodinated X-ray contrast media, which do not react directly with ozone, were only partially oxidized through reaction with $^{\bullet}$OH generated from ozone decay. While the removal of iopamidol, iopromide and iomeprol increased with increasing ozone dose, only 50-60% removal was observed at the highest ozone concentrations investigated (5 mg/L). Diatriozate, an anionic contrast agent, was most resistant and no statistically significant removal was found at any ozone dose. It is worth noting that the resistance of iopromide to ozonation has also been noted in studies focusing on simulated drinking water treatment [37, 47], suggesting that relative trends in PPCP activity toward ozone established for drinking water can be used to predict their susceptibility during ozonation of wastewater.

Snyder et al. [37] conducted bench-scale investigations of PPCP ozonation in surface water and wastewater matrices. For wastewater, their bench-top pilot plant utilized non-disinfected tertiary (filtered) effluent that contained PPCPs at naturally occurring levels. They also presented influent and effluent PPCP concentrations from one full-scale wastewater treatment facility utilizing ozone as a disinfectant. Generally, their results were in relatively good agreement with Huber et al. [40]. In bench scale studies with tertiary effluent and ozone doses ranging between 2.1 and 8.7 mg/L (which yielded ozone residuals required for disinfection), removal of most PPCPs was greater than >90%. Moreover, bioassays revealed that the estrogenicity of the treated effluent was reduced relative to that measured before ozonation, consistent with findings of Huber et al. [169] and Dodd et al. [170, 171], which have also found that ozonation diminishes the biochemical activity of many PPCPs. As was also observed in their drinking water studies, iopromide, musk ketone, dilantin (phenytoin) and meprobamate were most recalcitrant to ozonation, each undergoing only partial (~50% or less) removal. Studies with drinking water also revealed ibuprofen only undergoes partial oxidation, but this would not be important for wastewater treatment given the proficiency of secondary treatment to considerably degrade ibuprofen. Results from their bench scale studies also agreed with the measured performance of the full-scale wastewater treatment facility using ozonation. The facility used post-secondary treatment with ultrafiltration, pre-oxidation with a small ozone dose, a biological activated carbon (BAC) filter, and then disinfection and chemical oxidation with ozone. The use of this process train resulted in near complete removal for 8 of the 15 micropollutants considered in the plant's secondary effluent; for these 8 species, final concentrations were below the effluent MDL (typically less than 0.5 ng/L).

More recent examples of full-scale wastewater ozonation continue to demonstrate promising results for PPCP removal via ozonation relative to conventional wastewater treatment (Figure 2-10). Figure 2-10 compares influent and effluent PPCP concentrations at sites utilizing full-scale wastewater ozonation to concentration data obtained at facilities only employing conventional treatment practices. The data in Figure 2-10 are taken from the aforementioned work by Snyder et al. [37], as well as recent investigations by Nakada et al. [112] and Hollender et al. [117]. Nakada et al. [112] explored the removal efficiencies of 24 PPCPs via post secondary treatment with sand filtration and ozonation at a municipal sewage treatment facility in Tokyo. Hollender et al. [117] considered the fate of 220 micropollutants in a wastewater treatment facility Regensdorf, Switzerland that employed activated sludge. We also note that plant influent data were not reported in Snyder et al. [37], thus ozonated effluent concentrations are compared to values measured in secondary effluent prior to any tertiary treatment processes.

Similar to Snyder et al. [37], full-scale ozonation demonstrations by Nakada et al. [112] and Hollender et al. [117] report considerably enhanced PPCP removal, and far lower PPCP effluent concentrations than that attainable with secondary treatment alone. This improved removal is shown in Figure 2-10, with 58% of all data (50 out of 86) corresponding to removals of greater than 1-$\log_{10}$ concentration unit. Furthermore, percentile analysis (Figure 2-4) reveals that half of all effluent data points achieved removals greater than 94%, while 90% of all data correspond to removal efficiencies of 54% or higher. Most importantly, several compounds traditionally resistant or only partially transformed during biological treatment are amenable to treatment via ozonation. These include carbamazepine (see relevant data in Figure 2-6), as well as several compounds within the classes of beta blockers and anti-inflammatory drugs (Figure 2-11). These results constitute a clear improvement in PPCP removal over facilities employing only secondary treatment, and illustrate that ozonation will be a valuable treatment tool in the event toxicological evidence ultimately supports that such low effluent levels be mandated by regulation.

For wastewater treatment, ongoing efforts aim to better understand the influence of common aquatic chemical variables on ozone performance, as well as the relative importance of O_3 and $^\bullet OH$ as active oxidants during ozonation. Immediately after addition, ozone undergoes an initially rapid decomposition due to reaction with wastewater constituents such as EfOM or oxidizable species including nitrite and reduced forms of sulfur. This initial decay from reaction with the wastewater matrix is referred to as instantaneous ozone demand (IOD), and can critically influence the efficiency by of PPCP removal. Early work by Buffle et al. [172] suggested that this rapid decay of ozone coincided with an increase in $^\bullet OH$ to exposure levels typically found in AOPs. Although ozone is consumed, this would be beneficial for treatment because of the potency and non-specificity of $^\bullet OH$. Similarly, Nothe et al. [173] recently also provided evidence to suggest that ozonation can produce new sites for $^\bullet OH$ production on EfOM. However, conflicting results were found by Wert et al. [174], who examined the effect of effluent organic matter (EfOM), nitrite and alkalinity on ozone fate and reactivity toward 31 micropollutants. Unlike Buffle et al. [172] and Nothe et al. [173], Wert et al. [174] found that there is relatively limited $^{\bullet}OH$ available for contaminant destruction during initial stages of ozone decomposition (defined as less than 30 sec after addition). Thus, it appears that the relative ozone and $^{\bullet}OH$ exposure will be highly dependent upon the water matrix. One approach to overcome IOD is to use higher ozone doses during treatment. Based upon kinetic modeling, Nothe et al. [173] suggest that 5-10 mg/L of ozone would degrade even the most resistant micropollutants regardless of EfOM levels. Such doses would, however, increase the cost of treatment while also raising concerns over byproducts generated at such high concentrations.

2.3.2.6. PPCP Transformation during Advanced Oxidation Processes. Advanced oxidation processes (AOPs) encompass treatment technologies that rely on the production of $^{\bullet}OH$ or other radicals, which act as strong oxidants capable of degrading recalcitrant compounds. Many different AOP technologies for radical production exist, including heterogeneous photocatalysis using TiO_2 in combination with UV light or solar irradiation, Fenton's and photo-Fenton's reagent, ozone in combination with peroxide (H_2O_2) or UV light, UV light in combination with H_2O_2, electrolysis, sonolysis, ionizing radiation, ferrate reagent and others. The majority of research relating to PPCP degradation by AOPs has focused on heterogeneous photocatalysis, ozone-based AOPs and (photo-)Fenton's reagent [175]. However, studies investigating other technologies are currently emerging. Most to date have focused on PPCP removal from laboratory solutions or surface waters, while investigations using wastewater remain scarce. Of 80 recently reviewed papers addressing the removal of PPCPs by AOPs [175], only seven used WWTP effluents as the matrix. Of those studies, four were conducted in pilot- or full-scale systems, whereas the others were performed at a laboratory scale. As a result of this scarcity of wastewater data, we did not include AOPs in our influent-effluent analyses comparing unit operation performance.

While often viewed as a promising treatment approach, the advantages of AOPs over conventional chemical oxidation methods (e.g., chlorination and ozonation) remain unclear. In a study involving a wastewater matrix and 36 PPCPs and other micropollutants, Snyder et al. [37] determined that advanced wastewater treatment by O_3/H_2O_2 only marginally improved PPCP removal relative to treatment with O_3 alone. Similarly, Ternes et al. [49] showed that AOPs applied to wastewater (O_3/H_2O_2 and UV/H_2O_2) did not enhance the removal of iodinated X-ray contrast media, which are quite recalcitrant to O_3.These findings are in contrast to those obtained for AOP application to distilled or surface waters matrices. For example, Zwiener and Frimmel [176] reported a greater removal of clofibric acid, diclofenac and ibuprofen from distilled and surface water by AOP (O_3/H_2O_2) compared to O_3 alone. Similarly, Rosenfeldt and Linden [177] showed an enhanced removal of endocrine disruptors by H_2O_2/UV compared to UV alone in actual and simulated natural water. The comparison of these examples illustrates that AOP results obtained in waters with low organic matter content cannot be directly transferred to wastewater applications due to organic matter's role as a radical scavenger.

Notably, different AOP technologies can yield different degradation pathways for the same compounds. In a pilot-scale study of the removal of diclofenac by photo-Fenton's reagent using a compound parabolic collector (CPC) exposed to sunlight, complete oxidation was attained within 60 minutes, and complete mineralization in 100 min [178]. Comparison with other oxidative treatments, namely O_3, UV/H_2O_2 and photolysis, showed that degradation pathways differed between systems. Similarly, Radjenovic [179] found similar, but not identical pathways for the degradation of atenolol by heterogeneous photocatalayis and homogeneous photo-Fenton treatment in the same CPC setup. Furthermore, the photo-Fenton process was found to be more effective for PPCP removal compared to heterogeneous photocatalysis [179, 180]. Thus, not only PPCP degradation kinetics but also PPCP transformation pathways will need to be evaluated for AOPs when considering their application to wastewater. While AOPs can reduce the estrogenicity [85] and antimicrobial activity [171] of PPCPs, metabolites may exhibit other toxicity mechanisms. For example, the toxicity of wastewater effluent, measured by three bioassays (*Daphnia magna, Pseudokirchneriella subcapitata* and *Lepidium sativum*), was not fully eliminated upon treatment by heterogeneous photocatalysis using TiO_2 [181].

2.3.2.7. PPCP Photochemical Transformation during UV Disinfection: During disinfection with high energy UV light, PPCP degradation can occur via direct photolysis. For such a scenario, the PPCP must be a chromophore (i.e., be capable of absorbing light energy) and the energy of light must be sufficient to result in breaking of chemical bonds in the PPCP structure. To date, there are no data available on the transformation of PPCPs in wastewater as a result of UV radiation. Although some work has been conducted in systems representative of water treatment, less PPCP removal would be expected in a more complex wastewater matrix, which will include higher levels of organic matter and other light scattering and absorbing constituents.

In one of the most detailed water treatment studies to date, Canonica et al. [182] considered the UV-induced phototransformation of 17α-ethinyl estradiol, diclofenac, sulfamethoxazole and iopromide. In dilute solutions of buffered water at pH 7.0, only modest removals (0.4-27%) were observed at a fluence of 400 J/m^2, a standard value for drinking water disinfection using UV. Rosenfeldt et al. [177] also conducted work examining the transformation of endocrine disrupting compounds (bisphenol A, 17α-ethinyl estradiol, and 17β-estradiol) upon exposure to UV radiation from either a monochromatic low pressure UV lamp or a polychromatic medium pressure UV lamp. As in the study by Canonica et al.[182], experiments were conducted in model laboratory systems or with samples of natural surface waters and limited (<20%) removal was observed due to direct phototransformation.

2.3.2.8. PPCP Removal using Membrane Filtration. Membrane technologies for the removal of pathogens, micropollutants and salts have gained importance in drinking water production over the past decades. More recently, this technology has also attracted interest as a method to achieve better PPCP removal from wastewater, particularly in instances of wastewater reclamation and reuse. Membrane application to full-scale or even pilot-scale wastewater treatment systems is still somewhat rare, but there is an increasing body of literature reporting on this topic.

In contrast to MBRs, where the function of membranes is predominantly the retention of sludge for biodegradation, membrane technologies function by rejecting constituents due to pore size restrictions or electrostatic repulsion. Adsorption onto the membrane also can contribute to compound rejection, in particular for neutral and hydrophobic substances [183]. Membranes are categorized as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) or microfiltration (MF) membranes, depending on their molecular weight cut-off (MWCO). Different membrane types are typically installed in series, with low-pressure membranes (MF or UF, alone or as MBR) providing pre-treatment, and one or more units of tighter, high-pressure membranes (RO or NF) for micropollutant removal. Based on the typical size of PPCPs, only RO and NF membranes are suited for PPCP removal by purely a size exclusion mechanism. However, if electrostatic repulsion or adsorption contributes or is the dominant mechanism, membranes with pores larger than the compound of interest have been found to lead to PPCP retention [184]. Kimura et al. [185] reported that negatively charged disinfection byproducts, PPCPs and endocrine disrupting compounds in Milli-Q water were rejected by RO/NF membranes independent of their molecular size. Conversely, RO membranes have also been found to retain compounds to a lesser degree than expected based on their molecular size. This was the case for the hormones estrone and estradiol [186], as well as for two trihalomethanes [187] in actual and simulated wastewater. This membrane breaching was attributed to cross-membrane diffusion of the compounds over longer operation times.

The efficiency of PPCP removal by membrane technology depends on a multitude of parameters. Besides MWCO, membrane material properties such as hydrophobicity, surface roughness, and charge will affect PPCP removal [188]. In addition, depending on the retention mechanism, different physical-chemical parameters of the individual substances can influence their retention. Critical parameters include the molecular weight and size, acid dissociation constant (pK_a), octanol-water partitioning coefficient (K_{ow}), polarity and aqueous diffusion coefficient [184, 188]. For example, the retention of antibiotics from the wastewater of a veterinary antibiotic production plant by RO/NF was a function of the molecular weight of the individual compounds [189]. Similarly, the retention of 11 neutral endocrine disruptors and PPCPs in distilled water by a polyamide RO membrane was correlated to the molecular weight of the individual compounds [190]. The retention mechanism in both cases was therefore attributed to size exclusion. In contrast, the retention of the same 11 compounds by cellulose acetate membranes increased with increasing polarity of the compound, indicating that mechanisms other than size exclusion influenced retention [190].

The composition of the feed water, in particular the organic matter content, water hardness and pH, also influence retention efficiency [188]. As with chemical oxidation strategies, the high EfOM content in wastewater represents an important distinction between membrane treatment for drinking water and wastewater. The effect of EfOM on PPCP rejection precludes simple extrapolation from drinking water to wastewater applications. The effect of membrane fouling by EfOM on wastewater treatment efficiency therefore warrants further investigation. Generally, EfOM has been found to exert a retention enhancing effect on the removal of charged compounds by various NF and RO membranes [186, 187, 191, 192]. This effect was attributed either to modification of the membrane surface charge [187, 191, 192], to interactions of the EfOM with the compounds [186, 192], or to restriction of the pore size in the case of loose membranes [191]. If adsorption to the membrane is the main rejection mechanism, however, the presence of EfOM may be detrimental. For example, Comerton et al. [193] reported that the rejection of the hydrophobic compound gemfibrozil decreased in the presence of EfOM, which was attributed to competition for adsorption sites.

Finally, operational conditions such as the transmembrane pressure [186] and the permeate flux rate [183] can affect PPCP retention. The importance of taking into account actual operational conditions including flux, recovery and membrane fouling in laboratory-scale experiments was stressed by Drewes et al. [187], who found that laboratory experiments underestimate contaminant removal compared to full-scale systems.

In a recent, extensive series of full- and pilot-scale investigations of wastewater treatment via different membrane types, makes and configurations, Snyder et al. [36] concluded that UF and MF were only effective for steroid removal, unless used in an MBR configuration, and that generally, MF outperformed UF. UF was also found to have limited impact on PPCP removal in an earlier work by this group [37]. Data from these studies pertaining to influent PPCP levels and their corresponding MF and UF effluent concentrations are summarized in Figure 2-12a and 2-12b**,** respectively. We note that influent data for UF studies correspond to PPCP levels reported in secondary effluent as levels in raw influent were not available. These figures clearly illustrate the relatively modest increase in effluent quality afforded by MF and UF relative to conventional treatment practices for wastewater. Removal of 1-$\log_{10}$ concentration unit is only observed for 64% (16 out of 25) of available MF data, whereas only 9% of UF data (4 out of 44) correspond to removal greater than1-$\log_{10}$ concentration unit.

In contrast, Snyder and colleagues [36, 43] report that wastewater treatment trains utilizing NF and RO, as well as an appropriate sequence of techniques to improve secondary effluent quality to a level suitable for membrane separations, achieve the best removal efficiencies for PPCPs. NF and RO effluent data from Snyder et al. [36] and Kim et al. [43] are summarized in Figures 12c and 12d, respectively, illustrating the significant PPCP removal exhibited by NF and RO for the vast majority of compounds. For example, roughly 90% of all RO effluent data correspond to PPCP levels below the method detection limit for analysis, which was typically on the order of 1-5 ng/L (data points indicated in Figure 2-12d by a center dot). Comparable results were reported for NF; all NF effluent levels corresponded to removal greater than 1-$\log_{10}$ concentration unit (16 out 16) and all but one compound (TCEP) being removed to levels below analytical MDLs.

Not surprisingly, PPCP removals in these systems are far superior than can be achieved in treatment trains utilizing other tertiary unit operations considered in this review. While we had insufficient data for NF and MF to conduct a comparison of percentiles, analysis of the available UF data showed that this membrane provides little, if any benefit, over secondary treatment (see Figure 2-4). RO, in contrast, exhibited a very high PPCP removal. Half of all compounds were removed to 98% or more, whereas only about 10% of all investigated substances were removed by less than 85% (see Figure 2-4). Notably, the list of PPCPs rejected by RO includes carbamazepine (see relevant data in Figure 2-6), which is notoriously difficult to remove by secondary treatment. RO is also among the most effective treatment approaches for iodinated contrast media (Figure 2-13), which as a class are recalcitrant to biological treatment and only partially degraded via chemical oxidation methods. A small subset of compounds, however, were occasionally detected in the RO permeate. The breakthrough of these substances cannot be rationalized by any common physical-chemical properties. However, membrane breaching frequently was reported for DEET, meprobamate, gemfibrozil and sulfamethoxazole, all of which were relatively poorly removed during the treatment steps preceding RO (MBR, UF or MF [36]), and were thus present at elevated concentrations in the RO feed. If a RO double-pass was installed, however, these remaining micropollutant traces could be fully removed during the second pass.

Several aspects of membrane treatment of wastewater have not conclusively been addressed to date. In a recent overview of the advantages and drawbacks of NF, van der Bruggen et al. [194] identified six key parameters that warrant further investigation. These include membrane fouling, better separation of solutes, treatment of concentrates, chemical resistance and lifetime of membranes, insufficient rejection of pollutants and the need of modeling and simulation tools. First steps toward resolving this last aspect, the development of simulation tools, have been attempted by Kim et al.[43]. They constructed a transport /rejection model for neutral and charged compounds, based on membrane properties, which differentiated between convective and diffusive contaminant transport through the membranes. As the authors point out, however, their model lacks predictive capabilities, and thus needs further improvement.

2.3.2.9. Passive Effluent Treatment Technologies: Soil Aquifer Treatment, Wetlands, and Treatment Lagoons. There is growing interesting in passive tertiary treatment techniques that utilize attenuation processes in natural systems to treat wastewater effluent as a final polishing step. These include soil aquifer treatment, engineered wetlands, and treatment lagoons. Unlike most oxidative or separative tertiary treatment options, these approaches hold the advantage of operating at low energy and cost, and do not require sludge or brine removal.

During aquifer recharge with reclaimed water, soil aquifer treatment (SAT) represents a sustainable strategy that can mitigate potential risks associated with persistent chemicals including PPCPs encountered in treated wastewater effluent [195]. SAT takes advantage of natural subsurface processes that occur primarily in the vadose or unsaturated zone to treat reclaimed water that is subsequently stored in the aquifer, and eventually extracted for municipal use [196] (i.e., managed underground storage and recovery operations [197]). Most often, recharge projects utilize rapid infiltration ponds (or surface spreading basins) built on permeable sediments to introduce treated effluent into aquifers, a process characterized by fluctuating organic matter concentrations and variable redox potentials arising from the repeated wetting and drying cycles associated with multiple recharge events [198].

The fate of effluent-derived PPCPs during SAT has been studied either using bench-scale column studies constructed from aquifer materials or via field-scale monitoring to track the fate of effluent-derived PPCPs at sites utilizing treated effluent for recharge [196, 199-205]. These studies have generally revealed that a wide variety of hormones and prescription drugs can be further degraded during SAT including anti-inflammatories, analgesics, steroids and some endocrine disruptors [199, 200, 203, 204], with biotransformation representing the most important attenuation processes for these species [106, 199, 204, 205]. Certain compounds, particularly those that are most resistant to biological degradation, are recalcitrant, however. For example, effluent-derived carbamazepine and primidone were reported to persist in the subsurface at reuse facilities for as long as 6 to 8 years [199, 200].

PPCP removal in wetlands and lagoons can occur by multiple mechanisms, including adsorption onto the wetland matrix, aerobic and anaerobic biodegradation, and photodegradation in the case of surface flow wetlands and lagoons. Wetlands and lagoons typically have longer HRTs than conventional treatment systems. This restricts their use to situations where a large footprint can be accommodated, or where the wastewater volume is small.

While nutrient removal in wetlands has been extensively investigated, information regarding the degradation of PPCPs has only recently started to emerge. In an early study, Gross et al. [206] investigated the fate of selected PPCPs and other wastewater-derived contaminants during river transport and subsequent passage through a constructed wetland with a residence time of 2-4 days. They reported a significant removal of gemfibrozil, ibuprofen and its metabolite hydroxyibuprofen in the wetland, although this effect was small compared to attenuation during river transport. Matamoros and co-workers [207-212] have extensively investigated the fate of PPCPs in wetlands of different configurations. In a performance comparison of two planted subsurface horizontal flow constructed wetlands with different water depths, they found that PPCP removal was better in the shallow wetland, which was a less anaerobic environment and therefore had a less negative redox potential [210, 211]. Of the PPCPs tested in these two studies, salicylic acid and carboxy-ibuprofene were removed at >80%, ibuprofen, hydroxyl-ibuprofen and naproxen at 50-80%, carbamazepine at < 50 %, and clofibric acid, ketoprofen and diclofenac were recalcitrant. Degradable PPCPs were removed by biodegradation, whereas musks were removed by adsorption onto the gravel bed. In a subsequent study, Matamoros et al. [208] compared PPCP removal in pilot-scale vertical subsurface flow constructed wetlands (VFCW) to sand filters. They found that both systems operated well at the design loading rate, but that the VFCWs maintained higher removal rates during overload conditions. Furthermore, the vegetation present in the VFCWs helped to prevent clogging. Finally, operation under unsaturated flow conditions achieved better removals than saturated flow conditions. Most recently, these authors compared the removal of 13 substances from secondary wastewater in different household-scale systems including five horizontal-flow constructed wetlands, four vertical flow constructed wetlands, sand filters and biofilters [209]. It was found that removal in all systems was > 80 %, except for the more recalcitrant compounds carbamazepine, diclofenac and ketoprofen. However, the vegetated, vertical-flow wetlands consistently performed better than the other systems. This was attributed to the unsaturated flow and presence of vegetation, which result in better oxygenation compared to the horizontal wetlands. As a summary of their work, the authors thus far advocate planted VFCWs as an appropriate treatment option because it required lower HRTs and achieved better removal than horizontal flow configurations.

Similar to wetlands, PPCP removal in lagoons has not received much attention to date. From one of the few studies published on this topic, it appears that lagoons perform as well as CAS treatment systems for the degradation of biodegradable compounds [105]. For more recalcitrant compounds, however, lagoons have been found to outperform CAS systems. This was the case for gemfibrozil and diclofenac removal in three Canadian lagoons treating municipal wastewater [105], as well as for carbamazepine removal in French treatment plants consisting of trickling filters followed by ponds, or of a sequence of ponds alone [132] . In the latter case, the enhanced removal of carbamazepine compared to CAS systems was attributed to adsorption onto organic matter as well as photodegradation in the maturation ponds.

The efficiency of PPCP removal in a combined lagoon/wetland treatment was investigated by Conkle et al. [213], who studied the fate of PPCPs in wastewater that first entered a series of aeration lagoons, followed by a constructed wetland, UV disinfection, and finally a natural wetland. Of the nine PPCPs followed throughout this treatment, most were removed to greater than 1-$\log_{10}$ concentration unit. The two most recalcitrant compounds, carbamazepine and sotalolol, were removed to a lesser extent (52 and 81%, respectively). Overall, the authors concluded that this natural treatment setup performed better than conventional wastewater treatments with respect to PPCP removal, behavior that was attributed to the long residence time of the system (~30 days). Similar conclusions were presented by Hijosa-Valsero et al. [207], who monitored the removal of selected PPCPs from primary treated municipal wastewater in three full-scale hybrid systems consisting of different arrangements of ponds, surface and subsurface wetlands in series. The observed removal efficiencies were compared to those obtained in a conventional WWTP. Removal in the passive systems mostly outcompeted that observed for at a conventional WWTP. Interestingly, the recalcitrant compound diclofenac, which was not removed in the WWTP, was degraded by 65-87% in the passive systems. The improved removal efficiency in passive systems was attributed to the coexistence of different microenvironments, which leads to a variety of parallel metabolic pathways for PPCP degradation. In WWTPs, in contrast, the physicochemical conditions tend to be more homogenous, limiting the number of degradation pathways that exist.

A compilation of influent and effluent data from studies documenting PPCP removal in lagoon and wetland treatment systems [93, 207, 209, 212-214] confirms that such passive or natural treatment approaches perform favorably relative to conventional wastewater treatment systems (Figure 2-14). Using the removal of one-$\log_{10}$ concentration unit as a basis for performance comparison, 48% of available data (38 out of 79) achieve this threshold for treatment facilities utilizing lagoons and/or wetlands (natural or constructed). Furthermore, percentile analysis indicates that these treatment methods achieved PPCP removal on par to ozonation (see Figure 2-4). In fact, 90% of PPCPs treated at facilities using lagoons and/or wetlands obtained removal of at least 43%, performance that is an improvement over facilities using either CAS or MBR for biological treatment. While promising for PPCP treatment, additional research and full-scale performance data are needed to further validate the performance of these natural or passive treatment methods. Further, the advantages of lower energy requirement and operating costs conferred by these approaches must be weighed against the requirement of a considerably larger spatial footprint.

2.4 Predicting and Minimizing PPCP Occurrence in Wastewater Effluents

2.4.1. Recommendations for Optimizing PPCP Removal. In choosing between possible biological treatment options (e.g., CAS, MBR, etc.) to optimize PPCP removal, it is generally observed in Figures 1 and 2 that removal by CAS only exceeds 1-$\log_{10}$ concentration unit (or 90%) for a relatively small subset of PPCPs (Table 2-1). Interestingly, existing influent and effluent data indicate that for conventional biological treatment, PPCP removal appears relatively invariant with respect to microbial community composition, as well as the HRT and SRT conditions applied. We therefore conclude that the maximum removal potential by conventional biological treatment likely cannot be expanded much beyond current performance through simple manipulation of process operating conditions. Rather, it appears that improvements in biological treatment can only be achieved by upgrading to a more advanced technology such as MBRs, although increases in PPCP removal may only be marginal at best (see Figure 2-4). Based upon published reports, perhaps the best approach for targeting PPCPs are tertiary treatment technologies applied to secondary effluent that combine biodegradation with another route for compound degradation or sequestration. Although data are limited, promising approaches for improving effluent PPCP levels include biological activated carbon (BAC), which couples biodegradation and sorption, or natural/constructed wetlands, in which a multitude of PPCP removal mechanisms can occur in parallel.

Rather than choosing a tertiary technique that utilizes additional biological processing, PPCP removal also can be augmented by combining conventional biological treatment with abiotic treatment approaches. While the level of PPCP removal afforded by membrane technologies may be most appropriate when high quality effluent is desired (e.g., indirect or direct potable reuse), ozonation may be more broadly applicable for WWTPs simply trying to lower effluent PPCP loads because it can be directly applied to secondary effluent [117] without the extensive pretreatment required for NF or RO. Evidence also suggests that other chemical oxidation approaches including AOPs hold limited, if any, real advantage over ozonation [37].

Notably, there may be additional benefits for the sequential application of ozone and BAC to secondary effluent. During their full-scale evaluation of wastewater ozonation, Hollender et al. [117] recommended the use of a biological sand filter post-ozonation to remove byproducts of oxidation including nitrososdimethylamine (NDMA) and biologically assimilable carbon such as aldehydes. Treatment of ozonation effluent with BAC should provide comparable, if not greater, benefit due to the nature of the activated carbon sorbent used as the filter media. We caution, however, that these recommendations are based entirely on lowering PPCP effluent concentrations and do not fully consider the economic impact of increased reliance on advanced treatment technologies, which is discussed in greater detail subsequently.

2.4.2. Predicting PPCP Removal Efficiency and Occurrence in Treated Effluent. In addition to identifying optimal treatment scenarios for minimizing PPCP occurrence in effluent, it would also be beneficial to develop predictive models that reliably estimate PPCP persistence during wastewater treatment as a function of the compound's physical and chemical properties. The use of structure-activity relationships as predictive models have been developed with varying degrees of success for specific water treatment technologies targeting PPCPs [43, 47, 115, 146, 215]. Unfortunately, to date no single approach has emerged that accurately predicts PPCP removal during wastewater treatment over a wide range of treatment technologies, water quality conditions, and PPCP compounds and compound classes.

Predictions of PPCP persistence in effluent will likely have to be based on experimentally gathered evidence rather than simple physical and chemical principles governing their fate during treatment. For example, several substances are almost universally shown to persist during conventional wastewater treatment. From our literature survey, PPCPs for which a removal of less than 30% has been repeatedly reported include carbamazepine (n_{total} = 48; 74% of which report < 30% removal), diclofenac (35; 56%), metoprolol (9; 78%), sotalol (6, 100%), erythromycin (8, 50%) and clofibric acid (6, 67%). Our analysis is corroborated by others; carbamazepine and diclofenac have been found in > 90% and > 80%, respectively, of surveyed river water samples in Europe [216]. Glassmeyer et al. [217] detected carbamazepine in > 80% of samples in and around 10 WWTPs across the United States. Miege et al. [218], who conducted a similar review of PPCP occurrence in WWTPs, reported the presence of carbamazepine in all of 63 effluents considered, while diclofenac and metoprolol were also found with high regularity (85% and 97 % of effluents evaluated, respectively). It can thus be concluded that these compounds are among the PPCPs most resistant to biodegradation (Figure 2-15a). Moreover, any of these species could serve as a good indicator of wastewater inputs to surface water; they are consistently present in wastewater influent at concentrations well above MDLs, are recalcitrant to removal during conventional treatment, and their main environmental entry route is wastewater effluent.

Several methods have also been proposed utilizing the occurrence of select PPCPs with well-characterized behavior in WWTPs, referred to as indicator or marker compounds, to evaluate treatment system performance. As indicators of biodegradation-based treatment, two approaches have been proposed. Several authors suggest the use of enatiomeric ratios of substances such as naproxen [209] or propranolol [219] to determine the extent that a wastewater has undergone biological treatment. This method is based on the insight that microorganisms preferentially degrade one enantiomer in a racemic mixture, whereas dilution would affect both enantiomers equally. Other studies [217, 220] suggest monitoring the ratio of biodegradable PPCPs to recalcitrant species in wastewater effluent, a ratio that should decrease with increasing treatment efficiency. Based on the data compiled for this review, suitable choices for biodegradable compounds include acetaminophen, ibuprofen, thymol, aspirin or salicylic acid (Figure 2-15b and Table 2-1). Hormones such as estrone and estradiol could also be used, but their effluent concentrations are frequently below method detection limits. Among the most frequently detected, biologically recalcitrant compounds, we propose the use of diclofenac, erythromycin, and metoprolol (Figure 2-15a), as well as the class of iodinated X-ray contrast media (Figure 2-13).

WWTPs employing tertiary treatment may require a different set of indicators compounds. For example, biologically recalcitrant carbamazepine and diclofenac are readily degraded during ozonation, whereas several X-ray contrast media are not [117]. Using three sets of indicator compounds corresponding to (i) biodegradable PPCPs (Table 2-1, Figure 2-15b), (ii) biologically recalcitrant but oxidatively degradable PPCPs (e.g., carbamazepine and diclofenac), and (iii) generally recalcitrant compounds to both biodegradation and chemical oxidation (e.g., iopromide or other iodinated contrast media) can provide information not only about the overall treatment efficiency, but also regarding the treatment stage where failure occurs. This concept has been explored for ozonation of drinking water [18] and wastewater [221]. Dickenson et al. [221] recommended dilantin (phenytoin), DEET, meprobamate, and iopromide as indicators to assess optimized oxidation conditions during ozonation of tertiary treated wastewater for indirect potable reuse processes. These species represent those most resistant not only to biodegradation, but also to direct reaction with ozone. The detection of these compounds in the absence of PPCPs readily degradable by ozone (e.g., carbamazepine and diclofenac) would be indicative of an ozone system operating efficiently. Alternatively, the absence of these species after ozonation would indicate high exposure levels to $^{\bullet}OH$, and thus, be consistent with optimized chemical oxidation conditions that will degrade nearly all PPCPs. In contrast, identification of carbamazepine or diclofenac after ozonation would suggest inefficient oxidizing conditions.

We note that an alternative approach utilizing bulk water parameters as indicators for ozonation performance was explored by Wert et al. [222]. They suggested a simple method for monitoring PPCP removal that relies upon changes in UV_{254} absorbance and color of the wastewater upon ozonation. Oxidation of ozone-reactive compounds was found to correlate well with a reduction in UV_{254} absorbance between 0-50%, and PPCPs that react predominantly with hydroxyl radicals correlated well with a UV_{254} reduction of 15-65%. Similarly, the loss of true color also could be correlated with the extent of PPCP degradation during ozonation.

2.5 Current and Future Challenges Posed by PPCPs for Wastewater Management

Despite progress made in recent years toward better understanding of PPCP removal during water treatment, many challenges associated with PPCPs in wastewater remain. Here we introduce a selection of issues that will be critical for the development of reliable technologies for PPCP removal and sustainable practices for wastewater management. These include emerging methodologies for PPCP analysis and monitoring; byproducts generated during the transformation for PPCPs during wastewater treatment; and potential challenges associated with an increased reliance and the widespread application of advanced treatment technologies that have proven thus far to be best suited for PPCP removal. We do not address the pressing need for ecotoxicological data that convincingly demonstrates the adverse impacts associated with exposure to PPCPs or PPCP mixtures at levels anticipated in wastewater effluent, which is beyond the scope of this review. For a recent and detailed treatment of this topic, the reader is referred to a review of pharmaceutical ecotoxicology by Fent et al. [223].

2.5.1 Analytical Approaches for Real-Time PPCP Monitoring. The detection of PPCPs in wastewater influent and effluent can present an analytical and economical challenge for both research labs and wastewater treatment facilities. Much effort to date has therefore been spent to optimize techniques for the trace level analysis of PPCPs in complex environmental matrices so as to minimize detection limits, as well as the time and manpower required for analysis. Prior to detection and quantification of trace constituents, considerable sample clean-up is an obvious necessity. To this end, solid phase extraction (SPE) techniques have proven largely successful at minimizing potential interferences associated with the non-target components of these aquatic matrices. After sample clean up, the bulk of PPCP analysis, namely species identification and quantification, is conducted using either gas or liquid chromatography coupled to detection by mass spectrometry (i.e., GC/MS and LC/MS) or tandem mass spectroscopy

(GC/MS/MS or LC/MS/MS). Rather than address these topics herein, we refer the reader to outstanding reviews that cover many aspects of PPCP analysis in water and wastewater. These include a series of biannual reviews by Richardson focusing on analysis of emerging contaminants in water and environmental mass spectrometry [224-231], as well as recent special issues devoted to PPCPs in Trends in Analytical Chemistry (June 2007) and Analytical and Bioanalytical Chemistry (February 2007). The advantages and limitations of online-SPE coupled to LC-MS/MS are discussed in further detail by Rodriguez-Mozaz et al. [232].

Current frontiers in PPCP analysis are geared toward the identification and quantification of yet unidentified species, as well as transformation products generated during treatment. The identification of such unknown substances involves the application of high-resolution mass spectrometry methods, such as (quadrupole) time-of-flight-MS/MS and linear ion trap MS. These techniques allow the identification of non-target compounds in the absence of analytical standards. Applications of high-resolution mass spectrometry techniques to identify non-target compounds have recently been demonstrated [233, 234].

Another growing area in PPCP detection is the development of real-time analysis tools, which allow the continuous monitoring of PPCPs in effluents. Vanderford et al. [235] presented a mass spectrometry-based method capable of real-time monitoring of triclosan and its degradation products during chlorination. In this approach, samples were directly injected into a mass spectrometer, thereby avoiding the need for chromatographic separation, sample quenching or derivatization. While this technique has to date only been applied to controlled lab experiments, its expansion to applications involving real effluents could be envisioned.

For real-time monitoring, sensor-enabled technologies may prove more suitable than MS-based techniques. Sensors rely on contaminant detection via a recognition element, such as antibodies, enzymes or membrane-imprinted polymers. An overview of the current (bio)sensor-based applications for the detection of organic contaminants in environmental samples is presented by Rodriguez-Mozaz et al. [232, 236]. Compared to mass spectrometry applications, sensor-based technologies hold many favorable attributes. Potentially they can consume less sample volume, do not require trained personnel for operation, are less sensitive to matrix effects and are more cost-effective. Multi-analyte detection, however, remains challenging [232], and more studies evaluating the sensitivity, selectivity and robustness of (bio)sensor-based technologies in complex environmental matrices are required.

2.5.2 Next Generation Treatment Byproducts PPCPs undergo, to varying extents, chemical and/or biologically mediated transformations during wastewater treatment. As previously mentioned, however, degradation should not be equated with removal. All chemical and biological reactions result in the formation of products, many of which may share structural similarities with or retain the biochemical activity of the parent PPCPs from which they are derived.

To date, most concern has focused on the potential formation of hazardous transformation products during chlorination of PPCPs. Laboratory investigations with model systems have convincingly demonstrated that chlorination of common PPCPs can lead to the formation of known toxicants and probable carcinogens. Rule and Vikesland [237] demonstrated that free chlorine doses typically used in water treatment could react with the common antimicrobial triclosan to produce chloroform. Likewise, Bedner and MacCrehan [238] found that chlorination of acetaminophen under conditions simulating wastewater disinfection led to the production of several products, including known toxicants 1,4-benzoquinone and N-acetyl-p-benzoquinone imine, which are associated with lethal acetaminophen overdoses.

In addition to the formation of recognized toxicants, of further concern are those chlorinated transformation products uniquely formed during PPCP chlorination [239, 240]. At low doses or short contact times, reaction with chlorine is likely to only produce small modifications in the parent compound structure. For example, Dodd and Huang [152] found that trimethoprim reacts readily with free chlorine yielding products that were predominantly multi-chlorinated and hydroxylated. Early work examining the chlorination of 17β-estradiol [241, 242] observed similar phenomena; seven transformation products were identified including 2,4-dichloro-17β-estradiol, monochloroestrone, and 2,4-dichloroestrone, all of which maintained the characteristic five-ring steroid structure indicative of estrogens.

These unique species produced by chlorination represent the next generation of disinfection byproducts. They are viewed by many as a cause of concern with respect to their biological activity and possible toxicity, particularly mono- and di-chlorinated products that largely retain the structure of the parent PPCP. To date, several studies have employed *in vitro* cell assays to evaluate changes in biochemical activity induced by chlorination. The most widely applied of these approaches is the YES (Yeast Estrogen System) assay, which screens for estrogenicity. Several studies have used the YES assay or similar to conclude that chlorination of estrogenic hormones and endocrine disrupting compounds yields end products of lesser or no estrogenicity [243, 244]. As analytical methods for detecting, identifying and isolating these transformation products become more readily available, future research must continue to explore how physicochemical characteristics and biological activity of partially chlorinated transformation products differ from the behavior of the parent PPCP. Furthermore, additional toxicological studies with transformation products are warranted, so as not to place too strong an emphasis on the results of *in vitro* toxicity assays; PPCPs may result in toxic endpoints other than estrogenic response that may only be observed through investigation of whole organism (i.e.*, in vivo*) toxicity.

Even for chemical oxidation strategies such as ozonation, which effectively degrades most PPCPs, mineralization (i.e., the complete conversion into inorganic components such as CO_2) is not likely a realistic goal. Therefore, further identification and characterization of byproducts generated during wastewater treatment are urgently needed. Early work in this area conducted by Huber [169] examined the ozonation of 17α-ethinyl estradiol. Although small amounts of estrone and 17β-estradiol were observed, they concluded that most products exhibited chemical structures considerably altered from the parent, consistent with the loss in estrogenic activity measured in assays of the ozonation products. Notably, large changes in parent compound structure would not be anticipated from reaction with ozone, which tends to target specific moieties. Although not suggested by the authors, one might conclude that products of considerably altered structure relative to the products may be generated through indirect reaction with non-specific hydroxyl radical.

More recent analysis of ozonation products seems to support a larger role of hydroxyl radical than may have originally been anticipated for PPCP treatment with ozone. For example, Benner and Ternes [245] identified the products of metoprolol ozonation, primarily observing transformation products rich in aldehyde moieties and others indicative of hydroxylation reactions. Although they worked in model systems consisting of raw wastewater and secondary wastewater effluent spiked with metoprolol, these transformation products seem to suggest a significant role for $^{\bullet}OH$ during ozonation of PPCPs in wastewater matrices. Similarly, laboratory studies conducted by Radjenovic et al. [140] on the ozonation of antibiotics in both distilled water and secondary wastewater effluent revealed transformation products most consistent with $^{\bullet}OH$ reaction pathways, despite the relatively high affinity that many of the parent antibiotics exhibit toward ozone. Notably, two products of roxithromycin exhibited high refractoriness to ozonation. Both products maintained an intact tertiary amine moiety suggesting that antimicrobial activity may have been preserved after ozonation.

Other concerns over ozonation of wastewater stem from the traditional oxidation byproducts associated with ozone use. These include the formation of bromate (BrO_3^-) in bromide-containing waters, as well as a wide range of low molecular weight organic oxidation products including aldehydes, carboxylic acids, and other bioavailable forms of organic carbon. In a recent comparison of ozone to ozone-based AOPs, however, Wert et al. [246] found that ozone yielded a smaller amount of these byproducts relative to AOPs, which is a likely the result of the lower degree of $^{\bullet}OH$ exposure during ozonation.

Further research regarding the formation, ecotoxicological impacts and approaches for mitigation of byproducts produced from PPCP transformation is warranted if chemical oxidation is to become a commonplace wastewater treatment strategy. Indeed, such evaluation should be conducted before these treatment measures are routinely implemented. As pointed out by Snyder [85], however, future research should not only focus on the ecotoxicity of oxidation metabolites. Because organic matter is present in wastewater at much higher concentrations than micropollutants, organic matter-derived oxidation products also merit consideration.

2.5.3 Challenges of Increased Reliance on Advanced Treatment Technologies

An oft-cited detriment of advanced wastewater treatment, including chemical oxidation and membrane technologies, are their high energy requirement and the associated ecological and economical costs. If advanced treatment of wastewater is deemed necessary, a careful evaluation of these costs should be performed when identifying an optimal treatment method. For example, energy consumption was recently evaluated at a full-scale plant using ozonation to degrade micropollutants in wastewater [117]. Results indicated that micropollutant concentrations could be drastically reduced with an energy demand from ozonation that amounted to only 12 % of the total energy cost of a typical nutrient removal plant. This energy cost increased by approximately 30 % if the production of pure oxygen for ozone generation was taken into account.

In a comparison of energy consumption associated with different advanced treatment methods, Rosenfeld et al. [79] compared the energy use for different H_2O_2-based AOPs and ozone applied to surface and ground water. They found that at a low $^{\bullet}OH$ yield, ozone was the most efficient technology, whereas at higher yields the difference became negligible. Future direct comparisons of chemical oxidation-based treatment technologies should also include AOPs that can be operated with sunlight as the energy source and without the addition of H_2O_2, the use of which contributes greatly to operation costs. Two examples of AOPs that can use sunlight as the main energy source are homogeneous photo-Fenton using ferrous iron and hydrogen peroxide, and heterogeneous solar photocatalysis based on titanium dioxide. A life cycle analysis of these two AOPs coupled to biological treatment was evaluated in a noteworthy study by Munoz et al. [247], taking into account the impact categories global warming, ozone depletion, human toxicity, freshwater aquatic toxicity, photochemical ozone formation, acidification, eutrophication, energy consumption, and land use. Results showed that solar photo-Fenton has a lower environmental impact than solar heterogeneous photocatalysis for the treatment of industrial wastewater. The solar photo-Fenton process thus seems to be a more reasonable option if AOPs are to be employed.

In addition to those advanced methods already demonstrated as effective for PPCP removal, emerging oxidants, such as ferrate (Fe(VI)) and permanganate (Mn(VII)), could be scrutinized for their efficiency and environmental impact. Because these oxidants are not as commonly used as chlorine and ozone, PPCP removal by permanganate and ferrate has received less attention to date. However, it has been shown that they are capable of efficiently degrading endocrine disruptors and antimicrobials [248, 249], as well as carbamazepine [250]. Furthermore, their disinfection byproducts are considered benign [251] and the products of their reduction (i.e., MnO_2 (s) and $Fe(OH)_3(s)$) can be exploited as coagulants to further contribute to the removal of PPCPs and EfOM (see Hu et al. [250] and references therein).

Similar considerations should also be applied for membrane technologies. Snyder et al., who have conducted the most comprehensive study of membrane technology for wastewater treatment to date [36], emphasized that while membranes show great potential for enhancing wastewater quality, the benefits of membrane treatment must be weighed against possible detriments. Besides high energy requirements, this also includes the removal and disposal of the concentrated brine produced during the process. An economic analysis conducted by Jones et al. [44] indicates that the use of membrane technology for wastewater treatment is ultimately both economically and ecologically undesirable as a result of the high energy demand.

2.6 Conclusions

Based upon available data, technological solutions currently exist that can be used to lower PPCP levels in wastewater effluent to sub-ng/L levels that push the limits of current analytical instrumentation. Experimental evidence clearly demonstrates that current limitations in conventional treatment practices can be overcome with advanced treatment strategies including chemical oxidation with ozone or the use of membrane technologies such as RO and NF, all of which improve considerably effluent quality when incorporated into wastewater treatment trains. We caution, however, that zero is neither a reasonable nor achievable treatment goal for PPCPs. Recent advances in engineered wastewater treatment must now be matched by ecotoxicological data that establish acceptable levels of PPCPs in wastewater effluent and regulations regarding thresholds for PPCP removal. Until these questions are resolved, appropriate treatment technologies will be difficult to identify with certainty.

Ultimately, adequate removal of PPCPs from wastewater may require rethinking current paradigms in wastewater treatment and its associated infrastructure. For example, available data suggest that the use of passive treatment options oftentimes affords better PPCP removal than conventional treatment systems, while also providing the benefits of low energy input and minimal operation and maintenance costs. In populated areas, however, implementation of such systems may be limited by their large space requirement. Therefore, a model for future wastewater treatment infrastructure may involve decentralized systems that serve smaller population segments. Such systems could include primary or secondary treatment, followed by passive tertiary treatment with

SAT, constructed wetlands or lagoons. Another logical approach would be localized treatment of highly contaminated sources. Hospital effluents and industrial wastewater could be treated with advanced technologies before being combined with municipal systems. This would limit the most intensive treatment to lower volumes of water, which in return yields lower energy expenditures.

Coupling wastewater treatment with other applications, in particular irrigation or potable reuse, may improve both the economical and ecological cost of treatment in water-stressed regions. Therefore methods must be developed that attempt to quantify the ecological benefits of advanced treatment practices that enable water reuse strategies. For example, Munoz et al. [252] used life cycle analysis to compare the toxicity implications of different water reuse strategies. They considered direct reuse of secondary effluent, as well as three tertiary treatment options (RO, ozonation and H_2O_2/O_3). Their findings highlight the importance of non-regulated pollutants, including PPCPs, in the toxicity assessment of reclaimed water. Specifically, tertiary effluents exhibited lower ecotoxicity than secondary effluent, indicating tangible ecological benefits associated with advanced treatment. In the future, these benefits must be better quantified and weighed against more easily identifiable detriments commonly associated with advanced technologies, such as the emission of greenhouse gases associated with RO.

In all the scenarios outlined above, it is important to emphasize the need for more research involving actual wastewater and full-scale WWTPs. In particular for applications such as membranes, oxidative treatment and activated carbon, the divide between water and wastewater research needs to be closed, under consideration of the special challenges posed by the presence of effluent organic matter. Furthermore, more analyses needed to evaluate the commensurability of different water treatment scenarios aimed at the removal of PPCPs with respect to economic and ecological effects resulting from treatment.

Table 2-1. Compounds most susceptible to removal via traditional wastewater treatment (i.e., solids removal and conventional activated sludge).

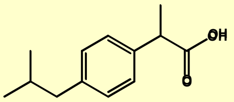
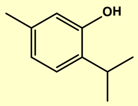
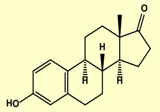
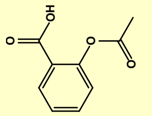
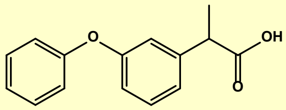
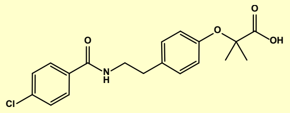
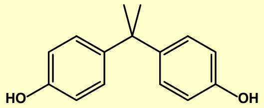
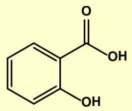
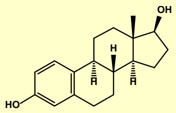
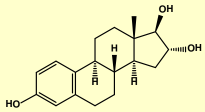
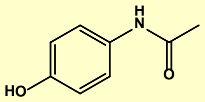
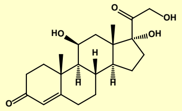
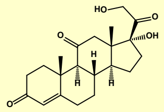
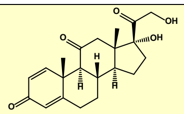
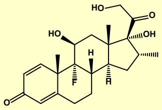
Compound (CAS #)	Chemical Structure	Compound Class	Number of Studies (n)	> 1-log Removal (% of Studies)
Ibuprofen (15687-27-1)		Anti-inflammatory	65	44 (69%)
Thymol (89-83-8)		Anti-microbial	18	16 (89%)
Estrone (53-15-7)		Hormone	18	8 (44%)
Aspirin (88566-80-7)		Analgesic	17	16 (94%)
Fenoprofen (29679-588-1)		Anti-inflammatory	17	7 (41%)
Bezafibrate (41859-67-0)		Lipid Regulator	15	5 (33%)
Bisphenol A (80-05-7)		EDC	14	5 (35%)
Salicylic Acid (69-72-7)		Anti-inflammatory	13	10 (77%)
17β-Estradiol (50-28-2)		Hormone	13	9 (69%)
Estriol (50-27-1)		Hormone	8	6 (75%)
Acetaminophen (8055-08-1)		Analgesic	7	7 (100%)
Cortisol (8056-11-9)		Gluco-corticoid	7	7 (100%)
Cortisone (50-22-6)		Gluco-corticoid	7	7 (100%)

Table 2-1, continued.

Prednisone (53-03-2)		Gluco-corticoid	7	7 (100%)
Dexamethasone (50-02-2)		Gluco-corticoid	6	6 (100%)

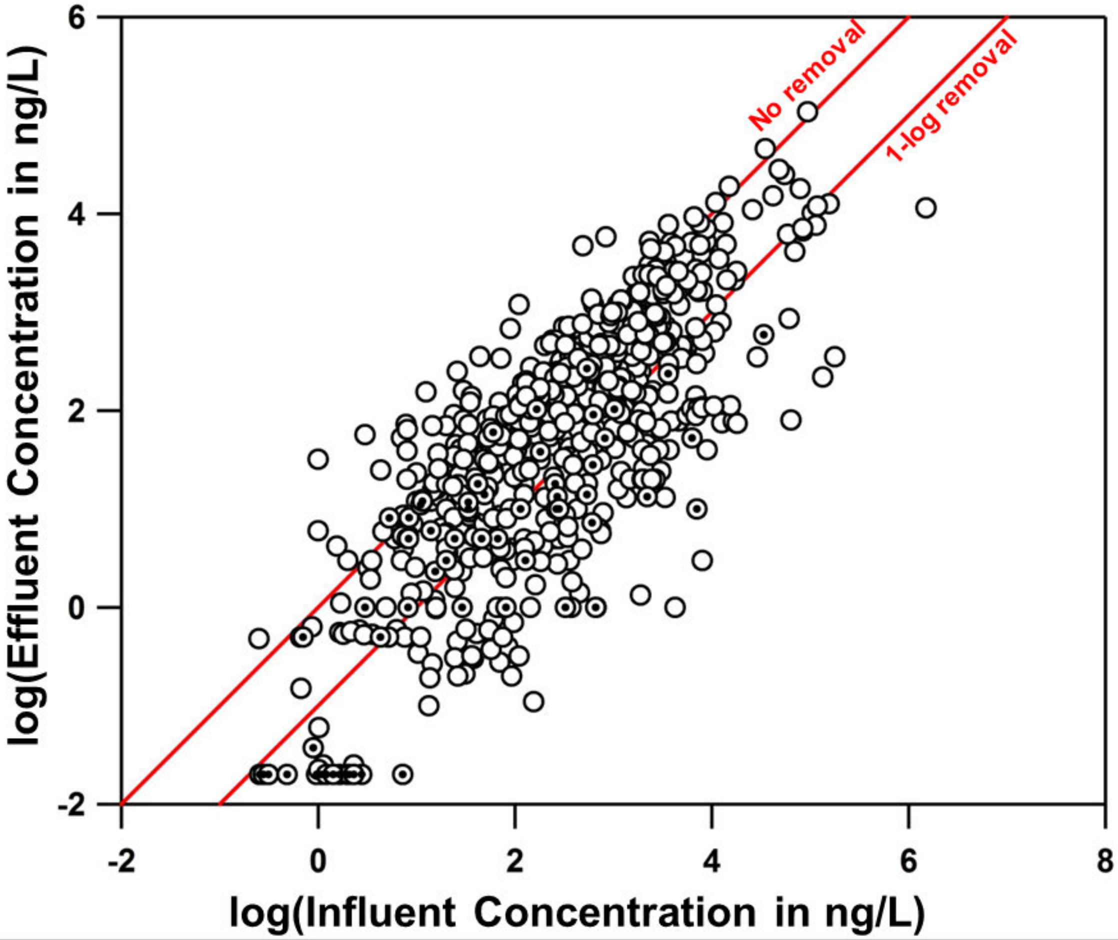


Figure 2-1. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing traditional treatment operations (i.e., solids removal and conventional activated sludge). Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL. Additional details regarding data compilation are provided in the text.

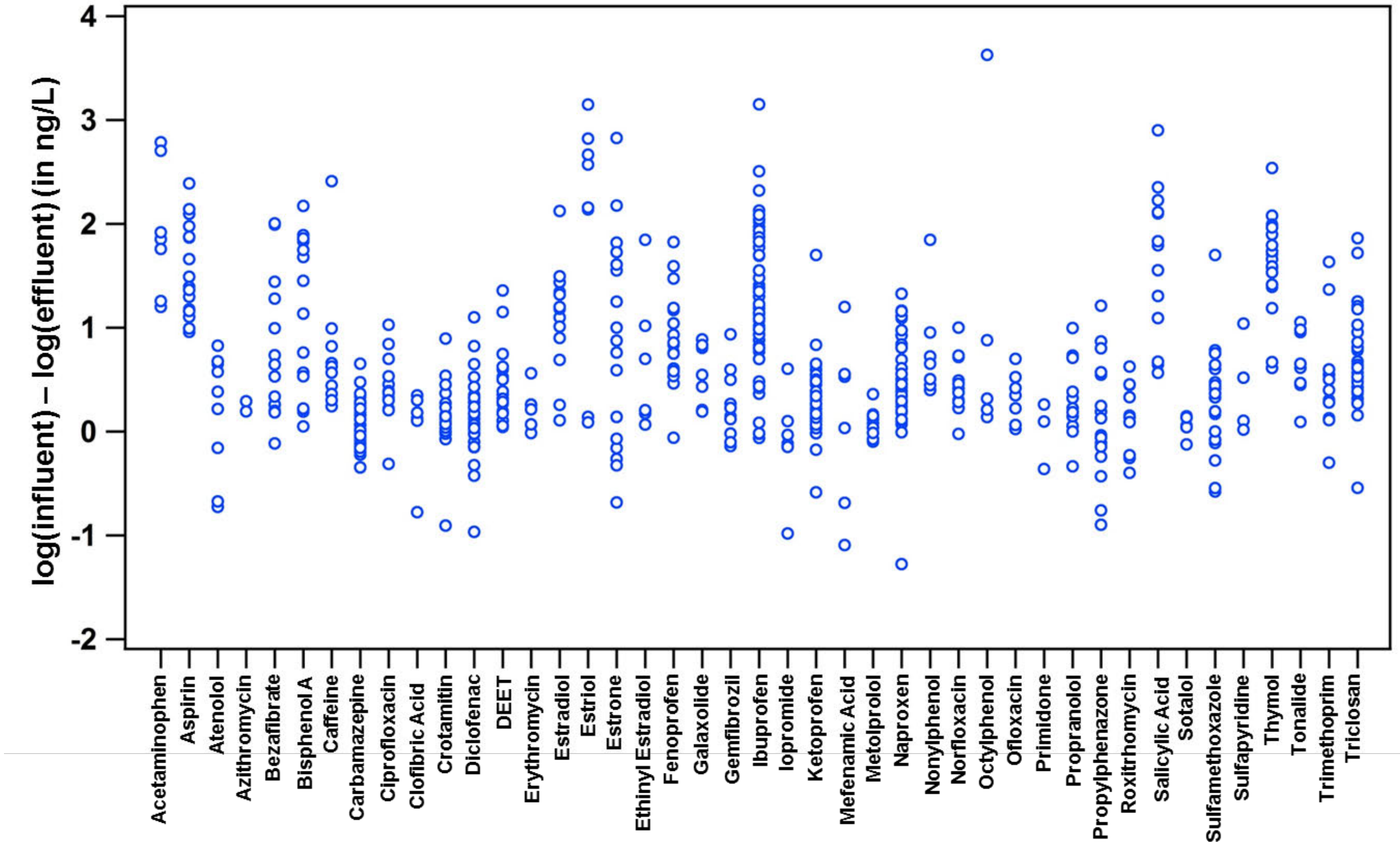


Figure 2-2. Log_{10} removal efficiencies for select compounds at WWTPs utilizing traditional wastewater treatment operations (i.e., solids removal and conventional activated sludge). Each data point corresponds to a published report of influent and effluent concentration for a PPCP at a WWTP using these treatment technologies. Dashed lines show thresholds indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit.

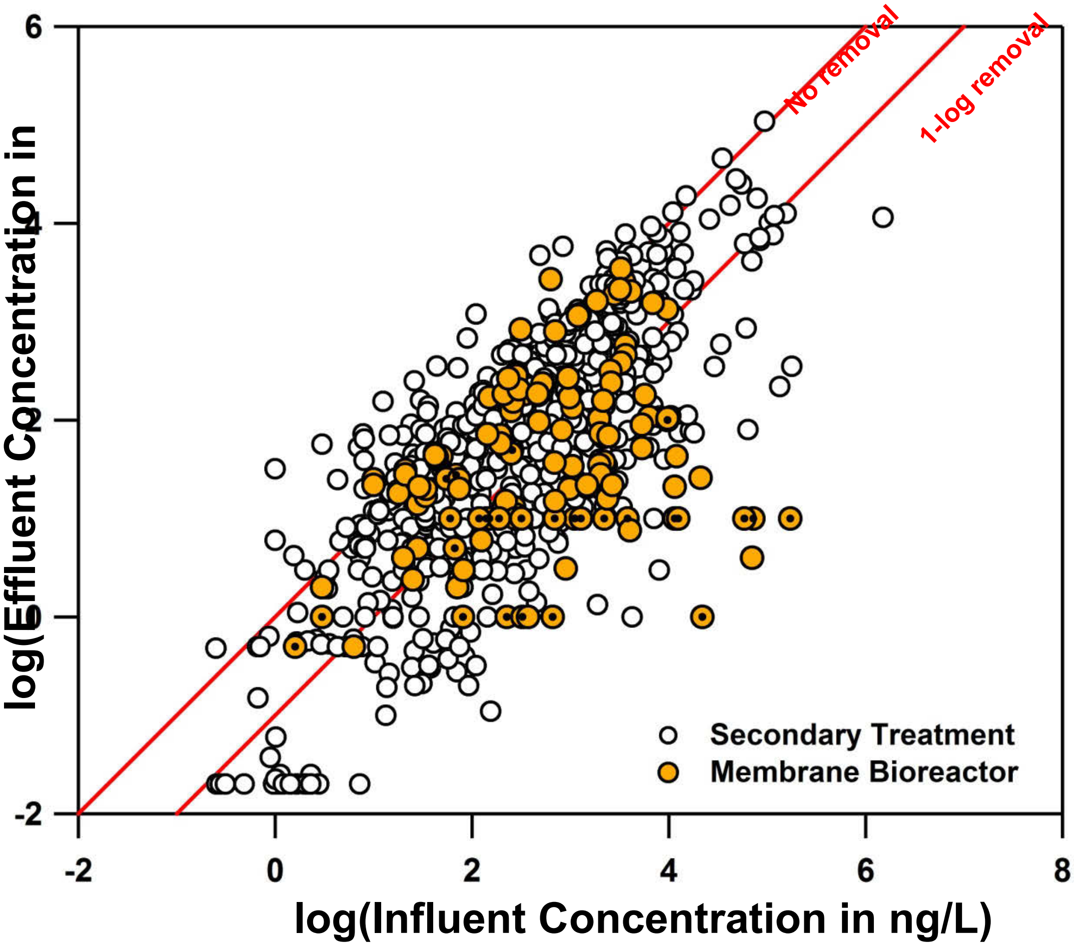


Figure 2-3. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing a membrane bioreactor (MBR) for biological treatment. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL.

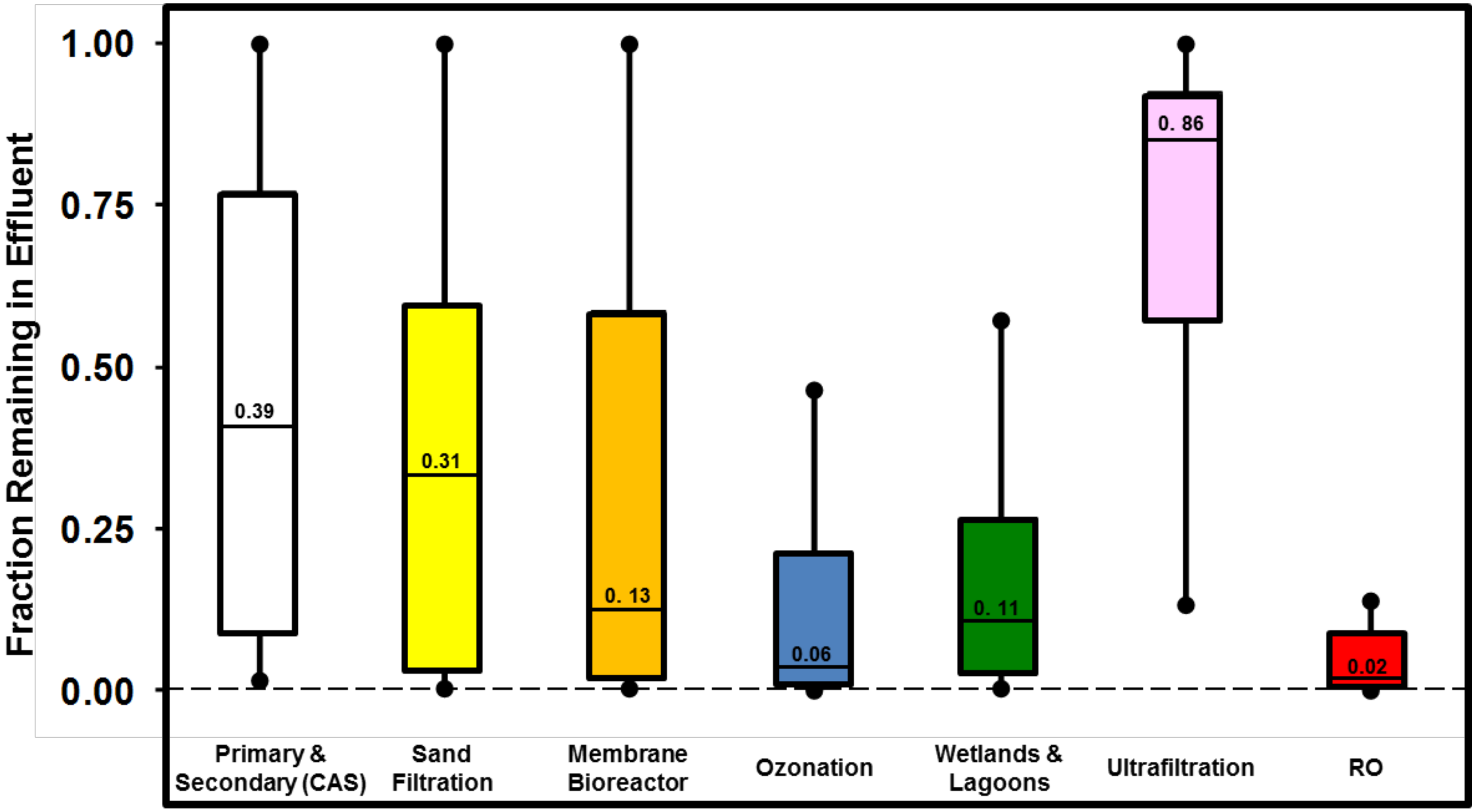


Figure 2-4. Box plot comparing PPCP removal efficiencies of the different wastewater treatment technologies considered herein. Plots show the distribution of removal efficiencies, expressed in terms of fraction of PPCP remaining in the treated effluent, for each treatment approach. Maxima and minima correspond to the 90th and 10th percentile for effluent fractions, whereas boxes span the range from the 25th to the 75th percentile. The solid line in each box represents the 50th percentile (median). Results of percentile analysis are only shown for treatment approaches for which there were over *n*=30 instances of influent-effluent data for different PPCPs.

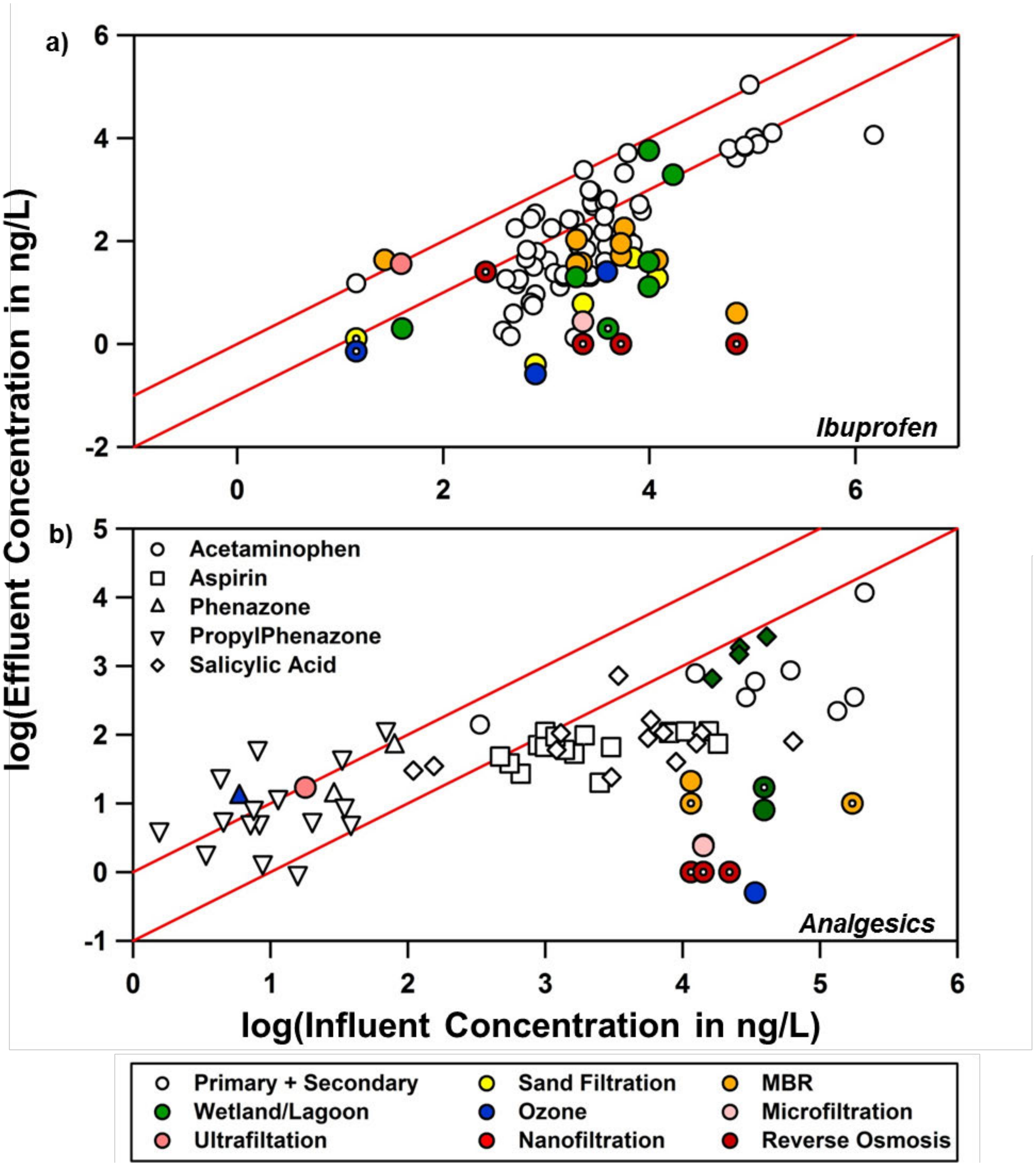


Figure 2-5. Influent and effluent concentration comparison for ibuprofen and analgesics. Data are shown for (a) ibuprofen and (b) common analgesics during wastewater treatment with various technologies. Where appropriate, data shape corresponds to different PPCPs, whereas the color of the data represents the different treatment technologies utilized. Data with a center point indicate those instances where reported effluent concentrations were below the MDL, in which case effluent data represent the reported MDL. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit.

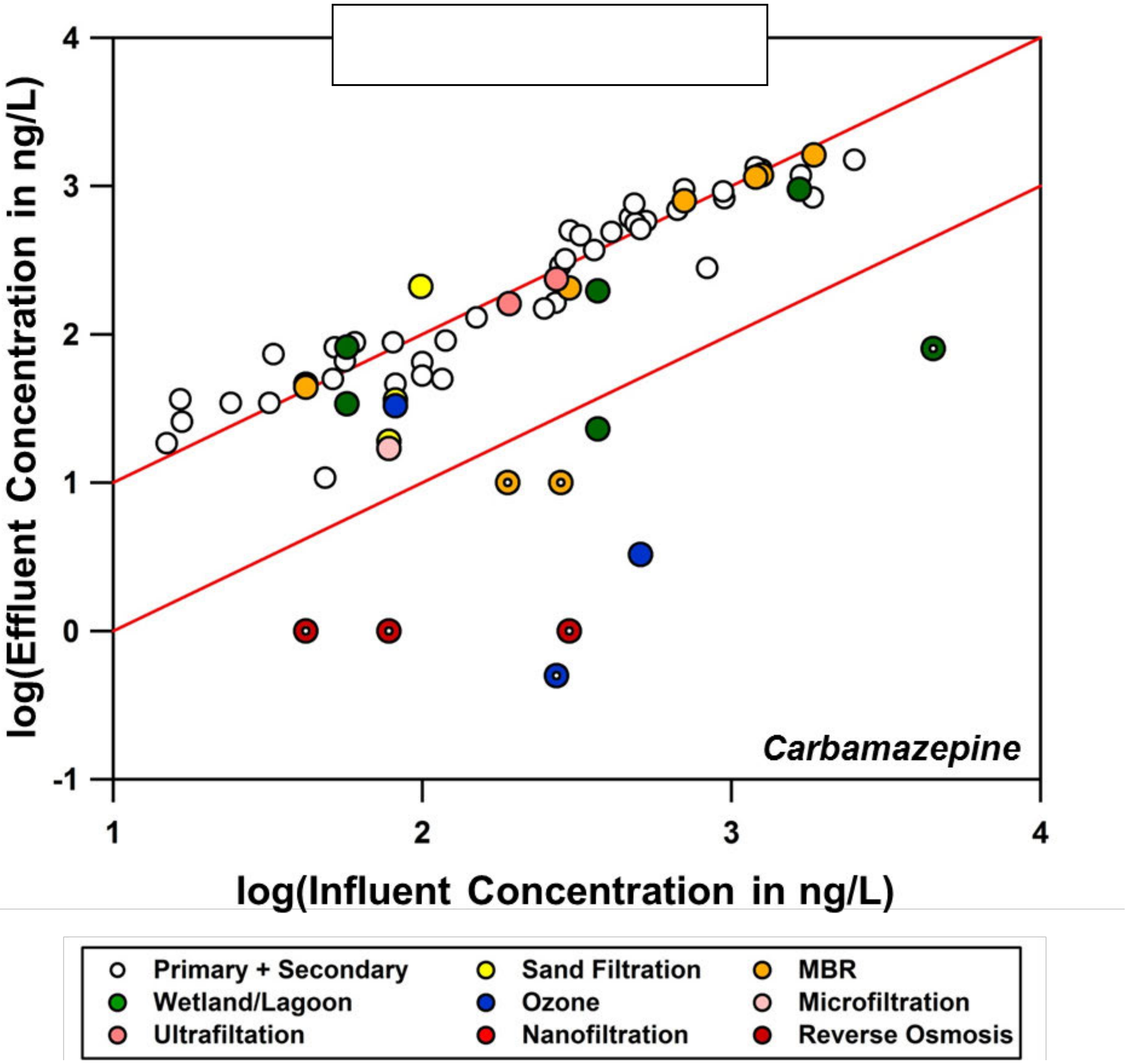


Figure 2-6. Influent and effluent concentration comparison for carbamezapine during wastewater treatment with various technologies. Data with a center point indicate those instances where reported effluent concentrations were below the MDL, in which case effluent data represent the reported MDL. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit..

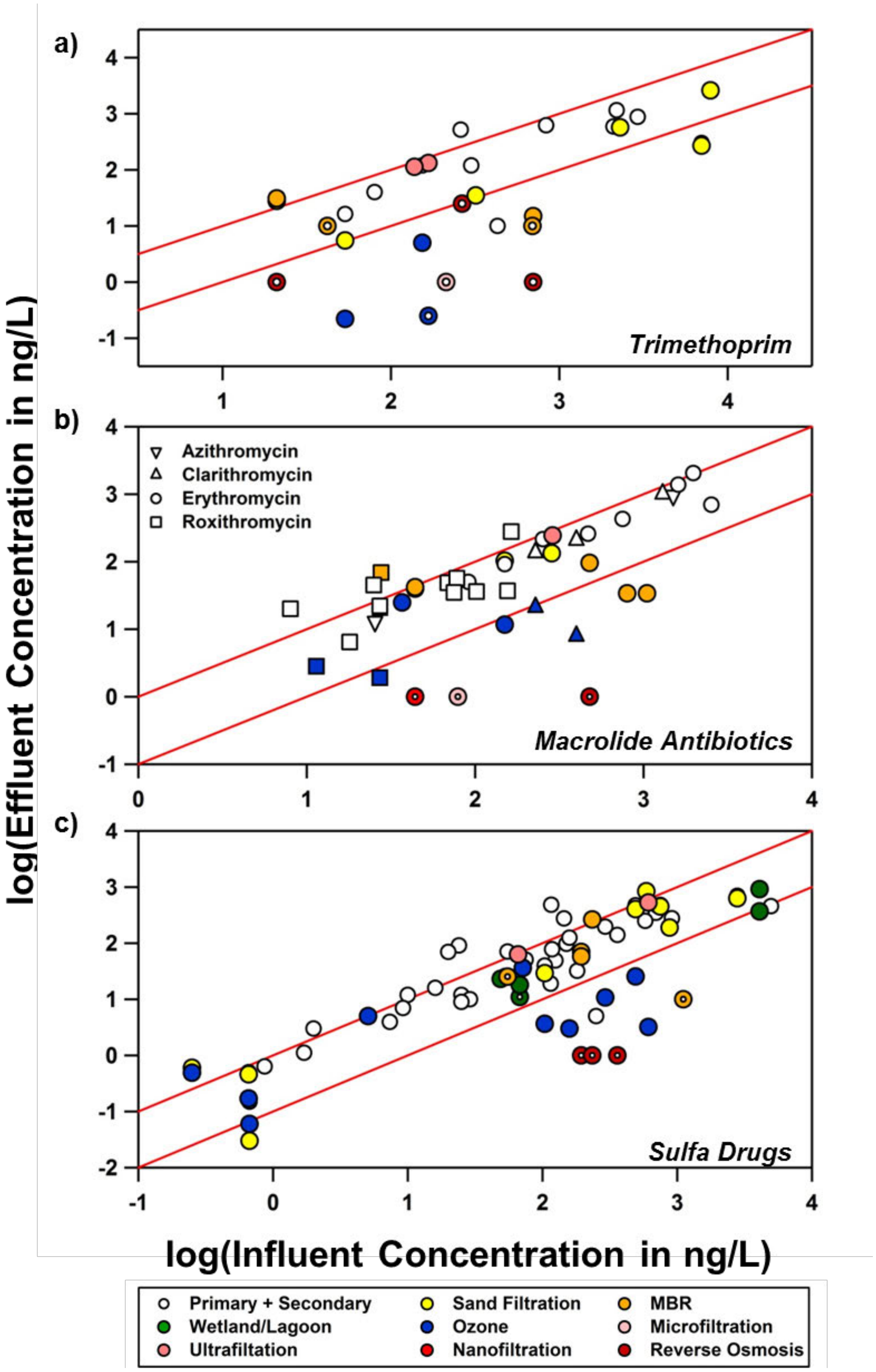


Figure 2-7. Influent and effluent concentration comparison for trimethoprim, macrolide antibiotics and sulfa drugs. Data are shown for (a) trimethoprim, (b) macrolide antibiotics and (c) sulfonamides during wastewater treatment with various technologies. Where appropriate, data shape corresponds to different PPCPs, whereas the color of the data represents the different treatment technologies utilized. Data with a center point indicate those instances where reported effluent concentrations were below the MDL, in which case effluent data represent the reported MDL. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit.

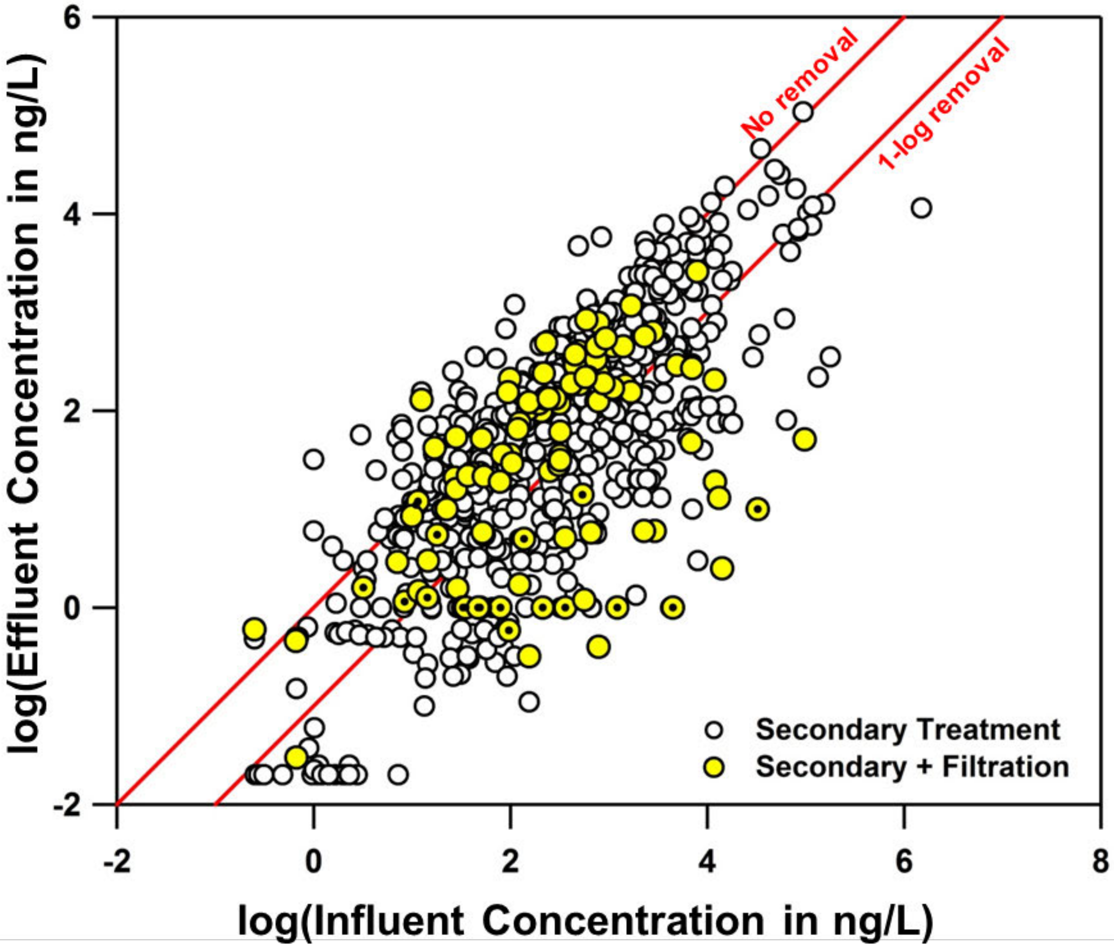


Figure 2-8. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing sand filtration for tertiary treatment of secondary effluent. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL

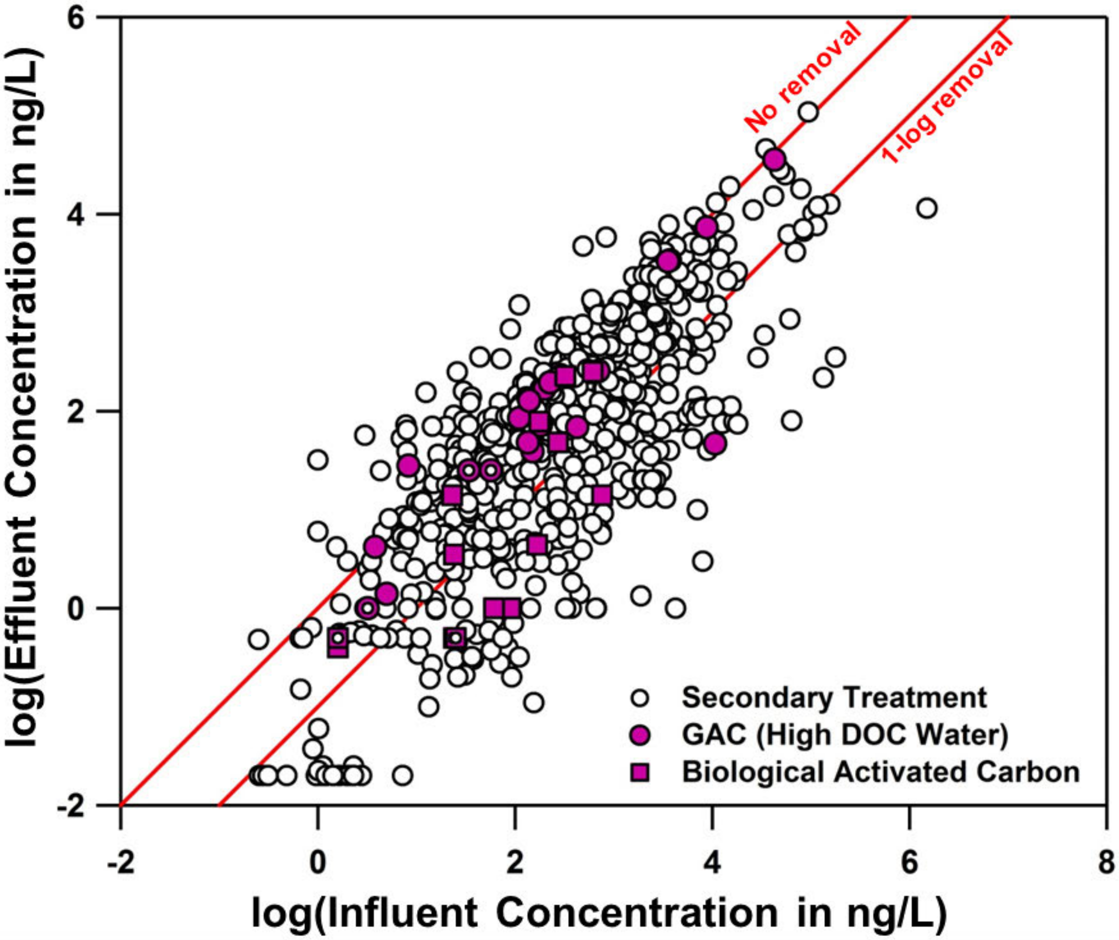


Figure 2-9. Comparison plot of PPCP effluent concentration as a function of influent concentration for applications of activated carbon for PPCP removal. As described in the text, data are shown for the application of GAC to a high TOC water source (purple circles) and the use of biological activated carbon for tertiary wastewater treatment (purple squares). Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL.

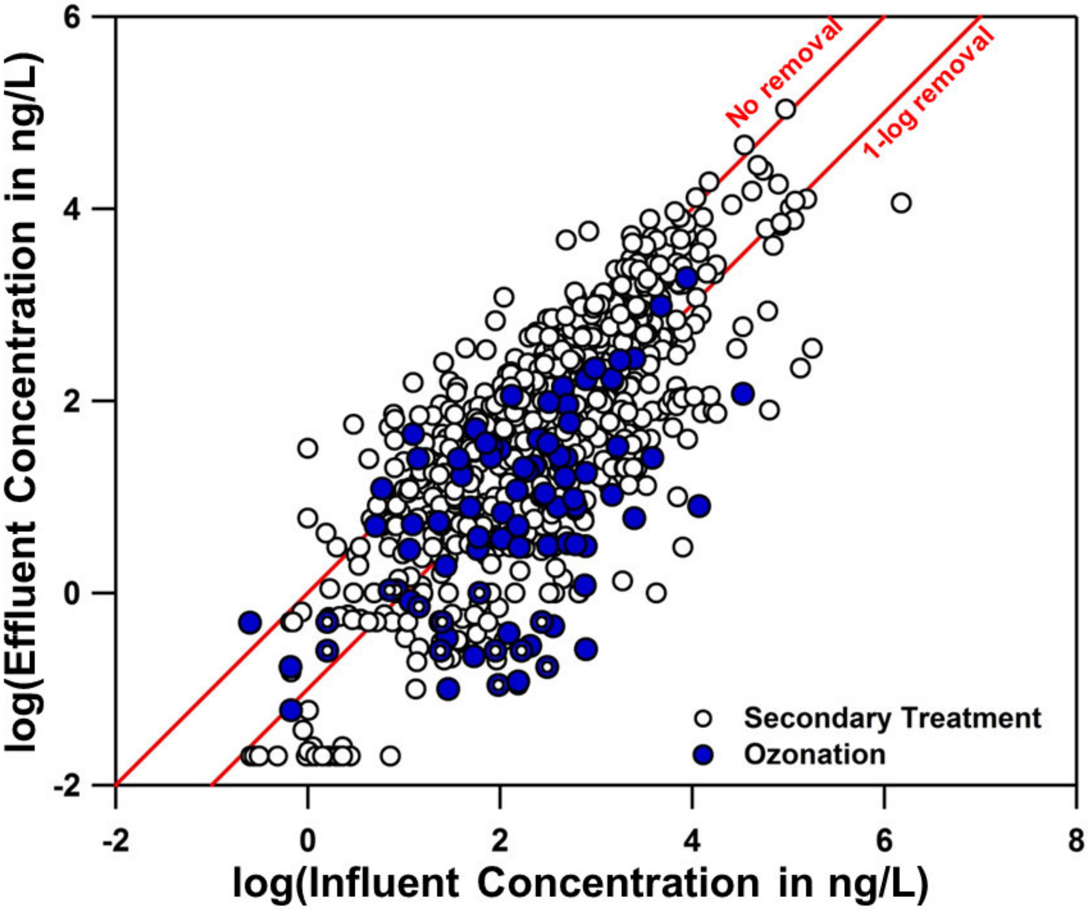


Figure 2-10. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing chemical oxidation with ozone as tertiary treatment of secondary effluent. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-log concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL.

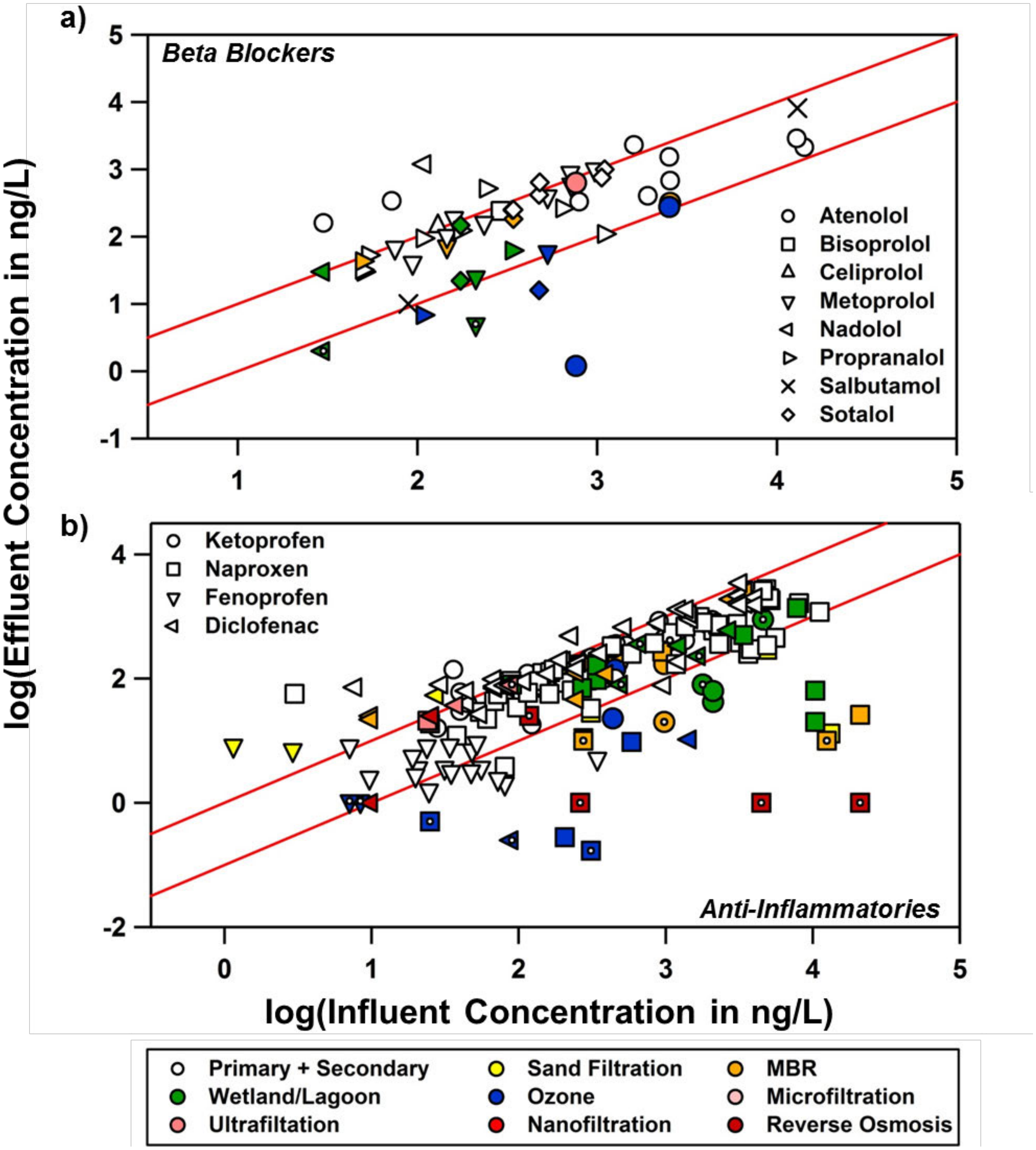


Figure 2-11. Influent and effluent concentration comparison for beta blockers and anti-inflammatory compounds. Data are shown for common (a) beta blockers and (b) anti-inflammatory compounds during wastewater treatment with various technologies. Where appropriate, data shape corresponds to different PPCPs, whereas the color of the data represents the different treatment technologies utilized. Data with a center point indicate those instances where reported effluent concentrations were below the MDL, in which case effluent data represent the reported MDL. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit

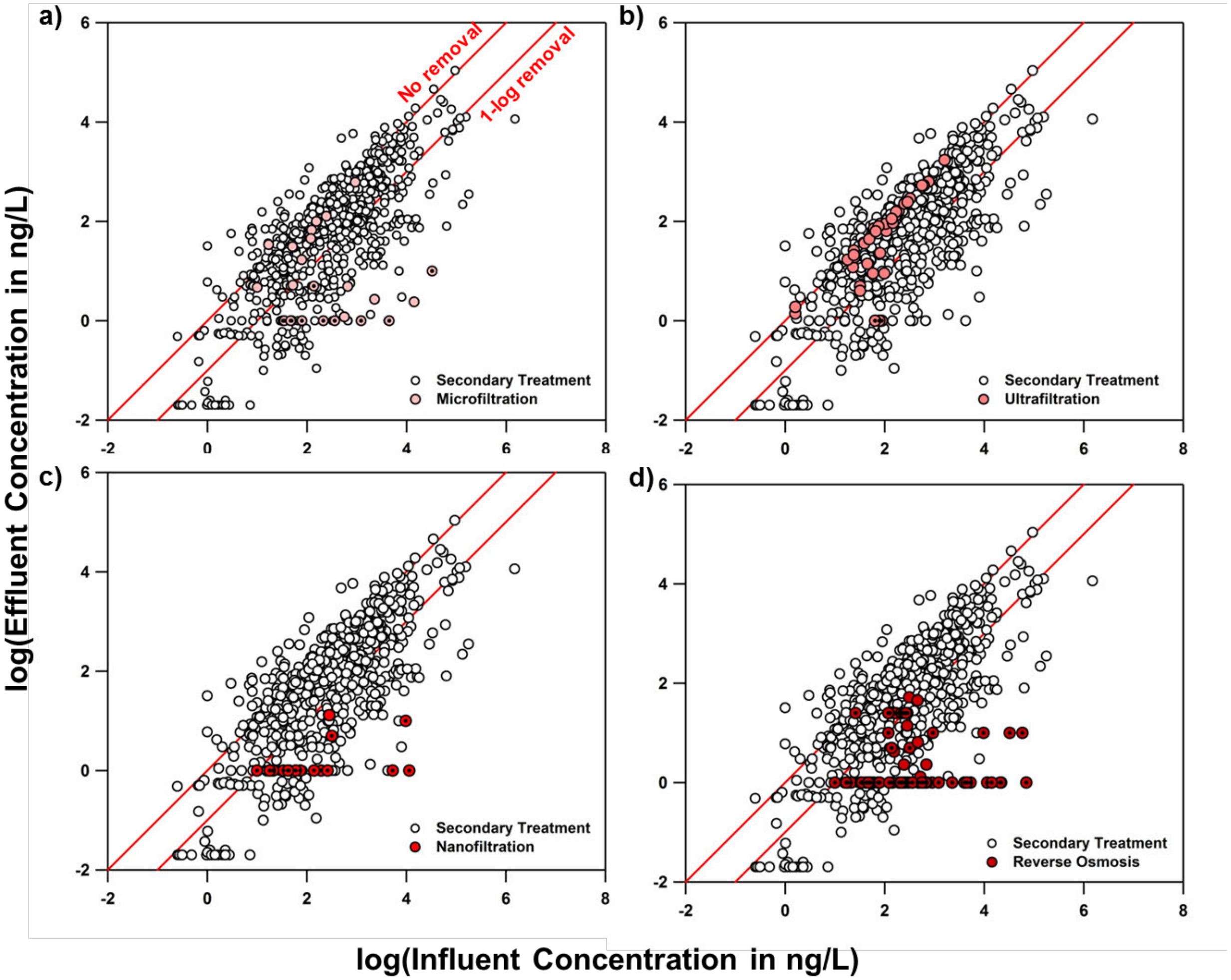


Figure 2-12. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing various membrane technologies for tertiary treatment. Shown are (a) microfiltration, (b) ultrafiltration, (c) nanofiltration and (d) reverse osmosis. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL.

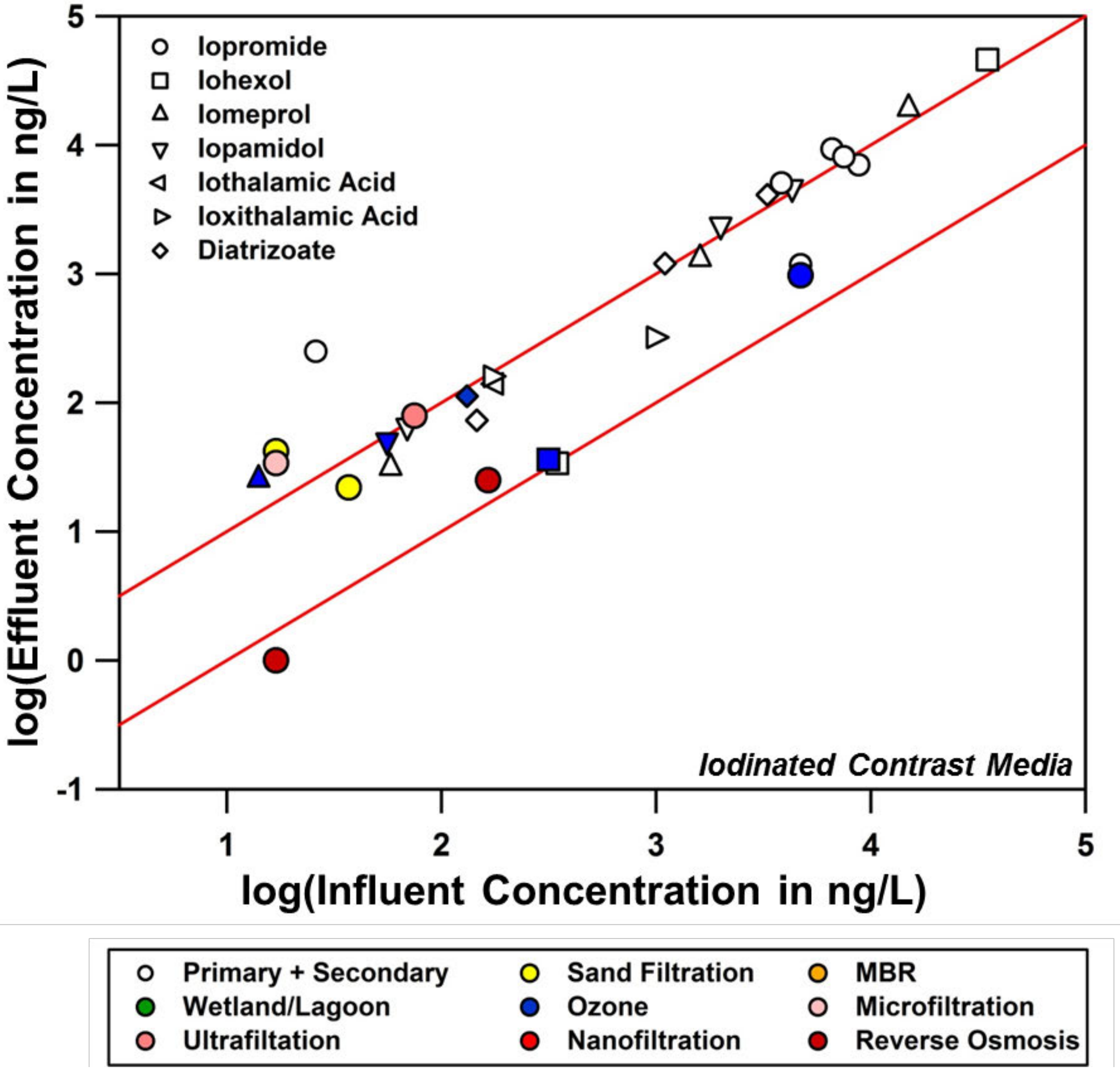


Figure 2-13. Influent and effluent concentration comparison of common types of iodinated contrast media during wastewater treatment with various technologies. Where appropriate, data shape corresponds to different PPCPs, whereas the color of the data represents the different treatment technologies utilized. Data with a center point indicate those instances where reported effluent concentrations were below the MDL, in which case effluent data represent the reported MDL. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit.

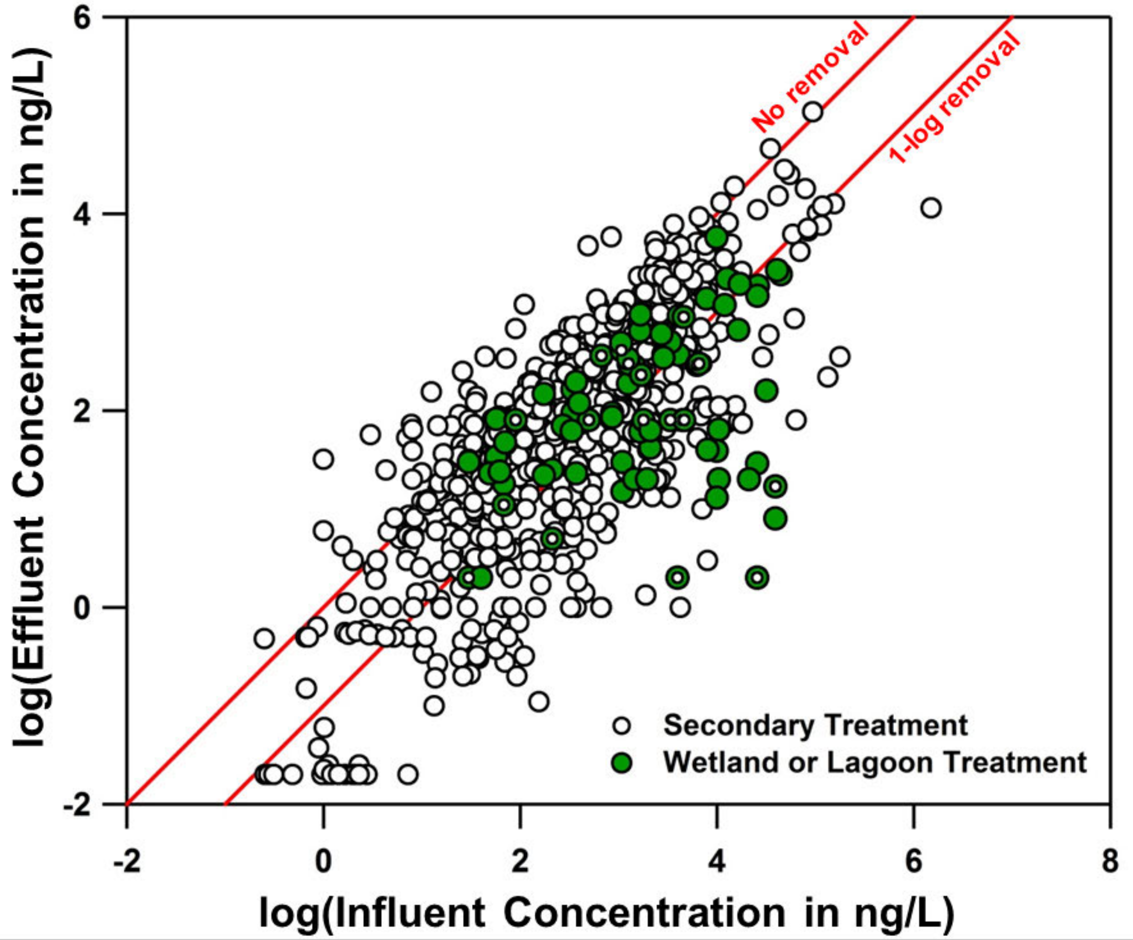


Figure 2-14. Comparison plot of PPCP effluent concentration as a function of influent concentration for WWTPs utilizing wetland or lagoon treatment systems. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit. For comparison, influent-effluent data obtained with traditional wastewater treatment (data from Figure 1) are also shown as open circles. Data with center dots indicate instances where effluent PPCP concentrations were below the MDL, in which case effluent data represent the reported MDL.

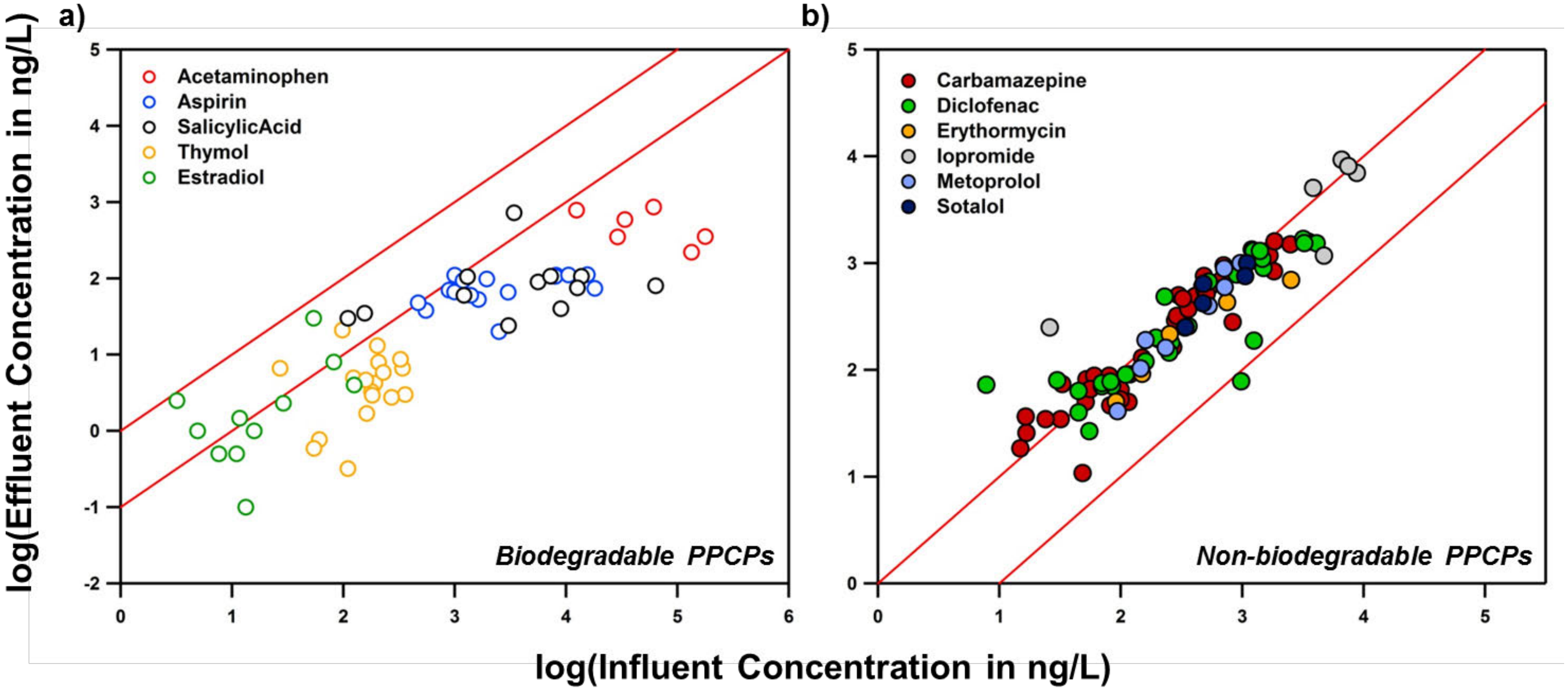


Figure 2-15. Influent and effluent concentration comparison of identified compounds. Data includes compounds identified as (a) highly susceptible to biological transformation or (b) highly resistant to biodegradation. Also shown in red are lines indicating no PPCP removal and removal corresponding to 1-$\log_{10}$ concentration unit.

CHAPTER 3: USE OF MULTI-WALLED CARBON NANOTUBES TO PROMOTE HYDROXYL RADICAL FORMATION DURING OZONATION

3.1 Abstract

Substrates including activated carbon are known to promote hydroxyl radical ($^{\bullet}OH$) formation during ozonation, a process known as "catalytic ozonation". Here, we show that multi-walled carbon nanotubes (MWCNTs) represent another viable substrate, promoting $^{\bullet}OH$ formation during ozonation to levels exceeding activated carbon and equivalent to conventional ozone-based advanced oxidation processes (e.g., O_3 /H_2O_2) based on R_{CT} values (a standard metric for $^{\bullet}OH$ exposure during ozonation). When used as-received from multiple vendors, MWCNTs consumed O_3 but yielded limited, if any, $^{\bullet}OH$. In contrast, MWCNTs oxidized with nitric acid (HNO_3) exhibited vastly greater rates of both O_3 consumption and $^{\bullet}OH$ formation. Some of this enhanced reactivity undoubtedly reflects the greater suspension stability of oxidized MWCNTs. However, a simple increase in reactive surface area via improved dispersion cannot fully explain the greater $^{\bullet}OH$ formation in suspensions of oxidized MWCNT. Notably, we observed a strong correlation between R_{CT} values and MWCNT surface oxygen concentrations measured via X-ray photoelectron spectroscopy. We interpret this relationship as evidence that oxygen-containing surface functional groups added during MWCNT oxidation with HNO_3 are responsible for $^{\bullet}OH$ formation. The ability to optimize MWCNT surface chemistry for $^{\bullet}OH$ formation during ozonation makes them a promising alternative in oxidative treatment processes.

3.2 Introduction

Catalytic ozonation, in which a surface promotes ozone (O_3) decay into hydroxyl radical ($^{\bullet}OH$), has been proposed as a promising alternative to traditional advanced oxidation processes (AOPs) [51]. While metal oxides [51, 253-258] have been extensively utilized in this process, activated carbon (AC) represents another attractive substrate because of its widespread use in water and wastewater treatment [53]. Jans and Hoigne [259] discovered that the combination of O_3 and granular activated carbon (GAC) promoted $^{\bullet}OH$ formation relative to traditional ozonation, and subsequent explorations with O_3/GAC revealed comparable removal of $^{\bullet}OH$-specific probe compounds to that achieved by O_3 with H_2O_2, albeit at a slower rate [260]. Indeed, O_3 in combination with AC has been shown to provide many of the positive treatment outcomes associated with traditional AOPs, including improved removal of total organic carbon [46, 260-263], reduced ecotoxicity levels of treated effluent [263, 264], and enhanced degradation of common O_3-recalcitrant compounds (e.g., low molecular weight acids [261, 265, 266]) and micropollutants [263, 264].

Mechanistically, O_3 decomposition and $^{\bullet}OH$ formation are surface processes that scale with AC concentration or surface area [4], yet some $^{\bullet}OH$ remains available in the bulk solution where it oxidizes dissolved targets [51]. For AC, oxygen-containing surface sites from activation (e.g., hydroxyl, carbonyl, and carboxyl [3, 46, 51] or pyrones and chromenes [3, 51, 52, 263]) are often implicated in $^{\bullet}OH$ formation because they contain lone electron pairs that are ideal for attack by electrophilic O_3. It has also been suggested that delocalized π-electrons in the graphene planes of the AC can function as Lewis base sites that initiate reaction with ozone to generate H_2O_2 [51, 52], which is believed to be a critical intermediate in $^{\bullet}OH$ formation. Reduced metal impurities, which are occasionally encountered in AC, may also contribute as they would be prone to oxidation by O_3 [51, 253]. There remains debate over whether $^{\bullet}OH$ production is truly catalytic, with some prior work suggesting that AC activity diminishes over prolonged exposure to ozone [46, 52].

Despite the existing body of fundamental research, the practical application of AC during ozonation has been limited because of perceived shortcomings in material properties. For example, the vast majority (typically >90%) of AC surface area is internal [267], most of which will not be accessible to highly reactive O_3 via mass transfer limitations [264]. Further, AC may lack the structural integrity to withstand the highly oxidizing environment during ozonation, as evidenced by loss of both surface area and mesopores after repeated ozonation [3, 46, 261, 268].

A likely alternative for use in combination with O_3 are carbon nanotubes (CNTs) because many properties of AC linked with $^{\bullet}OH$ production are shared or likely to be more pronounced with CNTs. CNTs exhibit significantly higher external surface area than AC, and their surfaces can be chemically functionalized [269-272] to optimize the type and density of oxygen-rich surface sites believed responsible for transforming O_3 into $^{\bullet}OH$. Based upon their growing application as catalysts and catalyst supports [273, 274], CNTs are also known to be relatively stable in extreme chemical environments and thus are more likely to maintain their mechanical integrity during ozonation. Furthermore, CNTs are currently the research and development focus for a number of environmental quality control applications [4] including their use as sorbents [275-277], antimicrobial agents [82, 278-280], and components in selective high-flux filtration membranes [281-285]. Therefore, when used in combination with O_3 to promote chemical oxidation processes, CNTs may also offer unrecognized treatment benefits through their potential multi-functionality.

A few recent studies have explored the use of CNTs for promoting $^{\bullet}OH$ production during ozonation [286-290], generally demonstrating the viability of CNTs for this process. Nevertheless, both practical and fundamental questions surround their use in catalytic ozonation. Notably, nearly all work to date has been conducted under conditions far from those representative of water and wastewater treatment (e.g., pH 3 [286, 288, 290] or at high temperature and pressure [289]). Also, other than a single instance demonstrating the improved performance of CNTs relative to AC [290], it is not yet known how CNTs in combination with O_3 compare to more traditional ozone-based AOPs such as O_3 with H_2O_2. Therefore, the practical value of CNTs as an alternative for $^{\bullet}OH$ formation during ozonation remains unclear.

From a more fundamental perspective, studies [286-290] to date have provided conflicting results as to the influence of surface oxidation on CNT ability to generate $^{\bullet}OH$ during ozonation. Liu and co-workers [286-288] found that increased surface oxidation decreased CNT reactivity, whereas Goncalves *et al*. [290] observed little to no difference between the reactivity of oxidized and non-oxidized CNTs. Notably, both results run counter to expectations for the role of oxygen-containing surface groups in $^{\bullet}OH$ formation anticipated from results with AC. Further, a complicating factor in these studies is the interdependence between CNT surface oxidation and suspension stability, and its certain influence on CNT performance. Because CNT oxidation increases their dispersion in suspension [3, 75, 271, 272, 291] and nearly all reactivity studies to date have been conducted in suspension [286-288, 290], changes in reactivity observed as a function of CNT surface oxidation may result from either the addition (or loss) of reactive surface sites during functionalization or changes in the stability and behavior of CNTs in suspension. This distinction is critical to future efforts to engineer CNTs with optimal properties for $^{\bullet}OH$ formation.

Here, we examine the ability of two commercially available multi-walled carbon nanotubes (MWCNTs) to enhance $^{\bullet}OH$ exposure during ozonation. Working in aqueous suspensions, $^{\bullet}OH$ exposure during ozonation of MWCNTs was quantified at pH 7 using the radical probe *para*-chlorobenzoic acid and the R_{CT} concept developed by Elowitz and von Gunten [292]. Performance of MWCNTs was then compared to a common ozone-based AOP (O_3/H_2O_2), as well as to the O_3 and GAC system. In addition to work with as-received or non-functionalized MWCNTs, which were strongly hydrophobic and of limited stability in suspension, functionalization with various strengths of nitric acid (HNO_3) was used to systematically vary the extent of MWCNT surface oxidation. Characterization of the MWCNT surface chemistry and aggregation in suspension, in complement with reactivity studies quantifying $^{\bullet}OH$ formation, allowed us to assess directly how surface oxidation influences MWCNT reactivity and whether observed reactive trends result from changes in the nature of reactive surface sites induced by functionalization or the stability and behavior of CNTs in suspension.

3.3 Experimental Section

*3.3.1 Reagents***.** All reagents were used as received unless otherwise indicated. Ozonation experiments used *para*-chlorobenzoic acid (*p*-CBA) (Sigma Aldrich; 99%), *tert*-butanol (*t*-ButOH) (Sigma Aldrich; ≥99%), anhydrous sodium sulfite (Sigma Aldrich; ≥ 98.0%) and potassium phosphate monobasic (Sigma Aldrich; ≥99%). Ozone concentrations were measured colorimetrically using potassium indigo trisulfonate, phosphoric acid (ACS reagent, ≥85 wt. % in H_2O), and methanol (HPLC grade). All solutions were prepared in deionized water (Millipore, Q-Grad 2). Phosphate buffer solutions were pre-treated with ozone to remove any organic matter in the solution prior to use in experimentation.

MWCNTs were acquired from two different commercial sources, CheapTubes.com (www.cheaptubes.com; Brattleboro, VT) and Nanolabs, Inc (www.nano-lab.com; Waltham, MA). Both had vendor-specified purities >95% and were synthesized via chemical vapor deposition. TEM images of the as-received CNTs are shown in Figure 3-1.

3.3.2. Batch Experiments for Quantifying $^{\bullet}$OH Production during Ozonation. Ozonation experiments used both as-received (or non-functionalized) MWCNTs and MWCNTs that were oxidized with concentrated nitric acid (HNO_3) using established protocols [75]. The functionalization procedure consisted of sonicating MWCNTs in an HNO_3 solution (20, 40, or 70% HNO_3) for one hour, then refluxing the MWCNT/HNO_3 mixture in an oil bath at 140°C for 1.5 h. After cooling overnight, the MWCNTs were captured on a 0.2 μm nitrocellulose filter. They were cleaned via repeated washing with DI water using a vacuum filter until the rinse water read a pH value greater than 5. Recovered MWCNTs were then dried overnight at 100°C and pulverized with a ball mill to form a powder. MWCNTs will heretofore be referenced by commercial source (NL for Nanolabs or CT for Cheaptubes) and the strength of acid used in functionalization (e.g., “NL-NF” refers to non-functionalized MWCNTs from NanoLabs, Inc., whereas “CT-70” refers to MWCNTs from CheapTubes.com oxidized with 70% HNO_3).

Concentrated (1 g/L) stock suspensions of all MWCNTs were prepared in DI water. To promote dispersion, these suspensions were then subjected to extended (20 h) sonication (Bransonic Ultrasonics Corporation, 42 kHz ± 6%). Immediately prior to use in reactivity studies, MWCNT stock solutions were once again sonicated for at least 15 minutes, with experimentation revealing that longer sonication times had no effect on suspension reactivity. All CNT stock suspensions were used within 30 min of sonication, after which we observed slight losses in suspension reactivity, presumably due to reaggregation.

For comparison purposes, our experimental conditions were similar to those used previously in catalytic ozonation studies with GAC [46, 253, 260]. Reactions were conducted in well-mixed (via digital magnetic stir plate) MWCNT suspensions with loadings between 1-40 mg/L. Solutions were maintained at pH 7.0 with 5 mM phosphate buffer and no change in pH was observed during our experiments. All solutions and glassware were initially pre-treated with O_3 and O_3 stock solution, respectively, to remove any O_3-active compounds, an approach previously recommended to yield more consistent results.[293]

Aqueous stock solutions of O_3 were produced using a DelOzone LG-14 ozone generator with a high purity (99%) O_2 feed. The O_3/O_2 gas mixture discharged from the generator was bubbled through a glass dispersion tube into 125 ml of a 5 mM phosphate buffer in an ice bath to create a concentrated O_3 stock solution. Tests showed that a steady-state dissolved O_3 concentration was achieved after roughly five minutes of bubbling. Ozone stock solutions typically had an initial concentration of ~20 mg/L, which is near the solubility limit for O_3 at 3°C when using a feed gas ozone concentration of ~2-3 wt %.[16, 294]

Reactors also contained 2 μM of *p*-CBA as an $^{\bullet}$OH probe. *p*-CBA reacts quickly with $^{\bullet}$OH ($k_{p\text{-CBA}/^{\bullet}\text{OH}} = 5\text{x}10^{9}$ $M^{-1}s^{-1}$) [295], but shows little reactivity toward O_3 ($k_{p\text{-CBA/O3}}$ ≤ 0.15 $M^{-1}s^{-1}$) [296] and does not sorb significantly on most organic materials [260]. Accordingly, decreases in *p*-CBA concentration represent an indirect measure of $^{\bullet}$OH production during ozonation. As is common in studies with O_3 [46, 52, 253, 260, 263, 265, 266, 297], reactors also contained 320 μM *t*-ButOH as a model $^{\bullet}$OH scavenger. The *t*-ButOH helps to ensure that the $^{\bullet}$OH produced in our experimental systems results primarily from O_3 reaction on the MWCNT surface; it quenches a catalytic cycle initiated by $^{\bullet}$OH that yields superoxide anion radical ($O_2^{\bullet -}$), and ultimately, more $^{\bullet}$OH [259, 298].

To initiate reaction, an aliquot of the concentrated O_3 stock solution was added to the MWCNT suspension to achieve the desired initial O_3 concentration, which typically ranged between 80 and 240 μM (3.8 mg/L to 11.5 mg/L). Periodically, samples were collected over time. Samples for *p*-CBA analysis were quenched with excess sulfite ($NaSO_3$ two- to four-times in molar excess of original O_3 concentration) to consume residual O_3. The quenched sample was then passed through a 0.2 μm Nylon syringe-driven filter (P.J. Cobert Associates) to remove suspended MWCNTs (tests showed that filtration had no effect on *p*-CBA stability or analysis). Samples were transferred to 2.5 mL (nominal volume) amber autosampler vials for immediate analysis via HPLC. Separate samples for O_3 analysis were taken simultaneously, in which an aliquot of suspension was added directly to vials containing indigo blue solution. Independent tests verified that the presence of CNTs did not affect colorimetric analysis of O_3 with IB. After IB addition, samples were protected from light until analysis to prevent possible photoreactions.

Control systems included O_3-free experiments to determine the extent of *p*-CBA sorption onto MWCNTs. Experiments were also conducted with O_3 in the absence of MWCNTs to quantify *p*-CBA loss via direct reaction with ozone. To ensure $^{\bullet}$OH formation was not attributable to any dissolved species leaching from the MWCNT surface, control studies were also conducted with supernatants removed from MWCNT suspensions after centrifugation.

3.3.3 Comparison of MWCNT Performance to Ozone-Based AOPs. A parallel set of reactivity experiments was performed with granular activated carbon (GAC) from Calgon Carbon Corporation (Pittsburgh, PA) that was specially prepared for use with O_3. We also explored $^{\bullet}$OH production via the combination of O_3 and H_2O_2, a conventional O_3-based AOP. Experiments with GAC were performed using the same procedures as described for MWCNTs. Typical concentrations of GAC used in ozonation experiments were $\geq$ 40 mg/L. Experiments with O_3/H_2O_2 also generally followed the procedures outlined above. To initiate reaction, a volume of 10 mM H_2O_2 stock (Sigma, 30% W/W) solution prepared in DI water was added to the reactor to achieve in an initial H_2O_2:O_3 molar ratio of 1:1, a ratio previously used for comparison to catalytic ozonation with GAC [260].

3.3.4. Quantifying $^{\bullet}$OH Exposure during Ozonation of CNT Suspensions. The R_{CT} concept of Elowitz and von Gunten [292] was used to quantify $^{\bullet}$OH exposure in all experimental systems. R_{CT} is defined as the total exposure to $^{\bullet}$OH relative to the total O_3 exposure (eq 1)

$$R_{\mathrm{CT}} = \frac{\int [^{\bullet}\mathrm{OH}]dt}{\int [\mathrm{O_3}]dt} \qquad (1)$$

where larger R_{CT} values indicate a greater $^{\bullet}$OH exposure in solution. R_{CT} values allow a single metric for comparing the extent of $^{\bullet}$OH formation in different O_3-based AOPs. While O_3 exposure is quantified from the change in its concentration over time, total $^{\bullet}$OH exposure is measured experimentally via degradation of *p*-CBA over time as illustrated in eq 2.

$$R_{\mathrm{CT}} \cdot k_{p\text{-CBA}/\bullet\mathrm{OH}} = -\frac{\ln\left(\frac{[p-\mathrm{CBA}]}{[p-\mathrm{CBA}]_0}\right)}{\int [\mathrm{O}_3]dt} \quad (2)$$

Accordingly, plots of $\ln\left(\frac{[p-\mathrm{CBA}]}{[p-\mathrm{CBA}]_0}\right)$ versus $\int [\mathrm{O}_3]dt$ should be linear, with a slope from which R_{CT} can be determined using the reported value of $k_{p\text{-CBA}/^{\bullet}\mathrm{OH}}$.

3.3.5. Analytical Methods. The concentration of O_3 in stock solutions was measured via UV/vis spectrometry (ε = 2900 L/mole/cm @ 258 nm) [293] using a Thermo Scientific Genesys 10S Spectrophotometer. At lower concentrations in reactors, aqueous O_3 was measured colorimetrically using the indigo blue method [293]. Concentrations of *p*-CBA were quantified using high performance liquid chromatography with diode array detector (HPLC/DAD). The analytical method for *p*-CBA analysis used an isocratic 60:40 methanol:water eluent adjusted to pH 2.7 with H_3PO_4 [299]. The Agilent 1100 HPLC/DAD used an Eclipse XBD-C18 column (4.6 × 150 mm, 5 μm particle size) and a 100 μL injection volume and a 1 mL/min flow rate.

3.3.6. Characterization of MWCNTs. The size and morphology of MWCNTs were characterized via imaging with transmission electron microscopy (TEM). TEM images were collected on a high resolution JEOL 2100F transmission electron microscope in bright field mode operating at 200 kV. Samples were prepared for TEM analysis through the addition of a drop of dilute MWCNT suspension prepared in DI water onto a holey carbon Cu TEM grid.

The specific surface area of as-received MWCNT powders was measured via N_2 BET adsorption isotherms performed on a Quantachrome BET Nova 4200e automated surface area analyzer. Samples were outgassed overnight at 100°C under vacuum prior to analysis via a seven point N_2 BET adsorption isotherm.

Surface chemical composition, specifically the concentration of surface oxygen arising from functionalization via nitric acid, was determined via X-ray photoelectron spectroscopy (XPS) analysis conducted on a custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system, per established methods [92]. The surface analysis chamber is equipped with monochromatic radiation at 1486.6 eV from an aluminum Kα source using a 500 mm Rowland circle silicon single crystal monochromator. Survey scans were collected using the following instrument parameters: energy scan range of 1200 to -5 eV; pass energy of 160 eV; step size of 1 eV; dwell time of 200 ms and an X-ray spot size of 700 × 300 μm. High resolution spectra were acquired in one sweep of all regions of interest using the following experimental parameters: 20 to 40 eV energy window; pass energy of 20 eV; step size of 0.1 eV and dwell time of 1000 ms. All spectra were calibrated using C1s peak at 285.0 eV. A Shirley-type background was subtracted from each spectrum to account for inelastically scattered electrons that contribute to the broad background. CasaXPS software was used to process the XPS data. Transmission corrected relative sensitivity factor (RSF) values from the Kratos library were used for elemental quantification.

The behavior of MWCNTs in aqueous suspension was also extensively characterized using dynamic light scattering (DLS), zeta potential analysis, and sedimentation studies. Solution-phase characterization was performed on 20 mg/L suspensions of various MWCNTs prepared in a 5 mM phosphate buffer. Dynamic light scattering (DLS) and zeta potential analyses were conducted with a ZetaPals analyzer (Brookhaven Instruments Corporation, Holtsville, NY). Mean hydrodynamic particle diameters via DLS were measured at pH 7, whereas zeta potential analysis was conducted as a function of pH. Suspensions were adjusted to their desired pH value (pH 2, 5, 7 and 9) prior to analysis using dilute NaOH or HCl to adjust the pH to the desired value. Measurements were repeated five times for quality control. The stability of CNT suspensions at pH 7 as a function of surface oxidation was also examined using sedimentation tests. Suspensions (20 mg/L) were prepared in 5 mM phosphate buffer. A portion of suspension was then transferred to a 1-cm quartz cuvette and rates of settling were measured by the change in light transmittance (λ of 300 nm) as a function of time using a UV/visible spectrophotometer (Thermo Fisher Scientific, Genesys 10S).

3.4 Results and Discussion

3.4.1. Characterization of MWCNTs and their Suspensions. Generally, MWCNT dimensions and morphology matched expectations provided by the vendor, as shown in Table 3-1.

Table 3-1

Mean hydrodynamic diameter as measured by DLS for as-received and oxidized MWCNTs considered in this study.

MWCNT	Mean Hydrodynamic Diameter (nm)
NL-NF	3.4 (± 0.8) x 10^4
NL-70	330 (± 20)
CT-NF	4.3 (± 0.5) x 10^4
CT-70	320 (± 9)

Measurements were conducted at pH 7 on 20 mg/L suspensions of MWCNTs prepared as described above.

Measured specific surface areas from N_2-BET were 250 and 280 m^2/g for NL and CT MWCNTs, respectively. Surface chemical composition via XPS revealed no elements other than C and O, in contrast to bulk elemental analyses via SEM/EDX provided by the vendors that suggest some impurities from the catalysts used during synthesis [e.g., Fe (0.94% w/w) and S (0.14%) for NL MWCNTs and Ni (0.94), Cl (0.45%), and Fe

(0.26%) for CT]. The disagreement between XPS and SEM/EDX characterization is consistent with other recent investigations of MWCNTs [300], suggesting that impurities are primarily located in the interior of the MWCNTs rather than the surface. Consistent with expectations for oxidized MWCNTs [301], Figure 3-2 shows a roughly linear relationship between surface atomic oxygen concentration, as quantified by the O(1s) region from XPS, and the strength of HNO_3 used during functionalization of CT and NL MWCNTs. No other changes in MWCNT morphology or composition were evident in oxidized samples relative to as-received materials.

As observed in other studies [75], increasing surface oxidation resulted in greater MWCNT dispersion and suspension stability. For example, Table 3-1 shows that the mean hydrodynamic diameter measured via DLS for suspensions of CT-70 and NL-70 were two orders of magnitude smaller than those in suspensions of as-received materials. A lower degree of aggregation (i.e., greater suspension stability) for oxidized MWCNTs was also reflected in sedimentation experiments (Figure 3-3), in which as-received suspensions were far more prone to settling over 2 h than their oxidized counterparts. The relationship between surface oxidation and suspension stability is more quantitatively presented in Figure 3-4, which shows that settling rate coefficients, k_{settling} values estimated by modeling sedimentation as a first-order process (i.e., exponential decay), decreased monotonically with increasing surface oxygen concentration.

Finally, values of zeta potential generally became increasingly negative with increasing pH, with oxidized MWCNTs being more negatively charged at all pH values than their non-functionalized analogues (Figure 3-5). Functionalization adds ionizable oxygen-containing moieties to the MWCNT surface including surface hydroxyl (-OH) and carboxyl (-COOH) groups [301]. The deprotonation of these surface groups are responsible for the negative surface change on oxidized CNTs over the entire range of pH values investigated, including those used in subsequent ozonation experiments (i.e., pH 7).

*3.4.2. Ozone and p-CBA Decay in MWCNT Suspensions***.** Figure 3-6 shows degradation of O_3 (Figure 3-6a) and *p*-CBA (Figure 3-6b) in 20 mg/L suspensions of CT and NL MWCNTs. Data are shown for MWCNTs reacted with 160 μM ozone as-received (CT-NF and NL-NF) and after oxidation with concentrated nitric acid (CT-70 and NL-70). Shown for comparison are corresponding data collected in a system with only O_3 (i.e., without MWCNTs). Data shown represent averages (and standard deviation) from at least triplicate experiments.

In all cases, MWCNT suspensions enhanced O_3 decay compared to systems free of MWCNTs. There was remarkable consistency in reactivity between the MWCNTs supplied from different vendors, with essentially identical reactivity exhibited by CT and NL MWCNTs. Nitric acid oxidized MWCNTs were considerably more reactive per unit mass than as-received MWCNTs; oxidized MWCNTs nearly completely consumed O_3 over two minutes whereas only 40% decay was observed for as-received materials. Considerably less (< 20%) O_3 decay was observed in the systems free of MWCNTs over the same time scale. In all systems, the change in O_3 concentration over time followed exponential decay (fits from nonlinear regression are shown in Figure 3-6a), allowing coefficients for ozone decay (k_{O3} values) to be determined from semi-log plots of O_3 concentration versus time. From k_{O3} values measured at 20 mg/L, as-received and oxidized MWCNTs enhanced O_3 decay by as much as 3- and 8-fold, respectively.

Corresponding analysis of *p*-CBA (Figure 3-6b) suggests O_3 decay is accompanied by $^{\bullet}OH$ formation in most, but not all, MWCNT systems. NL-NF systems exhibited little to no reactivity toward *p*-CBA, with concentration data often over-lapping with those observed for *p*-CBA in systems without MWCNTs. This is in contrast to CT-NF systems, which exhibited a near-immediate ~25% drop in *p*-CBA after which its concentration remained relatively unchanged over the remainder of the experiment. The greatest degree of *p*-CBA loss, and thus $^{\bullet}OH$ production, was observed in CT- and NL-70 systems, in which the rate of *p*-CBA decay closely mirrored O_3 consumption. As with their reactivity toward O_3, the rate and extent of *p*-CBA loss in CT- and NL-70 suspensions were nearly identical, suggesting that any differences in their purity or other physicochemical properties originating from their respective vendors appear to exert little influence on their capacity for $^{\bullet}OH$ formation.

We note that in O_3-free control systems, adsorption of *p*-CBA onto MWCNTs was in most cases minimal. The greatest extent of *p*-CBA sorption over timescales relevant to our ozonation experiments occurred on non-functionalized MWCNTs, corresponding to approximately 20% of the initial *p*-CBA concentration in 20 mg/L suspensions of CT- and NL-MWCNTs (or ~3 μg *p*-CBA/mg CNT). Trends in *p*-CBA sorption are most consistent with hydrophobic interactions being responsible for uptake, as increasing surface polarity via oxidation essentially made sorption negligible in CT-70 and NL-70 suspensions. Unless otherwise noted, all *p*-CBA concentration data from reactivity studies presented herein have been adjusted to account for sorption based upon uptake measured in O_3-free controls. Thus, all losses in *p*-CBA concentration shown in Figure 3-6b resulted from oxidation. Additional control experiments found that supernatants collected via centrifugation of CT-NF and NL-NF suspensions were unreactive toward O_3 and *p*-CBA, consistent with a surface-mediated oxidation process in MWCNT suspensions.

There are several noteworthy observations from the trends in O_3 and *p*-CBA decay in Figure 3-6. For example, despite promoting O_3 decay, NL-NF suspensions resulted in essentially no additional *p*-CBA decay. Thus, not all MWCNT surface sites capable of reacting with O_3 are also suitable for $^{\bullet}OH$ production. This is also supported by the abrupt but limited *p*-CBA decay in CT-NF suspensions, consistent with a small number of highly reactive surface sites capable of producing $^{\bullet}OH$, whereas O_3 consumption over longer time scales does not yield $^{\bullet}OH$. Results from CT-70 and NL-70 suspensions, on the other hand, indicate that the limitation in surface sites capable of $^{\bullet}OH$ production is relieved via surface oxidation. The greater reactivity of oxidized MWCNTs either implicates surface oxides (e.g., carboxyl groups) known to be generated via functionalization with HNO_3 as the primary entities responsible for O_3 consumption and $^{\bullet}OH$ formation, or may simply reflect easier access to the same types of reactive sites available on non-functionalized MWCNTs due to the greater dispersion of the oxidized materials in suspension.

3.4.3 Performance Comparison of O_3/CNT to Alternative O_3-based AOPs.

Figure 3-7 shows R_{CT} plots (i.e., $\ln([p\text{-CBA}]/[p\text{-CBA}]_o$ versus $\int[O_3]dt$) for CT-70 and NL-70 suspensions, as well as for O_3 in the absence of MWCNTs, a combination of O_3 and GAC (40 mg/L) and a 1:1 molar ratio of O_3 and H_2O_2. Relative to O_3 alone, the GAC suspension provided a modest, two-fold enhancement in $^{\bullet}OH$ exposure, a value that agrees reasonably well with the 5-fold increase in R_{CT} observed by Sanchez-Polo *et al.* [260] for 500 mg/L of a commercially available GAC. Production of $^{\bullet}OH$ was considerably greater in suspensions of oxidized MWCNTs. Specifically, 20 mg/L suspensions of CT-70 and NL-70 yielded R_{CT} values approximately 30-fold greater than in O_3 systems and at least an order of magnitude greater than observed with 40 mg/L of GAC, which represents the lowest GAC loading at which enhanced $^{\bullet}OH$ production could be observed.

Our results also show that oxidized MWCNTs produce $^{\bullet}OH$ to a nearly equivalent extent as the combination of O_3 and H_2O_2. R_{CT} plots for suspensions of CT-70 and NL-70 essentially overlapped with those of the H_2O_2/O_3 system (Figure 3-7a). Furthermore, as is to be expected for a surface-mediated process, the reactivity of MWCNTs scaled with their suspension concentration. As shown in Figure 3-7b, R_{CT} values generally increased with the concentration of CT-70 and NL-70 in suspension in a matter essentially independent of the two initial O_3 concentrations we utilized (either 80 or 160 μM). This behavior in R_{CT} is attributable to similar increases in k_{O3} values (Figure 3-8) and the rate of *p*-CBA decay (Figure 3-9) that were also observed with increasing MWCNT suspension concentration.

Aside from the magnitude of R_{CT} values, there is another noteworthy similarity between MWCNTs and other O_3-based AOPs. A useful metric in O_3-mediated oxidation processes is the yield of $^{\bullet}OH$ per unit O_3 consumed, which can be assessed experimentally through the change in *p*-CBA concentration at some point along the reaction coordinate normalized to the change in O_3 concentration measured at that same point in time (i.e., [Δ*p*-CBA]/[ΔO_3]). This ratio calculated as a function of time is shown in Figure 3-7c for CT-70 and NL-70 suspensions, as well as for the O_3/H_2O_2 system. In all cases, this ratio is roughly constant over the duration of reaction, but most importantly, it is essentially equal in magnitude across systems (average [Δ*p*-CBA]/[ΔO_3] values range between $9.8 (\pm 0.5) \times 10^{-3}$ to $1.25 (\pm 0.08) \times 10^{-2}$). Notably, these yields are nearly identical to those reported by Sanchez-Polo *et al.* [260] for various O_3-based oxidation processes including GAC-enabled catalytic ozonation. The uniformity in $^{\bullet}OH$ yields suggests a shared mechanism for its production from O_3 across all systems. Accordingly, we propose that MWCNTs, especially those with extensive surface oxidation, function in a matter analogous, if not identical, to H_2O_2 upon exposure to O_3.

3.4.4. Influence of MWCNT Suspension Stability and Surface Oxides on $^{\bullet}OH$ Production. It is possible that the greater $^{\bullet}OH$ production observed for oxidized MWCNT suspensions relative to as-received materials is simply due to their greater suspension stability. Certainly, greater MWCNT dispersion increases the surface area available for reaction with O_3, and such behavior must contribute, at least in part, to the greater reactivity for oxidized MWCNT suspensions.

Experimental evidence indicates, however, that increased suspension stability alone cannot explain the observed changes in $^{\bullet}OH$ production arising from surface oxidation. For example, in a subset of experiments we considered the influence of O_3 concentration on $^{\bullet}OH$ formation in CT-NF systems (Figure 3-10). Although faster in CT-70 suspensions, O_3 decay was a first-order process (i.e., its rate was independent of initial ozone concentration) in both CT-NF and CT-70 suspensions (Figure 3-10a). In CT-NF suspensions, however, the rate and extent of *p*-CBA decay was invariant over a three-fold increase in initial O_3 (from 80 to 240 μM; Figure 3-10b), suggesting that $^{\bullet}OH$ formation in these systems is limited by something other than available O_3. We propose this limitation relates to the availability of surface sites in CT-NF suspensions suitable for generating $^{\bullet}OH$ during O_3 decay. In contrast, CT-70 systems exhibited a roughly two-fold increase in *p*-CBA removal when the initial O_3 concentration was doubled, consistent with an excess of surface sites on oxidized MWCNTs capable of generating $^{\bullet}OH$ via O_3 decay.

Additional evidence obtained with NL MWCNTs also suggests that surface oxidation adds reactive sites capable of producing $^{\bullet}OH$ during ozonation. As previously noted, NL-NF suspensions showed only a minimal increase in *p*-CBA degradation relative to the loss observed in the system free of O_3 (Figure 3-11). Such behavior is consistent with the majority of *p*-CBA loss in NL-NF suspensions resulting from its sorption onto the hydrophobic MWCNT surface. Behavior of NL-70, on the other hand, was markedly different. Relative to NL-NF, not only was *p*-CBA degradation considerably increased in the presence of O_3, but the extent of *p*-CBA sorption in suspensions without O_3 also decreased (Figure 3-11), as would be expected for the more polar MWCNT surface arising from oxidation with HNO_3. We contend that if the increased reactivity associated with functionalization was purely a result of increased MWCNT dispersion, the fraction of *p*-CBA loss attributable to sorption in NL-70 systems would match that measured with as-received materials. Instead, even with greater MWCNT surface area available in suspension due to improved dispersion, the amount of *p*-CBA loss attributable to sorption decreased in the NL-70 systems. In this case, therefore, it appears that oxidation with HNO_3 changes the inherent nature of the NL MWCNT surface from that of a sorbent to a substrate capable of generating $^{\bullet}OH$ during ozonation.

3.4.5. Tailoring $^{\bullet}$OH Exposure via the Extent of MWCNT Surface Oxidation. Concentration profiles for *p*-CBA as a function of time for NL MWCNTs oxidized with 20, 40 and 70% HNO_3 are shown in Figure 3-12a. The rate and extent of *p*-CBA loss increased with increasing strength of HNO_3, with similar reactivity trends also observed for ozone decay. In Figure 3-12b, R_{CT} values from these suspensions (NL-NF, 20, 40 and 70) are shown as a function of surface oxygen concentration as quantified via XPS spectra (see Figure 3-2), revealing a strong, linear correlation between $^{\bullet}$OH exposure and NL MWCNT surface oxidation. This relationship, albeit somewhat weaker, is also observed for R_{CT} values measured in suspensions of CT-NF, 20, 40 and 70. Thus, it appears that $^{\bullet}$OH production during ozonation is linked to the availability of oxygen-containing functionalities present on the MWCNT surface, and that this relationships is generalizable regardless the origin of the MWCNTs.

A number of different surface oxide sites are generated during MWCNT oxidation with HNO_3 including carboxyl (-COOH), which is typically produced in the greatest abundance, hydroxyl (-OH), and carbonyl (–C=O) moieties [301]. We propose these oxygen-containing surface functionalities are the reactive entities primarily responsible for $^{\bullet}$OH formation. However, aggressive oxidizing agents such as HNO_3 can also produce amorphous carbon on the MWCNT surface and induce surface defects [301], the density of which may also scale with surface oxygen concentration. Additional work is therefore needed to elucidate the exact nature of the entities responsible for $^{\bullet}$OH production and explore possible contributions from defects and amorphous carbon

3.4.6. Environmental Implications. MWCNTs effectively promote formation of $^{\bullet}$OH during ozonation, behavior that is exhibited for CNTs regardless of their commercial source. Most notably, we find that MWCNT surface chemistry, specifically their degree of surface oxidation, positively influences the extent of $^{\bullet}$OH production. While increased dispersion undoubtedly contributes to the enhanced reactivity of oxidized MWCNTs, surface sites created during oxidation with HNO_3 also appear to promote O_3

decomposition into $^{\bullet}$OH. As a practical consequence, surface oxygen content should be viewed as a metric for optimizing MWCNT performance, as highly oxidized MWCNTs (i.e., surface oxygen atomic concentration ~ 10% from XPS) exhibit reactivity near equivalent to some traditional ozone-based AOPs (e.g., O_3 with H_2O_2).

For these highly oxidized MWCNTs (i.e., CT-70 and NL-70), enhanced formation of $^{\bullet}$OH was observed at relatively low suspension concentrations (2 and 5 mg/L, respectively), and their reactivity increased with MWCNT mass loading. We expect, therefore, that R_{CT} values exceeding those of traditional ozone-based AOPs can be readily achieved at higher solid-to-water ratios, as might be encountered within a porous mesh network or filter mat composed of CNTs. There have been several recent demonstrations as to the utility of CNTs in filtration, typically applied as a thin CNT layer deposited on an underlying membrane support [4, 82, 302-304]. We contend that modification of robust ceramic microfiltration membranes with a coating of CNTs, in an manner analogous to their modification with metal oxide nanoparticles [83], could potentially couple membrane filtration with the highly oxidizing microenvironment generated within the CNT layer upon exposure to an ozonated feed stream.

CNTs appear ideally suited for such an application platform. The short timescales associated with O_3 and *p*-CBA decay (on the order of minutes in mg/L suspensions) suggest that CNTs can effectively enhance $^{\bullet}$OH production without the need for long contact or residence times. Furthermore, relative to other reagents used to activate O_3 such as H_2O_2, CNTs provide comparable reactivity with the promise of greater treatment longevity; while H_2O_2 will be completely consumed upon dosing with O_3, CNTs will persist and may exhibit sustained reactivity toward O_3 over their entire lifetime. In fact, O_3 is a recognized oxidizing agent for CNTs,[305-310] such that sustained reaction with O_3 may continually regenerate the surface sites most responsible for $^{\bullet}$OH formation. Finally, while a detailed examination of costs is outside the scope of this study, production costs continue to decrease for a multitude of non-research grade (i.e., “industrial grade”) CNTs (currently on the order of $65/kg) [311] such that their use in full-scale treatment applications may one day not be cost prohibitive.

We note that for both CT and NL MWCNTs across the range of surface oxidation explored, we consistently observed that faster rates of O_3 decay coincided with greater rates of *p*-CBA loss (i.e., $^{\bullet}OH$ production). This behavior is somewhat undesirable from an application standpoint; while MWCNTs can greatly enhance $^{\bullet}OH$ exposure, it requires a corresponding increase in O_3 demand. Ideally, high $^{\bullet}OH$ production would be achieved with only modest conversion of O_3, thereby maximizing the amount the $^{\bullet}OH$ generated per unit of O_3 consumed. Future studies with CNTs and other carbonaceous nanomaterials must aim to identify system conditions (e.g., solution variables or materials properties) that optimize this ratio.

Finally, the results presented herein fit well into the existing body of knowledge regarding the reaction of different forms of carbon with O_3. In addition to the reactivity of AC, enhanced $^{\bullet}OH$ production has also been reported during the reaction of O_3 with various forms of organic matter including effluent organic matter [42, 81, 172, 312, 313]. The surface moieties present on functionalized MWCNTs are analogous to many of the functionalities encountered in dissolved organic matter that are believed to be promoters of $^{\bullet}OH$ from O_3 [42, 81, 172, 312, 313]. This similarity between functionalized CNTs, AC and certain types of dissolved organic matter should not be overlooked when considering the implications and applications of CNTs in the environment.

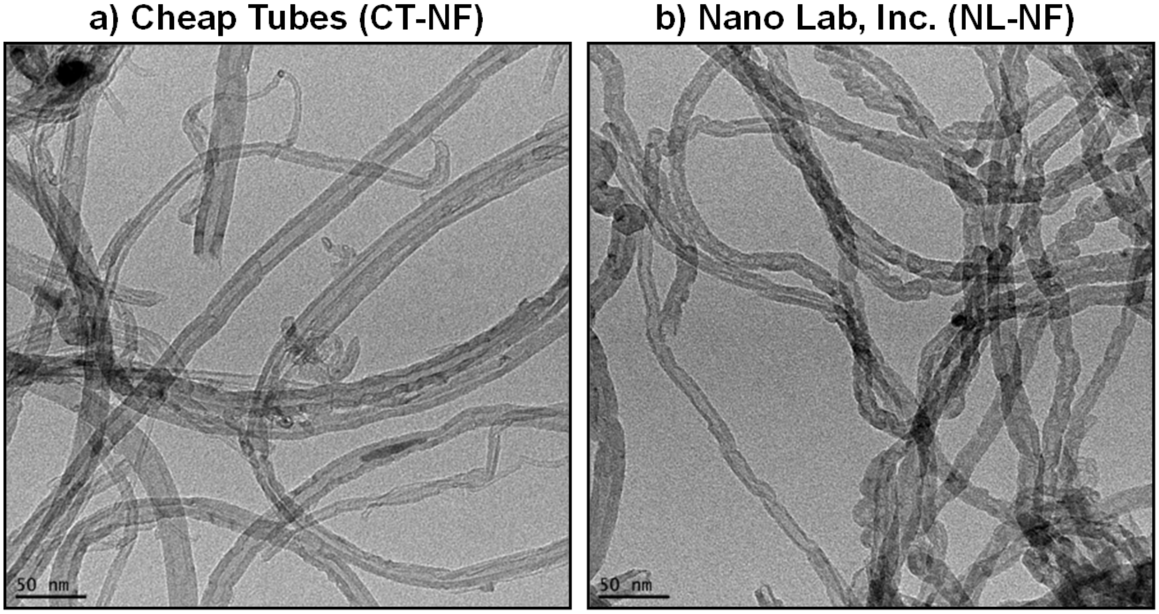


Figure 3-1: TEM images of as received multi-walled carbon nanotubes. Images show CNTs from (a) CheapTubes.com (CT-NF) and (b) NanoLabs, Inc (NL-NF). The outer diameter (OD) of MWCNTs generally fell within the range expected from the vendor (15 ± 5 nm for NL and between 20-30 nm for CT). Length and inner diameters were not quantified via TEM imaging, with vendor reported lengths of 1-5 mm and 10-30 mm for NL and CT, respectively, and inner diameters of 7 ± 2 nm and 5-10 nm for NL and CT, respectively.

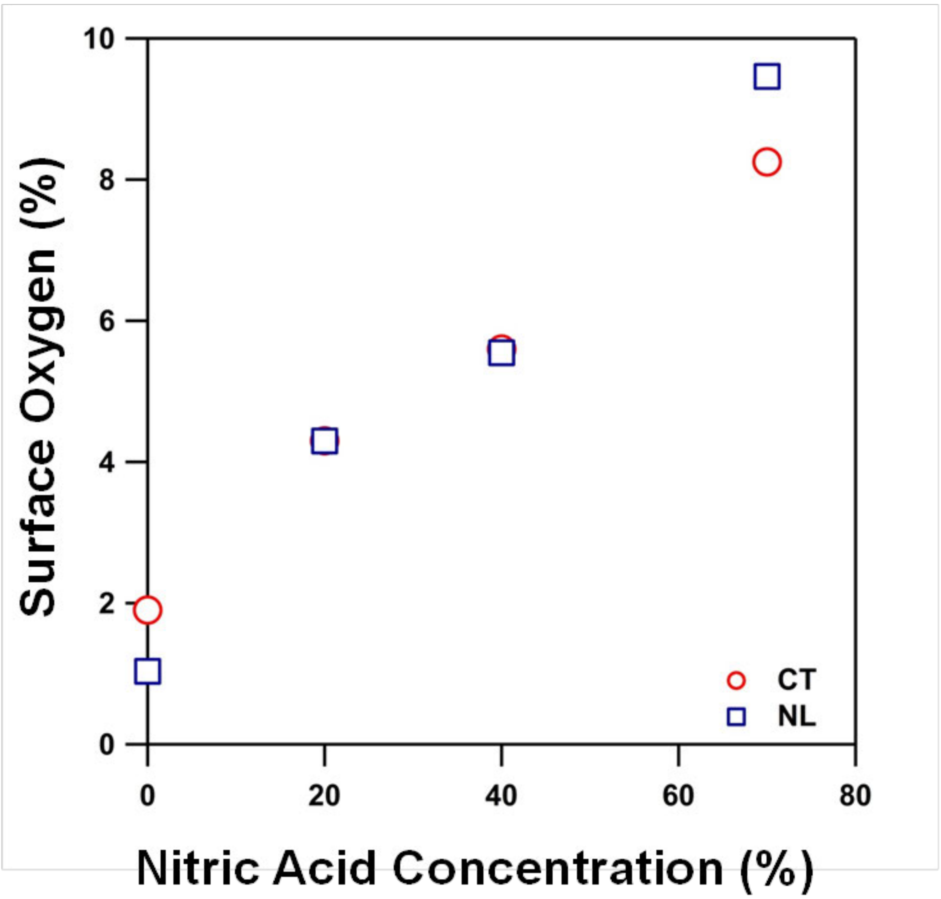


Figure 3-2: Surface oxygen concentration in atomic percent (from O1(s) region of XPS) as a function of the strength of nitric acid (%) used during MWCNT functionalization. A direct linear relationship is evident between total surface oxygen and strength of HNO_3, and the extent of oxidation at a specific HNO_3 concentration was comparable on MWCNTs from each vendor.

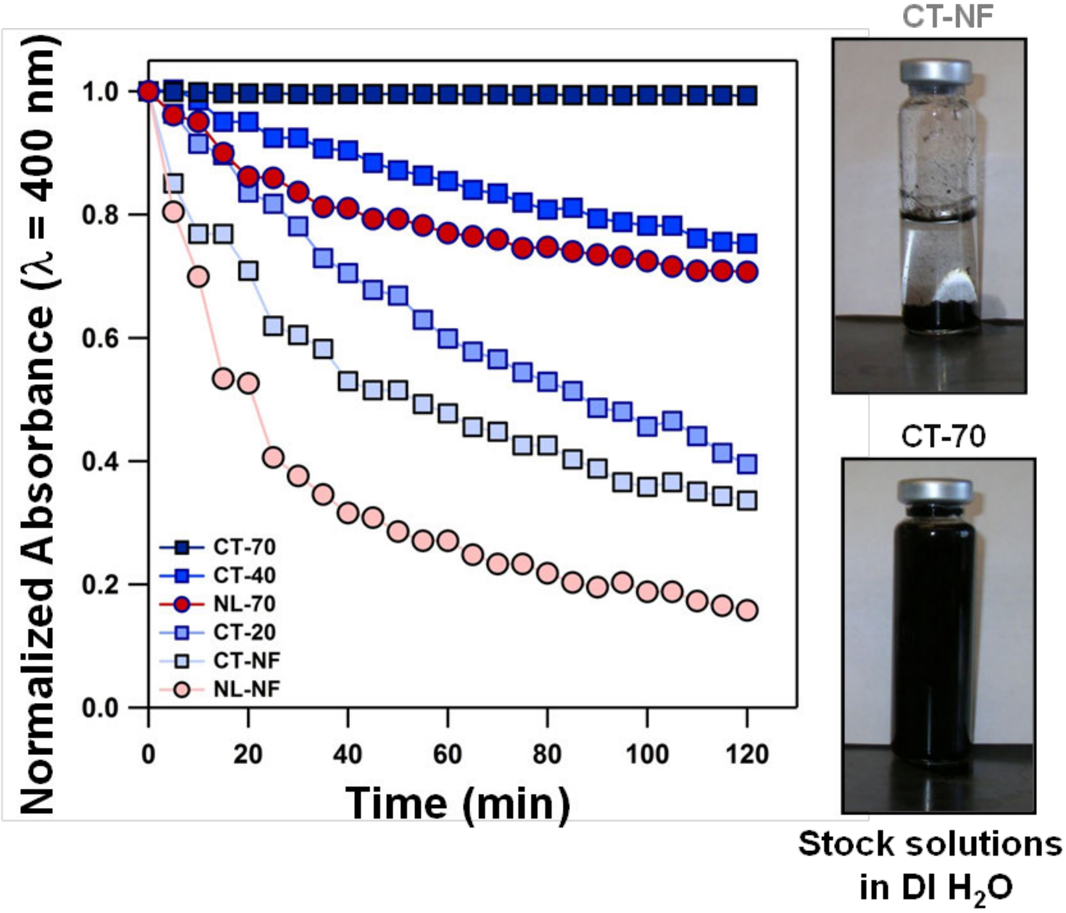


Figure 3-3: Results from sedimentation studies with CT and NL suspensions with various degrees of MWCNT surface oxidation. Suspensions (20 mg/L) were prepared in 5 mM phosphate buffer. A portion of suspension was then transferred to a 1-cm quartz cuvette and rates of settling were measured by the change in light transmittance (l of 300 nm) as a function of time using a UV/visible spectrophotometer. Generally, suspension stability increased with the degree of MWCNT surface oxidation. This outcome is shown on the right in photographs of 1 g/L stock suspensions of CT-NF and CT-70 prepared in DI water. Images were taken 1 h after the stock suspensions were removed from the sonicator.

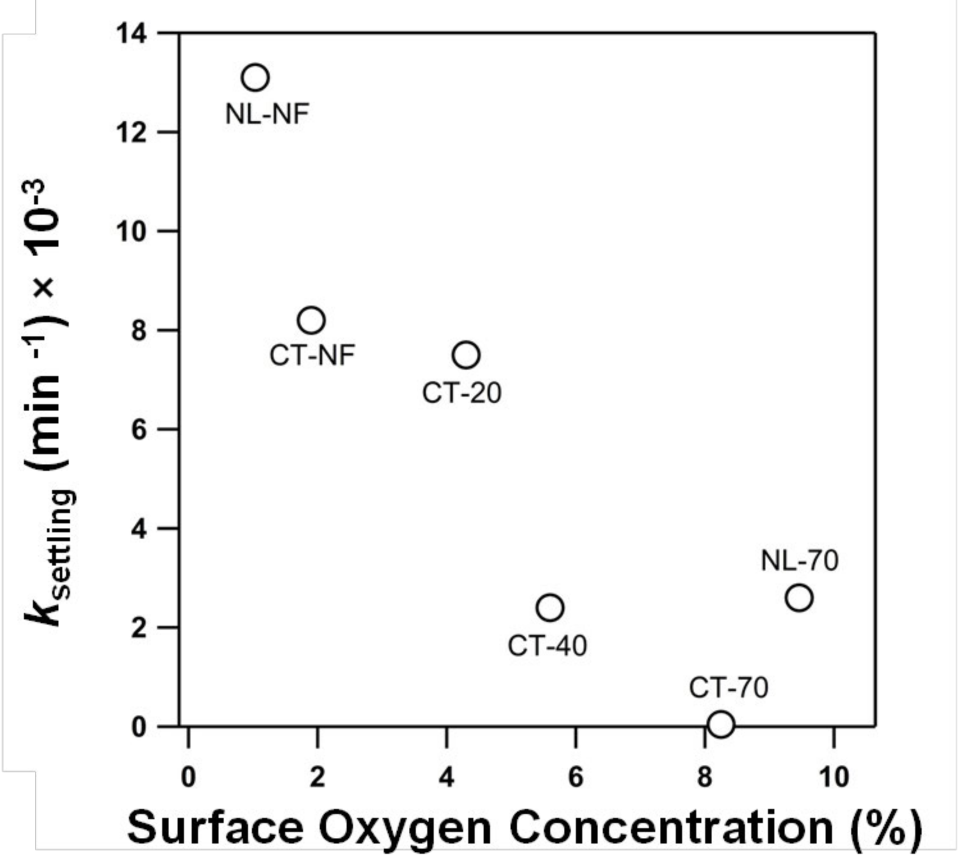


Figure 3-4: First-order rate coefficients for MWCNT settling ($k_{settling}$ values) as a function of surface oxygen concentration (in atomic % as quantified by the O(1s) region via XPS). Values $k_{settling}$ were quantified by using an exponential decay model to fit the sedimentation data shown in Figure S3. Generally, suspensions with oxidized MWCNTs were more stable, an indicated by the decrease in $k_{settling}$ values observed with increasing surface oxidation. The impact of this change in MWCNT aggregation state on their reactivity toward ozone is addressed in the main text.

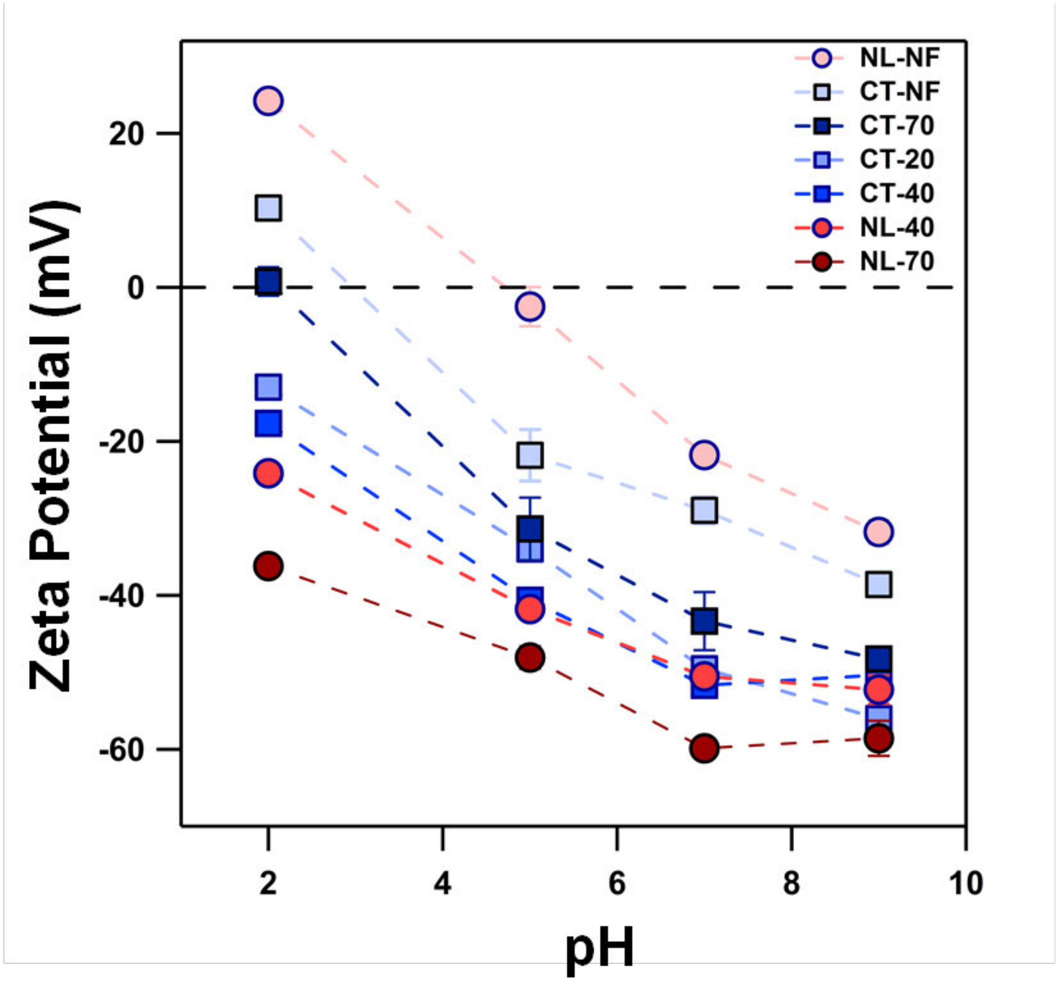


Figure 3-5: Zeta potential of MWCNT suspensions as a function of pH for CNTs exhibiting various degrees of surface oxidation. All solutions were prepared using 5 mM phosphate buffer, adjusted to the indicated pH value. MWCNT concentrations were adjusted so that the final suspensions used in analysis exhibited an absorbance between 0.3 and 0.35 at 546 nm. Values shown are the means and standard error for five readings. The results show that the zeta potential on all MWCNTs decreases (i.e., becomes more negative) with increasing pH. Also, oxidized MWCNTs tend to exhibit more negative zeta potential values at all pH relative to as-received or non-functionalized MWCNTs. Results support the surface sites present on oxidized MWCNTs (e.g., surface carboxyl and hydroxyl groups) are deprotonated at the pH value (pH 7) used in reactivity studies with ozone.

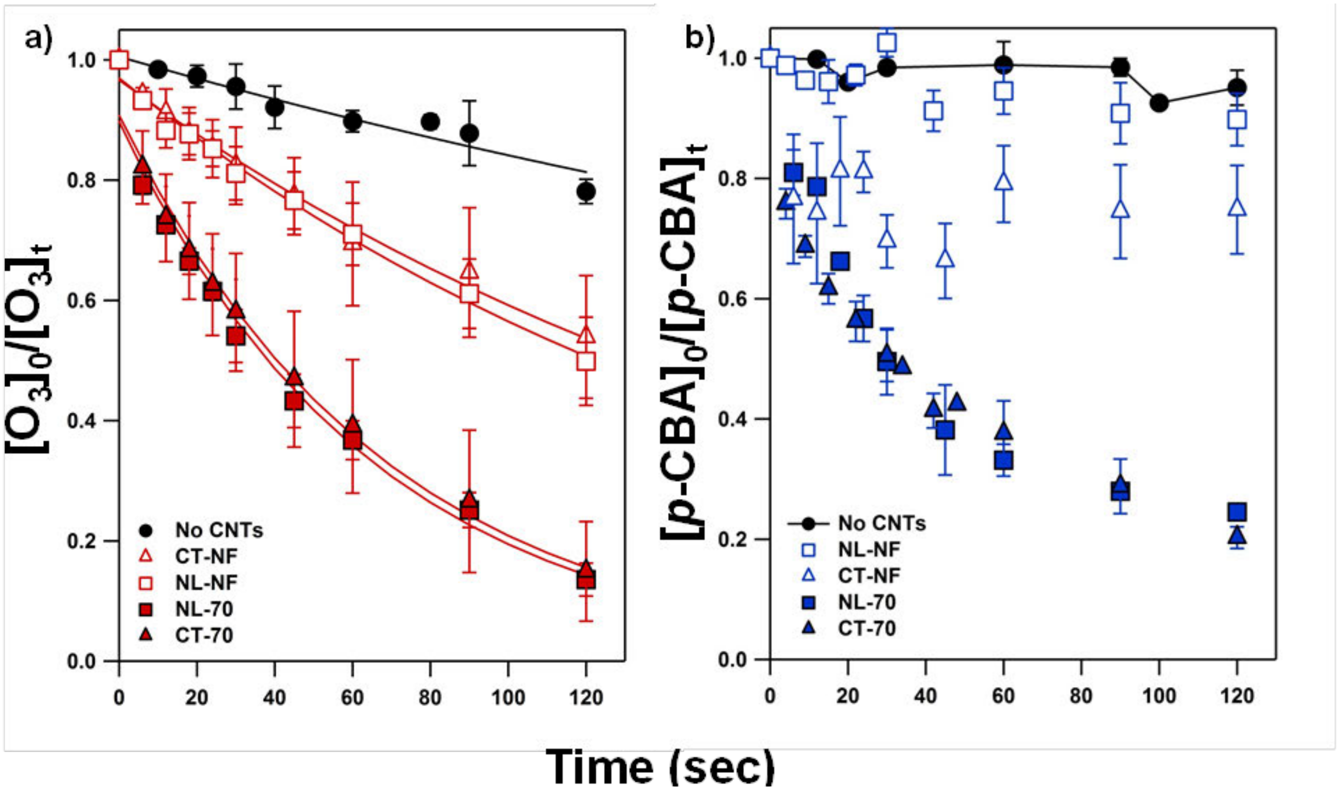


Figure 3-6. Ozone and *p*-CBA concentration as a function of time in 20 mg/L suspensions of MWCNTs. Data are shown for ozone (a) and p-CBA (b) degradation in suspensions of CT and NL MWCNTs that were reacted with ozone as-received (CT-NF and NL-NF; open symbols), as well as after oxidation with 70% HNO_3 (CT-70 and NL-70; solid symbols). Also provided for comparison are O_3 and *p*-CBA data collected in a system free of MWCNTs. In all instances, concentration data were normalized to the initial value measured in the reactor. Uncertainties represent standard deviations for at least triplicate experiments. Pseudo-first order fits to describe O_3 decay are shown in panel (a), as determined by regression analysis. Data were collected in systems with 20 mg/L of MWCNT and an initial O_3 concentration of 160 mM. Systems also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM. Suspensions were prepared in a 5 mM phosphate buffer at pH 7.

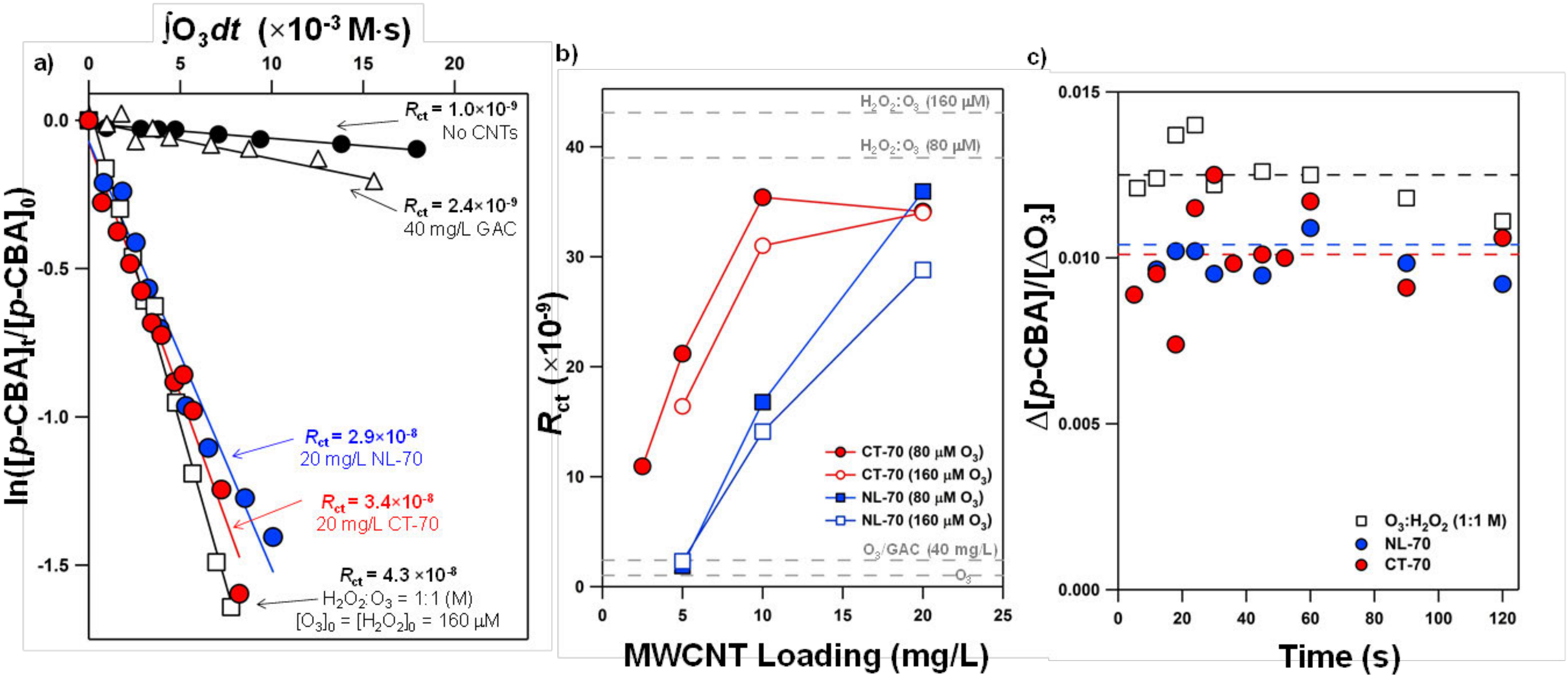


Figure 3-7. Comparative $^{\bullet}$OH Production Efficiency. (a) R_{CT} plots for CT-70 and NL-70 suspensions. Results from systems with O_3 in the absence of MWCNTs, O_3 with GAC, and an equimolar (1:1) mixture of O_3 and H_2O_2 are provided for comparison. As shown in equation 2, values of R_{CT} were determined from the slope of best-fit linear regressions fit to each data set, results of which are shown. (b) Values of R_{CT} for CT-70 and NL-70 systems as a function of MWCNT suspension concentration. The dashed lines indicate R_{CT} values in an O_3 system without CNTs, an O_3 system with GAC, and an equimolar mixture of O_3 and H_2O_2. Values for R_{CT} are shown for initial O_3 concentrations of 80 and 160 mM, as noted. (c) Values of [D*p*-CBA]/[DO_3] as a function of time in CT-70 and NL-70 suspensions, as well as in an equimolar mixture of O_3 and H_2O_2. The average values of [D*p*-CBA]/[DO_3] from each system are indicated by dashed lines [(1.25 ± 0.08) × 10^{-2}, (9.8 ± 0.5) × 10^{-3}, and (1.01 ± 0.14) × 10^{-2} for O_3:H_2O_2, NL-70 and CT-70, respectively]. In all cases, experiments with MWCNT were conducted at 20 mg/L, whereas the GAC system was conducted at 40 mg/L. Unless otherwise noted, systems contained an initial concentration of 160 μM of O_3 and 2 μM of *p*-CBA, as well as 320 μM of *t*-ButOH. Suspensions were prepared in a 5 mM phosphate buffer at pH 7

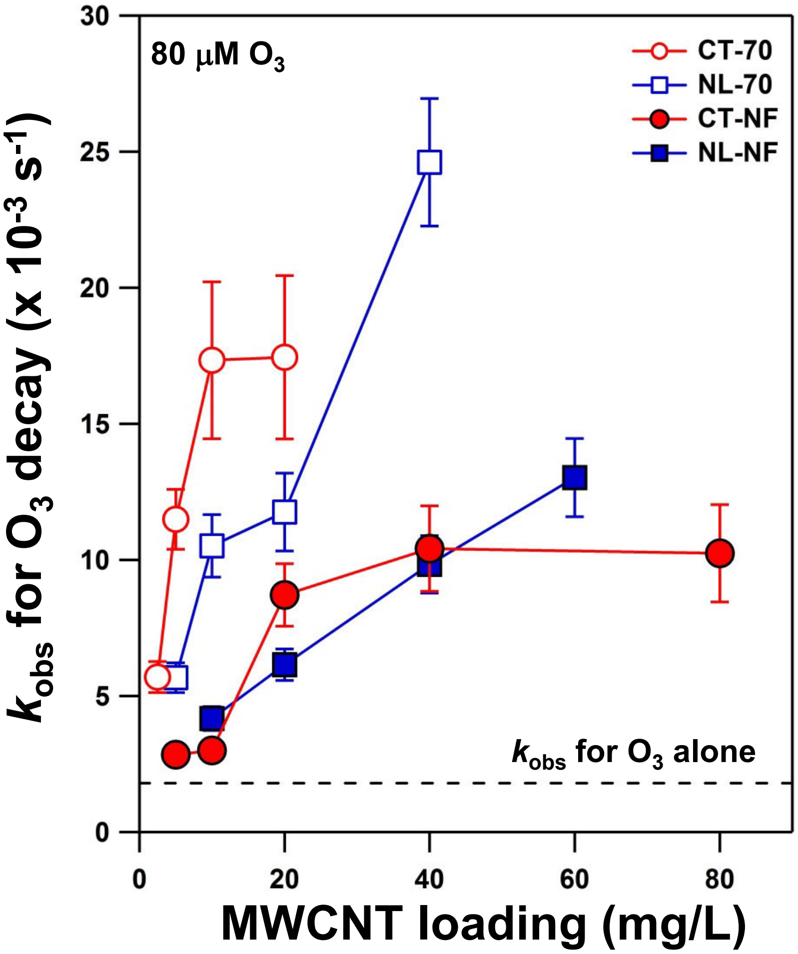


Figure 3-8: Plot of the pseudo-first-order rate constant for ozone decay (k_{obs} value) via reaction with MWCNTs. Results are shown for CT and NL MWCNTs used in reactivity studies as received (or non-functionalized, CT-NF and NL-NF) and after oxidation with 70% HNO_3 (CT-70 and NL-70. Also provided for comparison is the rate constant for ozone decay in a system free of MWCNTs (dashed horizontal line). Uncertainties represent the 95% confidence interval associated with the regression analysis used to quantify the value of k_{obs}. Results show that the rate of ozone decay typically increased with increasing MWCNT concentration in suspension. Also, oxidized MWCNTs were always more reactive toward ozone than their non-oxidized counterparts. Interestingly, while NL MWCNTs showed the expected monotonic increase in k_{obs} values with increasing solid loading, both CT-NF and CT-70 appeared to reach a regime in which the rate coefficient was independent of the MWCNT concentration (i.e., a zero-order dependence on MWCNT mass or reactive surface area). Such behavior with increasing CT-NF and CT-70 concentrations may indicate the presence of a large excess of MWCNT surface sites in these systems that are suitable for O_3 consumption.

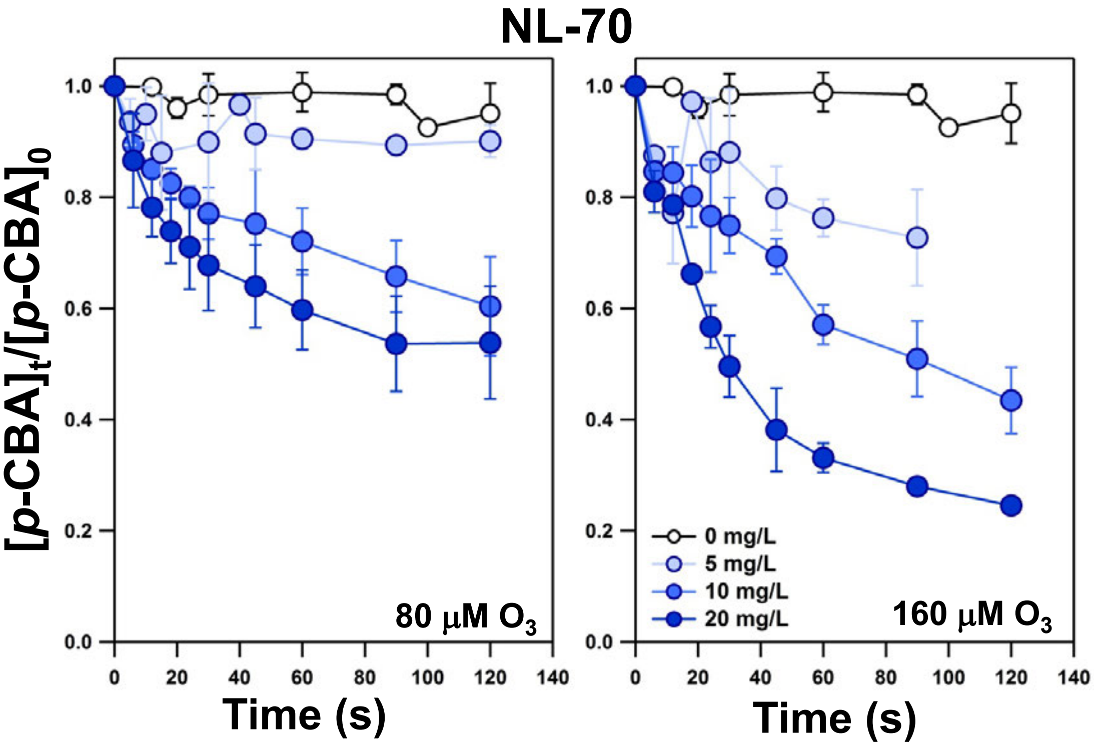


Figure 3-9: Plots of normalized *p*-CBA concentration as a function of time in suspensions of NL-70 MWCNTs. Concentration data are shown as a function of MWCNT concentration in suspension and initial ozone concentration. Uncertainties represent one standard deviation determined from at least triplicate analyses. Data were collected in systems with 20 mg/L of MWCNT, and an initial O_3 concentration of either 80 mM (left) or 160 mM (right). Systems also contained 320 μM of *t-ButOH* and an initial *p*-CBA concentration of 2 μM. Suspensions were prepared in a 5 mM phosphate buffer at pH 7. Data are consistent with $^{\bullet}$OH formation being a surface-mediated process, with the rate and extent of *p*-CBA decay generally scaling with MWCNT concentration. Differences in the total amount of *p*-CBA loss over the course of the reaction are attributable to the different initial concentration of ozone used in each system. As discussed in the main text (see Figure 2c) the amount of *p*-CBA degraded per unit ozone consumed is constant in these systems. Thus, the amount of *p*-CBA loss observed in systems with an initial ozone concentration of 80 mM is limited by this stoichiometry (i.e., almost all of the ozone is consumed over the timescales shown, thus there are no oxidizing equivalents available to further degrade the remaining *p*-CBA). At higher initial concentrations of ozone (160 mM), this limitation in oxidizing equivalents is relieved, and greater removal of *p*-CBA is observed.

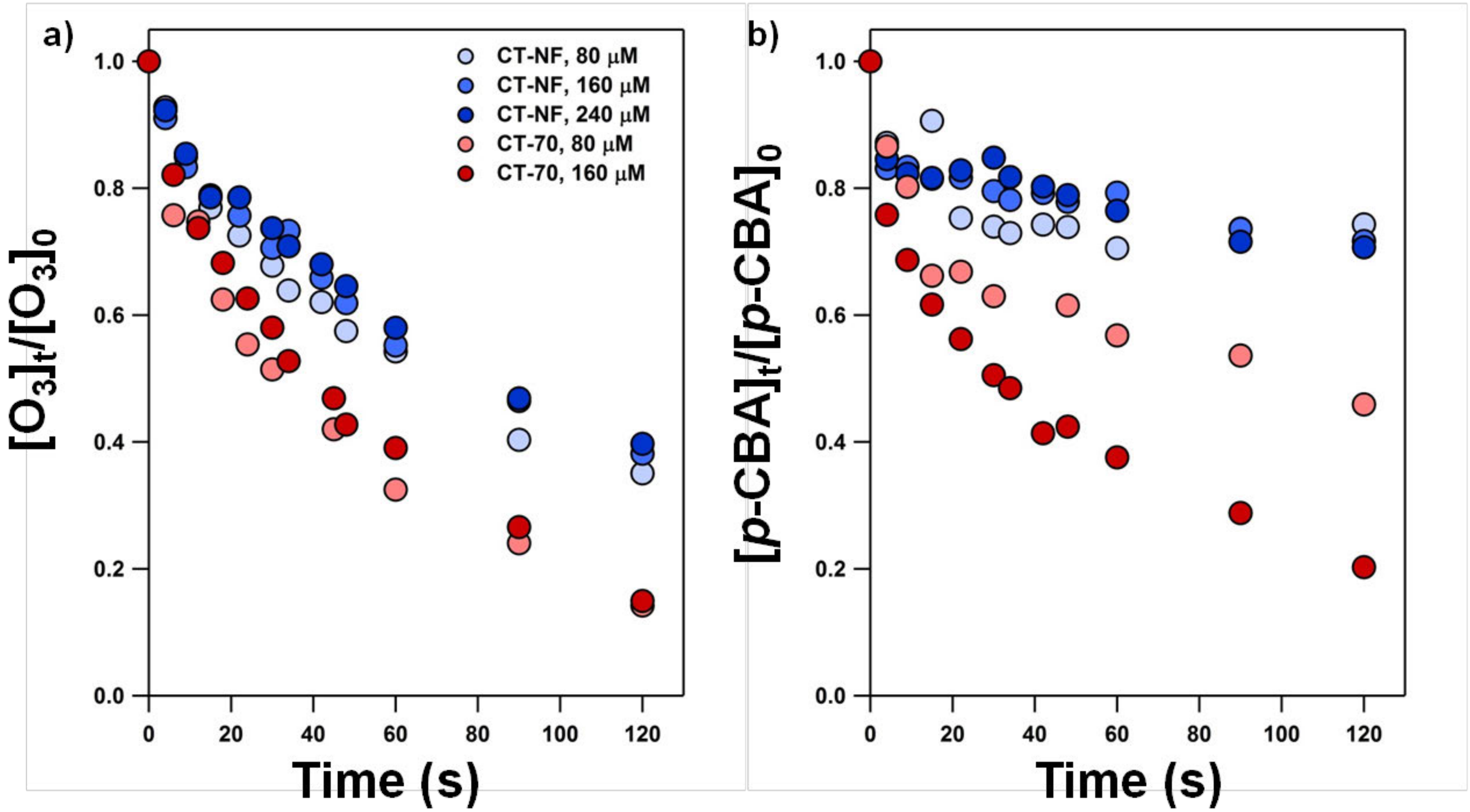


Figure 3-10. Normalized concentrations profiles for O_3 and *p*-CBA as a function of time under a range of initial O_3 concentrations. Data were collected in systems with CT-NF and CT-70 suspensions (20 mg/L) containing a range of initial O_3 concentrations (from 80-320 mM). Representative data are shown. Systems also contained 320 μM of *t-ButOH* and an initial *p*-CBA concentration of 2 μM. Suspensions were prepared in a 5 mM phosphate buffer at pH 7.

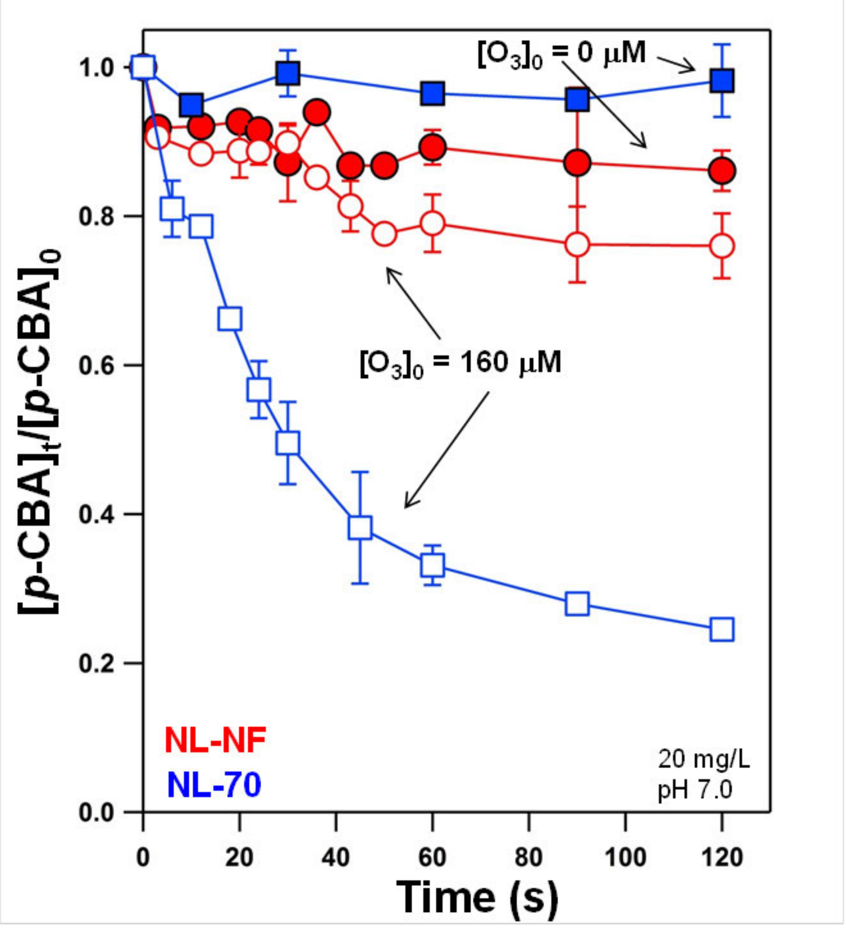


Figure 3-11: Plots of normalized *p*-CBA concentration as a function of time for NL-NF and NL-70. For both suspensions, *p*-CBA data are shown for systems in the presence (open symbols, 160 mM) and absence (solid symbols) of O_3, and *p*-CBA concentration data collected in the presence of O_3 have not been corrected for sorption losses. Uncertainties represent standard deviations for at least triplicate experiments. Data were collected in systems with 20 mg/L of MWCNT. Systems also contained 320 µM of *t-ButOH* and an initial *p*-CBA concentration of 2 µM. Suspensions were prepared in a 5 mM phosphate buffer at pH 7. As discussed in the main text, NL-NF suspensions showed only a minimal increase in *p*-CBA degradation relative to the system free of O_3. Such behavior is consistent with the majority of *p*-CBA loss in NL-NF suspensions resulting from sorption. Behavior of NL-70, on the other hand, was markedly different. Relative to NL-NF, not only was *p*-CBA degradation considerably increased in the presence of O_3, but the extent of *p*-CBA sorption in suspensions without O_3 also decreased. We contend that if the increased reactivity associated with MWCNT functionalization was purely a result of increased MWCNT dispersion, the fraction of *p*-CBA loss attributable to sorption in NL-70 systems would match that measured with as-received materials. It appears, therefore, that oxidation with HNO_3 changes the inherent nature of the NL MWCNT surface from that of a sorbent to a substrate capable of generating $^{\text{Ÿ}}$OH during ozonation

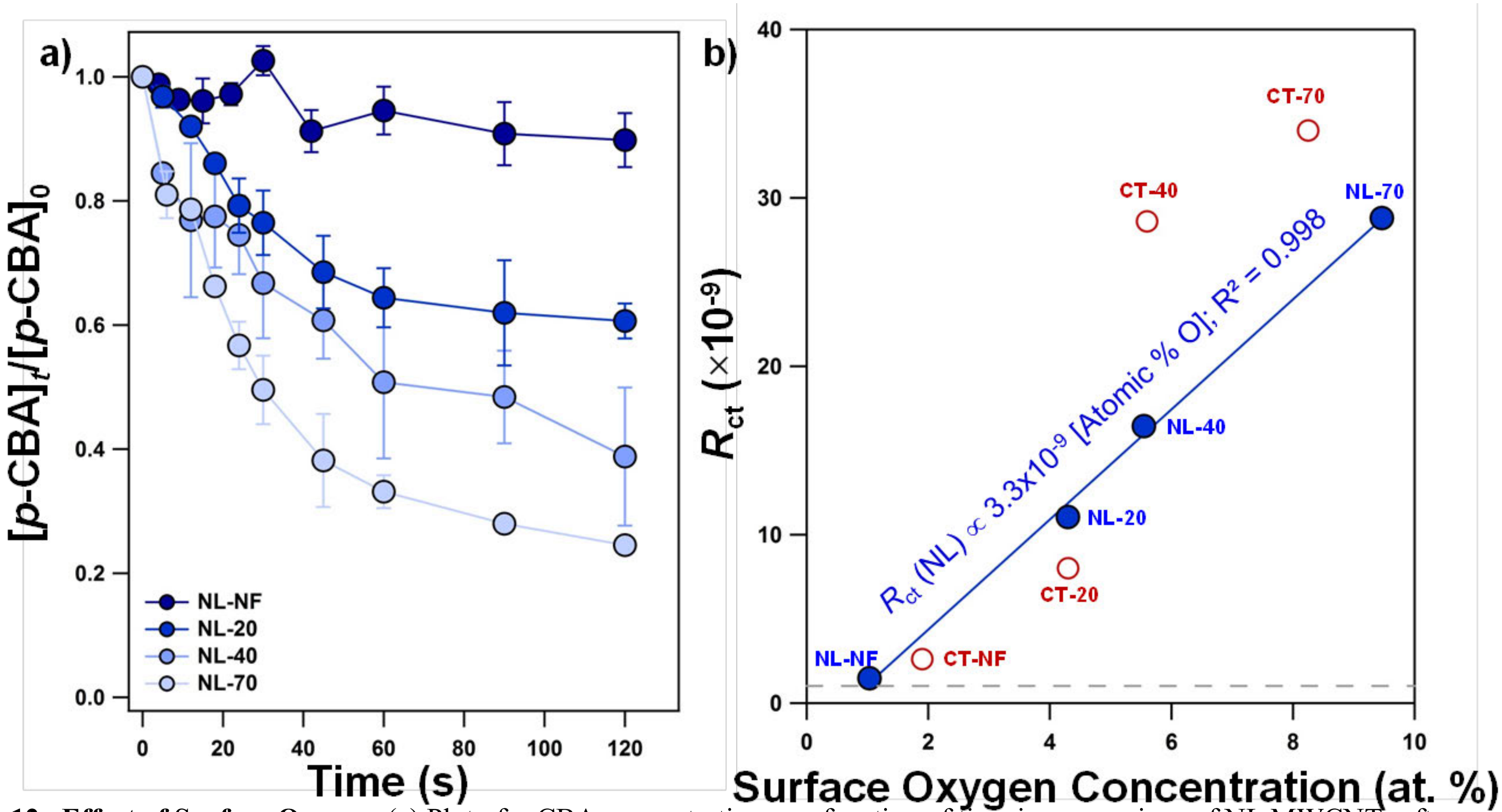


Figure 3-12. Effect of Surface Oxygen. (a) Plot of *p*-CBA concentration as a function of time in suspensions of NL MWCNTs after treatment with various strengths of nitric acid (0, 20, 40 and 70%). Uncertainties represent one standard deviation determined from at least triplicate analyses. (b) Plot of corresponding R_{CT} values as a function of surface oxygen concentration (as quantified from the O(1s) region of XPS analysis). Values of R_{CT} are presented for both CT and NL MWCNT. Given the limited reactivity in as-received MWCNT systems, these R_{CT} values represent estimates for the purpose of comparison only. The blue line represents the result from best fit linear regression analysis for the relationship between R_{CT} and surface oxygen concentration for NL MWCNTs. Data were collected in systems with 20 mg/L of MWCNT, and an initial O_3 concentration of 160 mM. Systems also contained 320 μM of *t-ButOH* and an initial *p*-CBA concentration of 2 μM. Suspensions were prepared in a 5 mM phosphate buffer at pH 7

CHAPTER 4: ROLE OF CARBON NANOTUBE SURFACE CHEMISTRY, STRUCTURE, AND PURITY IN PROMOTION OF HYDROXYL RADICALS DURING OZONATION

4.1 Abstract

We have previously shown that multi-walled carbon nanotubes (MWCNTs) increase hydroxyl radical ($^{\bullet}$OH) production during ozonation, and that this increase correlates with the degree of surface oxygen on the MWCNT surface. Here, we explore the effects of CNT surface chemistry, structure, and composition on $^{\bullet}$OH production during ozonation. Using standard oxidation routes to systematically vary the extent of surface oxygen on the CNTs, we show that $^{\bullet}$OH production is linked to the type of oxygen-containing functional groups on the MWCNT surfaces. Based on correlation analysis coupling reactivity data with surface chemical composition from X-ray photoelectron spectroscopy with chemical derivatization, our results suggest that deprotonated carboxyl groups and possibly also lactone moieties on the CNT surface are integral to CNTs reactivity toward ozone (O_3) and corresponding $^{\bullet}$OH formation. We also found that although single-walled (SW) CNTs tend to exhibit greater reactivity toward O_3 than MW or double-walled (DW) CNTs, this increased reactivity does not necessarily correspond with an improved efficiency of $^{\bullet}$OH generation. With respect to their composition, N-doped CNTs fail to promote $^{\bullet}$OH formation despite being reactive toward O_3, whereas the presence of amine functional groups on the CNT surface promote $^{\bullet}$OH formation, albeit to a lesser extent than the most active oxygen-containing functional groups. Finally, lower purity, industrial grade (IG) MWCNTs exhibited similar $^{\bullet}$OH production as their research-grade counterparts, suggesting that residual metal impurities within the CNT have little influence on their performance. Collectively, new insights obtained herein as to the effect of surface chemistry, structure, and composition on $^{\bullet}$OH formation during ozonation can be used to optimize CNT performance, while cost

savings afforded by equally reactive IG CNTs may help to overcome current hurdles in materials costs that currently limit technology maturation.

4.2 Introduction

The ubiquity of pharmaceuticals and other organic micropollutants in water sources and wastewater effluents dictates that new treatment technologies are needed to address the global water crisis. These technologies must be capable of treating a broad spectrum of pollutants over a wide range of water chemistries, in a cost- and energy-effective manner. We contend that recent advances in nanotechnology and the unique reactivity of engineered nanomaterials may play a key role in development of such innovative, next-generation technologies.

We previously showed that multi-walled carbon nanotubes (MWCNTs) could be used to enhance $^{\bullet}OH$ levels during ozonation to levels comparable with traditional ozone (O_3)-based advanced oxidation processes (AOPs). We also found that surface oxygen, generated via MWCNT oxidation with concentrated nitric acid (HNO_3), was a key parameter in optimizing MWCNT reactivity. Specifically, we observed that increasing surface oxygen levels (as quantified by X-ray photoelectron spectroscopy (XPS)) resulted in greater exposure to $^{\bullet}OH$ during ozonation. Thus, the extent of MWCNT oxidation appears to be a key design variable that can be used to optimize CNT performance during their use in O_3-based AOPs.

As measured by XPS, surface oxygen concentrations represent a composite measure that includes many different oxygen-containing surface functionalities, including carboxyl (-COOH), hydroxyl (-OH), carbonyl (C=O), and lactone (O-C=O) groups (see Figure 1-4). There are numerous means for adding oxygen containing groups to CNT surfaces, including varying strength of HNO_3 to systematically tailor the level of MWCNT surface oxygen (from ~1-10%), as discussed in Chapter 3. Other commonly used methods of functionalizing CNTs include treatment with strong oxidants such as sulfuric acid/nitric acid mixture (hereafter S/N) and permanganate, as well as more mild oxidants including hydrogen peroxide (H_2O_2), persulfate (S_2O_8), and even O_3 [75]. Furthermore, these different oxidants produce different ratios of the aforementioned oxygen-containing functional groups on the CNT surface [300]. For example, more aggressive treatments with strong oxidants such as concentrated HNO_3 or S/N tend to result in a higher percentage of –COOH groups comprising the total surface oxygen, whereas more mild oxidants (e.g., O_3) often result in a roughly equal distribution between the different oxygen-containing groups analyzed [300].

Thus, while total surface oxygen is a useful composite metric from the practical standpoint of CNT reactivity optimization (e.g., methods of CNT oxidation are well established and surface oxygen is easy to quantify via XPS), a more fundamental understanding of O_3 decomposition and $^{\bullet}OH$ formation requires a closer consideration of the role of specific CNT surface sites. Different surface functional groups on CNTs have been shown to play different roles in aqueous environment. For instance, -COOH groups have been linked preferentially over –OH and C=O groups for Zn and Cd sorption [291] and have been found to play the most important role in the colloidal stability of oxidized CNTs in suspension [75].

With respect to reactivity toward O_3, there remains debate as to the role different oxygen-containing functional groups play in O_3 decomposition and $^{\bullet}OH$ generation. Some studies have proposed that $^{\bullet}OH$ formation on granular activated carbon (GAC) surfaces during ozonation results in the transformation of basic surface sites such as chromenes or pyrones into acidic sites such as carboxyl or lactone groups, which in turn reduce the effectiveness of the GAC for further $^{\bullet}OH$ production [261]. For example, Figure 4-1 (same as Figure 1-3) shows a proposed reaction pathway for O_3 decomposition on GAC at a pyrone site, in which O_3 reacts at with the available π electrons available in the double bond [3]. Some GAC studies suggest that –OH groups are more often associated with O_3 decomposition than –COOH or C=O groups, based on a multiple regression analysis which considered how carboxyl, carbonyl, lactone, hydroxyl, and basic surface groups on GAC affect O_3 decay rate in solution [3]. This result is also consistent with reports of surface –OH groups being the reactive site for O_3 decay on metal oxide surfaces used in catalytic ozonation [51]. In contrast, other studies have pointed to –COOH groups as being primarily responsible for O_3 decomposition on GAC, but only at pH values above the point of zero charge where they will primarily be deprotonated [314, 315].

A few recent studies have also considered the role of oxygen-containing surface groups on the reactivity of CNTs toward O_3. These studies have consistently found that increased levels of oxygen-containing surface groups, namely –COOH groups added via CNT oxidation, result in decreased O_3 decomposition and $^{\bullet}OH$ formation [286, 288, 290]. However, those studies were all carried out at pH 3, where fewer of the –COOH groups are likely to be deprotonated. Meanwhile, the role of specific oxygen-containing groups on ozonation of CNTs at neutral pH values most representative of water and wastewater treatment has yet to be determined. Given the conflicting range of scenarios proffered by previous investigators of GAC and CNT ozonation and the lack of studies under conditions most representative of treatment, there is need for greater understanding of the role played by specific oxygen-containing functional groups in $^{\bullet}OH$ production.

While focus on surface oxygen containing groups is warranted, one must not overlook other surface chemical variables that may also contribute to CNT reactivity during ozonation. For example, more aggressive oxidation routes are also linked to an increase in the amount of amorphous carbon debris left on the CNT surface [316, 317]. Some studies suggest that it is, in fact, oxygen groups associated with this amorphous carbon that causes the increased reactivity of functionalized CNTs toward O_3, rather than the oxygen-containing groups directly linked to the CNT surfaces themselves [316, 317]. Some of this debate stems from whether oxygen-containing groups form solely at CNT end caps and defect sites or also attach to CNT sidewalls [318]. Specifically, if oxygen-containing groups are limited to end caps and defects, amorphous carbon coating the

CNT surface would provide more defect sites for linking oxygen-groups. However, recent spectroscopic characterization of CNTs concluded that oxygen containing functionalities do indeed attach to CNT sidewalls [300], raising questions as to the relative contribution of oxygen groups associated with amorphous carbon and sidewalls on CNT behavior.

In this chapter, we explore the influence of CNT surface chemistry and the presence of surface-associated amorphous carbon on O_3 decomposition and $^{\bullet}OH$ formation. Expanding upon results in Chapter 3, we use a range of MWCNT oxidation routes to vary systematically the extent and distribution of surface-containing oxygen groups. Results from batch studies exploring $^{\bullet}OH$ formation during ozonation with these oxidized MWCNTs were then compared to characterization results obtained via XPS coupled with chemical derivatization. This methodology uses specific fluorinated compounds which react exclusively with either –OH, C=O, or –COOH groups on the CNTs, then measures the fluorine surface concentration of the reacted CNTs via traditional XPS. The end result indicates the relative surface concentration of identified surface oxide groups and residual surface oxygen, assumed to be largely lactones [319, 320]. Via this structure-activity analysis, we aimed to identify the surface site(s) most integral to $^{\bullet}OH$ formation during ozonation. In parallel, the influence of surface amorphous carbon on CNT reactivity during ozonation was explored via accepted practices (e.g., washes with moderately strong base) for its removal [316, 317].

In addition to identifying the exact nature of surface sites driving $^{\bullet}OH$ formation, a complementary portion of this work focuses on also determining the optimal CNT sidewall structure and chemical composition for use in O_3-based AOPs. While work in Chapter 3 was conducted exclusively on MWCNTs, single-walled (SW) and double-walled (DW) CNTs may have unique properties which could influence $^{\bullet}OH$ production. For surface-mediated decay of O_3, the greater specific surface area available of SWCNTs will likely make them more reactive per unit mass than their DW or MW counterparts.

Additionally, SWCNTs [69, 70] exhibit redox reactivity, which should improve their catalytic function because oxidizable centers promote $^{\bullet}$OH yields during ozonation. DW CNTs may combine both the redox properties of SW CNTs and the structural integrity of MW CNTs [321].

Another potentially important variable we consider is the chemical composition of the CNTs. Numerous studies have suggested that N-containing functional groups on GAC may be most effective at promoting $^{\bullet}$OH production during ozonation [46, 322, 323]. Thus, commercially available carbon nanotubes with amine- and amide-functional groups ($R\text{-}NH_2$ and $R(CO)NH_2$, respectively), or with nitrogen incorporated into the CNT sidewalls (so-called N-doped CNTs) may also promote reactivity. The purity of the CNTs may also influence their reactivity, with lower quality (so-called industrial grade (IG)) CNTs typically containing more metal impurities than higher purity research grade CNTs. While most of these impurities are generally believed to be internal to the CNTs, the existence of metallic surface impurities may enhance reactivity given that some dissolved metals and metal oxides can generate $^{\bullet}$OH formation during ozonation [51].

Ultimately, this work exploring these ranges of CNT surface chemical and structural variables will be used to identify the optimal CNT formulation to enhance $^{\bullet}$OH production during ozonation. These highly active CNTs will then be utilized in subsequent reactivity testing in more complex aquatic systems. Thus, the goal of this work is to establish the fundamental foundation upon which more practical considerations can be explored to develop a CNT-enabled ozonation treatment system.

4.3 Experimental Section

4.3.1 Reagents. A complete list of reagents is provided in Chapter 3. CNT vendors, structures, purities and functionalization methods are noted in Table 4-1. All CNTs were synthesized via chemical vapor deposition. Aminated CNTs were prepared by reacting ethylene diamine ($H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$) with –COOH surface groups on the CNTs, resulting in an amine functional group at the end of the carbon chain [324]. The

N-doped CNTs were prepared with 1 – 2% N in the CNT lattice, providing structural nitrogen for possible reactivity [325].

Table 4-1

Vendor-Provided CNT Specifications and Functionalization Treatments

CNT	**Vendor**	**CNT Purity**	**Diameter (nm)**	**Length (µm)**	**SSA (m^2/g)**	**Treatments**
MW	NanoLabs, Inc.	>95%	OD: 15 ± 5 ID: 7 ± 2	1-5	200 - 400	NF, HNO_3 20 - 70%, S/N, O_3, H_2O_2, S_2O_8, MnO_3, Water Washed, Base Washed, Furnace Treated
MW	cheaptubes .com	>95%	OD: <8 ID: 2-5	10-30	500	NF, HNO_3 20 - 70%
DW	NanoLabs, Inc.	>95%	4 ± 1	1-5	200 - 400	NF, S/N, HNO_3 70%
SW	NanoLabs, Inc.	>95%	~1.5	1-5	1000	NF, S/N, HNO_3 70%
IG	NanoLabs, Inc.	>85%	10 – 30	5-20	NA	NF, S/N, HNO_3 70%
N-doped (MW)	NanoTech Labs	8% residual iron	20-40	50 (avg)	NA	NF
Amine-Functionalized (MW)	NanoLabs, Inc.	>95%	1.5/15 ± 5	1-5	NA	NF

4.3.2 Batch Experiments for Quantifying $^{\bullet}$OH Production. Ozonation experiments were conducted as described in Chapter 3. Briefly, reactors contained 20 mls of 5 mM phosphate buffer at pH 7, 2 μM of p-CBA as an $^{\bullet}$OH probe, and 320 μM t-ButOH as a model $^{\bullet}$OH scavenger [46, 52, 253, 260, 263, 265, 266, 298]. Reactions were initiated by adding an aliquot of O_3 stock solution to create an initial O_3 concentration of 160 μM. Reactors also contained CNTs at solid loading levels ranging from 2 mg/L to 20 mg/L. For these studies, a variety of CNTs of various surface chemistries, sidewall structure, and chemical composition were considered, as shown in Table 4-1. Ozone-free control experiments were conducted as well.

As discussed in Chapter 3, we simultaneously measured O_3 and *p*-CBA degradation over the course of the reaction. These values were then used to calculate an R_{ct} value, a measure of the $^{\bullet}$OH exposure (as indicated by *p*-CBA degradation) relative to O_3 exposure (as indicated by O_3 degradation). R_{ct} values provide a comparative metric for efficacy of different O_3-based AOPs.

4.3.3 Tailoring of MWCNT Surface Chemistry. To study the effects of CNT surface chemistry, the CNTs used were treated via a variety of functionalization methods. Nitric acid (HNO_3) treated CNTs were functionalized as described in Chapter 3. CNTs were also treated with a mixture of H_2SO_4 and HNO_3 (S/N) per established methods [75]. Briefly, 100 mg of CNTs were added to a mixture of 6 ml H_2SO_4 and 2 ml HNO_3. The CNT/acid mixture was sonicated for one hour, then heated in a 70 °C oil bath for 8 hours without stirring. After cooling overnight, the CNTs were washed and processed as described in Chapter 3 for the HNO_3-functionalized CNTs. Other functionalization treatments were performed in the lab of Dr. Howard Fairbrother of Johns Hopkins University, and CNT samples were generously provided to us for experimental purposes. Functionalization methods employed by Dr. Fairbrother include O_3 treatment, hydrogen peroxide treatment, persulfate treatment, and permanganate treatment [75].

It is known that the harsh conditions of S/N functionalization treatments often leave some amorphous carbon remnants on the surface of the treated CNTs [316, 317]. To remove this amorphous carbon, a base-washing procedure was performed [316, 317]. The S/N-treated MWCNTs were cleaned initially with DI water as described in Chapter 3, then subsequently rinsed with a 0.01M NaOH solution (Sigma Aldrich ACS Reagent grade, purity >97%) until the rinse solution ran clear (approximately 2 L). CNTs were rinsed again with DI water until a neutral pH was achieved in the rinse water (approximately 1.5 L), then rinsed again with a 0.01M HCl solution until the rinse solution ran clear (approximately 500 ml). The CNTs received a final rinse with DI water until a neutral pH was again achieved (approximately 1.5 L). As a control, a separate batch of S/N-treated MWCNTs were subjected to a water wash with a total of 5.5 L of DI water, the same total volume of additional rinsing received during the base-washing procedure.

To specifically test the effects of –COOH groups on $^{\bullet}$OH production, CNTs underwent a furnace treatment at high temperatures to remove surface –COOH groups, subsequent to S/N functionalization [291]. Briefly, decarboxylation involved heating the CNTs to 500 °C under inert gas for 12 hours, which results in removal of between 32% to 58% of surface oxygen, particularly –COOH groups and residual (unidentified) O-containing groups [291]. The furnace-treated CNTs were also provided by Dr. Fairbrother.

The various CNT samples prepared by the aforementioned methods and used in reactivity studies are summarized in Table 4-1. Note that SW, DW, and IG CNTs were tested as-received (or non-functionalized) and after oxidation with 70% HNO_3 or the S/N mixture. Functionalization, subsequent cleaning, and suspension of the SW, DW, and IG CNTs were performed in the same manner as for the MWCNTs described above and in Chapter 3. All CNTs which received some post-functionalization processing (base washing, water washing, or furnace treatment) were subsequently dried and suspended in the same manner as described in Chapter 3 for the MWCNTs, prior to their use in batch reactions.

4.3.4 Analytical Methods. Analytical methods are described in Chapter 3. The concentration of O_3 in stock solutions was measured via UV/vis spectrometry ($\varepsilon = 2900$ L/mole/cm @ 258 nm) [293] using a Thermo Scientific Genesys 10S Spectrophotometer. Aqueous O_3 concentration in reactors was measured colorimetrically using the indigo blue method [293]. Concentrations of p-CBA were quantified using high performance liquid chromatography with diode array detector (HPLC/DAD). XPS with chemical derivatization was performed in the laboratory of Dr. Howard Fairbrother at Johns Hopkins University utilizing instrumentation and protocols previously described elsewhere [319, 320].

4.4 Results and Discussion

4.4.1 Influence of Oxygen-Containing Surface Functionalities in $^{\bullet}$OH Production. Figure 4-2 shows R_{ct} values for various MWCNTs, treated as indicated, as a function of surface oxygen concentration. The surface oxygen concentration, as atomic percent, was quantified via XPS. All systems had an initial O_3 concentration of 160 µM and a CNT solid loading of 20 mg/L. Data shown represent averages of at least triplicate experiments. Note that results are limited to high purity MWCNTs with only surface oxygen containing functional groups.

As observed in Chapter 3, for NL-MWCNTs oxidized with various strengths of HNO_3, there is a clear correlation between $^{\bullet}$OH production (as quantified by R_{ct} values) and surface oxygen concentration for MWCNTs. However, Figure 4-2 shows that this dependence of R_{ct} on surface oxygen concentration is maintained not only across the range of oxidants used for CNT functionalization but also different MWCNT vendors (Cheaptubes.com and NanoLabs, Inc.) Thus, surface oxygen appears to be a key variable that can be used to predict and optimize reactivity of a CNT-enhanced ozonated system.

To examine the contribution of specific oxygen-containing surface functional groups to $^{\bullet}$OH production, Figure 4-3 shows how R_{ct} values vary as a function of the amount of common oxygen containing functional groups, as quantified by XPS with chemical derivitization. Consistent with prior reports [300], the different MWCNT oxidation routes tended to primarily generate surface carboxyl groups, while other moieties are present at lower atomic concentrations. This analysis reveals a relatively strong correlation between R_{ct} values and the amount of surface carboxyl (-COOH) groups (Figure 4-3a), while no clear relationship is evident as a function of surface hydroxyl (-OH) (Figure 4-3b) or carbonyl (=O) group (Figure 4-3c) concentration. Correlation certainly does not equate to causality; however, the linear dependence between R_{ct} and –COOH surface concentration is consistent with these surface sites being important for O_3 decomposition and $^{\bullet}$OH formation. While this result may seem to contradict results found in previous studies of CNT ozonation [286, 288, 290], recall that those were performed almost exclusively at pH 3. At pH 7, which was the solution condition employed herein, our zeta potential analysis of CNT suspensions (see Chapter 3) indication that most, if not all, –COOH groups are deprotonated, and work by Hoigne and co-workers [314, 315] has shown that O_3 reactivity toward solution phase carboxylic acids can vary considerably depending on their protonation state.

Experiments performed with Furnace Treated CNTs further support this supposition. As discussed above, furnace treatment of the MWS/N CNTs was performed to preferentially remove –COOH groups. Experiments were then conducted to compare $^{\bullet}$OH production in MW Water Washed systems and MW Furnace Treated systems, represented by *p*-CBA decay as shown in Figure 4-4. The Water Washed CNTs exhibited significantly greater *p*-CBA decay than the Furnace Treated CNTs. Based upon XPS analysis, the most significant surface chemistry difference between the two systems is not total surface oxygen but –COOH group concentration (Table 4-2).

Table 4-2

Surface Oxygen and Oxygen-Containing Functional Groups

	O Total	**-OH**	**-COOH**	**C=O**	**O Residual**
Furnace Treated	10.1	1.6	1.7	1.3	5.6
Water Washed	12.2	0.6	6.2	1.7	3.8

This result supports the link between the presence of –COOH groups and p-CBA decay. While it is tempting to conclude from these lines of evidence that O_3 decay and $^{\bullet}OH$ formation occurs via reaction at –COOH sites, it is well known that dissolved carboxylic acids (e.g., oxalic acid) are essentially unreactive with aqueous O_3 [266, 314]. It is certainly possible that –COOH sites on MWCNTs exhibit reactivity toward O_3 that is inherently different from that of solution phase analogs. However, it is also possible that –COOH groups are not directly involved in the reaction with O_3, but that their presence on the CNT surface activates adjacent sites, making them more reactive toward O_3. For example, while –COOH groups are unreactive toward O_3, it has been shown that deprotonated –COOH groups (-COO-) make adjacent alkene and aryl groups more reactive toward O_3 [314, 326]. Thus, as the majority of surface –COOH groups will be deprotonated in solution at pH 7, we propose a scenario in which these deprotonated groups on the CNT surface enhance the reactivity of adjacent π-bonds in the graphene sheet toward O_3. O_3 would then react via its customary cycloaddition across the pi-bond to form an ozonide intermediate, as anticipated from the well-established Criegee mechanisms for O_3 addition to a pi-bond, as suggested for GAC in Figure 4-1. Numerous

O_3 reactions are then possible, resulting in generation of -OH, –O_2H, or –H_2O_2, and ultimately leading to generation of $^\bullet$OH [314].

We should note that an equally strong correlation was also observed between R_{ct} values and the amount of residual oxygen on the CNT surface (Figure 4-3d), defined operationally as

$$O_{RESIDUAL} = O_{TOTAL} - (O_{COOH} + O_{OH} + O_{CO}) \qquad (4\text{-}1)$$

This residual oxygen is assumed to be largely comprised of lactone groups. Note that this correlation does include negative values of residual oxygen, which corresponds to when the abundance of functional groups summed to be greater than the total oxygen determined by XPS. The correlation shown in Figure 4-3d is in fact stronger than that found for the –COOH groups (Figure 4-3a) because it includes CNTs from two different vendors (Nanolabs, Inc. and Cheaptubes.com), indicating perhaps a more universal correlation for predicting CNT activity. While speculative, we propose that these lactone sites may also contribute to $^\bullet$OH formation via O_3 decomposition in a similar manner similar to that discussed above for deprotonated –COOH groups, where the electron density from oxygen in these groups may make adjacent π-bond more prone to attack by O_3.

Regardless of their exact function in increasing $^\bullet$OH production during ozonation, it seems clear that increased –COOH groups on the CNT surface are beneficial to CNT performance in advanced oxidation processes. Thus, in designing a highly reactive substrate for optimal performance, strong oxidants such as nitric acid or mixtures of sulfuric and nitric acids will likely be best, as they tend to yield the greatest proportions of –COOH groups on the CNT surface [300]. Based on the criterion of –COOH group abundance, S/N treatment should result in the most reactive CNTs [300]. However, it is also the most aggressive functionalization treatment and can also lead to the presence of other species such as amorphous carbon on the CNT surface [317, 327]. The effect of these other species on CNT reactivity must be considered, therefore. For example, in

Figure 4-2, it is the S/N Water Washed CNTs (label "Water" in the figure) which fall on the expected correlation line, whereas unwashed S/N CNTs were highly reactive outliers and thus are not shown.

4.4.2 Role of Amorphous Carbon in ${}^{\bullet}$OH Production. In addition to resulting in a higher proportion of –COOH groups on the CNT surface, highly aggressive S/N treatments also result in deposits of amorphous carbon on the CNTs, likely from CNT breakdown during the functionalization process [317, 327]. Figure 4-5 shows representative O_3 degradation curves (Figure 4-5a) and *p*-CBA (Figure 4-5b) degradation curves for S/N treated MWCNTs that were then subject to either a thorough water wash or base wash. Both the Water and Based Washed MWCNTs exhibit slower degradation of O_3 compared to systems containing MW S/N utilized immediately after functionalization and initial cleaning without any additional post-processing (Figure 4-5a). In contrast, the Water Washed MWCNTs show virtually identical *p*-CBA degradation rates as the MWS/N samples, whereas the Base Washed CNTs exhibit a significantly reduced rate of *p*-CBA degradation (Figure 4-5b). Collectively, these observations suggest that the water washing physically removes some loosely bound material, likely amorphous carbon, from the S/N functionalized CNT surface that exerts an O_3 demand but does not translate into ${}^{\bullet}$OH formation. In fact, it is likely that the loosely-bound amorphous carbon removed during this washing procedure remains freely dispersed in the MWS/N suspension, increasing the rate of O_3 degradation without leading to ${}^{\bullet}$OH production. However, as the MWS/N CNTs are so well dispersed in suspension, it is too difficult to separate them from the suspension liquid itself to verify this theory. Base washing, on the other hand, appears to remove a more tightly bound amorphous carbon phase from the CNT surface, which in turn slows *p*-CBA degradation. Unlike the loosely bound amorphous carbon that is removed via water washing, this more tightly bound fraction appears to contribute to ${}^{\bullet}$OH production.

The exact mechanism by which this tightly bound amorphous carbon phase influences $^{\bullet}OH$ production remains unclear. A confounding factor is that the base washing procedure we have employed may also alter surface acids, such as –COOH groups on the CNT surface [317, 327]. Indeed, XPS analysis reveals that unprocessed S/N MWCNTs possess a surface –COOH concentration of 7.2%, whereas base washing decreases their abundance by nearly half (to 3.3%). It is not clear whether these –COOH groups are attached to tightly bound amorphous carbon that is removed via base washing or whether they are associated with the CNT sidewall but lost via incidental reaction under the basic conditions employed for the wash. While this distinction cannot be made herein, the decrease in reactivity toward *p*-CBA after base washing is once again consistent with a critical role for surface –COOH groups in $^{\bullet}OH$ production.

We also note that results from these post-processed S/N systems highlight some deficiencies in the use of R_{ct} values to compare the efficacy of O_3-based AOPs. As discussed above, the MWS/N CNTs are significantly more reactive toward O_3 than the Water Washed CNTs, but both systems result in nearly identical levels of *p*-CBA degradation. Notably, because R_{ct} values are calculated using the ratio of *p*-CBA loss relative to O_3 exposure, this rapid O_3 degradation produces a large, but misleading, R_{ct} value. In fact, it is for this reason that unprocessed S/N-treated MWCNTs are omitted from the R_{ct} correlation analysis in Figure 4-2; the resulting R_{ct} value (~2.4×10^{-7}) is considerably greater than those obtained for CNTs with a similar degree of surface oxidation despite resulting in comparable timescales and extents of *p*-CBA removal.

Another way to compare the relative $^{\bullet}OH$ production efficiency of different ozone-based systems is by comparing the change in *p*-CBA concentration (Δp-CBA) over the change in O_3 concentration (ΔO_3) over the same time period. This value essentially represents the yield of $^{\bullet}OH$ per unit O_3 consumed. The table in Figure 4-5b shows these efficiency values for the S/N, Water Washed, and Base Washed systems. Despite comparable or even reduced *p*-CBA decay, both the Water Washed and the Base Washed systems show greater $^{\bullet}$OH production efficiency than the S/N system, illustrating that the rapid O_3 degradation in the S/N system results in a misleadingly high R_{ct} value. In contrast, the Water Washed system results in comparable $^{\bullet}$OH production and more efficiently utilizes O_3 for $^{\bullet}$OH production.

4.4.3 Role of CNT Structure in $^{\bullet}$OH Production. While experiments thus far have been performed exclusively on MWCNTs, experiments comparing MW-, DW-, and SWCNTs were conducted with as-received materials (NF), as well as after oxidation with concentrated (70%) HNO_3 and S/N treatment. As was observed with non-functionalized MWCNTs, SWNF and DWNF systems were generally unreactive toward *p*-CBA, with the majority of the *p*-CBA loss resulting from sorption on the hydrophobic CNT surface.

However, the functionalized systems were more reactive. Figure 4-6 shows representative pseudo-first order rate constants (k_{obs}) for degradation of O_3 (Figure 4-6a) and *p*-CBA (Figure 4-6b) at various CNT loadings, while Figure 4-6c shows the R_{ct} curves for these CNT 70 systems at CNT loading of 5 mg/L. Generally, very few significant differences are observed across the various types of CNT wall structures. SWCNTs tended to be slightly more reactive toward O_3 than DW or MW, while k_{obs}(*p*-CBA) values were essentially equal across wall structure at each CNT concentration. Given the nearly identical k_{obs}(*p*-CBA) values, the modestly higher R_{ct} values observed for SW and DW CNTs likely reflects their greater O_3 demand (and thus shorter overall O_3 exposure as described above). CNTs oxidized with the S/N acid mixture exhibited similar behavioral trends, as shown in Figure 4-6d. Both Figures 4-6c and 4-6d also show the Δ *p*-CBA/ΔO_3 values for the indicated systems. Once again, while the SWCNTs consistently exhibited higher R_{ct} values, their efficiency in the 5 mg/L HNO_3 70% system is somewhat less than that of the DWCNTs. However, it is significantly higher than either the DW- or MWCNTs in the S/N system. At 10 mg/L, however, the Δ*p*-CBA/ΔO_3 value for MW70 is 0.019, almost twice that of SW70 at 0.010, though the

R_{ct} values at this loading show less disparity (2.9 x 10^{-8} for MW70 and 4.8 x 10^{-8} for SW70).

One possible explanation for the increased reactivity in the SW system could be greater surface area of the SWCNTs. Specific surface area for SWCNTs is approximately 4 times that of DW or MWCNTs. For surface-mediated reactions, increased available surface area will tend to result in increased reactivity. However, since surface area effects would be expected to be comparable in both S/N and HNO_3-treated systems, another possible scenario is related to the presence of loose amorphous carbon in the SW suspension. As discussed above for the MWS/N CNTs, loosely bound material generated during the functionalization process may be linked to increased O_3 reactivity and misleadingly high R_{ct} values. As SWCNTs lack the structural integrity of MWCNTs [321], they may be more likely to generate amorphous material during functionalization, not just for aggressive S/N but also concentrated nitric, which in turn may affect the reactivity of these SWCNT suspensions toward O_3. These effects may be more pronounced at higher loadings, at discussed above. In general though, our results suggest that sidewall structures do not show a clear effect on $^{\bullet}OH$ generation.

4.4.4 Role of CNT Composition in $^{\bullet}OH$ Production. In addition to oxygen-containing surface functionalities, aminated and N-doped CNTs are commercially available. These N-containing varieties may be ideal for promoting $^{\bullet}OH$ production given that (i) O_3 is known to be highly reactive toward amine functionalities [42] and (ii) studies on GAC-enhanced ozonation have suggested that the presence of nitrogen-containing surface groups ($-NH_2$ and pyrolle functionalities) can improve $^{\bullet}OH$ production during ozonation [46, 322, 323].

Figure 4-7 compares the change in O_3 (Figure 4-7a) and *p*-CBA (Figure 4-7b) concentration as a function of time in 10 mg/L suspensions of N-doped and aminated CNTs. For comparison, results are also provided for as-received MWCNTs, as well as MWCNTs that have been oxidized with concentrated HNO_3. N-doped and aminated

MWCNTs enhanced the rate of O_3 decay, compared to both O_3-only controls (not shown) and the MWCNT-NF system. In fact, these N-containing CNTs achieved similar levels of O_3 degradation to that observed in the highly reactive MW70 system. For aminated CNTs, this O_3 decay coincided with enhanced *p*-CBA removal compared to the NF system, but their ability to generate $^{\bullet}$OH remained less than that of the MW70 CNTs. This result is verified with the Δ *p*-CBA/ΔO_3 values, where MW70 CNTs ($\Delta = 0.019$) show roughly twice the efficiency of Aminated MWCNTs ($\Delta = 0.010$). Notably, the N-Doped CNTs, which have a unique structure known to make them effective as reduction catalysts [303] showed no measureable degradation of *p*-CBA at all. Thus, while surface nitrogen moieties may promote $^{\bullet}$OH production to some extent, bulk nitrogen clearly does not. Accordingly, surface oxygen groups, which notably are far easier to incorporate onto the CNT surface than N-containing moieties, appear superior for use in O_3-based AOPs.

A final aspect of CNT composition that merits consideration is their purity. Studies thus far have utilized research-grade CNTs with a CNT purity >95%. However, given concerns over the cost of such high purity (i.e., research grade materials at approximately $65,000/kg), maturation of CNT-enabled advanced oxidation processes will likely need to utilize less expensive, lower purity (so-called industrial-grade) CNTs to be commercially viable (at approximately $700/kg) [324]. The primary compositional difference between the research-grade CNTs and the IG CNTs is the presence of additional metal impurities in the CNTs, present as residuals of catalysts used in CNT fabrication. As these impurities are generally accepted to be inside the CNTs rather than at the surface, they are not expected to impact surface chemistry reactions.

Industrial-grade CNTs with a CNT purity of 85% were utilized for studies to compare reactivity against the results for the research-grade CNTs. Figure 4-8 illustrates O_3 (Figure 4-8a) and *p*-CBA (Figure 4-8b) decay curves in 10 mg/L suspensions of IGNF, IG70, and IGS/N systems, compared to the equivalent MW systems. We observed very little, if any, significant difference between the reactivity of research- and industrial grade CNTs. This result is promising from a $^{\bullet}$OH production standpoint; IG CNTs show similar reactivity to research-grade CNTs. However, more work is needed to verify that leaching of metal impurities from the IG CNTs is not a problem, particularly over long term application.

4.4.5 Environmental Relevance. Work herein provides fundamental insights to guide the rational design of CNT with optimal properties for generating $^{\bullet}$OH production during ozonation. Perhaps the most critical finding is the correlation we have observed between the extent of CNT surface oxidation and the propensity of CNTs to produce $^{\bullet}$OH during ozonation. In particular, -COOH groups are implicated in $^{\bullet}$OH production, likely because of the ability of deprotonated functionalities to activate adjacent π-bonds in the graphene plane and make them more prone to O_3 addition (see Figure 4-1). Thus, we have developed a structure-activity relationship that can be used to design reactive substrates ideal for use in O_3-based AOPs, an advance that may one day lead to an increase in the full-scale application of enhanced ozonation.

In addition to these fundamental mechanistic insights, we provide several practical outcomes that allow us to identify the CNT formulations most likely to be optimal in these applications. For example, those functionalization methods that preferentially result in surface –COOH groups provide a route to tailor and optimize $^{\bullet}$OH generation on CNT surfaces. However, we have also found that more aggressive functionalization treatments such as oxidation with mixtures of sulfuric and nitric acid should likely be avoided because of their ability to generate surface associated amorphous carbon that limits the efficiency of $^{\bullet}$OH formation per unit mass of O_3 consumed. Based on this evidence, a more moderate oxidative treatment such as 70% HNO_3 is preferable.

Another practical outcome is that CNT structure and carbon purity seem to have minimal effect on $^{\bullet}$OH production. SWCNTs may show some increased $^{\bullet}$OH production efficiency in single-use batch reactions, but they also may lack the structural integrity to have a long lifespan during continuous oxidizing conditions. Industrial production of the CNTs will be necessary for cost considerations as this technology moves toward development, so the fact that IGCNTs showed similar reactivity to their research-grade counterparts is encouraging. Looking into issues such as potential lifespan, cost, and performance of CNT-enhanced ozonation in more complex water systems will be the focus of the final chapter.

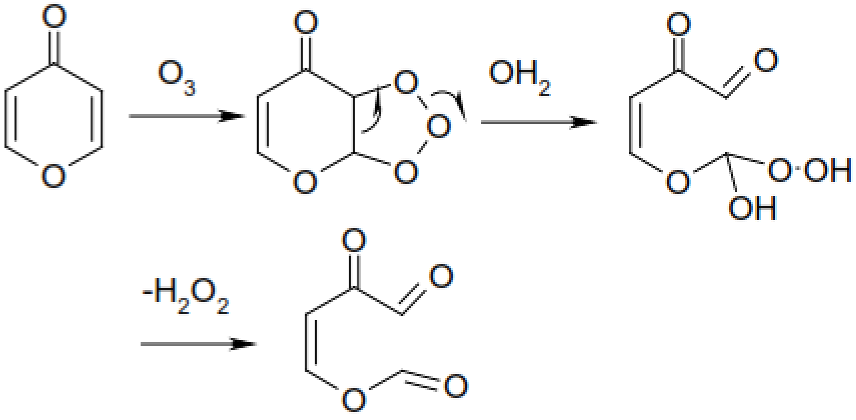


Figure 4-1. Proposed reaction pathway for ozonation of Granular Activated Carbon [3]

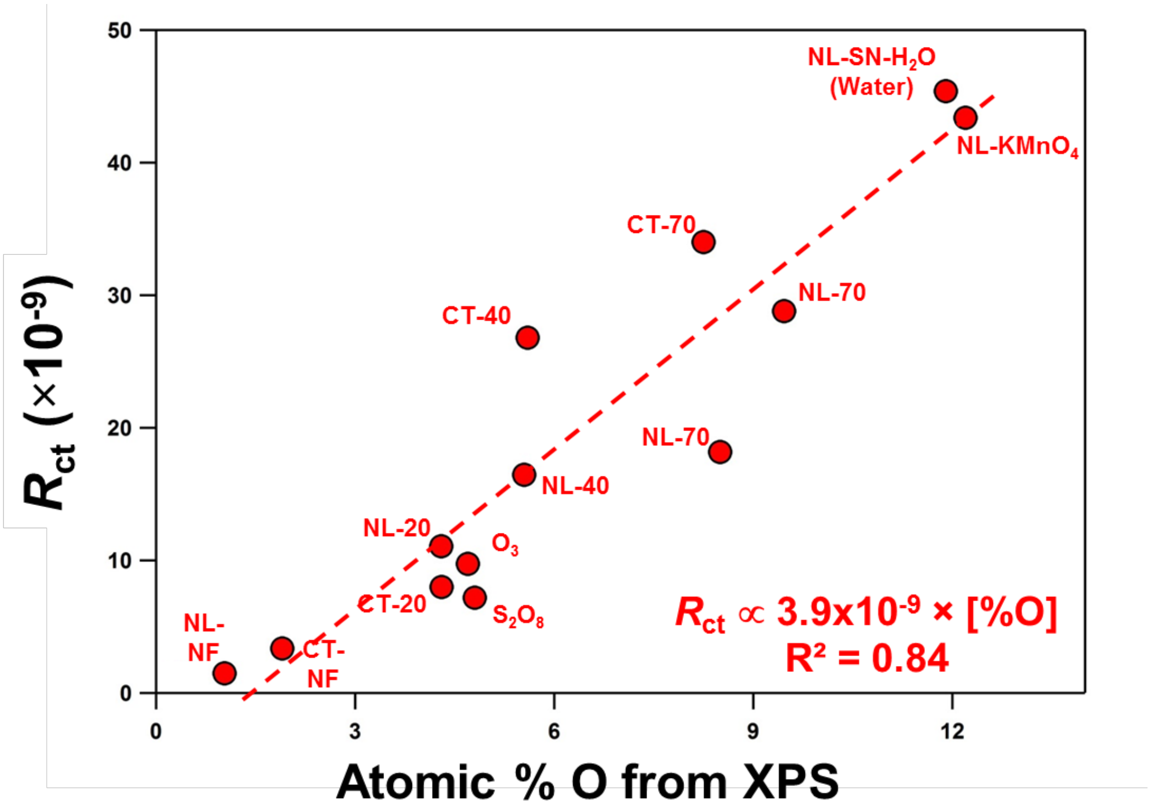


Figure 4-2. Correlation between R_{ct} values and atomic surface oxygen concentration (in %) measured via X-ray photoelectron spectrosocopy. Dashed line represents the results of linear regression analysis, with the slope and correlation coefficient provided. All data were collected in systems with a CNT concentration of 20 mg/L and an initial O_3 concentration of 160 μM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 μM of *t*-ButOH and an initial *p*-CBA concentration of 2 μM.

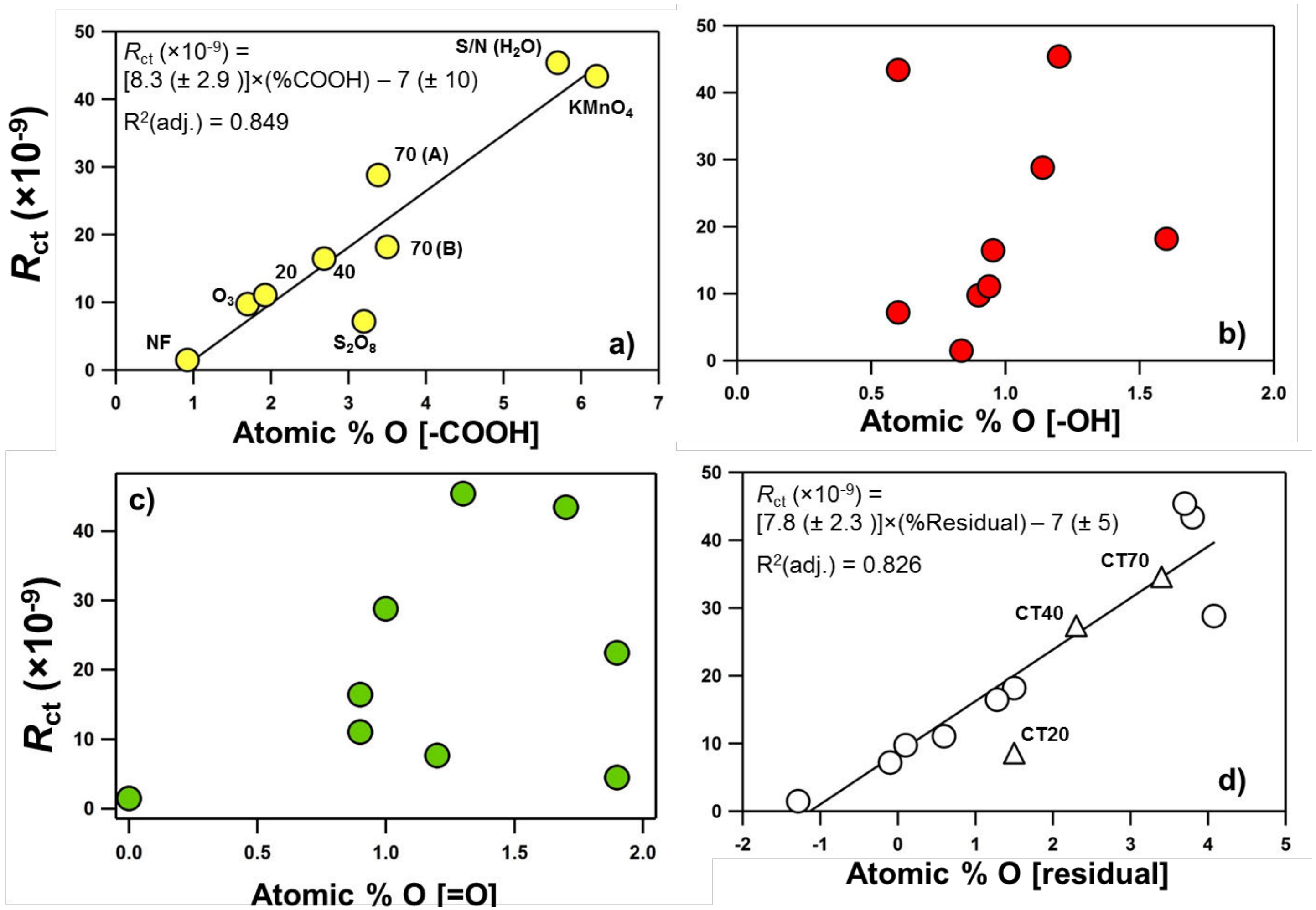


Figure 4-3. Correlation between R_{ct} values and the surface concentration of different oxygen-containing functional groups. Atomic concentrations (in %) were measured for (a) –COOH, (b) -OH, and (c) =O groups via XPS with chemical derivatization, whereas the amount of residual oxygen-containing groups (panel d) was found by subtracting the summed concentration of these groups from the total surface oxygen concentration measured via traditional XPS without derivatization. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM..

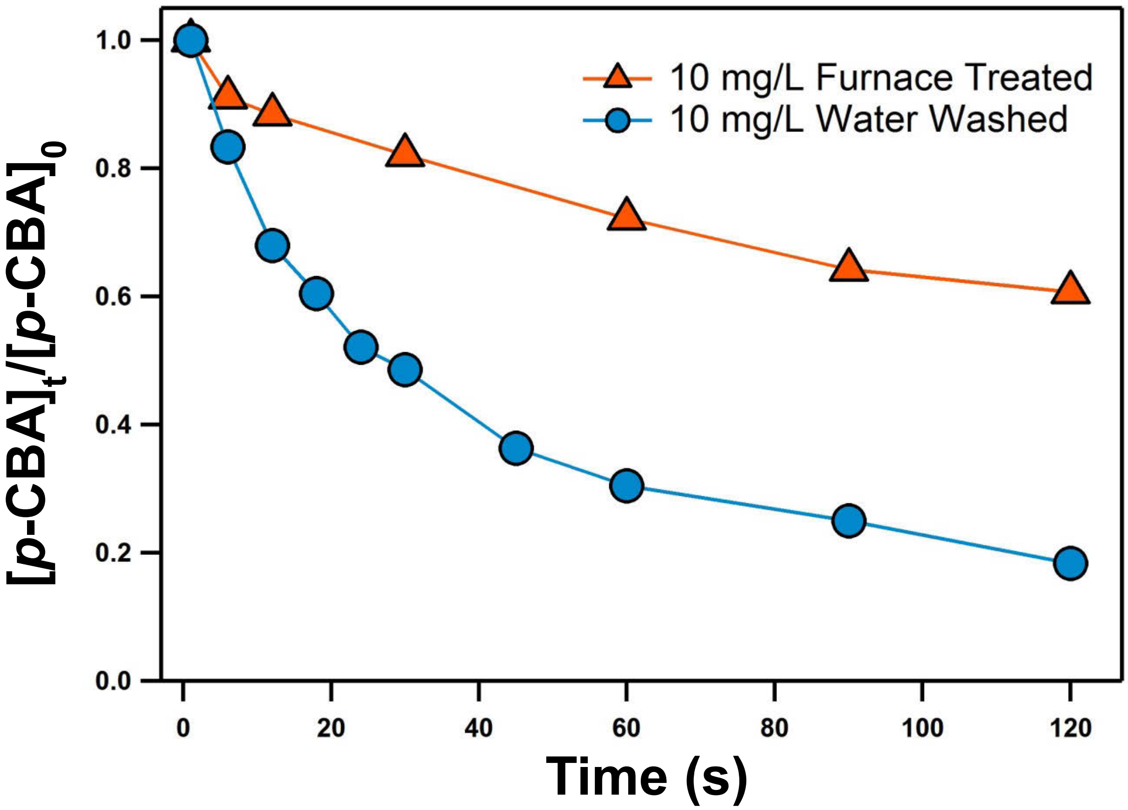


Figure 4-4. Degradation of *p*-CBA in ozonated suspensions of multi-walled CNTs. CNTs were first oxidized with a mixture of sulfuric and nitric acid (S/N) and then subsequently either washed with water (Water Washed) or annealed in a furnace (Furnace Treated) as described in the main text. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

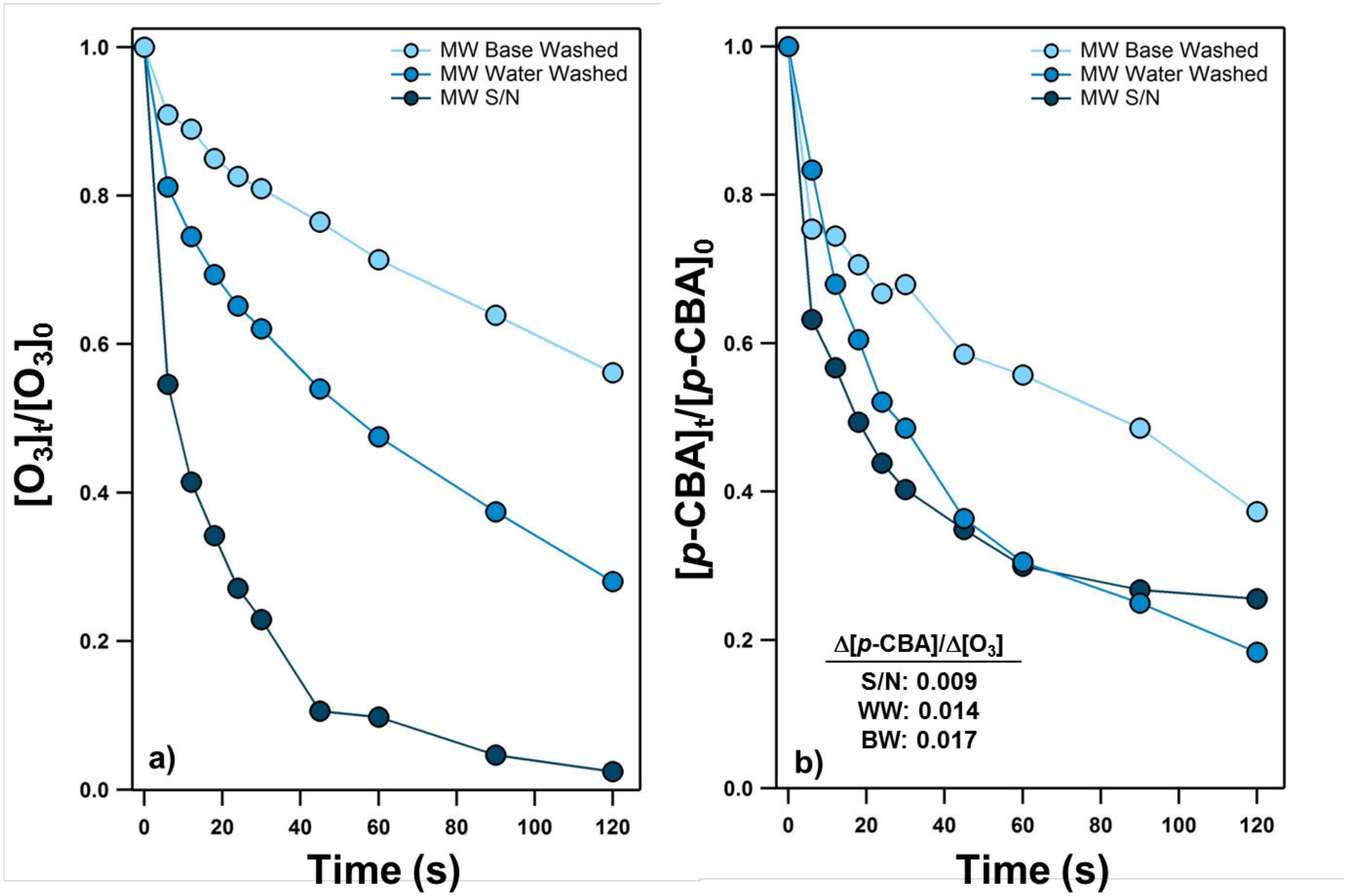


Figure 4-5. Representative degradation of ozone and *p*-CBA for multi-walled (MW) nanotubes that were oxidized via mixture of sulfuric and nitric acid (S/N). Data are also shown for this MWCNT formulation after post-oxidation water washing (Water Washed) or treatment with a strong base (Base Washed) according to protocols outlined in the main text. In (b), the yield of •OH (calculated by the relative change in *p*-CBA to O_3 over time in our systems) is provided. This ratio represents the average of all values measured at each sample collection point. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

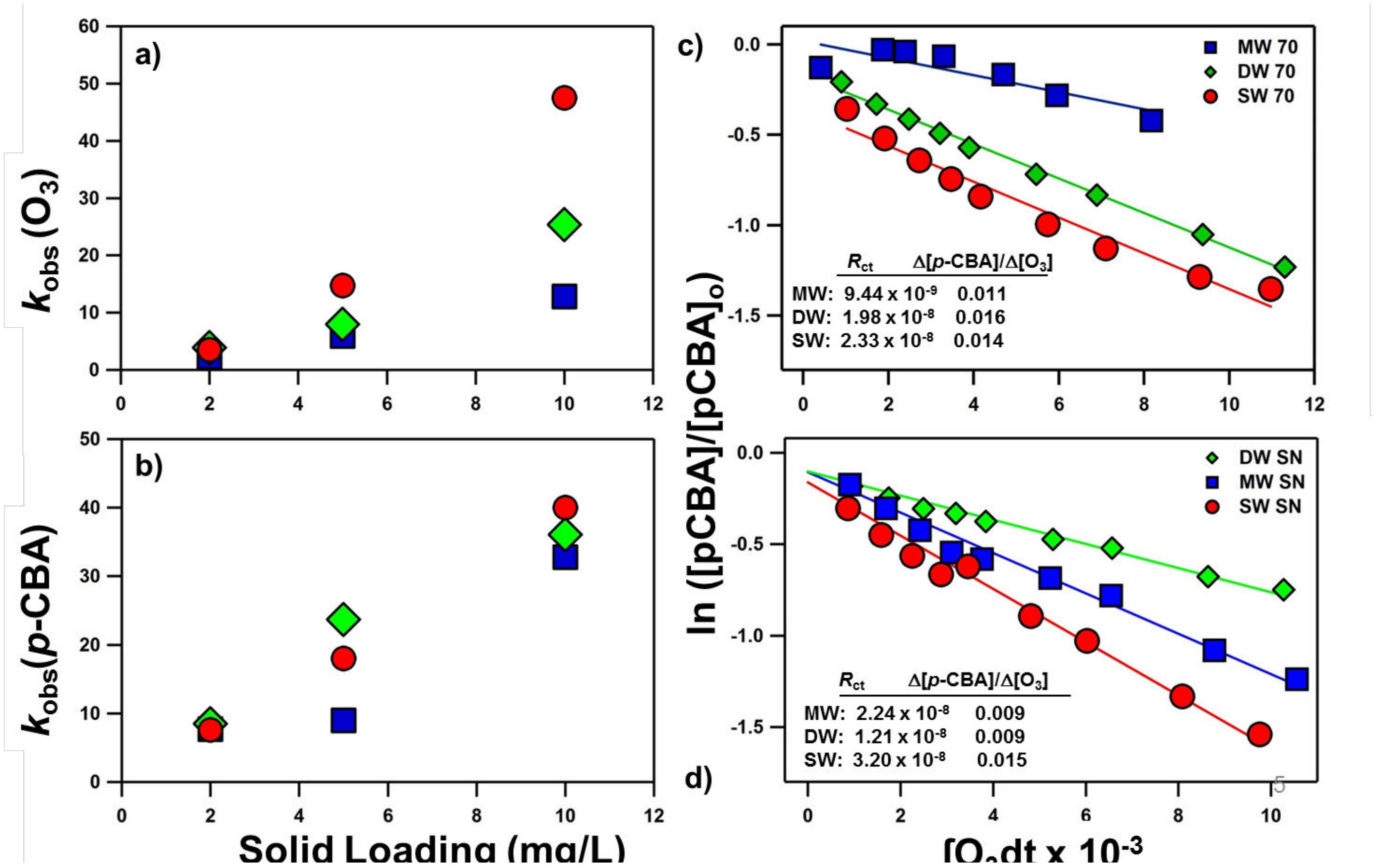


Figure 4-6. Values of pseudo-first-order rate constant for ozone decay [k_{obs}(O$_3$)] and *p*-CBA decay [k_{obs}(*p*-CBA)] as a function of CNT solid loading. Figures show data for SW (red), DW (green) and MW (blue) CNTs after oxidation with concentrated (70%) HNO$_3$. Also provided in are R_{ct} plots comparing reactivity of MW, DW, and SW CNTs that were oxidized via (c) concentrated (70%) HNO$_3$. and (d) a mixture of concentrated sulfuric and nitric acid (SN). R_{ct} plots were generated from systems conducted at 5 mg/L. In (c) and (d), the corresponding R_{ct} value and yield of •OH (calculated by the relative change in *p*-CBA to O$_3$ over time in our systems) is provided. This ratio represents the average of all values measured at each sample collection point. All data were collected in systems with an initial O$_3$ concentration of 160 μM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 μM of *t*-ButOH and an initial *p*-CBA concentration of 2 μM

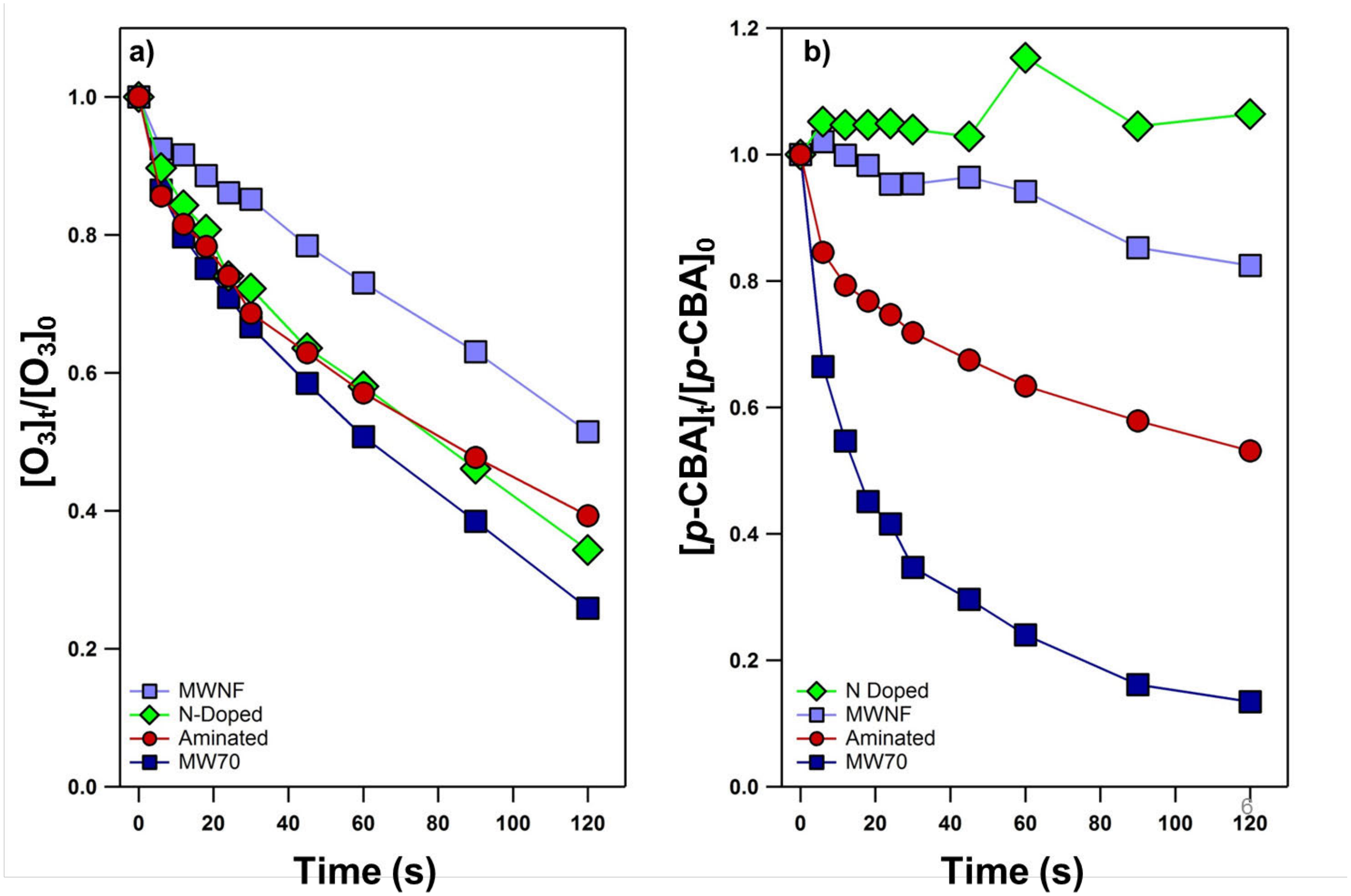


Figure 4-7. Representative degradation of ozone and *p*-CBA in N-containing CNT systems. Data are shown for N-doped and aminated MWCNTs. For comparison, we also present results obtained with MWCNTs that were used as received (NF) or after oxidation with concentrated (70%) HNO_3. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

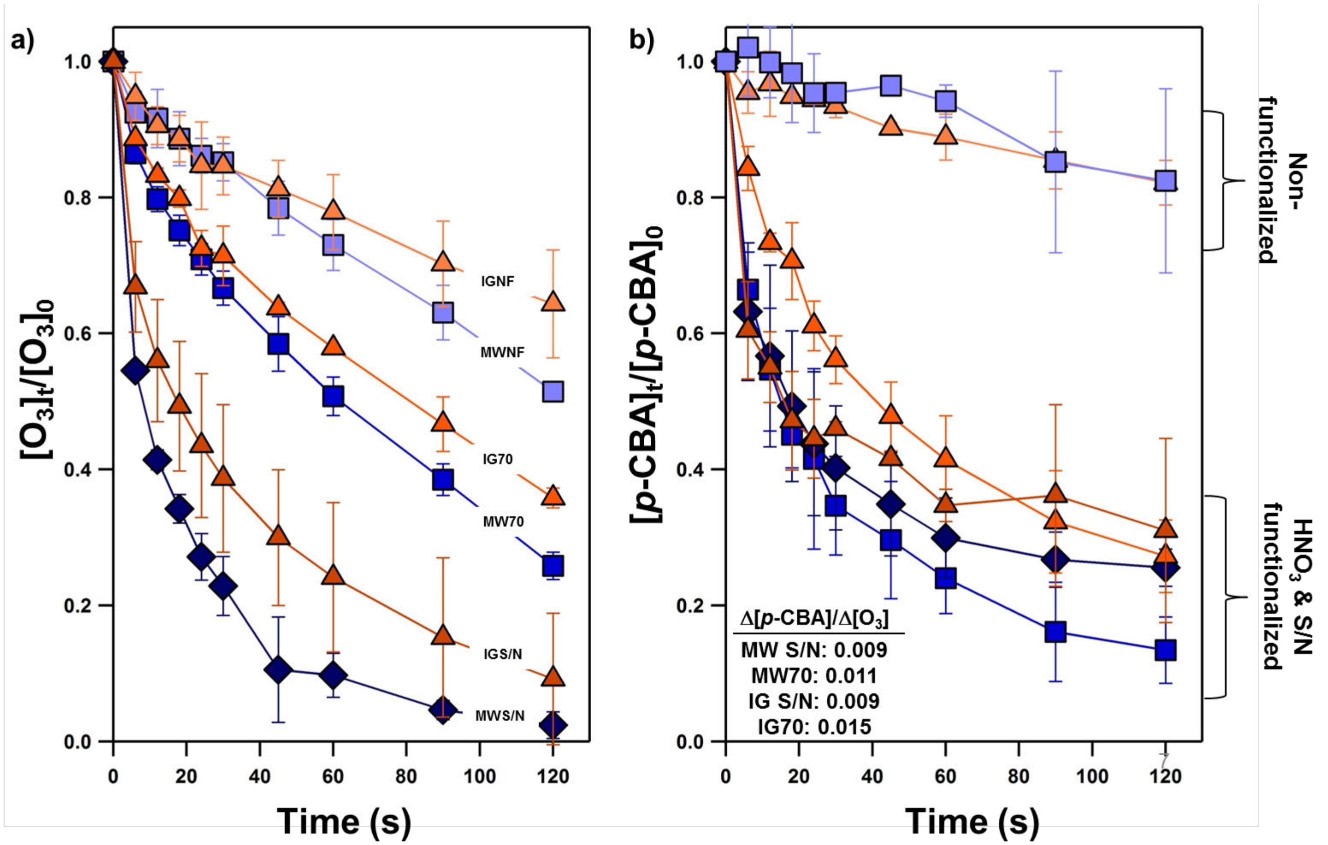


Figure 4-8. Representative degradation curves for ozone and *p*-CBA in research grade (high purity) and industrial grade (IG) MWCNTs from NanoLabs, Inc. Data are shown for MWCNTs that were used as received and after oxidation with either concentrated (70%) HNO_3 or a mixture of concentrated sulfuric and nitric acid (S/N). In (b), the yield of $^{\bullet}OH$ (calculated by the relative change in *p*-CBA to O_3 over time in our systems) is provided. This ratio represents the average of all values measured at each sample collection point. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 μM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 μM of *t*-ButOH and an initial *p*-CBA concentration of 2 μM.

CHAPTER 5: HYDROXYL RADICAL PRODUCTION IN COMPLEX WATER MATRICES AND MODEL TREATMENT SYSTEMS

5.1 Abstract

In ideal systems, multi-walled carbon nanotubes (MWCNTs) increase hydroxyl radical ($^{\bullet}$OH) production during ozonation, making them potentially viable substrates to enhanced ozonation treatment of organic microcontaminants. There remain, however, a number of practical considerations that must be addressed in order to advance the development of this technology. Here, we address these questions regarding the longevity or reactive lifetime of CNTs during oxidative treatment, the efficiency of $^{\bullet}$OH generation in more complex water matrices replete with scavengers, translation of results using a highly reactive $^{\bullet}$OH probe to ozone-recalcitrant pollutant classes, and performance demonstration in flow through systems more representative of engineered treatment. Simulated aging studies exposed various CNTs to a concentrated ozone stream for up to 36 hours, with results indicating that ozonation initially increases the propensity of CNTs for $^{\bullet}$OH generation by introducing reactive surface oxygen groups to the substrate surface. Notably, the reactivity of MWCNTs was maintained throughout the entire exposure period, whereas analysis of single-walled CNT suspensions revealed clear evidence of structural breakdown that coincided with decreased $^{\bullet}$OH generation after approximately 12 hours of aging. In model complex water matrices containing environmentally relevant levels of the known radical scavengers carbonate or dissolved organic matter, $^{\bullet}$OH generation by oxidized MWNCT was essentially unaffected compared to previous experiments. Similarly, studies using partially-treated water from the Iowa River also showed little to no inhibition of $^{\bullet}$OH generation compared to model water systems, which we interpret as evidence that the majority of *p*-CBA oxidation occurs in close proximity to the CNT surface rather than via free $^{\bullet}$OH in bulk solution. We also found that all trends in CNT reactivity established toward *p*-CBA also appear valid for transformation of the ozone-recalcitrant herbicide atrazine, which showed

significantly improved degradation during ozonation of CNT suspensions in both model and real water systems. Finally, a proof-of-concept study using a vacuum filtration assembly verified that results from batch systems can be replicated in a dynamic flow-through reactor utilizing CNTs immobilized on a ceramic membrane support, with treatment efficiency scaling with O_3 influent concentration and the amount of CNTs in the membrane coating. Though additional study is needed, the results of these practical consideration studies are promising and suggest that CNT-enabled advanced oxidation processes may one day grow into a viable treatment application.

5.2 Introduction

Motivated by the need for new technologies to advance society toward water sustainability, we have demonstrated previously the promise of carbon nanotubes (CNTs) in tandem with ozone (O_3) as a next generation advanced oxidation process (AOP). In model batch systems, we have found that various types of CNTs can enhance hydroxyl radical ($^{\bullet}OH$) formation during ozonation, and we have identified key CNT properties that influence their reactivity toward the radical probe para-chlorobenzoic acid (*p*-CBA). Most notably, optimal reactivity was achieved in suspensions of highly oxidized CNTs, with reactivity being greater for single-walled CNTs (SWCNTs) relative to multi-walled CNTs (MWCNTs), presumably because of the greater specific surface area available in SWCNTs suspensions.

Despite the progress made in our prior work in developing CNT-enabled AOPs (see Chapters 3 and 4), we have yet to address many of the practical challenges associated with their eventual application to water or wastewater treatment systems. Our model studies have been limited to single-ozone-dose, closed batch systems in idealized buffer solutions, but engineered treatment systems will generally be more complex in nearly every facet. Thus, this final Chapter explores practical aspects and potential hurdles that must be overcome to further the maturation of CNT-enabled AOPs. Specifically, we examine the lifetime or reactive longevity of CNTs in oxidizing environments, explore treatment efficiency in more complex water matrices that contain known scavengers of $^{\bullet}OH$, investigate the reactivity of ozone in combination with CNTs beyond model radical probes to a representative ozone-recalcitrant pollutant, and demonstrate the proof-of-concept application of CNTs as a reactive coating on a ceramic membrane exposed to an O_3-containing solution. The challenges presented by each of these practical considerations are discussed in greater detail in the following.

When considering the longevity of CNTs as a reactive substrate for promoting $^{\bullet}OH$ formation during ozonation, two competing factors are at play. First, O_3 is in and of itself an oxidant, albeit relatively mild, that may be used for adding oxygen-containing functional groups to CNT surfaces [328]. Accordingly, prolonged and continuous ozonation, as would likely be experienced if the CNTs were applied as a reactive coating on a ceramic microfiltration membrane, would be expected to increase the amount of oxygen-containing surface functional groups. Based on our previous findings in Chapters 3 and 4, therefore, extended exposure to O_3 would in turn also increase the CNT's propensity for $^{\bullet}OH$ production. Another consideration, however, is that extended oxidation may ultimately lead to CNT mineralization (i.e., conversion to CO_2). For example, studies with granular activated carbon (GAC) have shown that extended ozonation can lead to structural defects and performance loss for $^{\bullet}OH$ formation [3, 46, 261]. For CNTs, therefore, if O_3 decay and $^{\bullet}OH$ formation occurs via a reaction sequence that is not truly catalytic [329], CNT structural integrity and performance may be lost over time. This is especially a concern for SWCNTs, which are comprised of a single graphene sheet and thus lack the structural integrity of MWCNTs that often consist of sidewalls made of multiple graphene sheets [321]. Thus, in identifying the optimal CNT type for use during ozonation, consideration must not simply focus on the most reactive material but the most structurally robust in extreme oxidizing conditions. Longevity is also a key consideration when evaluating the cost-effectiveness of this technology, as any increase in reactive lifetime will provide a benefit relative to reagents used in traditional

O_3-based AOPs (e.g., hydrogen peroxide; H_2O_2), which is consumed entirely upon reaction with O_3.

In addition to CNT longevity during ozonation, another practical consideration relates to aquatic chemical variables that may influence $^{\bullet}OH$ formation and stability. Nearly all source waters and wastewater contain a plethora of known radical scavengers, with carbonate (CO_3^{2-}) and dissolved organic matter (DOM) representing two of the most well-known for inhibiting $^{\bullet}OH$ availability [42] and thereby potentially limiting AOP process efficiency. Carbonate, which is the dominant inorganic form of carbon in water above pH 10.3, reacts with $^{\bullet}OH$ to form carbonate radical ion (equation 5-1) [42].

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{-\bullet} + OH^- \qquad \text{(Eq. 5.1)}$$

Similarly, DOM acts as a scavenger when reaction with $^{\bullet}OH$ yields superoxide ion ($O_2^{\bullet-}$) (equation 5-2) [42].

$$\begin{aligned} &DOM + {}^{\bullet}OH \rightarrow DOM^{\bullet} + O_2 \rightarrow \\ &\qquad DOM\text{-}O_2^{\bullet} \rightarrow DOM^{\bullet} + O_2^{\bullet-} \qquad \text{(Eq. 5-2)} \end{aligned}$$

This behavior is analogous to the behavior of *t*-butanol, the model scavenger used in ozonation experiments in Chapters 3 and 4. DOM may also limit the reactivity of surfaces during ozonation simply through sorption and steric blocking of reactive sites on the substrate responsible for O_3 decay and $^{\bullet}OH$ formation. However, we also note that some forms of DOM may also function as promoters of $^{\bullet}OH$ production during ozonation. The product of Eq. 5-2, the superoxide ion, reacts with O_3 to form $^{\bullet}OH$ again (Equations 5-3 through 5-5) [42].

$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet}- + O_2$ (Eq. 5-3)

$O_3^{\bullet -} + H+ \leftrightarrow HO_3^{\bullet}$ (Eq. 5-4)

$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2$ (Eq. 5-5)

The impact of more complex water matrices on CNT performance during ozonation may reflect the behavior previously reported for GAC [46, 260]. In ozonated GAC suspensions in Lake Zurich water, $^{\bullet}OH$ production tended to be maintained despite the presence of these competitors [46, 260]. Lake Zurich water was measured to have a low natural alkalinity (2.6 mM as HCO_3^-) and DOM concentration (DOC = 1.4 mg/L) [46, 260]. The authors proposed that acidic sites on the GAC surface were able to neutralize the natural alkalinity in the water and minimize the impact of CO_3^{2-} on $^{\bullet}OH$ stability [260]. Furthermore, additional studies with GAC suggested that the dual role of DOM as both scavenger and promoter for $^{\bullet}OH$ ultimately may negate one another, so that the presence of DOM does not cause a significant reduction in $^{\bullet}OH$ production during GAC ozonation [46]. One might expect, therefore, that CNT-enabled $^{\bullet}OH$ production will show similar resilience during ozonation of more complex water matrices replete with known radical scavengers.

Finally, validation of CNT-enabled AOPs must consider the treatment targets and platform likely to be utilized at the field-scale. Thus far, all prior experiments have utilized the highly-reactive $^{\bullet}OH$ probe compound *p*-CBA ($k_{OH} = 5 \times 10^9$ $M^{-1}s^{-1}$) [295], yet the actual target of CNT-enabled AOPs will be the suite of established and emerging pollutants known to be ozone recalcitrant, which currently can be treated only with AOPs or alternative advanced treatment technologies like high pressure membranes (e.g., nanofiltration or reverse osmosis). Some ozone recalcitrant pollutants include the herbicide atrazine ($k_{O3} = 6.0$ $M^{-1}s^{-1}$, $k_{OH} = 3.0 \times 10^9$ $M^{-1}s^{-1}$ [80]), the lipid regulator bezafibrate ($k_{O3} = 590$ $M^{-1}s^{-1}$, $k_{OH} = 7.4 \times 10^9$ $M^{-1}s^{-1}$ [167]), the tranquilizer diazepam ($k_{O3} = 0.75$ $M^{-1}s^{-1}$, $k_{OH} = 7.2 \times 10^9$ $M^{-1}s^{-1}$ [167]), the x-ray contrast medium iopromide

($k_{O3} < 0.8$ $M^{-1}s^{-1}$, $k_{OH} = 3.3 \times 10^9$ $M^{-1}s^{-1}$ [167]) and numerous others. Validation of CNT-enabled AOPs must, therefore, extend our results with *p*-CBA to members of this persistent pollutant class, which represent some of the most challenging to remove during water and wastewater treatment.

We also envision that the ideal platform for CNT application during ozonation is as a reactive layer supported on a low-pressure (e.g., microfiltration) ceramic membrane. In this hybrid membrane platform, contact of the CNT layer with an ozone-containing influent stream would create an $^{\bullet}$OH-rich micro-environment within the permeable CNT coating that could be used to simultaneously chemically oxidize and physically separate undesirable constituents in the treatment stream. This platform is challenging, however, as the residence time within such a reactive CNT layer would be very small, requiring exposure to a high concentration of $^{\bullet}$OH to achieve sufficient contaminant degradation.

Here, we address these practical considerations in hopes of moving CNT-enabled AOPs closer to a field scale application as an accepted treatment technology for water and wastewater treatment. Outcomes from this series of studies include performance metrics of this new technology under “real world” conditions. Specifically, it will provide valuable insight as to the most optimal CNT type for long term use in chemical oxidation technologies, the influence of common aquatic chemical variables on $^{\bullet}$OH production via experiments conducted with model scavengers and in partially treated water from the Iowa River, the efficiency of the technology toward atrazine, a representative ozone-recalcitrant pollutant, and finally provide a proof-of-concept demonstration of CNT performance in a dynamic flow-through system more representative of water and wastewater treatment.

5.3 Experimental Section

5.3.1 Reagents. A complete list of reagents is provided in Chapters 3 and 4. Briefly, all CNTs used herein were acquired from Nanolabs, Inc. (www.nano-lab.com; Waltham, MA). Research-grade SWCNT and MWCNTs had vendor-specified purities

>95% and were synthesized via chemical vapor deposition. Industrial grade MWCNTs (hereafter IGCNTs) had vendor-specified purities >85% and were synthesized via chemical vapor deposition. Vendor-provided CNT characterization data are also provided in Chapter 3 and 4.

5.3.2 CNT Longevity Studies. The reactive lifetime, or longevity, of CNTs was investigated in studies with extended ozonation. The CNTs used for longevity studies were as received MWCNTs (MWNF) and MWCNTs treated with concentrated (70%) HNO_3 (MW70), single-walled (SW) CNTs, and industrial grade (IG) CNTs. For each CNT studied, 75 mL of a 1 g/L suspension of CNTs in DI water was prepared and sonicated extensively (~20 h) to promote dispersion. The CNT suspension was then diluted to 0.5 g/L with DI water (150 mL total) and added to a 2-neck round bottom flask. An oxygen and O_3 gas mixture (generated as described in Chapter 3 using a Del Ozone commercial ozone generator) was then bubbled into this suspension using a glass dispersion tube inserted into one neck of the flask, with the other neck remaining sealed. The average ozone concentration measured in a control flask without CNTs was approximately 20 mg/L (determined by direct UV/Vis spectrophotometry at $\varepsilon = 2900$ $mol^{-1}cm^{-1}$ at λ=258 nm [293]).

After 0, 4, 8, 12, 24, and 36 h of ozonation, a 10 mL sample of the ozonated CNT suspension was removed from the flask. Samples were allowed to sit overnight to dissipate any residual ozone in the sample and subsequently sealed for later use in reactivity studies with *p*-CBA in model systems as described previously in Chapter 3. We note that during ozonation a small volume of water was lost from the reactor due to evaporation. To account for these losses, which would concentrate the CNT suspension over time, the fluid level in the flask was marked after each sample was withdrawn. As needed, DI water was periodically added to the CNT solution to maintain the marked fluid level, thereby offsetting evaporative losses and maintaining a relatively constant CNT concentration during ozonation.

5.3.3 Reactivity Studies in Complex Aquatic Matrices. Reactivity studies with *p*-CBA were conducted to measure $^{\bullet}$OH production in systems with increased levels of alkalinity and DOM. For the alkalinity experiments, reactors contained 0.1 – 5 mM of sodium bicarbonate ($NaHCO_3$; SigmaUltra, purity 99.5%). This range (5-250 mg/L as $CaCO_3$) was selected to reflect relevant alkalinity levels found during typical treatment scenarios [53]. Stock solutions were prepared by adding an appropriate volume of 1 mM of carbonate to a 1 g/L suspension of MW70 CNTs that had been oxidized with 70% nitric acid (prepared as described in Chapter 3) so that a 280 – 400 μL aliquot of the stock CNT solution would deliver the desired concentrations of carbonate and CNTs to the reactor. Stock solutions were allowed to mix thoroughly and sit overnight in order to allow for the suspension to reach equilibrium. These stock suspensions were then used in reactivity studies with *p*-CBA according to the protocols described in Chapter 3, with the influence of carbonate being determined from differences in $^{\bullet}$OH production observed in systems with and without (control) carbonate.

Suwanee River Humic Acid (SRHA) was used as representative DOM. Reactors contained an initial SRHA concentration of 1-5 mg/L, a range selected to reflect relevant levels during water treatment [53]. Stock solutions were prepared using an appropriate volume of 250 mg/L SRHA obtained from the International Humic Substances Society (IHSS) [330] and 1 g/L MW70 CNTs so that a 300 μL – 800 μL aliquot of the stock solution would deliver the desired concentration of SRHA and CNTs to the reactor. These stock suspensions were allowed to mix thoroughly and sit overnight, thereby allowing any sorption of SRHA onto the CNT surface to achieve equilibrium. These stock suspensions were then used in reactivity studies with *p*-CBA according to the protocols described in Chapter 3, with the influence of SRHA being determined from differences in $^{\bullet}$OH production observed in systems with and without (control) SRHA.

As a final test of matrix effects on CNT performance, we also conducted reactivity studies in partially treated Iowa River water. A grab sample was procured from

Sediment Basin A at the University of Iowa water plant on April 18, 2013. At this point in the water plant process train, Iowa River water has undergone coagulation, flocculation and sedimentation. Based on characterization data available from the Water Plant, Sediment Basin A water exhibited a turbidity of 1-1.5 NTU, alkalinity of 170-200 mg/L as $CaCO_3$, a total hardness of 300-350, and a carbonate hardness of 220-250. The pH was between 6.8 and 7.5.

In reactivity studies, water from Sediment Basin A was used in place of phosphate buffer in the reactors and spiked to an initial *p*-CBA concentration of 2 μM. According to our typical protocol, an aliquot of ozonated phosphate buffer was then added to the Sediment Basin A sample to initiate reaction. Control experiments were conducted with CNT-free systems to monitor for *p*-CBA loss via sorption to DOM present in the water sample. Additionally, experiments were conducted with and without added *t*-butanol (*t*-ButOH) to assess the relative contribution of radical scavengers naturally present in the partially treated river water sample.

5.3.4 Reactivity Studies with Atrazine. The herbicide atrazine is known to be resistant to treatment via O_3 [80]. To verify that $^{\bullet}OH$ production during ozonation of CNTs can degrade not only model probe compounds (e.g., *p*-CBA) but also known ozone-resistant water pollutants, the degradation of atrazine was explored in ozonated CNT suspensions. Reactivity studies were conducted in a manner analogous to our standard protocol for quantifying $^{\bullet}OH$ formation. However, rather than using *p*-CBA, these reactivity studies monitored the loss of atrazine over time.

An atrazine solution was prepared by adding excess atrazine powder (Sigma Aldrich, purity of 98.8%) to 100 mL of DI water. This solution was allowed to mix overnight, then was passed through a 0.2 μm nylon syringe-driven filter (P.J. Cobert Associates) to remove excess undissolved atrazine. The final solution was assumed to be at the solubility level of atrazine in water, or approximately 30 mg/L [331]. Reactivity studies employed an initial concentration of approximately 2 mg/L. Reactors also contained 320 μM *t*-ButOH as a model $^{\bullet}$OH scavenger and 10 mg/L of MW70 CNTs. Atrazine experiments were performed in phosphate buffer model systems as well as in systems containing an equal volume of Sediment Basin A water and ozonated phosphate buffer.

5.2.5 Proof-of-Concept CNT-Hybrid Membrane Testing. Single-pass flow-through experiments were performed using MW70 CNT immobilized on ceramic filters and a vacuum filtration set-up. Variables included the solid loading of the CNTs on the ceramic filter, either 0.2 or 0.5 mg/cm^2, and the O_3 influent concentration, ranging from 1 to 8 mg/L.

Hybrid CNT-ceramic filters were prepared by first pre-rinsing a 0.2 μm anodic aluminum oxide (AAO) filters (mfg. Whatman) with 250 mL of DI water using a vacuum filtration assembly. The desired mass of oxidized CNTs was suspended in 100 mL of DI water and sonicated for at least 15 minutes prior to application on the ceramic filters. The CNT suspension was then passed through the AAO filter, with the near complete deposition of the CNTs producing a thin coating on the filter surface. While still wet, the CNT-embedded filter was then rinsed with 100 mL of concentrated ozone stock solution to remove any residual organic residue prior to use in experiments monitoring *p*-CBA removal.

Filtration experiments were modeled after the batch systems described in this work. Solutions were prepared in 20 mL beakers, each containing 2 μM *p*-CBA, 320 μM *t*-ButOH, and an appropriate volume of 5 mM phosphate buffer at pH 7. Aliquots of ozonated phosphate buffer were then added to each beaker to achieve the desired ozone concentration. Time zero samples were taken, and the contents of the beaker were placed into the reservoir of the vacuum filtration assembly and passed through the Hybrid CNT-ceramic filter. Pass-through time took between 2 and 5 minutes, depending on the CNT loading of the filter. Final samples were taken from the filtrate and analyzed for *p*-CBA concentration as described below. Ceramic-only control experiments were performed as well.

5.3.6 Analytical Methods. Analytical details are as provided in Chapter 3. Briefly, the concentration of O_3 in stock solutions was measured via UV/vis spectrometry (ε = 2900 L/mole/cm @ 258 nm) [293] using a Thermo Scientific Genesys 10S Spectrophotometer. At lower concentrations in reactors, aqueous O_3 was measured colorimetrically using the indigo blue method [293]. Concentrations of *p*-CBA and atrazine were quantified using high performance liquid chromatography with diode array detector (HPLC/DAD). The *p*-CBA HPLC method is described in Chapter 3. The analytical method for atrazine analysis used an Agilent 1100 HPLC/DAD with an Eclipse XBD-C18 column (4.6 × 150 mm, 5 μm particle size), with a 100 μL injection volume and a 1 mL/min flow rate. The diode array detector was set at 226 nm, and a 60:40 acetonitrile:water mixture was used as the mobile phase [80].

5.4 Results & Discussion

5.4.1 Longevity of CNTs during Enhanced Ozonation. The lifespan of CNTs during ozonation treatment was tested using MWCNTs that were used as-received and after oxidation with 70% HNO_3. Due to their high reactivity in prior batch experiments (see Chapter 4), as-received SWCNTs (hereafter non-functionalized or NF SWCNTs) were tested as well. Finally, due to their lower production cost, as-received industrial grade (i.e., NF IG CNTs) were also tested to provide comparison to their higher purity, research-grade counterparts. We note that as-received CNTs were used in these aging studies to monitor the evolution of reactivity as ozonation introduced surface oxygen groups to the CNT surface over time, as we have previously shown these groups to be critical to CNT activity toward O_3 and $^{\bullet}OH$ production (see Chapters 3 and 4).

Figure 5-1 shows *p*-CBA degradation curves for the four different CNTs as a function of the aging times noted on the curves. Generally, all CNTs regardless of structure and purity showed an increase in reactivity for $^{\bullet}OH$ production (*p*-CBA decay) over the first 12 h of exposure to a concentrated O_3 solution. Notably, this increase in activity was observed for non-functionalized CNTs. During 12 h of ozonation, we observed via XPS that surface oxygen concentrations on these as-received materials increased from approximately 1% to 12%, a value more commensurate with aggressively oxidized CNTs. Thus, the extended exposure to O_3 appears sufficient at inducing the same surface oxide groups we previously noted were critical for activating the CNT surfaces toward O_3 for $^{\bullet}OH$ production. This is a noteworthy observation, as one could envision the performance of a CNT-modified filter increasing in performance, or ripening, over time.

Beyond 12 h, the trends in reactivity varied across the different types of CNTs considered. For MWCNTs that were first oxidized with 70% HNO_3, reactivity modestly decreased after 24 of exposure to concentrated O_3. In contrast, NF MWCNTs showed nearly identical reactivity after 36 h, a promising result showing that MWCNTs are relatively robust and stable during extended oxidation with ozonation. A similar result was observed with IG MWCNTs, which actually showed greater reactivity after 36 h of ozonation, although these CNTs were initially less reactive than the other CNT formulations considered. Notably, XPS analyses of these MWCNTs after 24 to 36 h of aging reveal that the level of surface oxygen was essentially equivalent to that observed after 12 h. Thus, the nature of the surface sites responsible for O_3 decay and $^{\bullet}OH$ formation appears relatively constant during aging.

A clear contrast was observed with SWCNT during aging studies, for which reactivity toward *p*-CBA decreased almost to the initial (as-received) level after 36 h of ozone exposure. The trends in reactivity for SWCNTs likely reflect the loss of structural integrity and degree of mineralization that occurs via extended oxidation of their single graphene sidewall. Figure 5-2a and 5-2b compare photos of the MW-NF and SW-NF suspensions after ozonation for 0, 4, 12, and 36 hours. As expected, the as-received suspension (i.e., 0 h sample) has CNTs that fall easily out of suspension, typical for non-functionalized CNTs with low surface oxygen concentrations ($\leq 1\%$) in aqueous suspension. By 4 h, for which XPS reveals that surface oxygen concentrations has increased to ~9%, both SW and MW CNT suspensions show an increased degree of suspension dispersion and stability. This trend continues after 12 h of ozone exposure, as is anticipated for such highly surface-oxidized CNTs.

A notable difference in MW and SW suspensions was observed after 36 h of O_3 aging, at which time the MWCNT appeared, at least visually, relatively unchanged from the stability exhibited after 12 h. In contrast, the SW suspension had become slightly translucent and developed a brownish hue, a color that is most often associated with that expected when large amounts of CNT-generated amorphous carbon are present in solution [317, 327]. Visual evidence, therefore, suggests the SWCNTs have extensive loss of structural integrity after extended exposure to concentrated O_3 solutions, behavior that would reasonably explain the loss of reactivity toward *p*-CBA exhibited by these suspensions.

This scenario is supported by TEM images collected on samples of MW and SW suspensions after 36 h of aging (Figure 5-2c and 5-2d). Figure 5-2c shows a representative TEM image of the MWCNTs after 36 hours of exposure to concentrated ozone. Although some evidence of structural damage and amorphous carbon production appears evident, the aged MWCNTs largely retain their distinctive nanotube structure. In contrast, the image of SWCNT suspensions after 36 hours of exposure (Figure 5-2c) lacks any structures reminiscent of nanotubes. Clearly, the aggressive oxidizing conditions of extended ozonation result in the near complete loss of SWCNT structure, as well as extensive mineralization and formation of amorphous carbon via graphene sidewall oxidation. Thus, despite their greater reactivity in single-use batch experiments, SWCNTs are likely not an optimal choice for practical application relative to more robust MWCNTs because of their inability to withstand strong oxidizing conditions over the timescales required for treatment.

When considering implementation, the ability of initially non-functionalized CNTs to increase reactivity, or ripen, while exposed to ozone, suggests a design possibility. One can envision a CNT-hybrid filter than employs a two-layer CNT design. A thin top layer of functionalized CNTs would cover a thicker lower layer of initially non-functionalized CNTs. The top layer provides the desired high level of reactivity initially while the lower layer has an opportunity to increase in reactivity via ozone activation and surface oxygen group formation over time. Eventually, as the top layer breaks down, the functionalized lower layer will be able to sustain the high level of reactivity needed for effective treatment.

5.4.2 Effects of Model Radical Scavengers on CNT Production of $^{\bullet}$OH during Ozonation. Thus far, experiments have been performed in idealized, model water systems (e.g., relatively clean, buffered systems). A series of experiments were therefore conducted to explore the impact of more complex aquatic systems, specifically the presence of $^{\bullet}$OH scavengers, on CNT performance during ozonation. *We n*ote that MW CNTs oxidized with 70% HNO_3 (MW70) were used in these, and all remaining, experiments. These CNTs were selected as a representative "optimal" CNT formulation because they provide both a high level of reactivity and an extended longevity during ozone exposure.

Figures 5-3a and 5-3b explore the impact of carbonate and DOM, respectively, on *p*-CBA degradation in ozonated CNT suspensions. Results are shown for systems containing 0.1 mM to 5 mM carbonate (4-3a) or 0.5 mg/L and 5 mg/L SRHA (5-3b) as a model form of DOM. We note that analogous to our previous reactivity experiments, these systems also included 320 μM *t*-ButOH as a model scavenger because systems without *t*-ButOH were too reactive to furnish meaningful *p*-CBA concentration versus time data. Recall that for CNT suspensions containing carbonate or SRHA, CNTs were pre-equilibrated with solutions of the radical scavengers for at least 24 hours prior to conducting the reactivity study.

Somewhat surprisingly, results in Figure 5-3 show that over the range of concentrations explored, carbonate and DOM do not impose any additional inhibition to $^{\bullet}$OH production during CNT ozonation. In particular, a primary concern with SRHA is that it might bind to the surface of the CNTs, diminishing their ability to react with ozone and consequently reducing $^{\bullet}$OH production. Since the SRHA and the CNTs had sufficient time to equilibrate, it is likely some organic matter was associated with the CNT surface (although the amount was not quantified), but clearly this surface SRHA did not have a deleterious effect on $^{\bullet}$OH production. We note that the extent of SRHA sorption is likely to be reduced on more polar, oxidized CNTs [332]; thus it is possible that the SRHA did not bind to the CNTs in sufficient quantities to alter $^{\bullet}$OH production. We also note that in the CNT-free system, SRHA alone was able to promote modest amounts of $^{\bullet}$OH formation, presumably from the ability of some functional groups in SRHA to function as promoters of $^{\bullet}$OH formation during ozonation [42]. Therefore, this additional $^{\bullet}$OH production associated with SRHA may have been able to offset any decrease in $^{\bullet}$OH production resulting from SRHA binding to the CNT surface.

Generally, we interpret the lack of influence of these traditional radical scavengers as evidence that the majority of $^{\bullet}$OH production in CNT systems occurs in the near surface region. All scavengers present in our system (*t*-ButOH, carbonate and SRHA) are expected to predominate the dissolved phase. The persistence of *p*-CBA despite the presence of such high concentrations of known scavengers is often interpreted as evidence of a primarily surface mediated process, with elevated $^{\bullet}$OH concentrations in the near surface region that remain largely unaffected by constituents present in bulk solution.

Finally, we note that our results with carbonate and SRHA mirror those previously observed in catalytic ozonation studies utilizing activated carbon (AC) [46, 260, 333]. Specifically, no significant difference on $^{\bullet}$OH production was observed in studies with AC conducted in more complex model systems (e.g., including known radical scavengers) and system with water samples collected from surface waters (e.g., Lake Zurich) [46, 260, 333].

5.4.3 Reactivity of CNTs during Ozonation of a Natural Water Sample. Figure 5-4 shows the results of the *p*-CBA degradation in a solution consisting of 14 mL of partially treated Iowa River water (i.e., Sediment Basin A water) blended with a 6 mL aliquot of ozonated phosphate buffer to initiate reaction. Results from various systems using this basic aquatic matrix are provided, most notably data comparing the influence of the radical scavenger *t*-ButOH in river water systems with and without CNTs. For example, in river water systems containing 320 μM *t*-ButOH, Figure 5-4 shows that *p*-CBA degradation is essentially identical to what we observed in our model (i.e,. phosphate buffer) reactor. In addition to supporting a scenario in which our laboratory results will generally translate well to a real-world water treatment scenario, these data also support our proposition that a significant amount of *p*-CBA transformation is surface mediated in our systems, such that the composition of the bulk matrix will not be able to entirely quench CNT activity.

Results in Figure 5-4 are also presented for systems without any added radical scavenger. In a CNT-free system without *t*-ButOH, we observed significantly more *p*-CBA degradation than observed in systems with *t*-ButOH, which is likely due to the ability of DOM present in the Sedimentation Basin A water to promote $^{\bullet}$OH formation during ozonation. Notably, for systems containing 10 mg/L MW70, we observed greater rates of *p*-CBA decay in *t*-ButOH-free systems relative to systems with *t*-ButOH. This result is also consistent with our earlier findings for *t*-ButOH-free systems in the present of the model radical scavengers of carbonate and SRHA. We interpret the difference in *p*-CBA degradation in systems with and without *t*-ButOH to the amount of $^{\bullet}$OH available in the bulk solution. The inhibition of *p*-CBA decay resulting from added *t*-ButOH reflects consumption of the fraction of the generated $^{\bullet}$OH that is available in the bulk solution, an observation that generally mirrors results on the influence of *t*-ButOH on $^{\bullet}$OH formation during ozonation of GAC [3, 266, 334].

However, it is notable in our systems that higher concentrations of *t*-ButOH (up to 640 μM) and more complex aquatic matrices (e.g., carbonate- and SRHA-containing solutions, partially treated Iowa River water) do not result in any further inhibition. It appears, therefore, that the CNT surface remains active toward O_3 and capable of $^{\bullet}$OH formation even in dirtier real world systems. Furthermore, the persistent activity of the CNT surface provides guidelines for possible application platforms that may optimize performance. In fact, our proposed application platform of CNTs as a reactive coating immobilized on a ceramic microfiltration membrane seems well-suited for sustained reactivity, as the solid-to-water ratio in such mats (and thus the available surface area) will be quite large. This will promote a high degree of interaction between pollutant targets and the CNT surface, where the $^{\bullet}$OH formation is least affected by matrix effects.

5.4.4 Reduction of Ozone-Recalcitrant Compounds via CNT-enabled AOPs. The herbicide atrazine was selected for additional investigation, as it is known to be recalcitrant to treatment via ozone alone [80]. Atrazine degradation was studied in both the typical model water system used for the majority of experiments described herein and in a system using Sediment Basin A water (Figure 5-5). Atrazine exhibit limited degradation in the ozone-only system, consistent with its recalcitrance toward ozone. In contrast, both the model water system and the real water system revealed essentially identical atrazine removal.

The behavior of atrazine mirrors the fate of *p*-CBA under otherwise identical experimental conditions. We note the rate and extent of atrazine decay in these experimental systems is less than that observed with *p*-CBA, which should be expected given differences in their relative reactivity toward $^{\bullet}$OH ($k_{ATZ/^{\bullet}OH} = 3.0 \times 10^9\ M^{-1}s^{-1}$ [80], $k_{p\text{-}CBA/^{\bullet}OH} = 5 \times 10^9\ M^{-1}s^{-1}$ [295]). In fact, it is likely that the relative reactivity of O_3

recalcitrant emerging and legacy pollutant classes in these CNT systems can simply be predicted from previously measured second-order rate constants for oxidation by $^{\bullet}$OH.

5.4.5 Demonstration of Hybrid CNT-Ceramic Filter for Flow-through Treatment. A single-pass flow-through system was developed as a proof-of-concept study, utilizing a typical laboratory vacuum-filtration assembly and a CNT-embedded ceramic filter. SEM images of the CNT-coated ceramic microfiltration are shown in Figure 5-6a, which shows a cross-sectional image collected after deposition of MW70 CNTs on the AAO support. The deposition of the oxidized CNT suspensions creates a relatively uniform layer on the membrane surface, and the relatively easy method of hybrid membrane fabrication allows the density of CNTs within the coating to be tailored; herein, we explored the reactivity of CNT layers with densities of 0.2 and 0.5 mg/cm^2.

Results from flow-through reactivity experiments are shown in Figure 5-6 and generally support that the reactivity of CNTs demonstrated in closed batch systems can be extended to more dynamic flow conditions representative of treatment. Most notably, these results demonstrate two key design variables that can be tuned to optimize hybrid filter performance. First, Figure 5-6b shows that increasing O_3 levels produce a corresponding increase in the amount of *p*-CBA loss in a single pass through a 0.2 mg/cm^2 filter. Over O_3 concentrations ranging from 1 to 8 mg/L, the removal of *p*-CBA also increased at a rate of 4% per mg/L of O_3, ultimately achieving a maximum removal of ~40% in a single filtration event. Second, Figure 5-6c shows the CNT density on the ceramic filter is another key parameter for optimizing reactivity. At a fixed O_3 concentration of 5 mg/L, an increase from 0.2 to 0.5 mg/cm^2 produced a 15% increase in *p*-CBA removal in a single filtration even. We anticipate that even greater removals in a single pass can be achieved at higher CNT densities, but we were unable to test beyond 0.5 mg/cm^2 due to slow flow rates through denser filters. Performance at these higher loadings is currently being investigated in a higher pressure microfiltration system.

While preliminary, the results in Figure 5-6 are promising. Given the relatively thin CNT layer on the ceramic membrane support, the residence time of fluid within the CNT mat must be incredibly short. Nevertheless, we achieve significant removals of *p*-CBA in a single filtration event, and the extent of removal is likely to improve in pressurized systems in which greater CNT densities can be used. Even under the current levels of removal depicted in Figure 5-6, hybrid filters run in series or in a recirculating system could be used to achieve even greater removals of O_3 recalcitrant pollutants.

5.4.6 Environmental Relevance. The results from these practical studies offer encouragement that CNT-enabled ozonation may provide a viable means of targeted treatment for ozone-recalcitrant pollutants in water and wastewater. The results found in model water systems discussed in Chapters 3 and 4 translate successfully to real water systems, and tests with atrazine verify that the $^{\bullet}OH$ production predicted with *p*-CBA is in fact effective against more representative, environmentally relevant ozone-recalcitrant pollutants.

Additional study is certainly warranted to further advance this concept toward practical application. One important area of further study is use of a pressurized filtration apparatus for CNT-functionalized membranes, as such systems are more representative of treatment platforms currently utilized water treatment applications. The proof-of-concept study results herein offer two key design parameters that can be tuned to optimize performance in a flow-through setting: ozone concentration and CNT density. In current water treatment applications, a maximum ozone concentration of approximately 2 mg/L is typical [16], so increasing the density of CNTs on the hybrid filter is likely to be the most flexible design parameter. However, CNT density must be increased in a manner that does not result in too great of head loss across the hybrid filter, which in turn would increase the energetics and cost of treatment. More complex matrices must also be considered, as membranes will be more prone to fouling by colloidal or organic matter in a flow-through filtration system.

A reasonable question that also must be addressed is the material cost associated with use of CNTs in water treatment. Based upon the results of longevity studies discussed above, we can provide an initial estimate of the potential lifetime of a CNT-embedded hybrid ceramic filter and the associated cost this technology. For a hybrid ceramic filter, we can estimate the lifetime per unit mass of CNTs. For example, the CNTs were exposed to a concentrated ozone stream for up to 36 hours. Assuming, very conservatively, that this is the practical lifetime of the CNTs, we can estimate a lifetime ozone exposure level:

$$20\,{}^{mgO_3}\!/\!_{L} \times 36h = 720\,{}^{mgO_3-h}\!/\!_{L}$$

Given an initial CNT mass in the system of 75 mg, this translates to an exposure per unit mass of:

$$\frac{720\,{}^{mgO_3-h}\!/\!_{L}}{75mg\;CNTs} = \frac{9.6\,{}^{mgO_3-h}\!/\!_{L}}{mg\;CNTs}$$

The maximum CNT loading on the CNT-embedded filter used in the flow-through system was 0.5 mg/cm^2, over a 10 cm^2 filter area, for a total filter exposure of:

$$\frac{9.6\,{}^{mgO_3-h}\!/\!_{L}}{mg\;CNTs} \times 0.5\,{}^{mgCNTs}\!/\!_{cm^2} \times 10cm^2 = 48\,{}^{mgO_3-h}\!/\!_{L}$$

In a treatment scenario, we can assume a maximum O_3 concentration of 3 mg/L, giving a lifetime per filter of:

$$\frac{48\,{}^{mgO_3-h}\!/\!_{L}}{3\,{}^{mgO_3}\!/\!_{L}} = 16\;hours$$

In a higher-pressure system, this CNT loading could be increased, so this value is also conservative.

Now, to translate these calculations to a full-scale treatment operation, we can consider a moderately-sized industrial filter of 10 ft^2 with the same 0.5 g/cm^2 CNT loading:

$$0.5\,{}^{mgCNTs}\!/_{cm^2} \times 10\,ft^2 \times \frac{929cm^2}{ft^2} = 4{,}645\ mg\ CNTs$$

Resulting in a total filter lifetime of:

$$\frac{\dfrac{9.6\,{}^{mgO_3-h}\!/_{L}}{mg\ CNTs} \times 4{,}645\ mg\ CNTs \times \dfrac{day}{24\ h}}{3\,{}^{mgO_3}\!/_{L}} = 619\ days$$

These lifetime analyses have a direct relevance to treatment cost. An estimated cost for functionalized, industrial-grade CNTs is roughly $700/kg [335]. At a CNT density of 0.5 g/cm^2, a 10 ft^2 filter would require 0.004645 kg of CNTs. This equals a total CNT cost of only $3.25, and an estimated useful life of 1.7 years. A higher density filter would have additional CNT costs, but it should also have an extended lifespan. To compare, assuming an average flow rate of 5500 L/hr through that filter and a typical ratio of 1 mg H_2O_2 per 1 mg O_3 for treatment, H_2O_2 costs over that same 619 day period would be approximately $250. Due to CNT's potential for extended useful life, CNT-enhanced ozonation may offer a financially viable treatment alternative to existing AOPs.

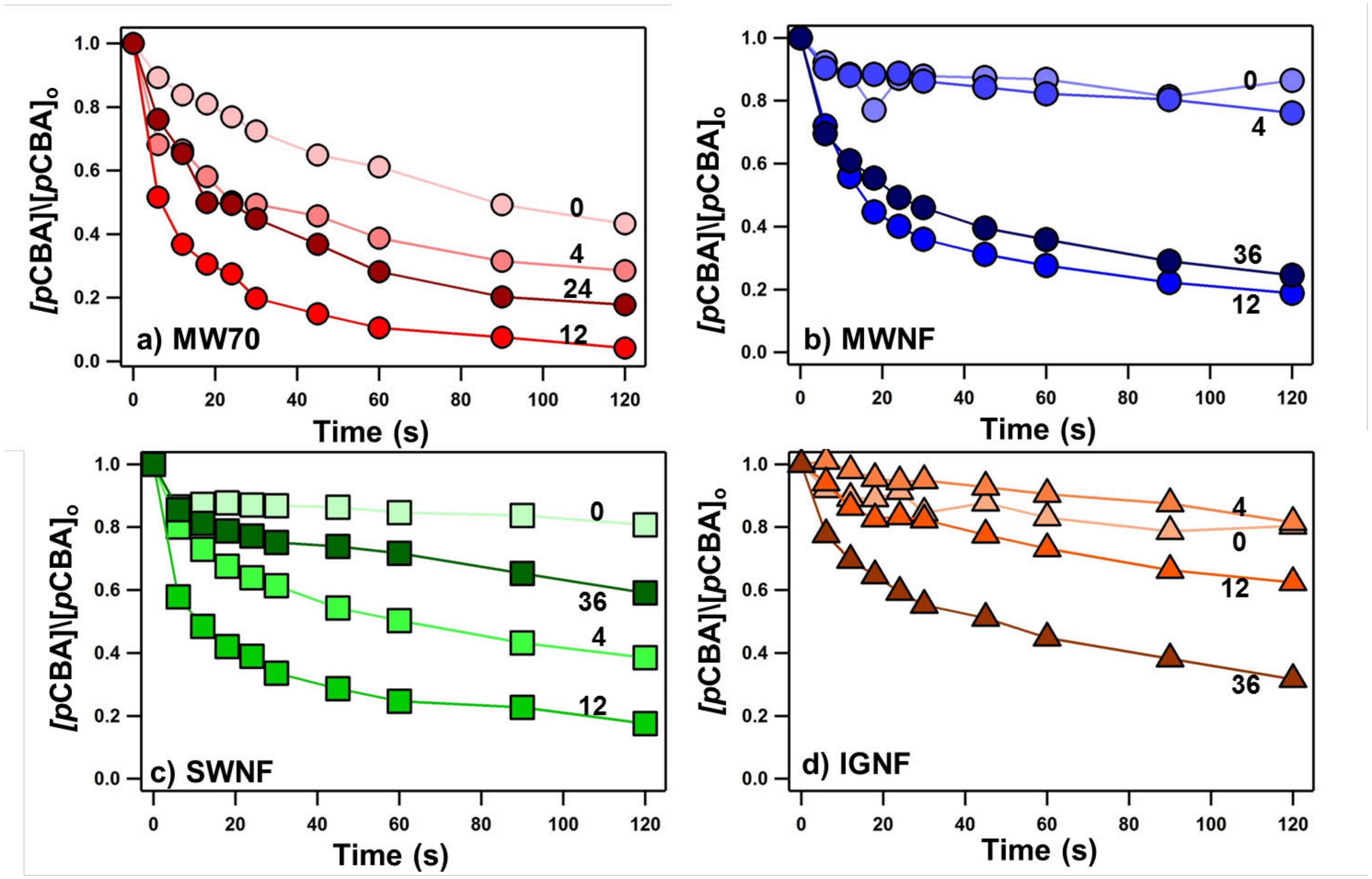


Figure 5-1. Representative curves for *p*-CBA as a function of ozone exposure time. Data are show for suspensions of (a) MW70, (b) MWNF, (c) SWNF and (d) IGNF. Data are shown as a function of exposure time (as indicated) to a concentrated ozone solution, as described in the text. All data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

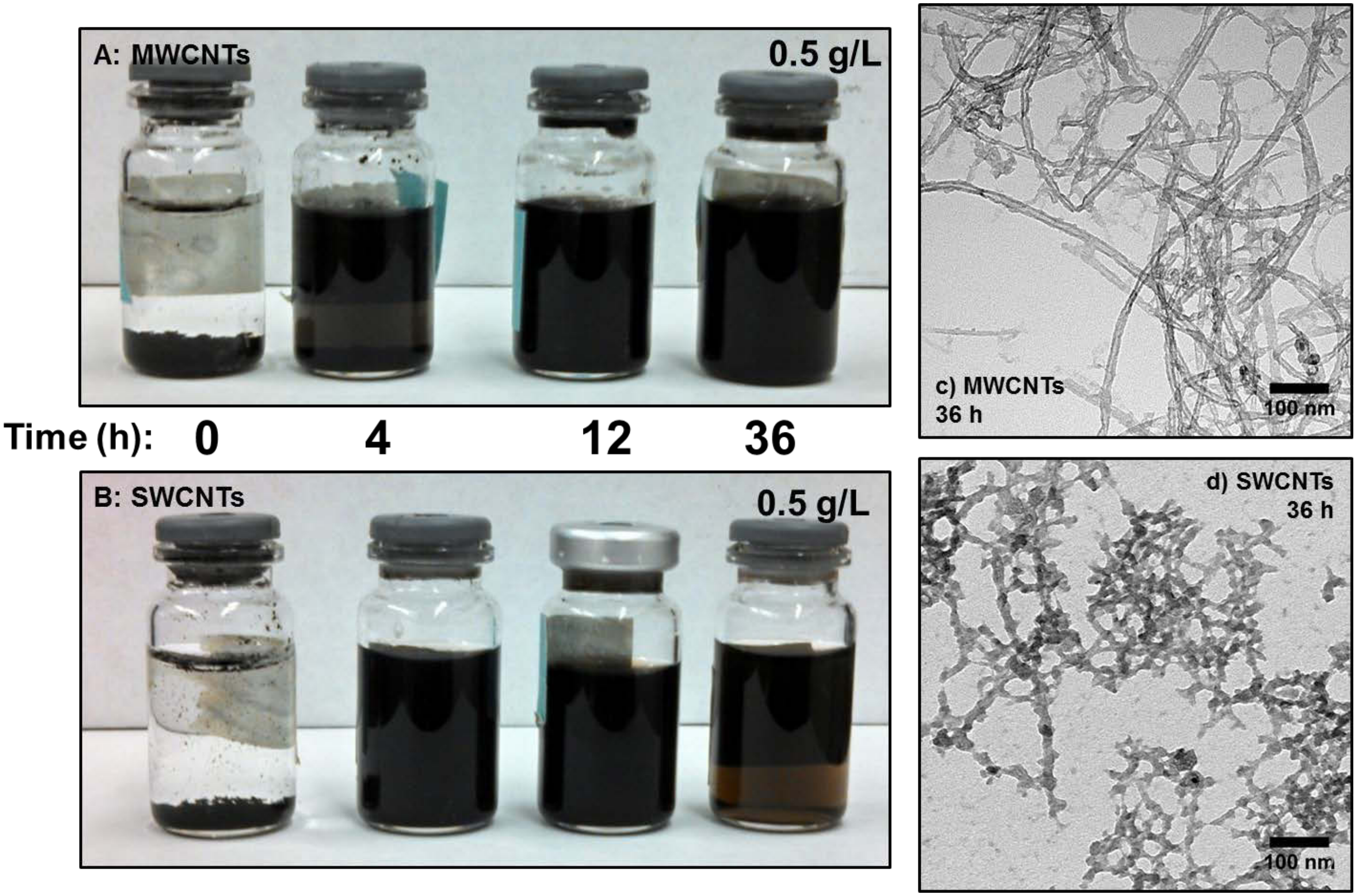


Figure 5-2. Images of CNT suspensions as a function of exposure time to a concentrated ozone solution. The photos show samples of 0.5 g/L MWCNT (a) and SWCNT (b) suspensions after the indicated number of hours of exposure to a concentrated ozone solution. Also shown in (c) and (d) are TEM images collected after 36 h of exposure to a concentrated ozone solution for these CNT suspensions, respectively.

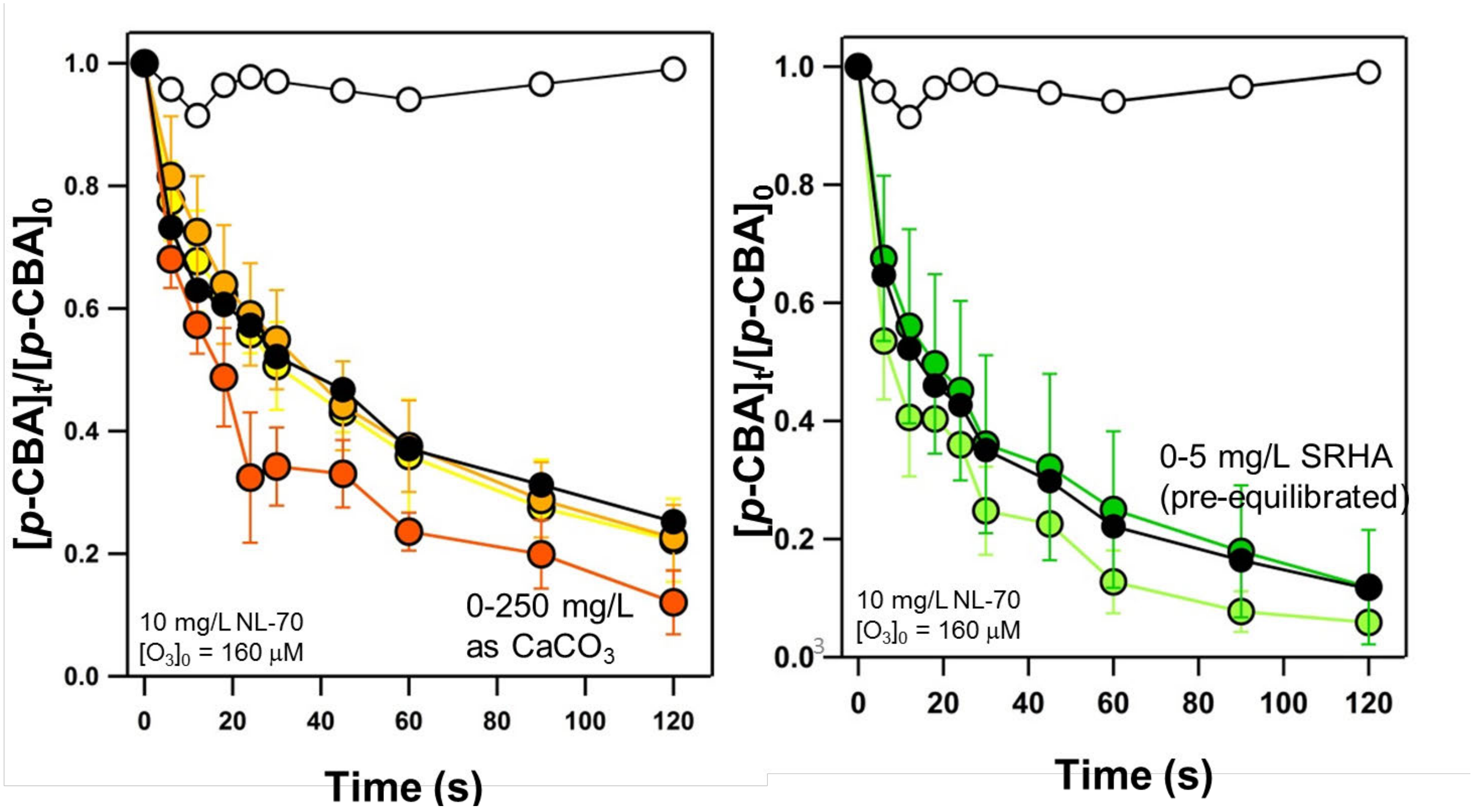


Figure 5-3. **Degradation curves for p-CBA in ozonated suspensions (10 mg/L) of MW70 CNTs containing model radical scavengers.** Systems included (a) carbonate and (b) SRHA over the range of concentrations indicated. Unless otherwise indicated, data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 μM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 μM of *t*-ButOH and an initial *p*-CBA concentration of 2 μM. Uncertainties represent one standard deviation from triplicate experiments.

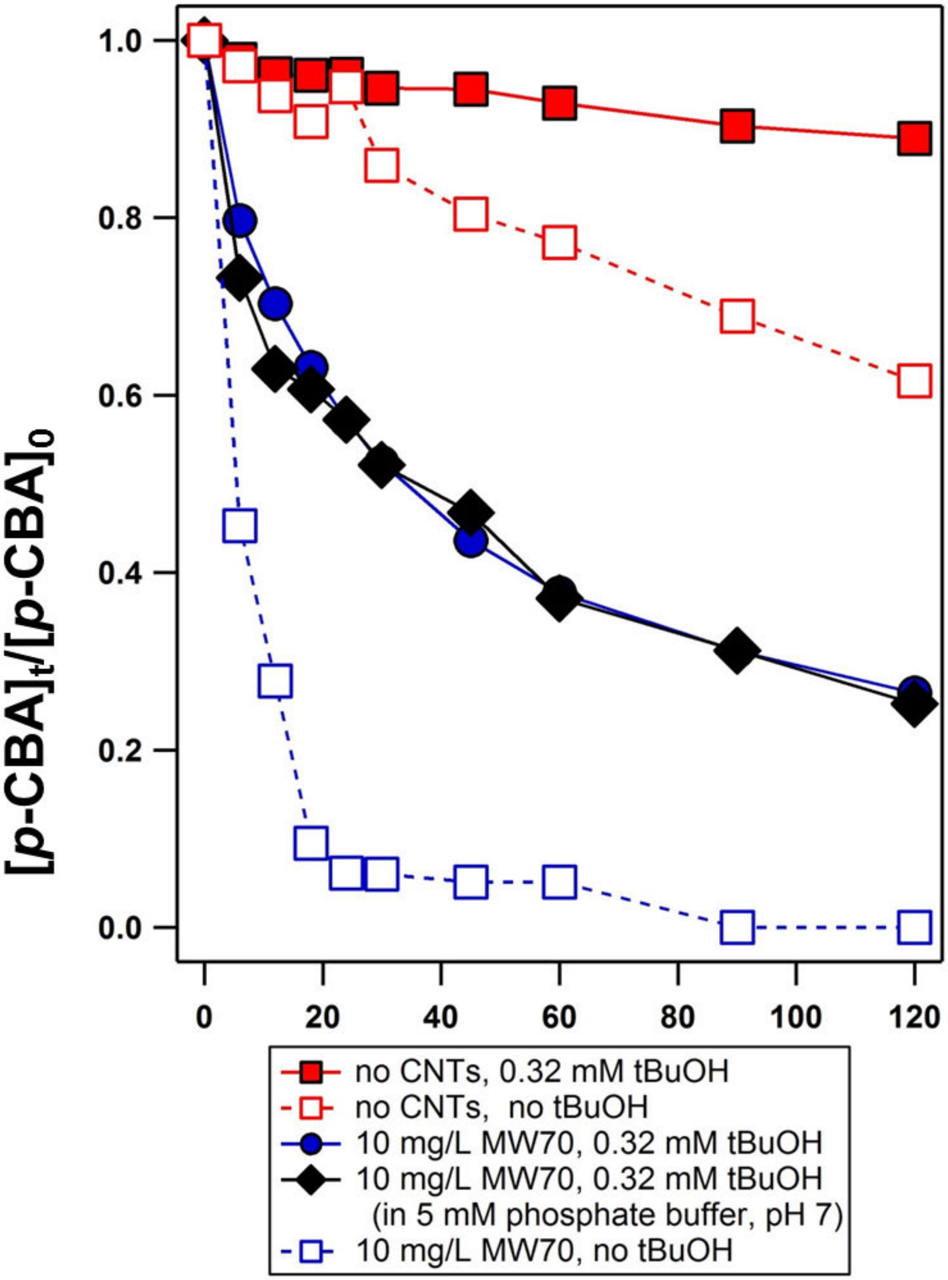


Figure 5-4. Degradation of pCBA in ozonated suspensions (10 mg/L) of MW70 CNTs prepared in partially treated Iowa River water (i.e., taken from Sediment Basin A). These suspensions contained approximately 14 mL of Sediment Basin A water and 6 mL of ozonated 5 mM phosphate buffer. Unless otherwise indicated, data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

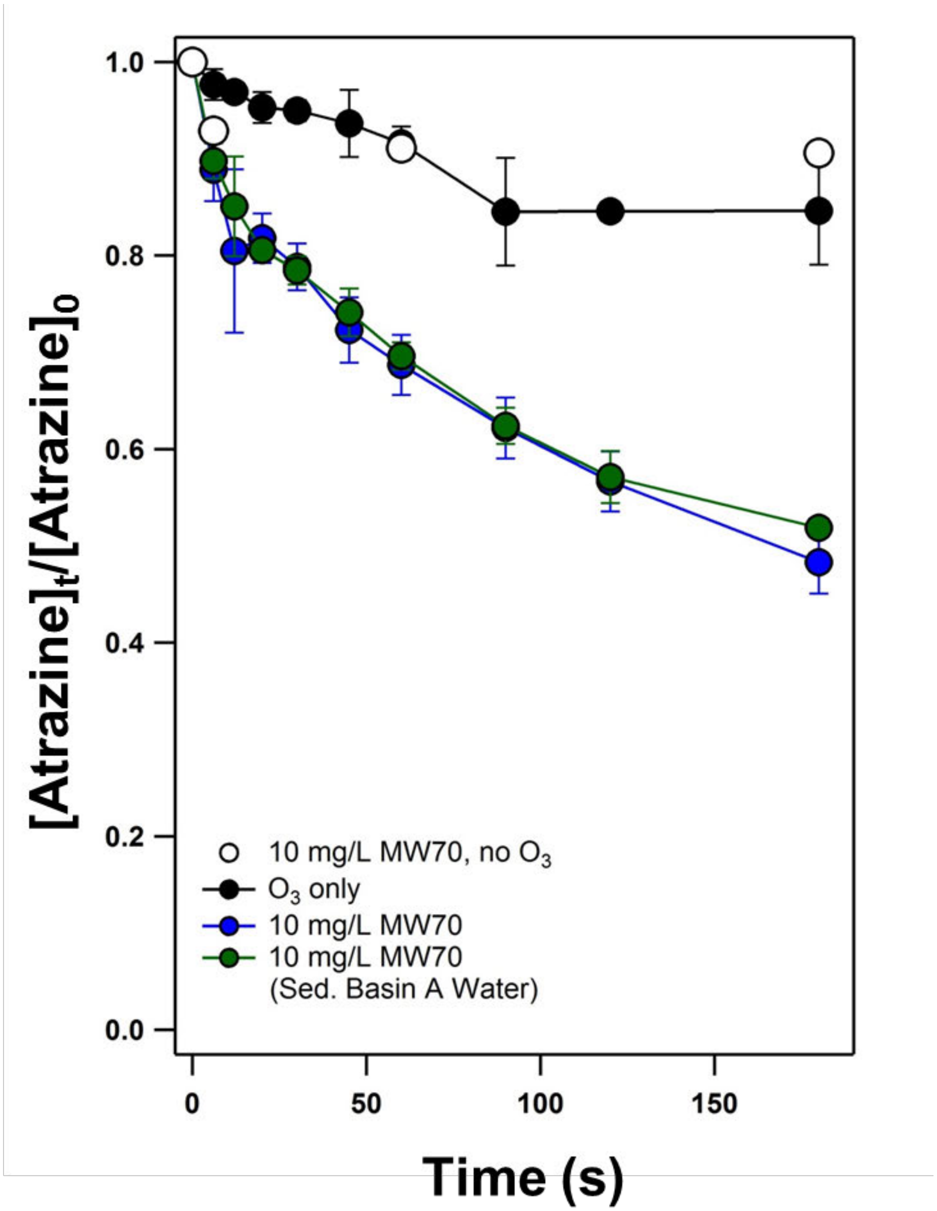


Figure 5-5. Degradation of atrazine in ozonated suspensions (10 mg/L) of MW70 CNTs. Data is presented from both model (phosphate buffer) systems and suspensions prepared in partially treated Iowa River water (i.e., taken from Sediment Basin A). Suspensions with Iowa River water contained approximately 14 mL of Sediment Basin A water and 6 mL of ozonated 5 mM phosphate buffer. Unless otherwise indicated, data were collected in systems with a CNT concentration of 10 mg/L and an initial O_3 concentration of 160 µM. Systems at pH 7 (5 mM phosphate buffer) also contained 320 µM of *t*-ButOH and an initial *p*-CBA concentration of 2 µM.

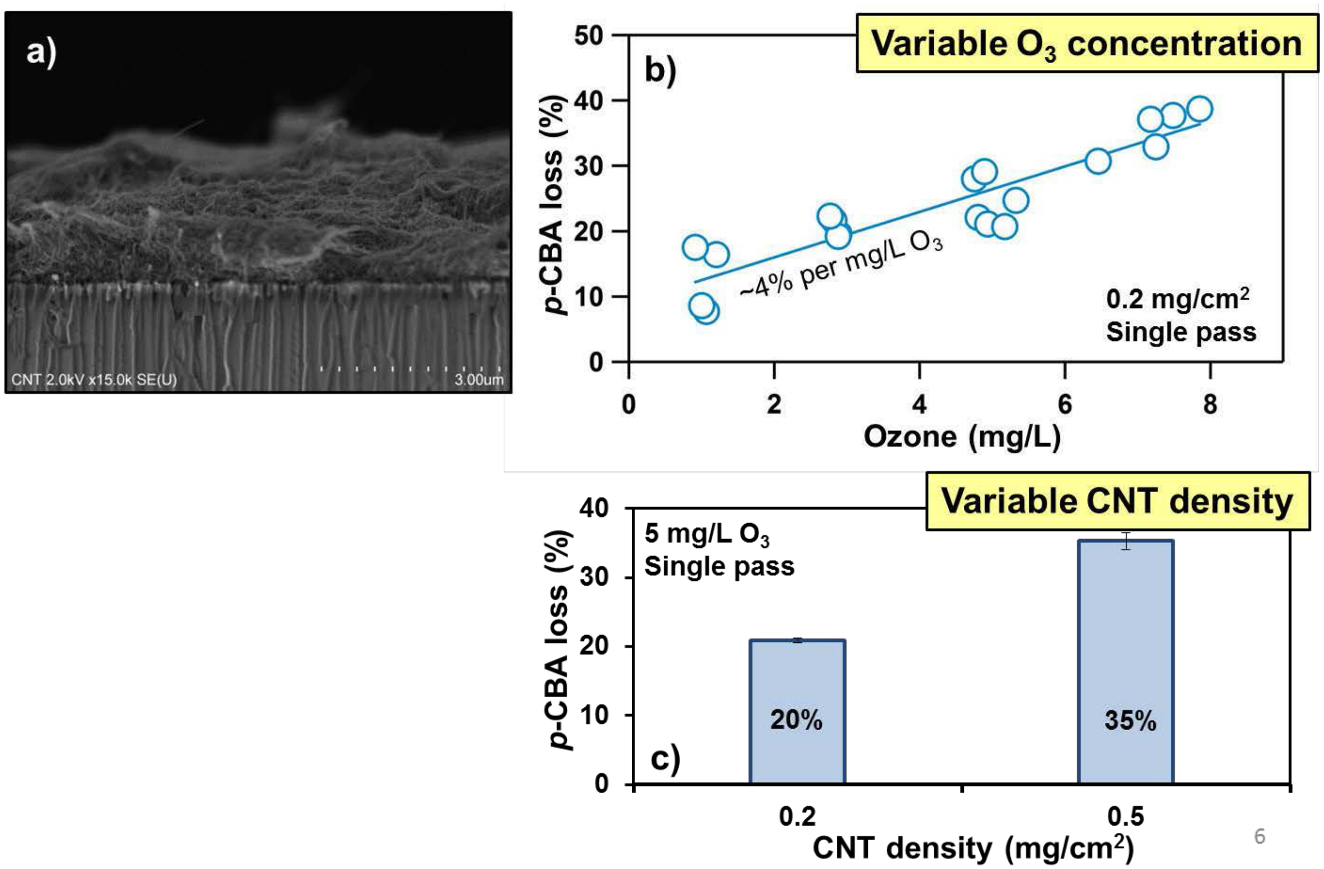


Figure 5-6. Flow-through system image and results. (a) Cross-sectional SEM image of hybrid CNT-ceramic microfiltration membrane prepared via the deposition of 0.2 mg/cm^2 MW70 CNTs on an AAO 0.2 λm microfiltration membrane. Performance results of this filter are provided in (b) and (c). Panel (b) shows the relationship between the extents of pCBA removal (as % of initial mass) in a single pass through this 0.2 mg/cm^2 filter as a function of the influent ozone concentration. Panel (c) illustrates the influence of CNT loading on filter performance, comparing the extent of pCBA removal (as % of initial mass) in a single pass through either a 0.2 or 0.5 mg/cm^2 hybrid filter. All influent solutions (pH 7) contained 320 μM of t-ButOH as a model radical scavenger and an initial p-CBA concentration of 2 μM.

CHAPTER 6: CONCLUSION

Collectively, this work provides a more comprehensive understanding of $^{\bullet}OH$ production during ozonation of CNTs, spanning from fundamental considerations of the role of CNT surface chemistry and structure to the practical considerations necessary to further develop this technology for full-scale application. Ultimately, we believe this work will allow chemical oxidation to become a viable alternative or complement to membrane treatment, thereby allowing for increased opportunities for water recycling. Each Chapter fills gaps in our current knowledge regarding the potential for advanced oxidation technologies to play a role in the treatment of emerging organic micropollutants. As with most research, it also revealed questions that merit further consideration and eventual study.

6.1 Need for New Advanced Treatment Options

The impetus for this work was the pressing need to develop alternatives for fresh water. All over the world, fresh water resources are being utilized at or beyond capacity. Continuing population growth and climate change will only exacerbate this problem in the future. Reuse of treated wastewater provides potential to significantly offset freshwater use. However, the ubiquity of organic microcontaminants such as pharmaceuticals in wastewater effluent poses a challenge for increasing use of this under-tapped resource. While human toxicology studies related to these microcontaminants in drinking water sources are ongoing, a clear link has been established between microcontaminants in wastewater effluent and ecotoxicological effects. The challenge of removing these pollutants must be addressed before wastewater reuse can truly be a viable alternative to fresh water.

Chapter 2 explored this challenge in greater detail. By reviewing published data on influent and effluent concentrations of 149 different pharmaceuticals, we found that, in general, conventional treatment exhibits limited effectiveness for pharmaceutical removal. In fact, many pharmaceuticals show no degradation at all during conventional treatment. The conventional treatment process was designed specifically to target removal of solids, BOD, nutrients, and pathogens. It is not surprising, therefore, that advanced treatment processes are needed to remove more complex chemicals.

Our data analysis identified that, currently, reverse osmosis is the best available technology for pharmaceutical treatment. However, reverse osmosis is prohibitively expensive for most wastewater treatment plants. Chemical oxidation is a lower-cost alternative that is more likely to be utilized in wastewater treatment. Chemical oxidation via ozone was found to be nearly as effective as reverse osmosis for a majority of microconstituents. However, as our statistical analysis revealed (Figure 2-4), there are still a number of pharmaceuticals which are resistant to treatment via ozone.

Current AOPs offer improved removal of these ozone-recalcitrant pollutants, but they tend to be energy intensive and/or rely on hard-to-store chemicals. This energy/water nexus poses significant challenge. Creating new energy requires fresh water; treating fresh water or fresh water alternatives to a safe level requires energy. As water treatment requirements increase, so generally do energy demands. Increased reliance on existing AOPs is not a sustainable solution to allow for increased wastewater reuse.

Ongoing research into granular activated carbon (GAC) -catalyzed ozonation is attempting to provide an alternative to these AOPs. Results so far are encouraging, though the process may not be truly catalytic, as GAC reactivity tends to decrease with repeated exposure to ozone because of changes in surface chemistry and reduced structural integrity [46, 260]. The factors of GAC which seem to be linked with $^{\bullet}$OH production include high surface area and presence of electron-rich surface sites that allow for reaction with ozone [46, 260]. Carbon nanotubes (CNTs) have higher external surface area than GAC and have easily-tunable surface chemistry [300]. Additionally, multi-walled (MW) CNTs are known for their mechanical strength, suggesting they may have the structural integrity to withstand the highly oxidizing environments which have proven problematic for GAC. These factors motivated us to explore whether CNTs are promising substrates for promotion of $^{\bullet}$OH during ozonation.

6.2 A Role for CNTs in Advanced Water Treatment?

We pursued an investigation into the viability of CNT-enabled ozonation. The focus of this work is novel; no other published study was found using ozonation of CNTs in conditions representative of water treatment at neutral pH levels. Several studies have looked at CNTs for catalytic ozonation of select constituents such as bezafibrate, metolachlor, or sulfamethoxazole [336-339]; however, these studies all utilized pH levels between 4 and 5. Further, they primarily explored the transformation of the selected constituents during treatment, rather than the CNT/ozone interactions specifically. The work discussed in Chapter 3 focused on ozonation of MWCNTs, to determine if they promote $^{\bullet}$OH production during ozonation and, if so, how those $^{\bullet}$OH production levels compare to current ozone-based AOPs.

One key outcome of this work was the determination that R_{CT} value scales with CNT mass loading in reactors. The finding that increased CNT mass results in increased $^{\bullet}$OH production implies that $^{\bullet}$OH production is initiated by a surface mediated reaction between the ozone and CNTs; increased available surface area results in increased levels of reaction. This result has obvious implications for application, in that higher levels of CNT loading will likely result in improved treatment levels.

The second key outcome has more important implications for achieving improved treatment efficiency. We determined that R_{CT} value also scales with increased levels of surface oxygen on the CNTs. This finding provides a predictive tool for estimating the reactivity of the CNTs during ozonation. Surface oxygen levels are easily adjustable by varying the strength of nitric acid used for treatment, and they are easily measured via XPS. We verified that this increased reactivity was not simply due to increased available CNT surface area due to reduced aggregation after functionalization. Rather, our results suggest that functionalization changes CNTs from a sorbent to a $^{\bullet}$OH promoter, via increased oxygen-containing groups on the CNT surface. Again, this finding has obvious implications for application, suggesting that increased levels of surface oxygen on the CNTs will likely result in increased $^{\bullet}$OH production.

Finally, we showed that functionalized CNTs can achieve similar R_{CT} values as current AOPs, represented by H_2O_2/O_3. As one motive for this work was to develop an alternative to existing AOPs, this result was encouraging. It also clarified that further research was needed to optimize this process and increase treatment efficiency. Optimizing CNT reactivity requires a better understanding of the mechanism of $^{\bullet}$OH production during ozonation of CNTs. This effort was the focus of Chapter 4.

6.3. Role of CNT Surface Chemistry, Structure, and Composition

Chapter 4 focused on identifying how to optimize $^{\bullet}$OH production during ozonation by examining effects of CNT surface chemistry, amorphous carbon on the CNT surface, CNT structure, and CNT composition. This work was highly fundamental in nature, though implications for application are discussed below.

One key result of this work served to confirm and expand on a key outcome of previous research. In Chapter 3, we discussed that R_{CT} scales with surface oxygen levels. In Chapter 4, we verified that the correlation between surface oxygen and R_{CT} value holds across a broad range of different oxidants and functionalization methods. More significantly, we found that –COOH functional groups specifically seem to be linked with increased reactivity. Likely, this result is not due to interactions between ozone and –COOH groups themselves; rather, the deprotonated –COOH groups may make the adjacent π bonds in the CNTs more reactive with ozone [314]. This result suggests that optimization of CNT reactivity will benefit from maximizing the density of –COOH groups on the CNT surface.

It has previously been determined that different routes of functionalization can result in different ratios of oxygen-containing groups on the CNT surface. More aggressive functionalization routes such as sulfuric/nitric treatment tend to result in a higher proportion of –COOH groups. However, these more aggressive routes may also result in higher levels of amorphous carbon bound to the CNT surface. Our results suggest that amorphous carbon acts as an ozone sink, reacting with ozone without generating $^{\bullet}$OH. The presence of amorphous carbon on the CNT surface may reduce the ozone available for reaction with the CNTs, thereby limiting $^{\bullet}$OH production. The more moderate functionalization route using concentrated nitric acid resulted in more efficient $^{\bullet}$OH generation.

We also verified that SW CNTs seem to be the most reactive of the structures tested, though they may lack the structural integrity for long term application. Finally, we found that industrial grade CNTs show similar reactivity as their research-grade counter parts, indicating that IGCNTs may offer significant cost savings as CNT-enhanced ozonation moves toward development.

The work in Chapter 4 offered some valuable insights into how to optimize CNT reactivity with ozone. Though it was early in the process of exploring this technology, we determined that consideration of certain practical aspects of application was relevant at this point, rather than pursuing additional work on optimization of CNT. If the CNT-enhanced ozonation process has challenges with practical aspects of water treatment in the bench-scale phase, those challenges will likely be increased as mechanical systems and water matrices become more complex. Consideration of some of these practical aspects was the focus of Chapter 5.

6.4. Practical Application Considerations

Chapter 5 focused on practical considerations that may influence overall viability of CNT-enabled ozonation during water treatment. Specifically, we explored potential lifespan of CNTs during ozonation, $^{\bullet}$OH production in more complex water matrices, and degradation of an ozone-recalcitrant pollutant rather than a $^{\bullet}$OH probe. Our results support moving forward with further development and optimization of CNT-enhanced ozonation.

The first issue addressed in Chapter 5 was the potential lifetime of CNTs during ozonation treatment. During treatment, ozone initially appeared to act as an oxidant, increasing the density of oxygen-containing functional groups on the CNT surface. Approximately 12% surface oxygen is the maximum amount typically seen; past this point, additional ozone seemed to mineralize the CNT surface and essentially etch it away. The MWCNTs showed sufficient structural integrity to withstand the concentrated ozonation processes for up to 36 hours of accelerated aging, but the SWCNTs showed evidence of structural break down. We concluded that they are not the optimal choice for use in a treatment application. The sustainable choice needs to show not just short term reactivity but also increased efficiency over the entire life of the treatment system.

Our study involving more complex water matrices revealed that CNT-enhanced ozonation is not impaired by increased levels of alkalinity or organic matter (OM) in the water. As found with similar GAC-enhanced ozonation studies, the CNTs seemed to neutralize the effects of alkalinity [46, 260]. Also like GAC, functionalized CNTs seemed to show reduced sorption of OM on their surfaces, or perhaps the reactive surface groups on the OM itself allowed for reactivity levels to be maintained [46, 260]. Even in minimally-treated real water samples from the Iowa River, $^{\bullet}$OH generation was not impaired by the more complex water matrix. Further, results with the highly reactive $^{\bullet}$OH probe *p*-CBA translated well to the ozone-recalcitrant herbicide atrazine, both in model and real water systems. Collectively, these results suggested that CNT-enhanced ozonation will be effective for treatment of micropollutants in real water systems.

The proof-of-concept study in a simplified flow-through system verified that results from initial batch reactions could be replicated in a simple flow-through system. Increased CNT loading resulted in increased *p*-CBA degradation, and increased ozone exposure also resulted in increased *p*-CBA degradation. Our work supports moving forward with further studies into optimization of CNT reactivity and design of more complex treatment applications.

6.5. Future Research

Our study has provided insight into both fundamental and practical aspects of CNT-enhanced ozonation for treatment of organic micropollutants. However, this work was in many ways preliminary and intentionally somewhat broad in scope. Further research is needed to achieve the treatment efficiency improvements necessary for this to be a sustainable technology. Several possible avenues of future research are presented in the discussions below.

6.5.1 Further testing of ozone-recalcitrant pollutants in complex water matrices. This study looked at degradation of the herbicide atrazine as a representative ozone-recalcitrant pollutant. Our results were encouraging, but further testing is warranted. A number of ozone-recalcitrant pollutants should be studied to ensure results translate across a broad range of pollutants. It would also be instructive to test a water system with a mixture of ozone recalcitrant pollutants, such as would be found in wastewater treatment, to determine how CNT-enhanced ozonation responds to a system with a variety of reaction rates. A key component of such a study would be a comparison of decay rates in ozonated systems to sorption trends in ozone-free systems. If the reaction is surface controlled, systems with greatest sorption would likely also exhibit the greatest degradation during ozonation. Such a study would provide both fundamental insights into the nature of the reactions and results that are directly applicable to a practical system.

Related to this work, study should also be done into the presence of breakdown products from these contaminants. Often, breakdown products have ecotoxic effects, generally, though not always, to a lesser degree than the parent compounds [24] The ultimate goal of a treatment system would be mineralization of the contaminants into their harmless base constituents. While this goal is unrealistic in practical application, a greater degree of breakdown generally means a lesser degree of toxicity. Previous work by Goncalves provides a model for this type of study into the degradation of ozone recalcitrant pollutants and their possible breakdown products [336-338].

6.5.2 Development and testing of a multi-functional filter in a flow-through system. From a practical standpoint, the batch reactions which comprised the vast majority of this study are by their nature limited; more complex process mechanisms must be developed and tested to truly consider the challenges of a water treatment application. The proof-of-concept study included in this work utilized a simple vacuum filtration mechanism. A system capable of handling higher pressures is necessary for development and testing of multi-functional filter in a flow-through system.

Such a system is currently under construction, as shown in Figure 6-1. This system has multiple sampling ports and a variety of ways to control flow through the filter housings and modify the concentration of ozone in the treatment stream. The currently ongoing work utilizing this testing unit will provide more in-depth information necessary for development and optimization of a hybrid CNT/ceramic filer mechanism.

6.5.3 Alternate nanocarbon structures. Recently, considerable progress has been made in the ability to decorate CNT surfaces with a range of nanostructures of well-defined composition, size, crystallinity, and morphology [76-78]. These hybrid nanomaterials display unique properties unlike the building blocks from which they are constructed, and their development has led to significant advances in the fields of sensing, optics, electronics, media storage and catalysis [76-78]. However, outside of sensor development, their potential as tools for water treatment is largely unrecognized. CNT hybridization with noble metals and metal oxides represents another route to promoting $^{\bullet}$OH formation, not only from participation of these surface additives in O_3 decomposition but also due to synergies arising from these additives' ability to alter the activity of the underlying CNTs. Other hybrid nanocarbons, such as grapheme or fullerols, may also be utilized. These other structures may be more reactive and/or easier to integrate into supported structures than CNTs.

Both noble metal/nanocarbon hybrids and iron oxide/nanocarbon hybrids may provide benefit for $^{\bullet}$OH production during ozonation. Au and Pt are noted for their role as gas-phase oxidation catalysts, their relative inertness in oxidizing environments, and activity toward ozone [340-347]. However, noble metals have rarely been investigated for enhancing ozonation, and exploration of their unique properties is worthwhile. Iron oxides have generated much interest for enhancing $^{\bullet}$OH production during ozonation [298, 348-351] because they are earth abundant and pose little risk, are readily synthesizable [352], and have generally proven to be effective $^{\bullet}$OH promoters. Previous studies have shown that hydroxyl groups density on nanoscale iron oxides is greater than that on larger materials [353], although aggregation often limits these materials' activity in solution [354]. A promising way to take advantage of the size-dependent hydroxyl group density on nanoscale iron oxides is to support them on nanocarbon materials via hybridization.

6.5.4 Treatment by-productions and leaching. While CNT-enabled ozonation shows much promise for achieving efficient $^{\bullet}$OH production for water or wastewater treatment, there are numerous concerns with this technology that must be addressed before it will become viable for practical use. One key issue is the possibility of creation of disinfection by products (DBPs). Already, numerous water treatment mechanisms create harmful byproducts even as they remove constituents of concern. In ozonation of bromide-containing waters, for instance, generation of carcinogenic bromate is a particular concern. Preliminary studies into the potential for DBP formation during CNT-enhanced ozonation have already raised some concerns in this regard. We have found that N-functionalized CNTs have the potential for developing unique CNT-derived byproducts during ozonation, including NDMA. They may also be a source of NDMA themselves, as unreacted N-functionalized CNTs have been found to release measurable amounts of NDMA. Formation and release of potentially toxic DBPs must be addressed for development of this technology to progress to application.

Another concern is the possibility of mobilization or leaching of CNTs from a hybrid filter during treatment. CNTs are themselves considered a pollutant and pose potential hazard to ecosystems. For instance, they are known to have antibacterial properties which are beneficial in a treatment scenario but inappropriate in the ecosystem [4]. The ongoing work with the flow-through system described in Section 6.5.2 will also allow for further study of this challenge. Mass loss due to leaching is too small to measure during operation. Techniques such as ICP/MS which can detect metal impurities in soluble CNTs must be utilized to study the problem of CNT breakthrough.

6.5.5 Further ecotoxicology studies. As discussed previously, this research was motivated by the fact that the presence of organic micropollutants in wastewater effluent makes wastewater reuse a challenge and a potential hazard for human and ecological health. The nature of that potential hazard, though, is still open for debate. The field of ecotoxicology has not come to a consensus on levels of emerging microconstituents that are considered “safe” for human consumption or ecological exposure. Coming to a consensus on this question is hampered by the fact that new products are developed and introduced to the market faster than ecolotoxicology studies can keep up with them. For instance, only a small percentage of the over 3000 registered pharmaceuticals are actively monitored in water systems or included in most research studies [21]. Further, many studies from multiple research groups focus on the same compounds. Only 11 of the top 25 most-prescribed pharmaceuticals had available data in 2009 [355]. To be effective, toxicology studies must reflect the pollutants likely to be found in water systems.

Studies into human and ecological toxicology drive regulations that are established for the protection of human and ecological health. Regulations, in turn, drive engineering decisions into how water and wastewater plants are managed and controlled. But, those regulations must also consider what is feasible, and as a society we must develop solutions that are sustainable. By working in parallel with ecotoxicologists, a determination can be made as to what levels of treatment are appropriate for emerging contaminants, while we simultaneously work to improve sustainable levels of microcontaminant treatment.

6.5.6 Water/energy nexus. Like all AOPs, CNT-enhanced ozonation requires significant energy use for ozone generation. Recent life cycle analysis (LCA) of advanced treatment technologies have shown that a 20-fold improvement in catalytic efficiency of the treatment process could mean the difference between a sustainable solution and an unsustainable one [356]. While it is hoped that exploitation of CNTs may allow for the necessary catalytic improvement to make this a sustainable option, concerns regarding energy use deserve specific attention. Translation of the energy use and economics of laboratory-based studies into practical application can be a challenge, but it is one worth pursuing as development of this technology progresses to determine if it is truly viable.

In looking at energy use, appropriate placement of this technology within the treatment train is an important consideration. For instance, point-of-use or decentralized treatment applications may be less energy intensive than centralized ones, and would allow for treating effluent to the quality desired for the specific end use. Also, the hybrid CNT/ceramic filter envisioned may allow for simultaneous chemical and physical treatment of microcontaminants, an advantage that would reduce the treatment train and improve overall efficiency of the treatment process. Alternatively, such a filter may be an effective pre-treatment mechanism to allow for more efficient use of membrane filters downstream.

A detailed LCA and a carbon/energy footprint study of proposed full-scale application of CNT-enabled ozonation would be a vital component in determining the potential sustainability of this technology. Such analysis would best be handled with a multi-disciplinary approach. Addressing complex environmental challenges requires a broad perspective and multiple avenues toward solution. Research in this area should provide opportunity for collaboration and symbiosis; sustainable solutions will only be found through sharing results and progress.

Our work revealed another promising opportunity for improved, energy-efficient wastewater treatment. Our review of treatment technologies in Chapter 2 identified that engineered wetlands are almost as effective as chemical oxidation for removal of pharmaceuticals. Engineered wetlands have the additional advantage of requiring very little energy input after construction. This combination makes them very desirable alternatives for addressing the water/energy challenge.

The primary concern with wetlands is the footprint or land area required for them to operate effectively. This space requirement presents a tremendous challenge for using wetlands to handle wastewater treatment on a municipal level. Instead, it would be valuable to study utilizing wetlands as a polishing step to treat municipal effluent for reuse on a site-specific or decentralized basis. Such an application would utilize smaller volumes of water, allowing for a smaller footprint. Additionally, it would be worthwhile to study means of tailoring wetland treatment to target specific constituents of concern according to the needs of the specific end user. Smaller scale engineered wetland application still may not be suitable in all areas, but nurseries, golf courses, and agricultural areas with a greater amount of available land are obvious potential end users. Others include industrial or commercial complexes and residential developments that can incorporate the wetland into their landscaping. Engineered wetlands can provide simultaneous green space and supplemental water treatment, in an energy efficient manner.

As environmental engineers, our goal is to understand the fundamental nature of the materials we work with, and use that understanding to optimize the performance of those materials for the benefit of the environment. This body of work has given insight into the importance of improving wastewater treatment methods. We have identified means of optimizing CNTs to improve $^{\bullet}$OH production during ozonation. We have addressed possibilities for utilization of CNT-enabled ozonation to improve microcontaminant removal during water treatment. Future research which expands on this work will move us closer to achieving one of the greatest challenges we face today: water sustainability.

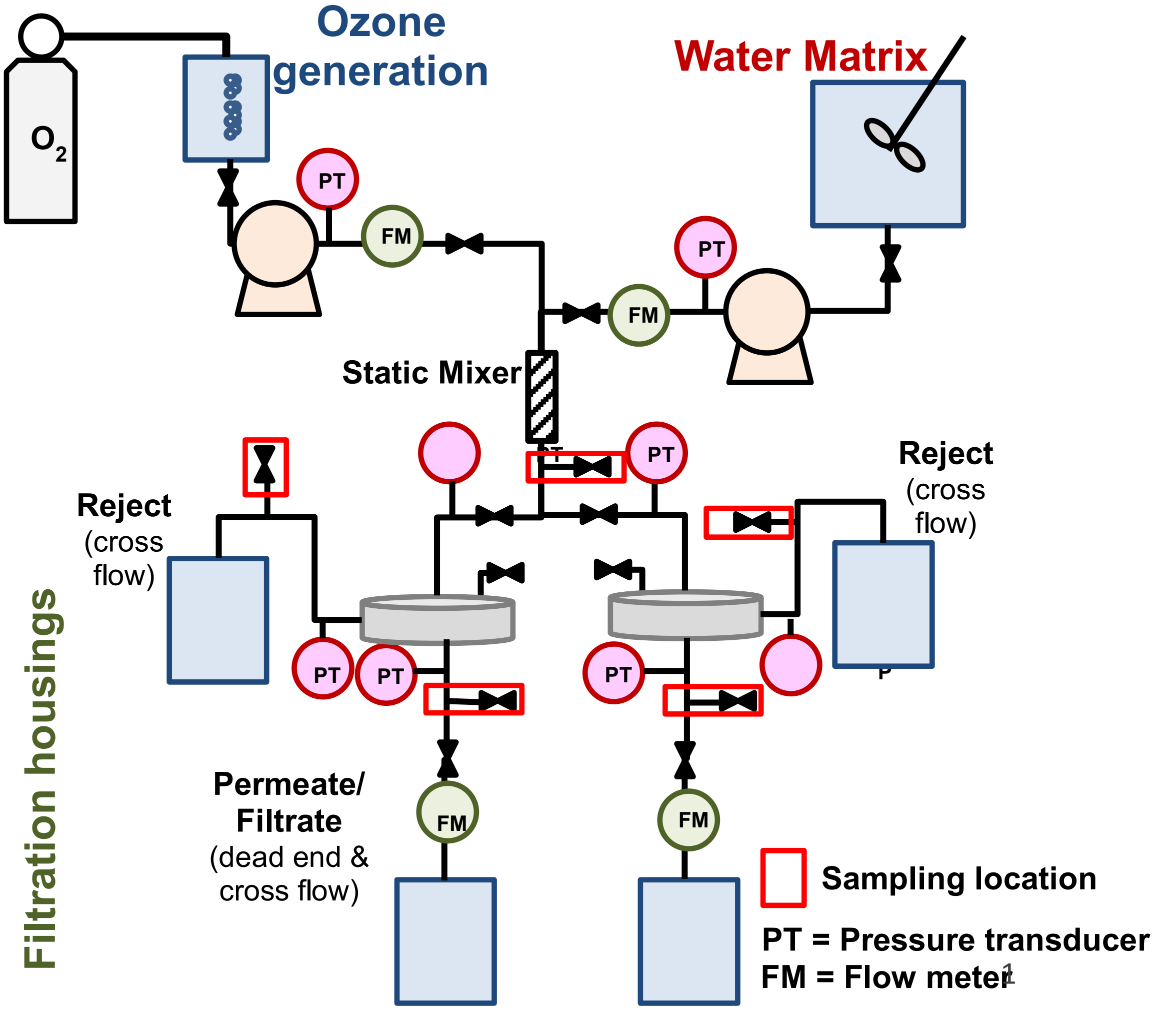


Figure 6-1. Schematic of flow-through testing system. Schematic created by Jason Haase.

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