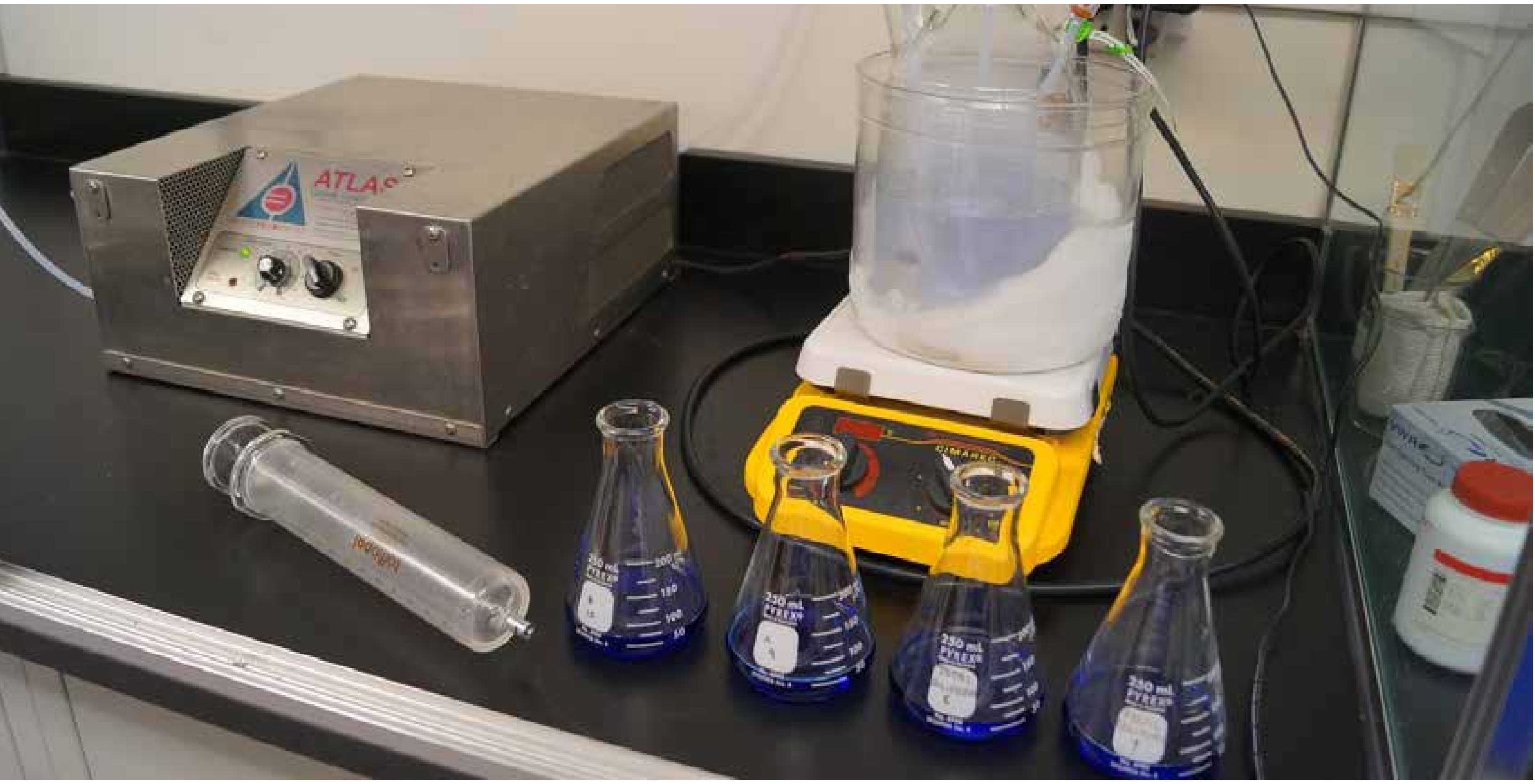

PROJECT NO.
4832

Evaluation of CEC Removal by Ozone/BAF Treatment in Potable Reuse Applications

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Co-sponsored by:
California State Water Resources Control Board

2023

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WRF ISBN: 978-1-60573-618-1
WRF Project Number: 4832

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Prepared by Trussell Technologies, Technical University of Munich, Stantec, AECOM, Brown & Caldwell, Data Instincts, and IBL Solutions.

Funding has been provided in full or in part through an agreement with the California State Water Resources Control Board. The California Water Quality, Supply, and Infrastructure Improvement Act of 2014 (Proposition 1) authorizes $7.545 billion in general obligation bonds to fund ecosystems and watershed protection and restoration, water supply infrastructure projects, including surface and groundwater storage, and drinking water protection. The contents of this document do not necessarily reflect the views and policies of the foregoing, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Contents

Tables

Figures

Acronyms and Abbreviations

AhR	Aryl hydrocarbon receptor
AOC	Assimilable organic carbon
ATP	Adenosine triphosphate
AVO	Operational availability
AWT	Advanced water treatment
AOP	Advanced oxidation process
BAC	Biologically activated carbon
BAF	Biologically active filtration
BAF_{eff}	BAF effluent
BDL	Below detection limit
BDOC	Biodegradable dissolved organic carbon
BEQ	E2-bioanalytical equivalent
BNR	Biological nutrient removal
BOD	Biological oxygen demand
BVT	Bed volumes treated
CA	California
CAS	Conventional activated sludge
CBAT	Carbon-based advanced treatment
CCP	Critical control point
CEC	Constituent of emerging concern
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
CT	Concentration multiplied by contact time
CTR	California Toxics Rule
DAF	Dissolved air flotation
DBP	Disinfection byproduct
DBPFP	Disinfection byproduct formation potential
DCTAWPF	Donald C. Tillman Advanced Water Purification Facility
DDW	Division of Drinking Water
DEET	N, N-diethyl-meta-toluamide
DMA	Dimethylamine
DMS	Dimethylsulfamide
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DPR	Direct potable reuse
DWTP	Drinking water treatment plant
EBCT	Empty bed contact time

EDR	Electrodialysis reversal
EEM	Excitation-emission matrix
EfOM	Effluent organic matter
EPA	United States Environmental Protection Agency
EPS	Extracellular polymeric substance
ER-α	Estrogen receptor alpha
EU	European Union
FAT	Full advanced treatment
FAQ	Frequently asked questions
FOEN	Swiss Federal Office for the Environment
FRI	Fluorescence regional integration
GAC	Granular activated carbon
gpm/sf	Gallon per minute per square feet
HAA	Haloacetic acids
HAA5	Regulated sum of five common haloacetic acids
HLR	Hydraulic loading rate
HRT	Hydraulic retention time
H_2O_2	Hydrogen peroxide
IPR	Indirect potable reuse
IX	Ion exchange
KPI	Key performance indicator
LASAN	Los Angeles Bureau of Sanitation
LD_{50}	Lethal dose 50
LECR	Lifetime excess cancer risk
LOAEL	Lowest observed adverse effect level
LOR	Limit of reporting
LOX	Liquid oxygen
LRV	Log reduction value
LT1ESWTR	Long Term 1 Enhanced Surface Water Treatment Rule
LT2ESWTR	Long Term 2 Enhanced Surface Water Treatment Rule
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MDH	Minnesota Department of Health
MEC	Measured environmental or effluent concentration
MF	Microfiltration
MGD	Million gallons per day
mg/L	Milligram per liter
MLD	Megaliters per day
MPN	Most probable number

MRL	Method reporting limit
MTL	Monitoring trigger level
MW	Molecular weight
NDBA	N-Nitrosodibutylamine
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NDN	Nitrification and denitrification
NDPA	N-Nitrosodipropylamine
NDPhA	N-Nitrosodiphenylamine
NF	Nanofiltration
NL	Notification level
NMEA	N-Nitrosomethylethylamine
NMOR	N-Nitrosomorpholine
NOAEL	No observed adverse effect level
NOM	Natural organic matter
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrrolidine
NTA	Non-target analytical
NTU	Nephelometric turbidity unit
OBP	Oxidation byproduct
OEHHA	Office of Environmental Health Hazard Assessment
ORP	Oxidation-reduction potential
O_3	Ozone
O&M	Operations and maintenance
PAC	Powdered activated carbon
PDT	Pressure decay test
Peroxone	Ozonation with hydrogen peroxide addition
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid

PFPeA	Perfluoropentanoic acid
PHG	Public health goal
PNEC	Predicted no effect concentration
PPCP	Pharmaceutical and personal care products
PSA	Pressure swing adsorption
RfD	Reference dose
RO	Reverse osmosis
RSSCT	Rapid small-scale column test
RWC	Recycled water contribution
SAT	Soil aquifer treatment
SMCL	Secondary maximum contaminant limit
SMP	Soluble microbial products
SRT	Sludge retention time
SWA	Surface water augmentation
SWRCB	California State Water Resources Control Board
SWTR	Surface Water Treatment Rule
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCEP	Tris(2-carboxyethyl) phosphine
TCEQ	Texas Commission on Environmental Quality
TCPP	Tris(1-chloro-2-propyl) phosphate
TDCPP	Tris(1,3-dichloroisopropyl) phosphate
TDS	Total dissolved solids
TF	Total fluorescence
ΔTF	Differential total fluorescence
THM	Trihalomethanes
TN	Total nitrogen
TOC	Total organic carbon
ToP	Total phosphorus
TP	Transformation product
TrOC	Trace organic contaminants
TSS	Total suspended solids
TTHM	Total trihalomethanes
UF	Ultrafiltration
UV	Ultraviolet
UV_{254}	UV_{254} absorbance
UVA	UV absorption
UVT	UV transmittance
UV/AOP	Ultraviolet light-based advanced oxidation
UV-VIS	process Ultraviolet-visible spectroscopy

VSA	Vacuum swing adsorption
WE&RF	Water Environment and Reuse Foundation
WHO	World Health Organization
WRD	Water Replenishment District of Southern California
WRF	The Water Research Foundation
WWTP	Wastewater treatment plant

Executive Summary

ES.1 Key Findings

The results of this research project are as follows:

- Ozone (O_3, used interchangeably) coupled with biological active filtration (ozone/BAF) is an essential and enabling technology with respect to pathogens, bulk organics, and a broad range of constituents of emerging concern (CECs) for potable reuse as part of a multiple barrier treatment strategy, especially for non-reverse osmosis (RO)-based applications but also as a pretreatment step for some RO-based applications (i.e., full advanced treatment [FAT])
- Regulators and practitioners should leverage existing health-based indicators and associated monitoring trigger levels (MTLs) on target compounds to assess the safety of ozone/BAF treated waters. Additional developments in bioanalytical monitoring techniques will continue to shed light on the toxicological relevance of recalcitrant compounds
- Ozone/BAF can be combined with other non-RO treatment processes to achieve viable multi-barrier, carbon-based advanced treatment trains (CBAT) for potable reuse, contingent on specific project type and location
- Ozone with biological activated carbon (ozone/BAC) is the most effective form of ozone/BAF; properly selecting a key list of design and operational criteria (e.g., ozone to total organic carbon [TOC] ratio [O_3:TOC], contact time, empty bed contact time [EBCT], loading rate, various online surrogates) will ensure a well-operating process capable of achieving various potable reuse goals
- A target O_3:TOC ratio of 0.6 should mitigate many CECs, while keeping bromate formation below its maximum contaminant level (MCL) of 10 µg/L and be sufficient to achieve 6-log virus and 3-log *Giardia* removal
- Granular activated carbon (GAC) is an effective treatment process to address recalcitrant CECs with health-based limits, such as long-chain per- and polyfluoroalkyl substances (PFAS), and provide TOC removal, which allows for the control of disinfection byproduct (DBP) formation
- CBAT can benefit the most in terms of both process performance and reducing costs from a robust upstream treatment that minimizes TOC concentration and other nutrients with addition of filtration, such as Biological Nutrient Removal (BNR) process coupled with media filtration or a Membrane Bioreactor (MBR).

ES.2 Background and Objectives

RO-based treatment trains pose significant implementation challenges for utilities around the world due to relatively high capital and operating costs and difficulty with managing the brine stream when ocean discharge is not available. To address concerns around the presence of CECs in reclaimed waters and to bring ozone/BAF into the mainstream for potable reuse application, technological challenges and knowledge gaps related to design and operation of ozone/BAF systems need to be addressed. The overarching goals of this project are to determine how an ozone/BAF-based treatment train complies with performance-based regulations and guidelines as well as identify and address knowledge gaps and additional optimization needs with respect to public health. Key objectives from this project include:

- Identifying CECs and degradation products that are persistent and not reliably removed by ozone/BAF;
- Benchmarking expected treated water quality from ozone/BAF-based treatment trains;
- Identifying surrogates for validation of CEC removal through ozone/BAF;
- Providing guidance on pretreatment and polishing steps required to achieve potable reuse goals;
- Identifying knowledge gaps that can be addressed through additional treatability testing;
- Developing ozone/BAF design and operational guidance based on scientific and engineering insights and regulatory public health protection requirements; and
- Developing communication and outreach tools to assist agencies with expediting the implementation of safe and sustainable ozone/BAF-based treatment trains in potable reuse applications.

ES.3 Project Approach

Design, operational, and water quality data from several pilot-, demonstration-, and full-scale ozone/BAF studies/projects around the world (e.g., United States, Australia, Namibia, Germany, Switzerland, and Austria) were collected as part of Chapter 1 through a curated questionnaire and interviews that were compiled into a comprehensive database. Chapter 2 builds on the results from Chapter 1 by defining persistent CECs, performance-based indicators and surrogates, and bioanalytical tools. Chapter 3 synthesizes the results from the survey in Chapter 1 and the presented approach to CEC prioritization regarding health-based concerns in Chapter 2 to identify information trends and knowledge gaps. Rapid small-scale column testing (RSSCT) also was performed as part of Chapter 3 to assess performance of virgin and reactivated GAC for removal of TOC and select PFAS. Chapter 4 builds off the findings from previous chapters to provide a guidance document to the design and operation of ozone/BAC systems to inform interested agencies of common and recommended design criteria. Finally, Chapter 5 provides examples of public outreach materials to address concerns around CECs and acceptance of the ozone/BAC treatment trains in potable reuse.

ES.4 Results

The critical results of this project are summarized in this section, broken down by chapter.

ES.4.1 Chapter 1 Results

In Chapter 1, 147 compounds along the ozone/BAF treatment train were compared across multiple studies and benchmarked by common treatment variables such as O_3:TOC ratio, initial media condition, and EBCT. Removal of CECs through Ozone/BAC is highly dependent on the influent water quality from the upstream secondary and tertiary treatment steps, therefore a highly treated influent with sufficient nutrient reduction (i.e., fully nitrifying plant) is needed for the best performance of ozone/BAC systems. From a public health perspective, fully nitrified effluent followed by ozone/BAC removed CECs effectively, just as RO based treatment does. Many compounds were effectively removed by ozonation alone, therefore, it was difficult to determine the performance of BAC in removing these compounds, especially as affected by different operational parameters (EBCT, type of media, etc.). On the other hand, BAC was shown to provide removal of oxidation byproducts, such as the low molecular weight (MW) nitrosamines, ketones, and aldehydes. This review provided a short list of compounds that can be candidates for performance surrogates and CEC indicators that are further discussed in Chapters 2 and 3 of this report. CECs were broken down into groups that were well removed by ozone and BAC, individually and collectively. Recalcitrant compounds were categorized into different examples. Most common examples of recalcitrant compounds with limited removals were PFAS, flame retardants, contrast agents, and artificial sweeteners, for which BAC also did not provide any significant removal due to limited remaining adsorption capacity. TOC removal by ozone/BAF was significant (20-50%) in most studies, whereas a higher removal of TOC could be achieved by RO-based treatment (>90%). A polishing step such as GAC filtration following ozone/BAF treatment can be used to provide additional TOC removal, minimize disinfection byproduct formation potential (DBPFP), and reduce PFAS. Similarly, ozone/BAC alone does not provide removal of salinity. Additional post-ozone/BAC treatment considerations to address remaining water quality targets is discussed in Chapter 3.

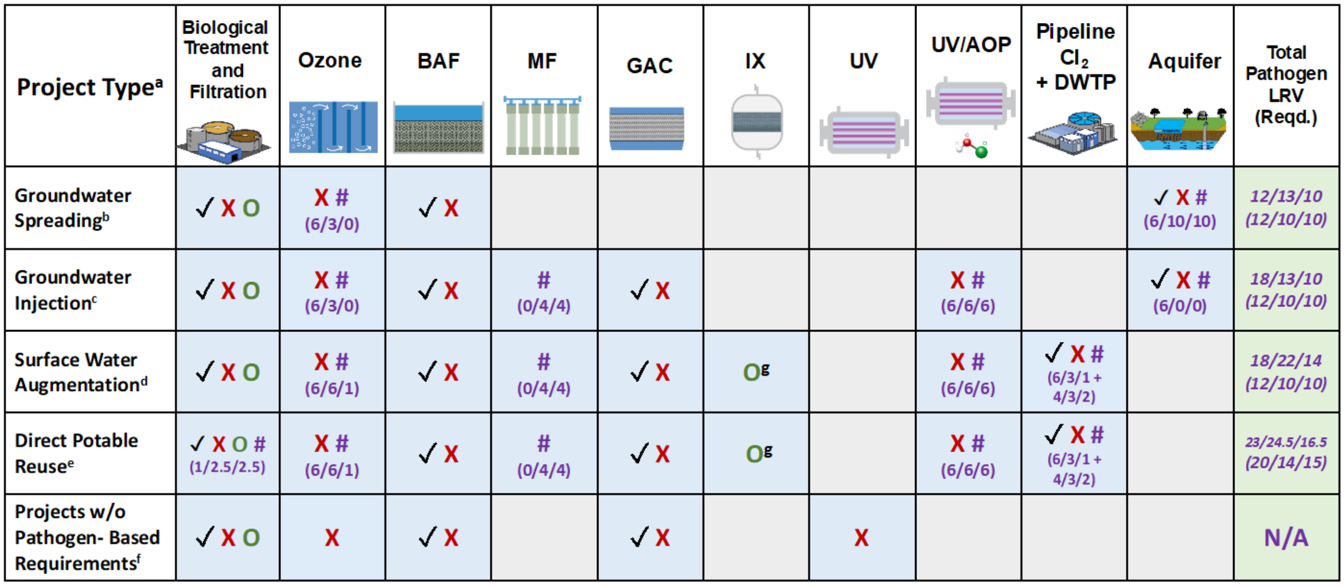
ES.4.2 Chapter 2 Results

Through prioritization of a wide array of CECs, Chapter 2 provides a shortlist of CEC data that can be utilized to identify potential performance-based indicators for both ozone and BAC treatment processes. In general, treating reclaimed waters with ozone results in oxidation and breakdown of many types of CECs through direct reactions with ozone or reactions with hydroxyl radicals. As a result, the treated waters are considered less toxic and more amenable to further biological treatment for additional removal of trace organic constituents and removal of oxidation by-products and/or transformation products (TPs). In some cases, TPs may be more toxic than the parent compound. However, the relative increase in toxicity of these TPs may still be balanced by a decrease in toxicity of other TPs that are less toxic than their respective parent compounds. Health-based indicators and associated MTLs for specific compounds are useful tools for assessing the safety of a treated effluent. Bioassays may provide additional information to assess the relative changes in toxicity before and after ozone, and after BAF. The current approach formulated by the regulators in California is to use two bioassay methods, the estrogen receptor alpha (ER-α) and the aryl hydrocarbon receptor (AhR) with MTLs defined as E2-bioanaltycial equivalent (BEQ) concentrations of 3.5 ng E2/L and 2,3,7,8-tetrachlorodibenzo-p-dioxin BEQ (TCDD-BEQ) concentrations of 0.5 ng TCDD/L for monitoring recycled waters. This is to investigate the occurrence and magnitude of CECs in recycled water and their impact on toxicity using these two endpoints. When the magnitude of exceedance is greater than a factor of 10 higher than MTLs, additional testing should be performed to identify specific CECs causing such exceedances. In time, more data should become available from the routine use of bioanalytical monitoring to further the understanding of toxicological relevance. Additional discussion of CECs and health-based levels is provided in Chapter 3.

ES.4.3 Chapter 3 Results

Chapter 3 synthesizes the results from the survey discussed in Chapter 1 and the presented approach to CEC prioritization regarding health-based concerns in Chapter 2. For the ozone process, the O_3:TOC ratio was identified as an effective surrogate to account for varying ozone demand and ensure an adequate ozone dose is applied for a target level of CEC removal. Change in UV_{254} absorbance (ΔUV_{254}) was also found to correlate well with CEC removal through the ozone process and is a simple analytical tool to include for ongoing performance monitoring of the system. For the BAF process, TOC removal was identified as the main performance surrogate to monitor the removal of organics through the system (including the acclimation period), with ΔUV_{254} useful as a potential secondary surrogate (especially if already being used in the ozone system). The recalcitrant CEC portion of Chapter 3 introduces a shortlist of the most relevant compounds that present health-based concerns and require additional treatment, which include DBPs and PFAS. Based on the findings, Chapter 3 outlines an approach to supplement ozone/BAF treatment with additional unit processes to provide additional protection from CECs, pathogens, and other important water quality objectives for different potable reuse projects, including direct potable reuse (DPR). RSSCT testing was conducted to assess TOC and PFAS removal and showed that for smaller MW PFAS, a smaller number of bed volumes occur before breakthrough than for larger compounds. Perfluoroalkyl sulfonic acids generally took higher number of bed volumes before breakthrough occurred than the perfluoroalkyl carboxylic acid analogs (i.e., PFAS with same carbon chain length). TOC removal by adsorption appears to be challenging because less bed volumes occur before breakthrough than for PFAS. For facilities targeting removal of both TOC and PFAS, the GAC system design would need to be balanced to accommodate target removal goals.

Hypothetical treatment train examples are presented in Figure ES-1 and are intended to illustrate the various tools that exist to achieve certain treatment goals. These alternative non-RO treatment trains need to demonstrate treatment equivalency in states such as California to comply with the potable reuse regulations, which may include minimum total pathogen log removals, TOC limits, and other water quality considerations such as nutrients.



Project Type[a]	Biological Treatment and Filtration	Ozone	BAF	MF	GAC	IX	UV	UV/AOP	Pipeline Cl_2 + DWTP	Aquifer	Total Pathogen LRV (Reqd.)
Groundwater Spreading[b]	✓ X O	X # (6/3/0)	✓ X							✓ X # (6/10/10)	*12/13/10* *(12/10/10)*
Groundwater Injection[c]	✓ X O	X # (6/3/0)	✓ X	# (0/4/4)	✓ X			X # (6/6/6)		✓ X # (6/0/0)	*18/13/10* *(12/10/10)*
Surface Water Augmentation[d]	✓ X O	X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O[g]		X # (6/6/6)	✓ X # (6/3/1 + 4/3/2)		*18/22/14* *(12/10/10)*
Direct Potable Reuse[e]	✓ X O # (1/2.5/2.5)	X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O[g]		X # (6/6/6)	✓ X # (6/3/1 + 4/3/2)		*23/24.5/16.5* *(20/14/15)*
Projects w/o Pathogen- Based Requirements[f]	✓ X O	X	✓ X		✓ X		X				N/A

✓=TOC X=CECs O=Nutrients #=Pathogen Credit: anticipated log removal values (LRV) for Virus/Giardia/Cryptosporidium

[Total pathogen LRV requirements are based on California's current and draft potable reuse regulations]

Figure ES-1. Examples of Ozone/BAF Treatment Trains for Different Potable Reuse Projects.

[a] These hypothetical treatment train examples are intended to illustrate the various tools that exist to achieve certain treatment goals. These alternative non-RO treatment trains need to demonstrate treatment equivalency in states such as California to comply with potable reuse regulations

[b] Groundwater spreading scenario assumes a minimum 6-month aquifer retention time and additional organics removal via soil aquifer treatment (SAT) which may eliminate need for GAC. Ozone dosing sufficient for concentration multiplied by contact time (CT) crediting is assumed, but ultraviolet light (UV) may also be used for disinfection credit. Ozone/BAF is included to help achieve TOC goals for recharge (depending on recycled water contribution [RWC])

[c] Groundwater injection scenario assumes a minimum 6-month aquifer retention time for additional virus credit. GAC is assumed to help achieve TOC goals (depending on RWC)

[d] Surface water augmentation (SWA) scenario assumes a higher ozone dose than the groundwater scenarios capable of achieving a CT value adequate for 1 log reduction value (LRV) for *Cryptosporidium*. Also assumes 100:1 dilution and a minimum 4-month retention time in the reservoir

[e] DPR scenario assumes Tier 1 MBR LRV credits based on WRF 4997 and a higher ozone dose than the groundwater scenarios, capable of achieving a CT value adequate for 1 LRV for *Cryptosporidium*

[f] Projects outside of California that do not have prescriptive pathogen LRV requirements

[g] Ion exchange is also effective at removing TOC and CECs and can be used to remove these constituents in addition to nitrate (with a higher resin regeneration frequency than nitrate alone)

ES.4.4 Chapter 4 Results

Chapter 4 provides high-level design and operational guidelines for implementing ozone/BAC for potable reuse applications. The O_3:TOC ratio is an effective monitoring and control strategy for ozone/BAC, especially for bulk and trace organics removal. Online TOC analyzers are reliable compared to dissolved ozone analyzers and other instrumentation in wastewater effluents. Attention must be given to correcting real-time monitoring of O_3:TOC ratio with nitrite demand, particularly when nitrite bleed-through occurs from upstream wastewater processes. ΔUV_{254} has been demonstrated to be an effective performance surrogate for CEC removal and may augment the O_3:TOC ratio control strategy. The optimal O_3:TOC ratio, ozone contactor hydraulic retention time (HRT), and EBCT for the majority of CECs are 0.6, 3 minutes, and 10-15 minutes, respectively. However, addressing the pathogen removal regulatory requirements with ozone is the most important design consideration for potable reuse. The ozone dose and contact time requirements are often determined by pathogens, not CECs, especially when ozone is needed to meet *Cryptosporidium* log removal targets.

One specific component of the ozone system that requires special attention is the off-gas collection system. Secondary wastewater effluent poses many challenges to an ozone system including the generation of foam in the contactor through the turbulent mixing of gas with wastewater and the relatively high gas to liquid ratios in potable reuse applications. This foam can foul air release valves, which are typically used in pressurized pipeline contactors, and allow water to pass from the contactor to the ozone destruct system rendering it damaged or inoperable. Mitigation measures via a proactive maintenance program on the air release valves, along with installing a liquid trap between the air release valves and ozone destruct system, are highly recommended to minimize downtime and equipment failure.

Startup of an ozone/BAC process is different from other unit processes typically used for potable reuse. The acclimation period for BAC with fresh GAC is typically around three months with respect to transitioning from adsorption to biodegradation as the dominant removal mechanism. This may pose challenges to a facility relying on steady-state performance of the system to meet overall plant performance goals. While fresh GAC in the BAC will improve removal of TOC and many adsorbable CECs when the dominant treatment mechanism is adsorption, some CECs such as N-Nitrosodimethylamine (NDMA) and aldehydes may not be as well removed until steady state via biological acclimation is achieved. Less and non-biodegradable CECs, such as PFAS and flame retardants, may be less removed as the sorption capacity of the GAC media is exhausted. Validating the performance of an ozone/BAC process after completion of startup to steady state may be best achieved by using a compound (intrinsic or spiked) that is biodegradable but not adsorbable.

ES.4.5 Chapter 5 Results

Chapter 5 built upon the key findings and recommendations from the previous chapters to develop examples of public outreach materials. These materials, a frequently asked questions (FAQ) page and a four-page handout, aim to enhance knowledge and awareness of how ozone/BAC based treatment trains can address concerns surrounding CECs. The FAQ provides answers to common questions about the use of ozone/BAC to address CECs based on the project findings. The handout delves slightly deeper than the FAQ page to provide a summary of the purpose, objective, and major outcomes from this project. The handout summarizes the findings of this project but does so by distilling the information into more easily digestible concepts that are more user-friendly for public outreach and educational purposes.

ES.5 Benefits

Significant information and analyses were completed as part of this project that will help practitioners of potable reuse better understand CEC screening for treatment performance and implement ozone/BAF. Chapter 3 provides a synthesis of the findings from Chapter 1 (Data Collection and Synthesis from Literature and Full-Scale Facilities of Ozone/BAF and CECs) and

Chapter 2 (Health-Based Water Quality Goals for CECs) that addresses challenges with ozone/BAF and recalcitrant CECs while also identifying remaining knowledge gaps for consideration and possibly future research. The findings from Chapter 3 will help utilities better understand the toxicological relevance of certain CECs and which ones may be persistent through ozone/BAF treatment. Furthermore, Chapter 3 discusses the importance of upstream treatment (i.e., secondary biological wastewater treatment) on CEC removal and ozone/BAF performance while also conducting much needed research using RSSCT to assess the performance of GAC for TOC and PFAS removal on ozone/BAC effluent. The design and operational guidelines developed in Chapter 4 can be used by utilities interested in evaluating and implementing ozone/BAF-based treatment trains as it provides information concerning equipment selection and sizing, process control strategies, and startup. Public outreach tools for use by utilities, including a handout and FAQ, were developed as part of Chapter 5. These tools can be customized on a project-specific basis to shorten the learning curve and assist utilities with messaging regarding potable reuse, ozone/BAC, and CECs.

ES.6 Related WRF Research

- Optimization of Ozone-BAC Treatment Processes for Potable Reuse Applications (4776)
- Impact of Wastewater Treatment Performance on Advanced Water Treatment Processes and Finished Water Quality (4833)
- Understanding and Improving Reuse Biofilter Performance during Transformation from GAC to BAC (5092)

CHAPTER 1

Data Collection and Synthesis from Literature and Full-Scale Facilities

1.1 Introduction

1.1.1 Ozone/BAF for Potable Reuse

Wastewater reclamation is increasingly being implemented around the globe, driven by an increase in wastewater disposal, energy costs, and water scarcity. Nevertheless, advanced treatment through a multi-barrier approach is needed to meet the potable water standards that are capable of protecting against a myriad of contaminants (National Research Council 2012). It is also desirable to implement reuse systems that are reliable and easy to operate with low carbon and energy footprint and cost.

A multi-barrier treatment train comprised of microfiltration (MF)/ultrafiltration (UF) and reverse osmosis (RO) in tandem with ultraviolet light-based advanced oxidation process (UV/AOP) is commonly implemented for water reuse, especially with the increasing interest in potable reuse without environmental buffers (Gerrity et al. 2013; EPA 2017a). This integrated system has been proven to be capable of mitigating the passage of a wide range of trace organic compounds in the finished water, including the most persistent constituents of emerging concern (CECs) such as per- and polyfluoroalkyl substances (PFAS), 1.4-dioxane, and nitrosamines such as N-Nitrosodimethylamine (NDMA) (Glover, Quiñones, and Dickenson 2018; Roback, Ishida, and Plumlee 2019). Nevertheless, the high capital and operational cost, as well as the cost for disposing RO brine waste, often limits the application of RO-based treatment trains. The cost barrier becomes even more pressing for inland applications as brine disposal sites may not be readily available (Tchobanoglous et al. 2015).

Ozone coupled with biologically active filtration (ozone/BAF)[1] has been a key enabling technology in drinking water treatment for decades due to its ability to simultaneously address pathogens and critical water quality challenges such as taste and odor compounds and disinfection byproduct (DBP) precursors (Sontheimer et al. 1978). The implementation of ozone/BAF in potable water reuse has been on the rise in recent years as an alternative to RO-based treatment trains, especially for inland application due to its lack of brine disposal requirement (C. Lee, Howe, and Thomson 2012; Gerrity et al. 2014; S. Snyder et al. 2014; Sundaram et al. 2020) and generally lower capital, operation, and maintenance costs compared to RO-based treatment over a range of plant capacities between 1 to 80 million gallons per day (MGD) or 3.78 to 303 megaliters per day (MLD) (Plumlee et al. 2014). Though its application in water reuse schemes is still relatively new, a number of studies have been conducted to gain a

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[1] For the purposes of this report, BAF is defined to mean any type of media for a fixed-film biological filter. This includes the use of GAC and the commonly used term biologically active carbon (BAC) and those applications that use anthracite. References to the specific use of ozone with BAC will be referred to as ozone/BAC. BAF does not mean biologically aerated filter in this report.

better understanding of ozone/BAF systems in terms of their capability to remove bulk organics and both regulated and unregulated trace organic carbon compounds such as CECs (Arnold et al. 2018; Bacaro et al. 2019; Bourgin et al. 2018; C. Lee, Howe, and Thomson 2010; C. Lee, Howe, and Thomson 2012; Hollender et al. 2009; Sun et al. 2018, Sundaram, Emerick, and Shumaker 2014; Sundaram et al. 2020), as well as optimization of process parameters such as ozone dose (Arnold et al. 2018; Bourgin et al. 2018; Sundaram et al. 2020); filtration media types such as sand, anthracite, or granular activated carbon (GAC) (Zhu, Wang, and Wieland 2015; Gifford, Selvy, and Gerrity 2018); initial media conditions (i.e. virgin/regenerated media versus exhausted media) (Bourgin et al. 2018; Sun et al. 2018); and empty bed contact time (EBCT) (Arnold et al. 2018; Sundaram et al. 2020).

Ozone/BAF treatment for water reuse application is an attractive alternative to RO-based treatment; however, its applicability is limited by the total dissolved solids (TDS) level in the incoming water. Ozone/BAF effluent might exceed the secondary maximum contaminant limit (SMCL) or local basin and/or groundwater limits for TDS for high salinity water (Vaidya et al. 2019). Therefore, ozone/BAF systems might be more applicable in locations where TDS removal is not required. In cases where TDS is still an issue, a treatment train with ozone/BAF may need to be augmented with a side-stream TDS removal technology such as nanofiltration (NF), RO, ion exchange (IX) or electriodialysis reversal (EDR) or blending the source water with a low TDS water, if available. Another ozone/BAF limitation includes nitrate levels in incoming water. Nitrate has a primary MCL of 10 mg/L and is not removed by ozone/BAF, therefore nitrate would need to be addressed with upstream wastewater process improvements, other advanced treatment technology, or side-stream treatment.

When TDS is not an issue, ozone/BAF can be more advantageous in terms of cost and performance compared to RO-based treatment (Hooper et al. 2020). While it may not provide similar total organic carbon (TOC) removal as RO-based processes, ozone/BAF can provide a similar overall level of CEC removal (Vaidya et al. 2019). For specific applications where ozone/BAF does not provide sufficient TOC removal and/or specific individual CEC removal (e.g., PFAS), GAC may be added after ozone/BAF, for additional bulk and trace organics removal, including oxidation byproducts (OBPs) and DBP precursors, to provide a finished water quality comparable to RO-based treatment. Alternatively, if used as a pretreatment step to RO-based treatment, ozone/BAF can also provide added benefits in achieving lower TOC (Tackaert et al. 2019) and reducing the organic fouling of both MF/UF and RO, as well as removing neutral, low molecular weight (MW), highly water miscible, and recalcitrant compounds such as formaldehyde and acetone, which cannot be removed well by physical processes, photolysis, and OH-radical chemical oxidation (e.g., UV/AOP) (Tackaert et al. 2019).

It is important to note, however, that the ability of ozone/BAF to remove both trace organic compounds and bulk organics (as measured by TOC, dissolved organic carbon [DOC], or change in UV absorption [UVA]) depends on site-specific factors, some of which are contingent upon primary/secondary/tertiary treatment in the wastewater treatment plants (WWTPs) and upstream source control. In fact, upstream source control and primary/secondary/tertiary treatment have the biggest impact on both water quality and the type and quantities of CECs, and, thus, the performance of an advanced water treatment (AWT) system, including ozone/BAF. Source control has become a standard regulatory requirement for potable reuse to minimize or prevent the release of trace organic compounds, especially from industrial dischargers. Maximizing nutrient reduction and TOC removal via secondary biological treatment may be essential to a developing cost-effective solution for potable reuse. Coagulation, flocculation, and sedimentation and/or filtration may also enhance the viability of an ozone/BAF based treatment solution. In terms of ambient temperature effect, BAF performance in cooler weather climates may be more limited than warmer water applications (Funk et al. 2018; Hooper et al. 2020; Lauderdale et al. 2018).

The design and operational parameters for ozone/BAF are determined by the project-specific goals and water reuse regulations. The most common project goals for considering the implementation of ozone/BAF include: i) evaluation of ozone/BAF as both a pathogen and chemical barrier; ii) comparison of ozone/BAF with RO-based treatment for potable reuse with respect to cost and other implementation factors; iii) evaluation of ozone/BAF as MF/UF and RO pretreatment; iv) assessment of ozone/BAF to remove specific contaminants that are not removed well by membranes such as aldehydes, glyoxals, acetone, and phenol (Sundaram et al. 2020). The robustness and reliability of ozone/BAF treatment to address pathogen log reduction and a wide array of CECs including pharmaceutical and personal care products (PPCPs), pesticides/herbicides/fungicides, hormones, artificial sweeteners, nitrosamines, PFAS, etc., is of interest, particularly for potable water reuse as an equivalent to an RO-based treatment train (Trussell et al. 2016). Nevertheless, the majority of ozone/BAF pilot- and full-scale facilities do not evaluate the full range of design and operational conditions and configurations needed to achieve potable reuse goals related to addressing concerns surrounding CECs (Sundaram et al. 2020). In addition, there are no clear guidelines for determining the design and operational parameters relative to potable reuse goals and regulations. Thus, understanding the removal mechanisms of CECs via ozone/BAF and its linkage to the design and operational variables are still evolving to fully identify the underlying key variables and optimization criteria. Bulk organic parameters such as TOC or DOC, UVA, and fluorescence excitation-emission matrix (EEM) are often utilized as surrogate indicators to predict the fate and transport of trace organic compounds in ozone/BAF systems (Arnold et al. 2018; Dickenson et al. 2009; Gifford, Selvy, and Gerrity 2018; Ibn Abdul Hamid et al. 2019; Im et al. 2019; G. Li et al. 2018; Sundaram et al 2020; Tackaert et al. 2019; Trussell et al. 2016). However, the complex matrices found in wastewaters with different degrees of susceptibility to oxidation and adsorption/biodegradation make it difficult for TOC or UVA alone to predict removal of CECs. As such, identification and utilization of the most appropriate surrogates along with health- and performance-based indicators, classified into multiple categories, would be beneficial in understanding ozone/BAF performance (Bourgin et al. 2018) and is warranted, especially for highly challenging contaminants such as PFAS, nitrosamines, and others.

1.1.2 Study Goal and Objectives

There are presently several ozone/BAF studies at pilot- and full-scale facilities in operation around the world. Selected CECs are commonly monitored in these facilities and can be linked to each project’s design and operational conditions. The goal of this study is to conduct an integrated assessment of ozone/BAF performance data obtained from multiple facilities to identify the most relevant and challenging CECs from which to develop performance criteria for ozone/BAF treatment trains. To achieve this goal, the specific objectives of this study are to:

- Collect design, operational, and water quality data from several demo-, pilot-, and full-scale ozone/BAF studies/projects through a curated questionnaire and interviews and compile the data into a comprehensive database;
- Benchmark the collected water quality data according to different design and operational configurations and systematically analyze the effects of various ozone/BAF operational parameters on removal of a wide array of CECs;
- Integrate the survey results with data from studies published in the literature; and
- Identify any inconsistencies or knowledge gaps that required additional evaluation.

1.2 Methodology

1.2.1 Data Collection Through Questionnaire and Literature Review

A questionnaire was developed for this study to obtain the critical operational parameters and configurations of ozone/BAF systems that potentially affect the fate and transport of CECs through the treatment train process from a multitude of projects located in different regions. The goal of the questionnaire was to identify the major process parameters being utilized to assess system performance and the impact of variations in system design parameters, including: i) the amount of ozone applied relative to the TOC in the influent, expressed as ozone to TOC (O_3:TOC) ratio; ii) the change in UVA; iii) EBCT; iv) type of ozonation (i.e., conventional ozone, ozone + peroxide); v) type of media used for biological filtration (e.g., GAC, sand, anthracite, etc.); vi) initial media conditions (e.g., virgin, regenerated, exhausted) and media specifications, etc. As influent water to the advanced treatment processes is generally influenced by nutrient reduction strategies, information about upstream primary, secondary, and tertiary treatment processes was also obtained. These data along with the water quality data provided by participating facilities were entered into a database that was utilized to identify and evaluate the effects of various parameters on the removal of a wide array of CECs. The database was further supplemented by additional relevant data (e.g., water quality, design and operation, system configurations, etc.) obtained from published and non-published reports shared by the participating facilities.

The project team received a total of 10 questionnaire responses but further augmented the database by identifying additional ozone/BAF studies and their corresponding data from literature and internal communications with the project team. Thus, a total of 37 demo-, pilot-, and full-scale studies around the globe were evaluated for their design and operational parameters. The general characteristics of these studies are presented in Table A-1 in the Appendix. Of these 37 studies, only 16 are supplemented with measured water quality data inclusive of CECs. Thus, discussions regarding CEC removal were based on these 16 studies. Note that some studies were conducted at the same facilities/sites but at different times, and in some cases utilized different pretreatment, design and/or operational conditions.

1.2.2 CEC Prioritization

Through the water quality data collected, the project team identified approximately 400 CECs in multiple classifications being monitored by multiple ozone/BAF studies. A list of these CECs can be found in Appendix A. To account for variability in water quality data in each dataset due to changing seasons, anthropogenic activities, and other factors, only compounds with at least two occurrences ($n \geq 2$) at detectable concentrations were considered. This was done to consider compounds with high temporal variability and to avoid handling skewed data. For concentrations that were below Limit of Reporting (LOR) values after ozone or BAF treatments, the concentrations were calculated as half of the corresponding LOR values, so that percent removal could be calculated. Some studies analyzed more compounds compared to the others, but there are some compounds that were consistently monitored across these studies. The concentrations of these compounds in the influent, post-ozonation step, and post-BAF step and their corresponding percent removals were then compared and benchmarked by common treatment variables such as O_3:TOC ratio, type of filtration media, initial media condition, media specification (e.g., iodine number etc.), and EBCT. Two reviewed projects corrected O_3:TOC with nitrite consumption, but for comparison purpose it is still referred to as O_3:TOC ratio. Of these 400 compounds, 147 compounds were then selected for prioritization based on adequate influent occurrence in multiple studies allowing calculation for their percentage removal during ozonation process.

The results from data benchmarking were used to classify the compounds into three operationally defined bins based on observed removal efficiencies during ozonation and two bins for removal during BAF, as shown in Table 1-1. The purpose of CEC binning is to identify compounds that are recalcitrant to ozone/BAF and compounds that can potentially serve as performance indicators which should satisfy the following criteria:

- Detectable in the feedwater of the ozonation unit at concentrations that are higher than the method reporting limit (MRL);
- Representable of different amenabilities to removal during ozonation and BAF; and
- Quantifiable with commercially available analytical methods.

Compounds with average percent removal greater than 90% during ozonation were considered as readily oxidized compounds. Compounds that fall into the second bin with average removal between 50% to 90%, were considered moderately removed by ozonation. Those with average removal less than 50% were considered poorly removed by ozonation, and in some cases were formed during ozonation. Only two operationally defined bins were considered for BAF treatment as the goal was to understand the capability of BAF to provide additional removal following ozonation. The simplification was also due to the complexity of BAF performance that is contingent upon many factors such as EBCT, type of media used, media conditions that changed over time, microbial activity, temperature, backwash regime and so on.

Table 1-1. Bin Assignment for Compound Removal by Ozonation and BAF.

Treatment	Bin Name	Bin Assignment Criteria	Treatment Parameter
Ozone	Readily oxidized	Average removal >90%	O_3:TOC = 0.1 to 2.0
	Moderately oxidized	Average removal between 50% and 90%	
	Poorly oxidized or formed during ozonation	Average removal below 50% or negative average removal	
BAF	>50% additional removal by BAF	Average removal above 50% following BAF	EBCT, media type, initial media condition (virgin/regenerated and exhausted)
	<50% additional removal by BAF	Average removal below 50% following BAF	

1.3 Effects of Pretreatments on Ozone/BAF Performance and CEC Removal

1.3.1 Primary Treatment

The preliminary and primary treatment in WWTPs mainly utilize physical processes such as screening and clarification to allow solids to settle and prepare the liquid stream for further nutrient and organic removal in the secondary biological treatment stage. Thus, preliminary and primary treatment processes are not expected to impact the concentration of CECs in the wastewater effluent (Hollender et al. 2009). Nevertheless, certain configurations in primary treatment, such as the absence of flow equalizations and/or combined return flows, may cause fluctuations in flow rate. Fluctuations in flow rate may impact the nutrient and organic loading to the secondary treatment which impacts the secondary treatment performance and potentially CEC removal in downstream processes. As shown in Figure 1-1, most facilities reviewed in this study employed screening, grit removal, and primary clarifiers in their primary treatment stage. Only a few studies indicated the inclusion of fat and grease removal as well as the use of primary clarifiers with chemical addition to aid in sedimentation. Two studies also indicated that dissolved air flotation (DAF) and microsieves were utilized. Nevertheless, only five studies clearly indicated that flow equalization basins were present in their systems.

Note that the implementation of pretreatment and source control strategies upstream of preliminary and primary treatment can be beneficial to minimize CECs from industrial wastes entering the secondary treatment stage and downstream AWT system (Drewes et al. 2018).

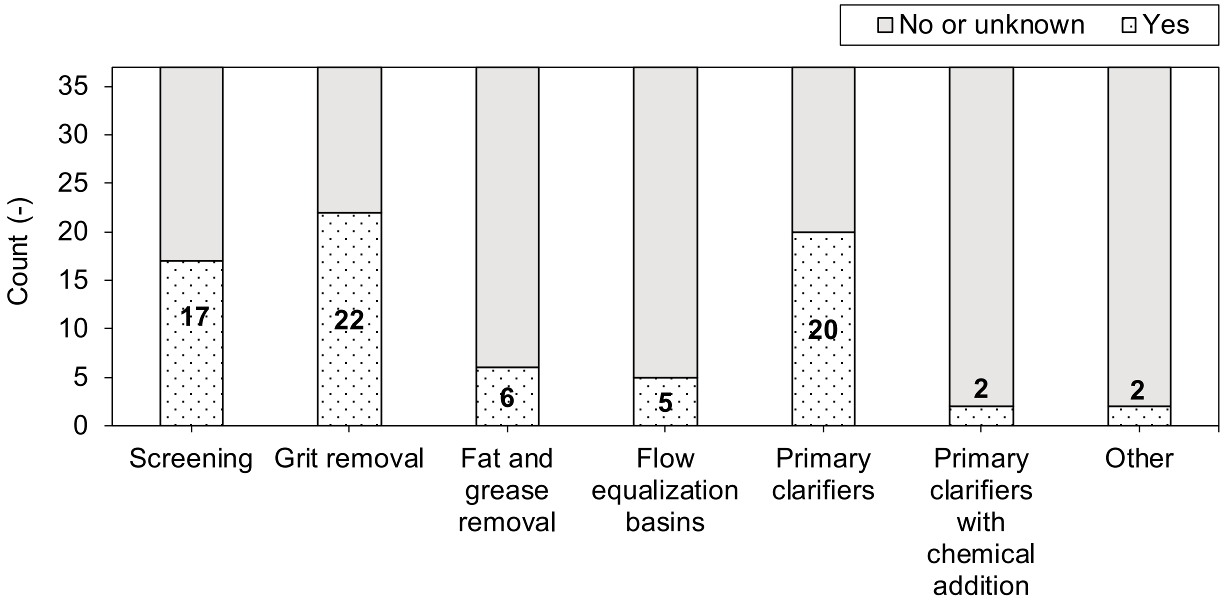


Figure 1-1. Type of Preliminary and Primary Treatments Employed by Wastewater Facilities Reviewed in this Study with the Number of 'Yes' Values shown for each Treatment.
Total number of studies (n) = 37

1.3.2 Secondary Treatment

Following primary treatment, wastewater is biologically treated in the secondary stage to reduce organic content and, depending upon process configuration, further reduce nutrients. The influent for ozone/BAF systems are sourced from secondary or tertiary effluent. As shown in Figure 1-2, most ozone/BAF studies sourced their waters from facilities that employ biological nutrient reduction systems targeting nitrogen and sometimes also phosphorus. Figure 1-3(a) shows that 15 out of 16 studies indicated that effluent water was fully nitrified (one is partially nitrified); thus, the effluents were most likely low in ammonia. Comparison between non-nitrified and nitrified wastewater effluents was not conducted in this study as some extent of nitrification was achieved in the reviewed projects. However, a previous study conducted in the City of Hollywood, Florida, demonstrated that high ammonia level (up to 9 mg/L) in the influent water to the ozone/BAF system (from PurOx plant with low sludge retention time [SRT]) may affect the NDMA formation potential through BAC, although more investigation is needed for confirmation (Stanford 2017).

In terms of nitrate concentration, most studies (25 out of 37) indicated that at least partial denitrification was achieved (Figure 1-3[b]). The typical nitrate concentrations in the secondary effluents as reported by these studies are presented in Figure 1-3(c). As shown, higher nitrate concentration was observed in a facility that only achieved partial denitrification.

When targeting CEC removal, advanced nutrient reduction strategies are warranted for ozone/BAF systems to prevent the passage of ozone-reactive scavengers such as nitrite that may impact ozonation performance. High ammonia loading may also impact the performance of BAF as it may shift the optimum proportion of carbon and nutrient availability (C:N:P molar ratio of 100:10:1 [LeChevallier, Schulz, and Lee 1991]) needed for microbial health to metabolize trace organic compounds and minimize extracellular polymeric substance (EPS) production in the biofilters (Lauderdale et al. 2018; Stanford 2017).

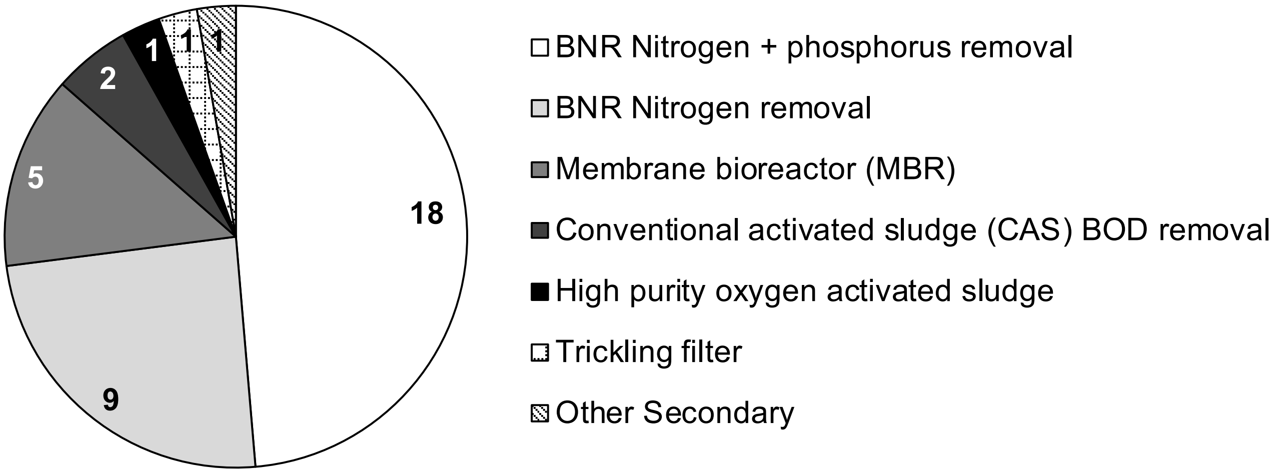


Figure 1-2. Type of Secondary Treatment Processes Employed in the Studies Reviewed.

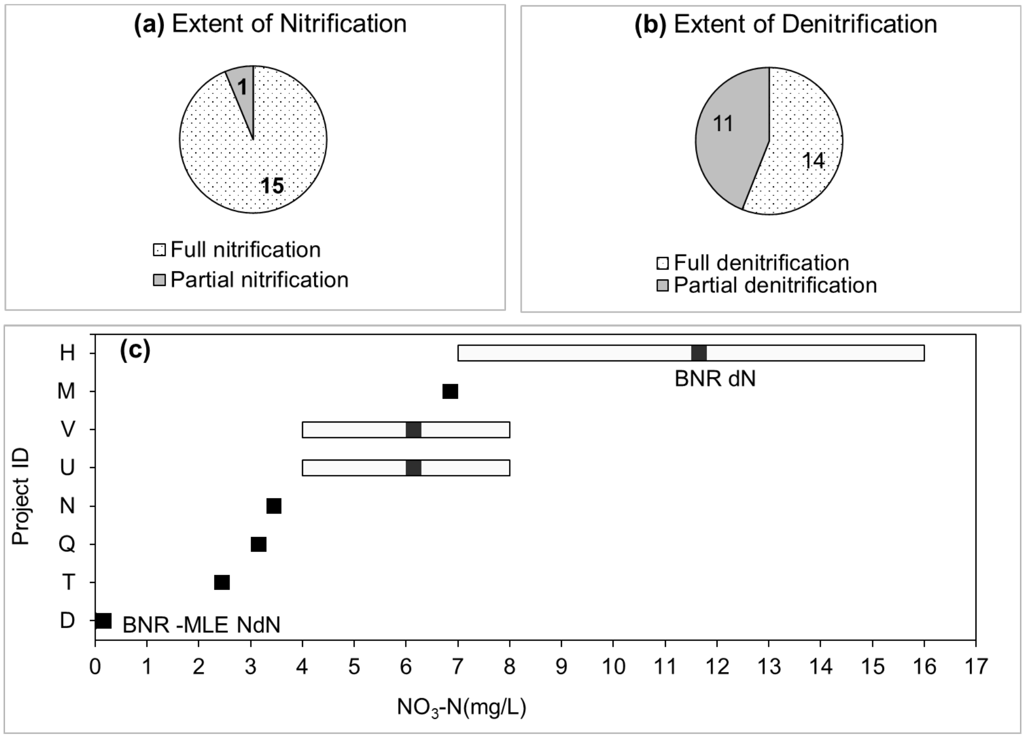


Figure 1-3. Information about Nitrification, Denitrification, and Nitrate Concentrations in the Studies Reviewed. (a) Extent of nitrification, (b) extent of denitrification, and (c) typical nitrate concentrations in the secondary effluents in the studies reviewed

1.3.2.1 Effect of Sludge Retention Time in the Secondary Treatment

The typical SRT for the studies reviewed are below 20 days (Figure 1-4), as expected in municipal facilities, with numbers varying according to the type of secondary treatment employed. However, the SRT can go beyond 20 days in a non-municipal setting, especially when employing a membrane bioreactor (MBR) as was the case for one of the study participants that was omitted from the SRT summary shown in Figure 1-4. SRT, which is a major design and operational variable in activated sludge secondary treatment, has been shown to impact the removal of xenobiotic compounds (Oppenheimer et al. 2007). Thus, investigation of its effect on the concentration of CECs in the influent of an Ozone-BAF system is warranted. Higher SRT values are expected to be more beneficial for CEC reduction as well as nutrient and bulk organic removal due to co-metabolic effects (Grady Jr., Daigger, and Lim 1980). The impact of different secondary treatments and their corresponding SRT on the concentrations of selected CECs in the ozone/BAF influents is demonstrated in Figure 1-5. Despite influent concentrations being dependent on multiple factors such as the population density, regional differences in consumer patterns, and proximity to industrial facilities, the CEC concentrations in each facility influent were relatively similar. However, when comparing the concentration of each compound across different SRTs, the effect of SRT warrants further investigation. While recalcitrant compounds such as Tris(2-carboxyethyl) phosphine (TCEP), primidone, and carbamazepine are poorly removed at all SRTs, compounds such as N,N-diethyl-meta-toluamide (DEET) and triclosan appear to be an order of magnitude higher at the facilities with low SRTs. The elevated concentrations of DEET and triclosan at lower SRTs are consistent with a previous study demonstrating that these compounds occur frequently in wastewater influents and are poorly removed until a critical SRT (>5 days) was provided (Achermann et al. 2018; Gerrity et al. 2013; Oppenheimer et al. 2007).

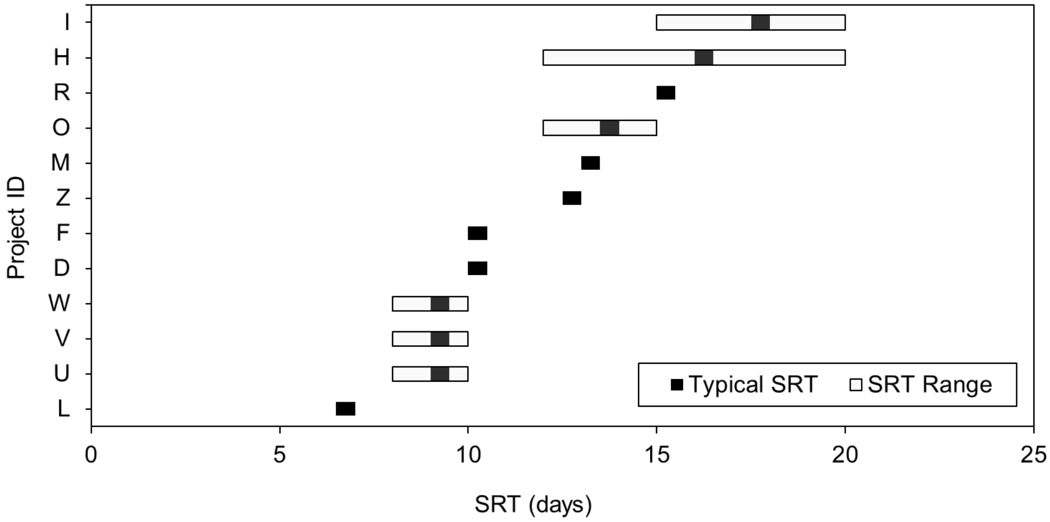


Figure 1-4. Typical SRT across Multiple Facilities.

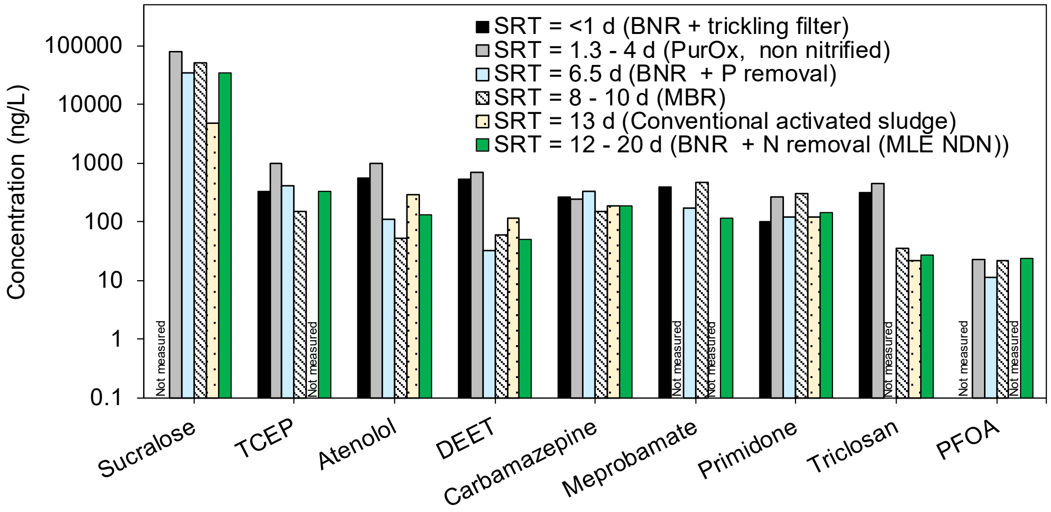


Figure 1-5. Comparison of CEC Concentrations in Ozone/BAF Influents from Facilities that Utilize Different Secondary Treatment Processes and SRTs.

Data Sources: Bacaro et al. 2019; Bourgin et al. 2018; Trussell et al. 2016.

Note that standard deviations are not provided from these studies.

1.3.3 Tertiary Treatment

As shown in Figure 1-6(a) and (b), 11 of 13 studies indicated that the ozone/BAF studies were sourced from tertiary effluents, mostly employing sand or granular media filtration (with or without coagulation pretreatment). Five of the studies also indicated that the ozone/BAF influents were taken after tertiary disinfection although there was insufficient information about quenching after disinfection when chlorination/chloramination was applied.

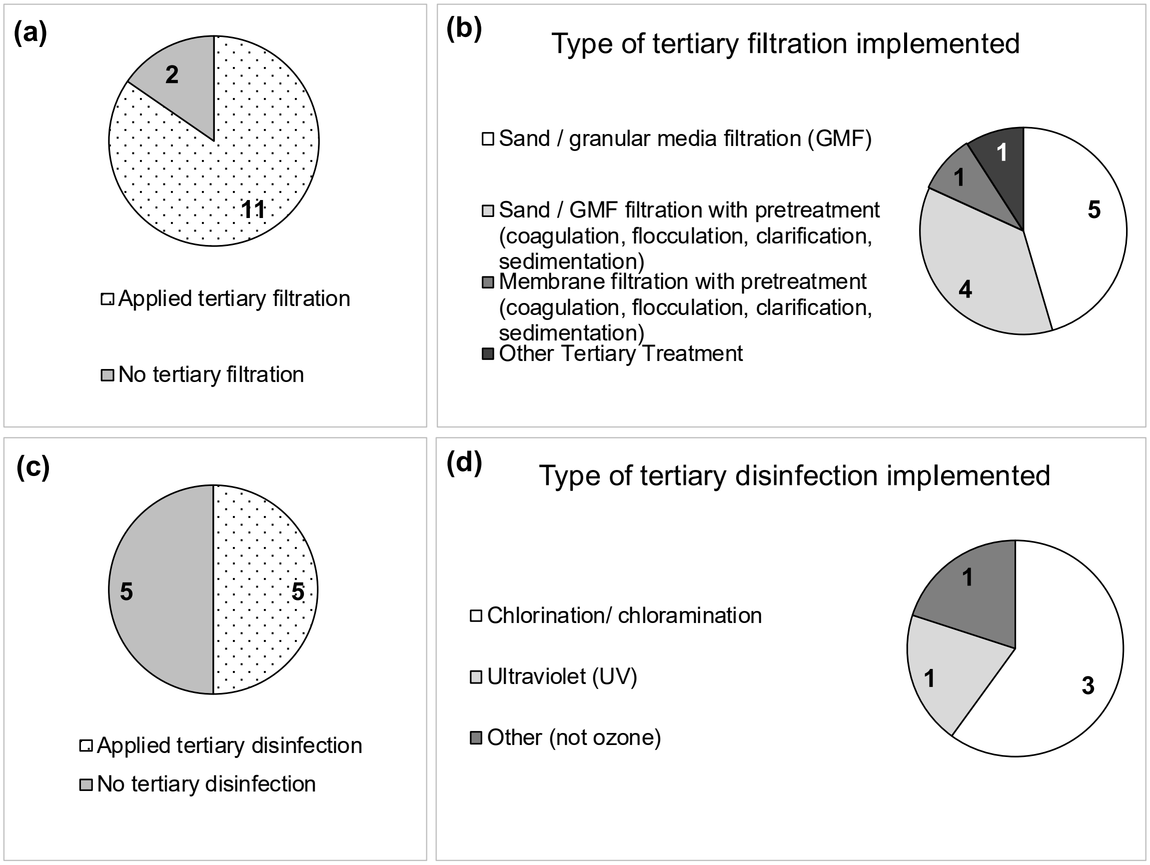


Figure 1-6. Information about Tertiary Treatment Implemented in the Studies Reviewed.
(a) Number of studies that sourced ozone/BAF influents from tertiary effluents**,** (b) type of tertiary filtration implemented**,** (c) number of studies that applied tertiary disinfection**,** and (d) type of tertiary disinfection implemented.

Plants that utilize coagulation in the treatment train may benefit from organic carbon and phosphorus removal. Chemical pretreatment reduced organic fractions that exert instantaneous ozone demand, ozone consumed by rapid reactions with readily degradable compounds; thus, more oxidant is available for CEC oxidation (Bourgin et al. 2018). However, coagulation preferentially removes the hydrophobic fraction of natural organic matter (NOM) and thus is not effective in removing the small, uncharged, hydrophilic fraction of NOM. In addition, in the absence of filtration, there is a chance of floc carryover to the biofilter, which can remove phosphorus, depending on the pH, but still can clog the filter (Lauderdale et al. 2018).

In terms of CEC concentrations in the ozone/BAF influents, there was no significant difference between facilities that sourced the water from secondary or tertiary effluents, as shown in Figure 1-7. As previously mentioned, the CEC concentrations in the influents also depend on various seasonal, anthropogenic, and regional factors, thereby adding complexity in understanding the effect of pretreatment processes relative to CEC concentrations in the ozone/BAF influents. Nevertheless, plants that utilize tertiary effluents may benefit from better incoming water quality in terms of TOC, nutrients (e.g., ammonia, nitrate nitrite), turbidity, etc., which can improve the performance of downstream Ozone-BAF systems.

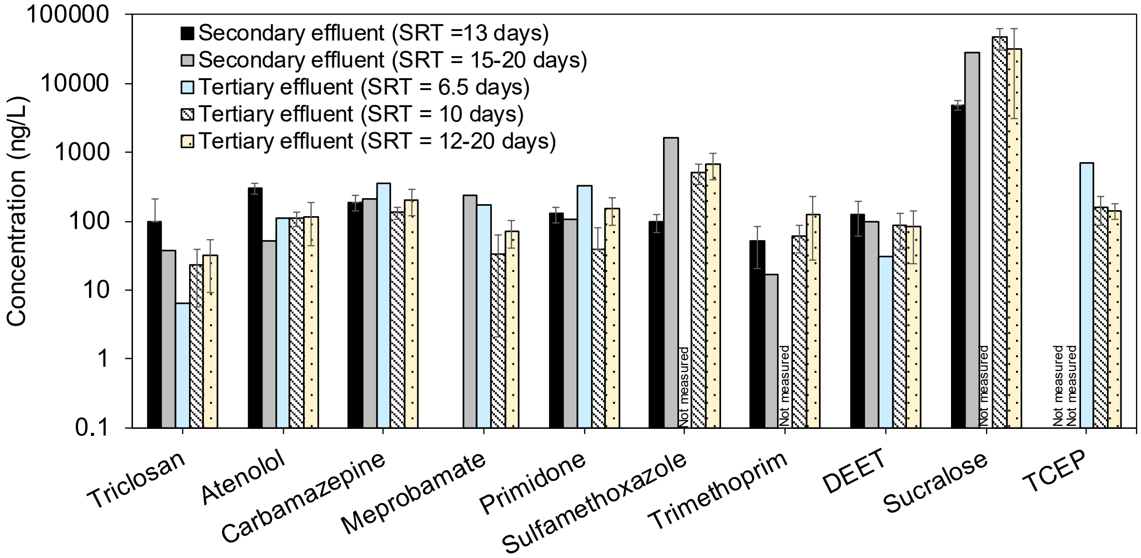


Figure 1-7. Effect of Secondary and Tertiary Treatments on CEC Concentrations in the Ozone/BAF Influents. The error bars denote standard deviation.

1.3.4 Other Pretreatment Considerations

To ensure successful operation of ozone/BAF systems in removing CECs, better nutrient reduction strategies are warranted in the upstream treatment processes. This is especially important for the ozonation step, as carryover of potential radical scavengers such as alkalinity (carbonate and bicarbonate), nitrite, and chloramine, and bromide have been shown to impact the efficacy of the ozonation process (Bourgin et al. 2018; Chys et al. 2018b). For plants that have upsets or challenges with fully nitrifying, then continuous monitoring of nitrite in the influent stream might be beneficial as the data can be used to calculate the nitrite-based ozone demand. Adjusting the ozone dose to compensate for the nitrite demand (as nitrite is an ozone scavenger) was shown to increase TOC removal by 8-10% (Brown and Caldwell and Trussell Technologies 2018). Bromate formation is another concern during ozonation and is dependent on the bromide concentration in the influent stream and ozone dose. Common bromate control strategies include using a chlorine-ammonia process, hydrogen peroxide addition (peroxone), and pH adjustment (Soltermann et al. 2017).

In terms of BAF performance, the proportion of bioavailable organic carbon, nitrate- and ammonia-nitrogen, and orthophosphate-phosphorus concentrations in the BAF influent is also important for maintaining microbial health to metabolize trace organic compounds (Lauderdale et al. 2018). While maintaining the ideal proportion of C:N:P of 100:10:1 is more of a concern for BAF system in drinking water plants (LeChevallier, Schulz, and Lee 1991), high loading of ammonia due to lack of nutrient reduction in the upstream WWTPs may also impact the performance of downstream BAF. For example, a pilot study conducted in Florida, USA, demonstrated sustained NDMA formation through BAF when sourcing the influent water from a PureOx plant with high ammonia concentration (Stanford 2017). However, the impact of high ammonia loading to BAF performance, especially in terms of CEC removal, needs to be further investigated.

1.4 Ozone System Design and Operation for CEC Removal

The following sections discuss the various ozone design and operation considerations in the context of CEC removal. Ozone system is generally installed to pre-oxidize bulk and trace organic compounds (as well as removal of color, taste, and odor) ahead of the BAF, but post-ozonation can also be implemented for disinfection purpose in addition to further removal of color and UVA (Mieog et al. 2011).

1.4.1 Overview of Ozone System Designs Implemented

There are several commercially available ozone systems that offer design and feature variations. However, there are only two major types of ozonation: i) conventional ozonation and ii) peroxone. Figure 1-8(a) shows that most of the studies implemented conventional ozonation rather than peroxone. Addition of peroxide is mostly performed for bromate control since peroxide addition does not provide significant benefit in enhancing removal of trace organic compounds during wastewater treatment compared to surface water treatment (Pisarenko et al. 2012). Twelve studies indicated that the ozone contactors were designed as multi-compartment tanks designed to maximize plug flow conditions, while pipeline ozone contactors were utilized in seven studies, as indicated in Figure 1-8(b).

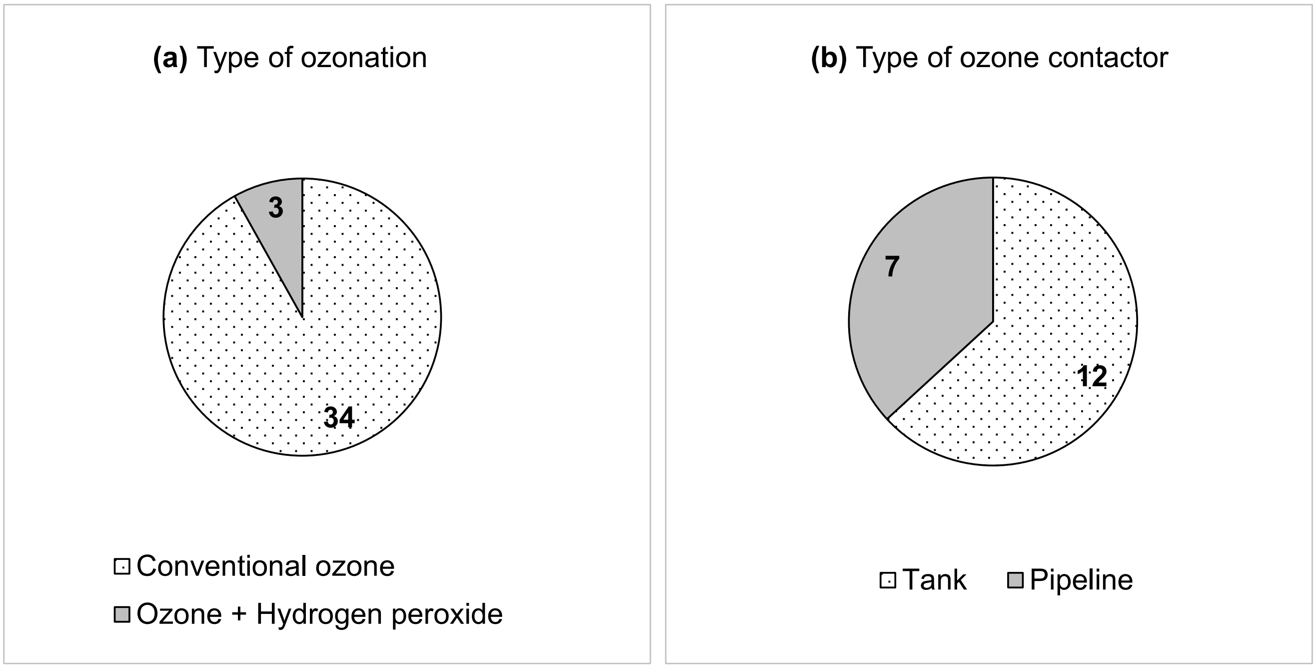


Figure 1-8. Ozonation and Contactor Types in the Studies Reviewed.
(a) Type of ozonation and (b) ozone contactor.

Ozone is produced from a dry oxygen source using corona discharge. The most common oxygen sources include dried air, oxygen concentrated from air using pressure swing adsorption (PSA) and liquid oxygen (LOX). Based on the questionnaire responses (Figure 1-9[a]), approximately half of the 15 respondents utilize LOX (seven studies), with the remainder utilizing PSA (three studies), dried air (one study), and four studies not specifically mentioning how the oxygen was concentrated from air for their systems. Venturi injection (either from the main stream or side stream) seemed to be utilized more than other methods such as fine bubble diffusion, addition within a static mixer, or direct gas injection, as shown in Figure 1-9(b). Selecting the most effective ozone dissolution system is important to meet the ozone transfer efficiency goal. Based on the limited questionnaire results (n = 5), the average ozone transfer efficiency ranged between 92% to 99%.

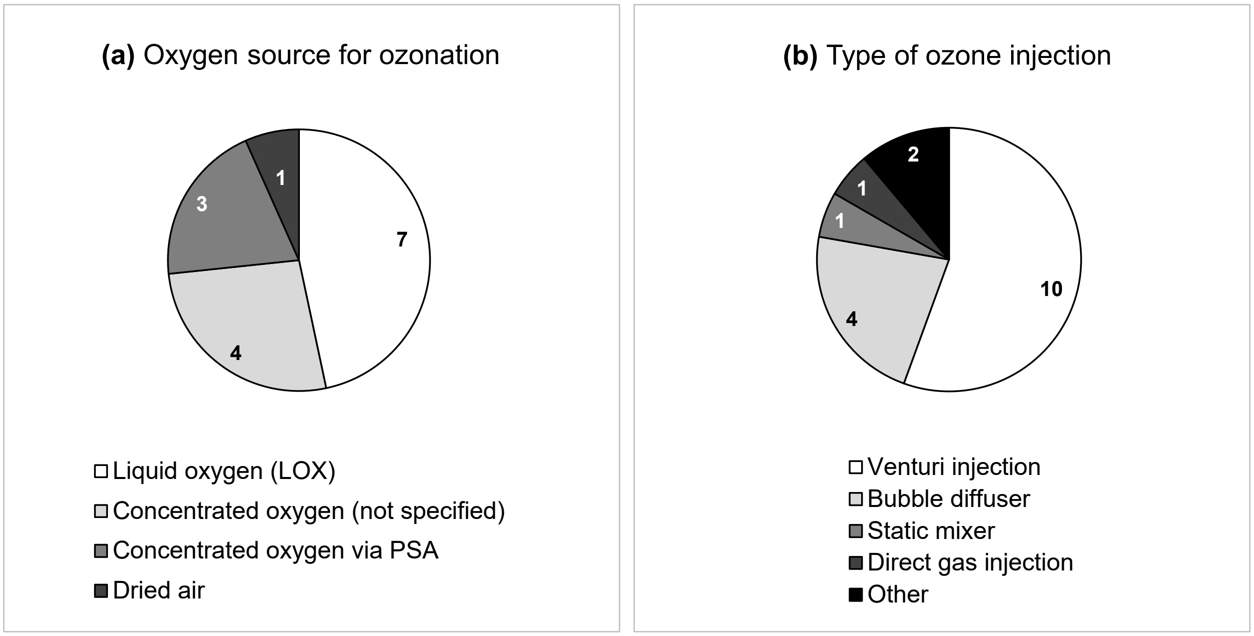


Figure 1-9. Oxygen Sources and Ozone Injection Methods in the Studies Reviewed.
(a) Oxygen source and (b) type of ozone injection method.

1.4.2 Effect of Process Parameters and Process Control on CEC Removal

The main parameters affecting the stability of ozone are temperature, pH, organic matter content and composition, alkalinity scavengers (carbonate and bicarbonate), and the presence of highly ozone-reactive inorganic constituents such as nitrite and bromide (Chys et al. 2018b). Nevertheless, the dynamic behavior of the physicochemical characteristics of the influent due to variations in the water matrix may require a more flexible approach in ozone dosing. Overdosing may result in the formation of ozonation byproducts that might be harmful to human health such as NDMA, PFAS, and bromate. Thus, optimization of ozone dosing is of paramount importance and may require online monitoring of surrogate parameters.

Ozone doses normalized by the amount of organic carbon (measured as TOC or DOC), i.e. mg O_3:mg TOC, in the wastewater can be used to compare micropollutant oxidation efficiencies achieved at different organic concentrations (Reungoat et al. 2012). Nevertheless, such normalization only accounts for the oxidation capability of organic constituents, without consideration of inorganic constituents. Thus, chemical oxygen demand (COD) might potentially provide a more useful representation of oxidation capability of both organic and inorganic constituents in the wastewater following ozone addition (Ekblad et al. 2019). Both TOC and COD include the organic wastewater fraction; however, COD provides further information on the number of electrons required for complete oxidation of organic compounds to carbon dioxide, water, and other inorganic compounds to a higher oxidation state (i.e., Fe^{2+}, Al^{2+}, etc.). Furthermore, COD also includes oxidation of other ozone-reactive inorganic compounds such as nitrite and bromide. A recent modelling study by Ekblad et al. (2019) showed that the dose response curves observed for organic micropollutants were similar to the predicted model when COD, rather than DOC, was used to normalize ozone doses. The study also demonstrated that using DOC alone for normalization resulted in an offset in the removals of selected organic micropollutants between two trials due to the differing nitrite concentrations in the influents.

Another similar accounting approach for influent nitrite is achieved by continuous monitoring of nitrite for calculation of the nitrite-based ozone demand. Correcting O_3:TOC for the nitrite consumption of O_3 was shown to increase TOC removal by 8-10% during ozonation (Brown and Caldwell and Trussell Technologies 2018). The manifested change in TOC removal, however, is site-specific and nitrite-concentration specific.

In addition to CEC removal, some plants may require pathogen removal credit, and thus ozone concentration multiplied by contact time (CT) can be used for process control. A study conducted in Melbourne, Australia has shown inactivation of all viruses (poliovirus 1, echovirus 11, coxsackievirus B5, and adenovirus 2) and surrogates (*Escherichia coli*, coliphage T1, T4, PRD-1, ΦX174, and MS2) greater than 4-log at ozone CT levels of less than 1 mg-min/L (Sigmon et al. 2015). Based on the survey, however, one study indicated ozone CT of 2.24 mg-min/L to achieve 1-log of *Cryptosporidium* removal.

1.4.3 Effect of O_3:TOC Ratio on Selected CEC Removal

One major process variable driving the design of ozone systems is the O_3:TOC ratio. As shown in Figure 1-10, the O_3:TOC ratios employed in the reviewed studies ranged from 0.1 to 2.25 mg O_3/mg TOC, with an average of 0.8 mg O_3/mg TOC. Earlier research studies have shown that increasing the O_3:TOC ratio improved organic removal, as measured by the change in TOC and UVA (Gerrity et al. 2014; Sundaram et al. 2020; Trussell et al. 2016). Nevertheless, bromate was also shown to increase at O_3:TOC ratio >0.4 mg O_3/mg TOC (Soltermann et al. 2017), while typical ozone-reactive contaminants require O_3:TOC ratio of ~0.5 mg O_3/mg TOC when targeting removals above 98% (Y. Lee et al. 2014). Thus, a wide range of O_3:TOC ratios are commonly assessed to optimize bulk and trace organic removal while minimizing bromate formation. Note that quenching of residual ozone may be needed when applying high ozone doses to safeguard structures and operator health and safety.

Interestingly, there is also a regional difference in the ratios employed, with lower ratios (<0.5) more common in European regions than the US. This can likely be attributed to the different treatment goals of the two regions. Ozone-BAF systems in Europe and Australia are mostly applied as a pathogen treatment barrier (with ozonation as the dominant pathogen barrier), while in the U.S. (and in Australia) there is increasing interest in the use of ozone/BAF as both a pathogen and CEC treatment barrier due to the more stringent regulations for potable water and common use of this technology as a viable alternative to membrane processes for inland application.

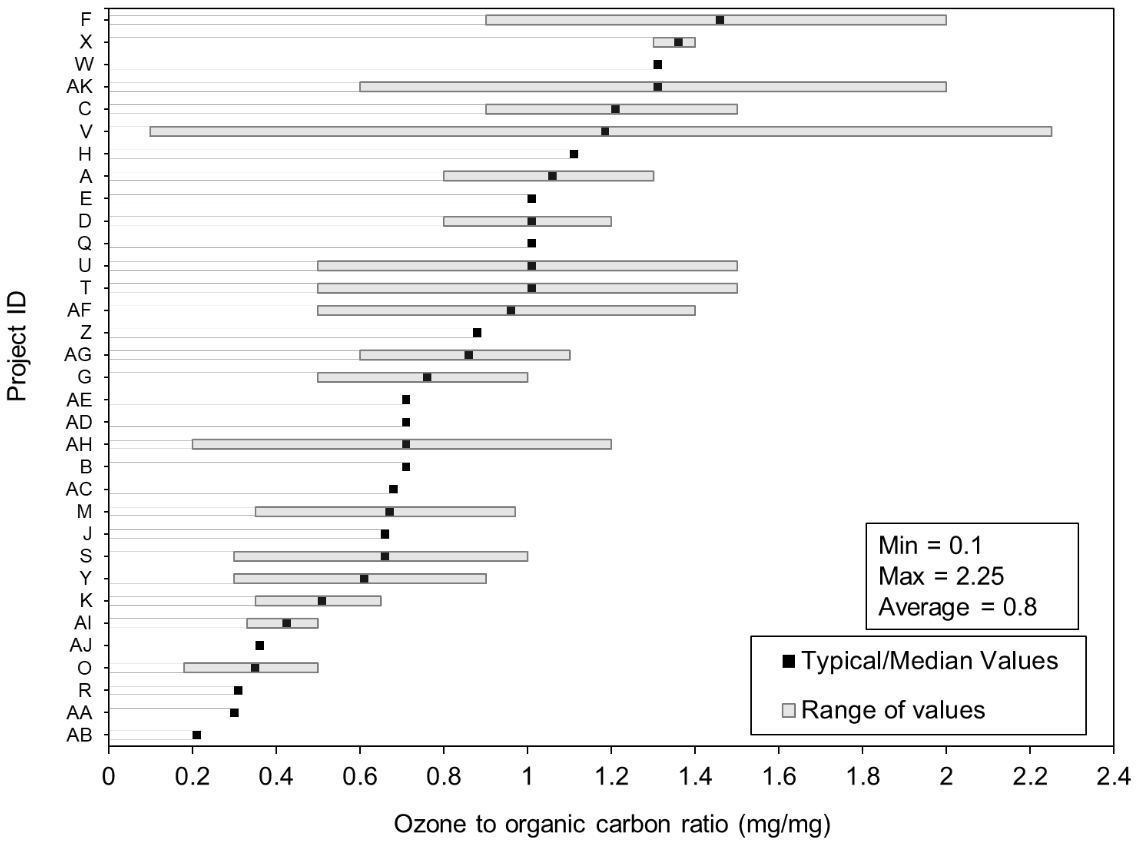


Figure 1-10. Typical O_3:TOC Ratios Employed in the Reviewed Studies.

Three discrete studies that systematically evaluated the effect of different O_3:TOC ratios on CEC removals were analyzed, wherein 13 common compounds from these studies were selected and compared for their susceptibility to ozonation (Figure 1-11). As expected, compounds with high ozone reaction rates (k_{O3} >10^3 $M^{-1}s^{-1}$, please refer to Table A-2 in Appendix) such as triclosan, gemfibrozil, carbamazepine, sulfamethoxazole, and fluoxetine exhibited high removals (>95%) even with the lowest applied O_3:TOC of 0.33 in some cases.

Atenolol, a moderately to highly oxidizable compound (k_{O3} =1.7 x 10^3 M^{-1} s^{-1}), was also expected to be removed well by ozonation; however, results showed variability in its removal. Based on the results from Project H in Figure 1-11(a), atenolol seemed to be susceptible to increasing O_3:DOC ratio (from 0.33 to 0.65), as atenolol removal increased from 79.5 ± 15.3% to 99.5 ± 0.10%. Nevertheless, atenolol removal at Project A in Figure 1-11(b) was only 74.7 ± 0.45%, despite the use of a higher O_3:TOC ratio of 1.2. Atenolol removal, however, increased when the O_3:TOC ratio was increased to 1.3 (98.5%, 1 measurement only). Similarly, atenolol removal also increased when the O_3:TOC ratio was increased from 1.5 to 2 at Project F (from 88.7% to 100%), though only one measurement for each O_3:TOC ratio was conducted (Figure 1-11[c]). These results imply that atenolol's susceptibility to increasing O_3:TOC ratio could be influenced by other factors when making multi-study comparisons. Such variations might potentially be attributed to the differences in the ozone/BAF influent composition in these studies or the presence of compounds that can scavenge ozone and/or hydroxyl radicals such as nitrites, carbonates, and chloramines in the influents.

For some compounds with low k_{O3} values (<10 M^{-1} s^{-1}) such as DEET, primidone, and meprobamate, moderate removal was still observed, most likely due to their susceptibility to hydroxyl radical oxidation (k_{OH}>10^9 M^{-1} s^{-1}) rather than by molecular ozone alone, as observed in other studies (Gerrity et al. 2014; Stanford 2017). As previously discussed regarding atenolol, increasing the O_3:TOC ratio seemed to impact the removal of these compounds; however, the level of removals varied across these three projects possibly due to differences in the influent matrix.

The rest of the compounds in Figure 1-11 represent those that are recalcitrant to ozonation such as sucralose, TCEP, NDMA, N-Nitrosomorpholine (NMOR), and Perfluorooctanoic acid (PFOA) at a wide range of O_3:TOC ratios of 0.33-2.0 mg O_3/mg TOC. Sucralose, as expected, showed low removal by ozonation due to its three electron-withdrawing chlorine atoms (Hollender et al. 2009). While other studies reported moderate susceptibility of sucralose to increasing ozone dose (Sundaram et al. 2020; Vatankhah et al. 2019a), only minor sensitivity was observed for sucralose. The removal of NDMA was also limited by ozonation due to its low k_{O3} (0.052 M^{-1} s^{-1}) and low susceptibility to hydroxyl radical oxidation (k_{OH} = 4.5 x 10^8 M^{-1} s^{-1}), as also reported by others (Bacaro et al. 2019; Hollender et al. 2009; D. Li et al. 2017; Sundaram et al. 2020). NDMA was also shown to increase after ozonation in Project H. NDMA formation has been consistently observed with ozonation of treated wastewaters (Hollender et al. 2009; Pisarenko et al. 2012). Chlorinated flame retardants like TCEP and PFAS like PFOA, which are engineered to be extremely stable, were marginally oxidized as expected. TCEP, furthermore, exhibited negative removal after ozonation in Project H and F. Note that TCEP was not formed during ozonation; instead, TCEP concentrations in the influents and post-ozone effluents were generally at a similar level with slight variations. These slight variations, which are still within analytical/sampling variability, apparently caused negative calculated removals after ozone/BAF treatment in some cases.

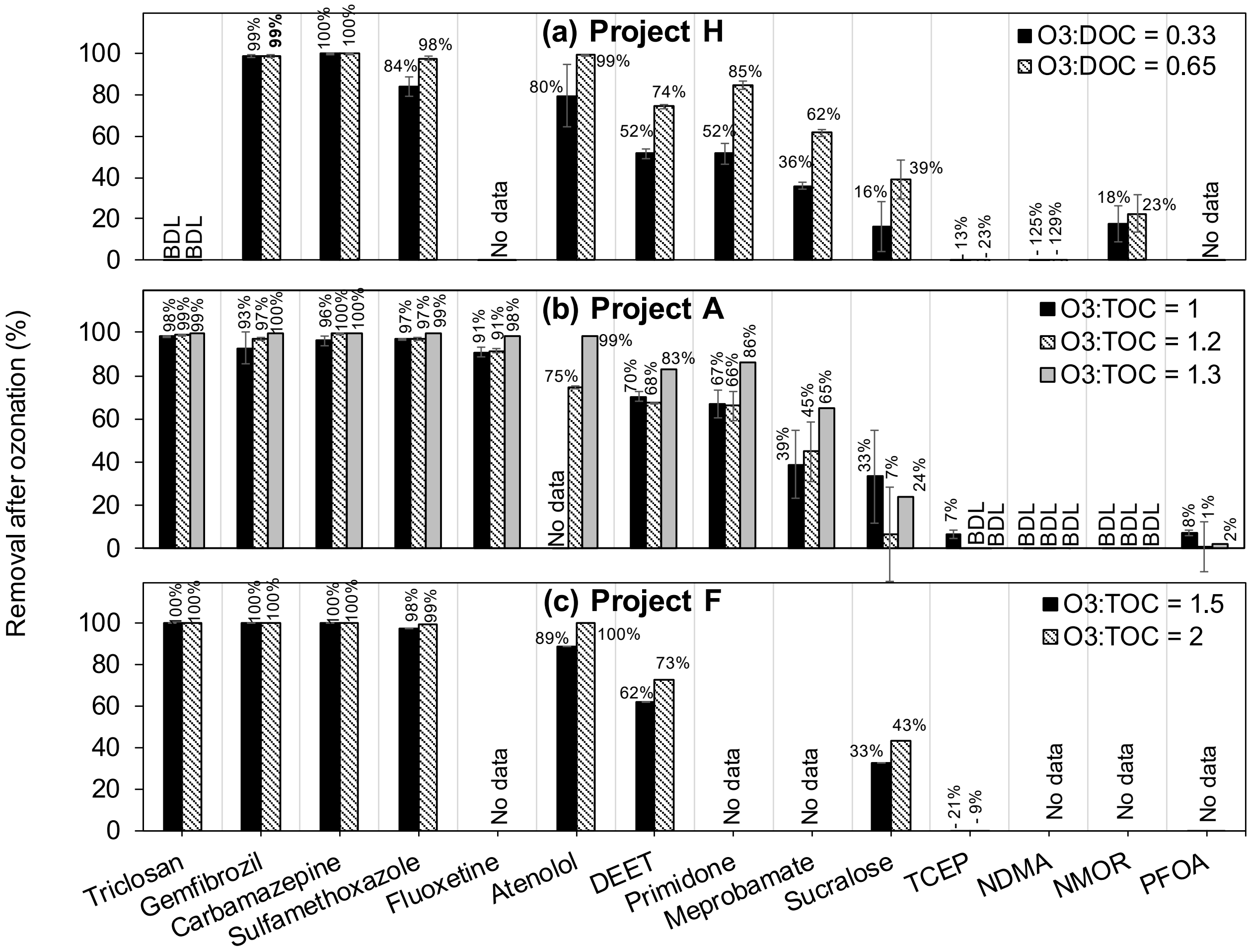


Figure 1-11. Removal of Selected CECs from Three Facilities Evaluating Different Range of O_3:TOC Ratios. (a) Facility H, O_3:DOC ratios of 0.33 and 0.65; (b) Facility A, O_3:TOC ratios of 1, 1.2, and 1.3; and (c) Facility F with O_3:TOC ratio of 1.5 and 2. Compounds marked as below detection limit (BDL) indicate that the concentrations in the influent and post treatment were below the detection limits. Percent removal after ozonation and BAF treatments are provided on top of the bars. The error bars denote standard deviation.

1.4.4 Common Issues with Ozone Systems and Mitigation Strategies

1.4.4.1 Bromate Formation and Mitigation

One concern related to ozonation is bromate formation, which is dependent on the incoming bromide concentration and the transferred ozone dose (Soltermann et al. 2017) along with the presence of scavengers including bulk organics. Bromate is a concern as it is a DBP regulated under United States Environmental Protection Agency's (EPA's) Stage 1 Disinfection Byproduct Rule with a maximum contaminant level (MCL) of 10 µg/L. A bench-scale study and work on the full-scale Windhoek plant in Namibia showed that an O_3:TOC ratio >0.9 lead to increased bromate concentration in ozonated effluent (Trussell et al. 2016); thus, the investigators concluded that there should be a balance between oxidation of trace organic compounds and bromate formation. Common bromate control strategies include bromide quenching (specifically the oxidized form, HOBr) using chloramine-ammonia process or hydrogen peroxide (H_2O_2) addition (Soltermann et al. 2017).

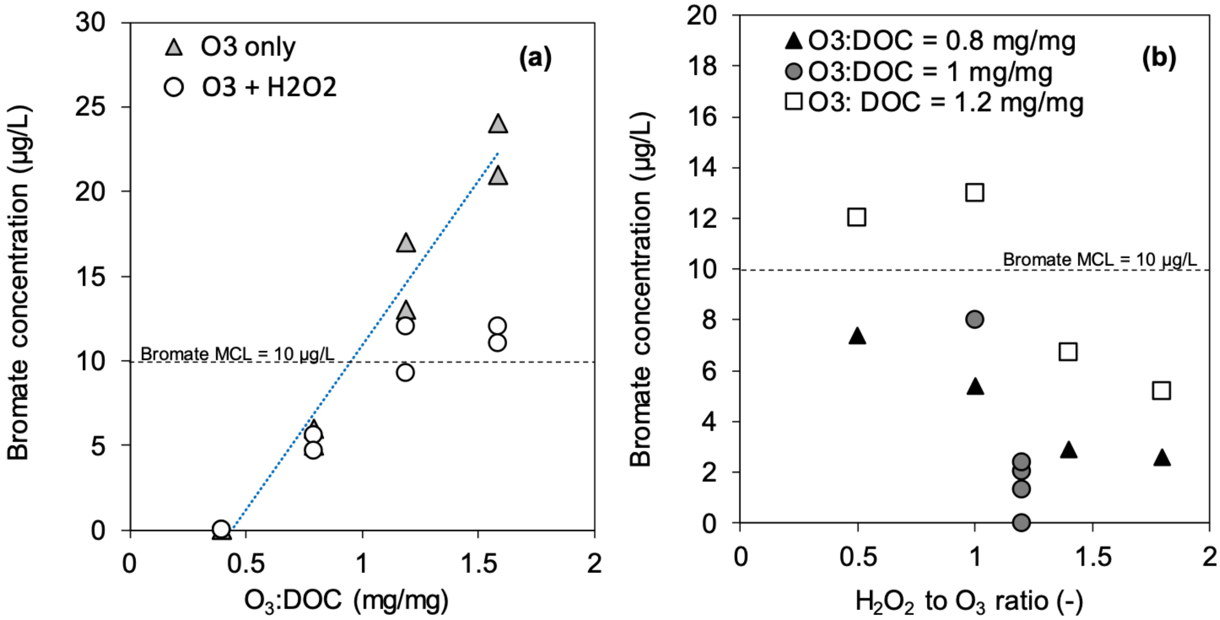


Figure 1-12. The Effect of Increasing (a) O_3:DOC Ratio and (b) H_2O_2:O_3 Molar Ratio to Bromate Formation during Oxidation using Ozone Alone and Ozone + Peroxide in Project I.

Figure 1-12(a) shows increasing bromate concentration with increasing O_3:TOC ratio in a systematic study (Project I). Increasing O_3:TOC ratio above 0.8 mg O_3/mg DOC resulted in bromate formation above the MCL for bromate (10 µg/L). However, when ozone was applied in tandem with peroxide, bromate formation could be suppressed to below the MCL despite increasing the O_3:DOC ratio beyond 0.8 mg O_3/mg DOC. Peroxide addition is useful in quenching the intermediates (HOBr) of the bromate formation pathway, thus minimizing bromate formation (Soltermann et al. 2017). Figure 1-12(b) also shows that high O_3:DOC ratios require higher H_2O_2:O_3 molar ratios to adequately reduce bromate formation. As shown, a molar ratio above 1.2 is needed to reduce bromate formation below its MCL when applying an O_3:DOC ratio above 0.8 mg O_3/mg DOC.

To assess the effect of peroxide addition on CEC removal, the concentrations of DEET, which is a moderately ozone-reactive compound (k_{O3}=10 M^{-1} s^{-1}) with high susceptibility to hydroxyl radical oxidation (k_{OH}= 4.95 x 10^9 M^{-1} s^{-1}), were analyzed from three different facilities employing similar O_3:TOC ratios (Figure 1-13). Using ozonation alone, DEET's removal appeared to be influenced by the initial concentrations (initial DEET concentrations in Project D and Project F were 86±47 ng/L and 177±128 ng/L, respectively). However, addition of peroxide in Project C seemed to result in slightly higher removal of DEET. Comparison of other compounds, nonetheless, yielded mixed results, due to other factors that may affect specific CEC removal such as initial concentration, O_3:TOC ratio, H_2O_2:O_3 molar ratio, etc. A previous study also showed that the presence of hydroxyl radical scavengers can impact removal of CECs with high k_{OH} (Tackaert et al. 2019).

The above results where a slight improvement in oxidation of ozone-resistant compound following peroxide addition are consistent with the previous study evaluating ozonation using secondary effluents collected from multiple facilities (S. Snyder et al. 2014). The study demonstrated that while peroxide addition may be beneficial in improving oxidation of ozone-resistant compounds, the increase in removal was only about 10%. Only marginal improvement was also provided by peroxide addition for other trace organic compounds. Peroxide addition for improved CEC removal, however, may be more beneficial for drinking water treatment compared to wastewater treatment. This is because, at sub-residual ozone doses, ozone demand in a wastewater matrix must be satisfied first before peroxide can react with residual ozone to accelerate the formation of hydroxyl radicals.

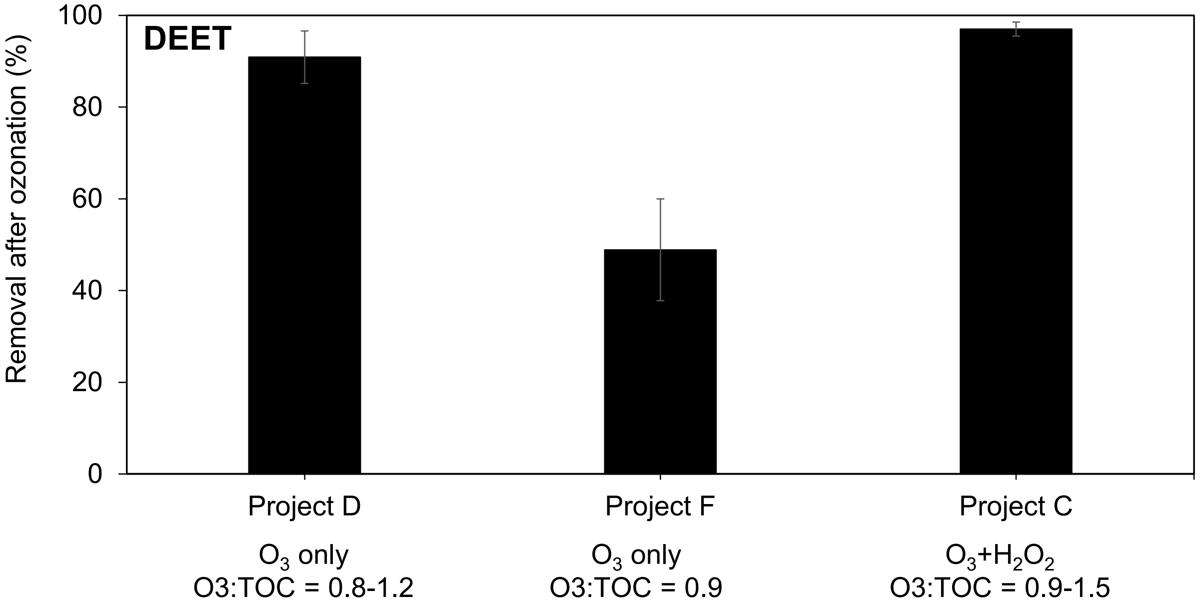


Figure 1-13. Removal of DEET by Ozonation across Three Studies.

Project D (ozone only, O_3:TOC = 0.8-1.2), Project F (ozone only, O_3:TOC = 0.9), and Project C (ozone + peroxide, O_3:TOC = 0.9-1.5). The error bars denote standard deviation.

1.4.4.2 Other Ozonation Byproducts

Organic macromolecules with highly susceptible sites for ozonation such as aromatic and amino acids functional groups can act as precursors of OBPs such as aldehydes, ketones, carboxylic acids (Legube 2003), and nitrosamines such as NDMA and NMOR (Bacaro et al. 2019; Bourgin et al. 2018; D. Li et al. 2017). The presence of NDMA and NMOR in ozonated effluents was also observed in several reviewed studies as depicted in Figure 1-14(a) and (b), respectively. Moreover, the concentration of NDMA in the ozonated effluents were higher than in the influents in most cases, suggesting the presence of precursors such as secondary, tertiary, or quaternary amines with at least one dimethylamine (DMA) (Dickenson et al. 2015; Marti et al. 2015; Roback, Ishida, and Plumlee 2019; S. Snyder et al. 2014; Sundaram et al. 2020). BAF, however, has been demonstrated to reduce the NDMA concentration to levels similar or lower than in the influents (Gerrity et al. 2015). It is also important to note, however, that NDMA concentrations in the ozone/BAF influents may have a temporal variation (Roback, Ishida, and Plumlee 2019; Sundaram et al. 2020), which affects its removal.

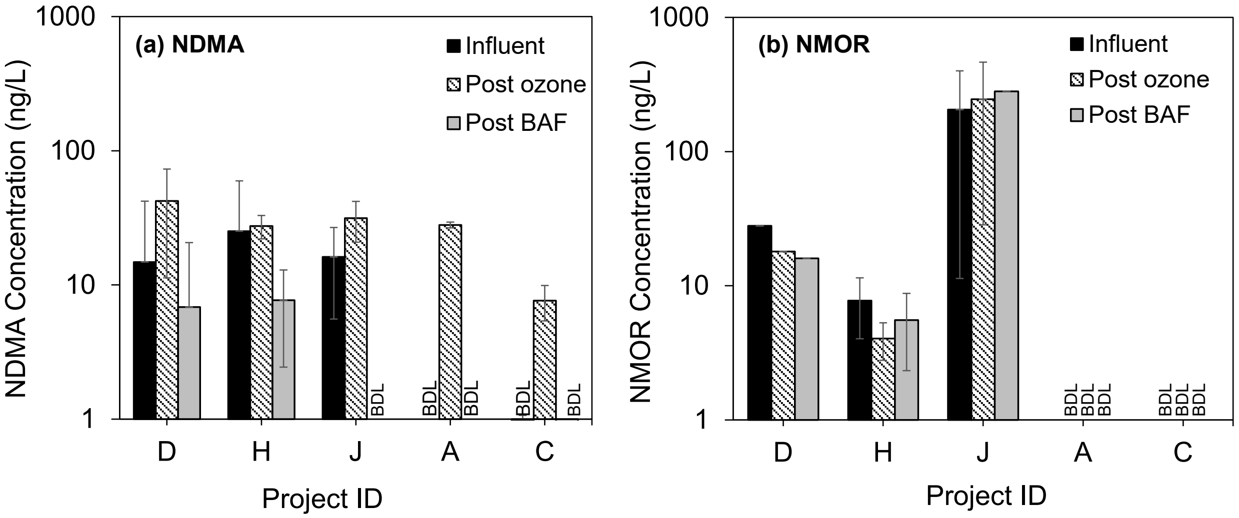


Figure 1-14. (a) NDMA and (b) NMOR Concentrations along the Treatment Train at Multiple Facilities.
The error bars denote standard deviation.

In contrast to NDMA, NMOR concentrations were similar at various points along the treatment train (i.e., at influent, post-ozonation, and post-BAF), as shown in Figure 1-14(b), demonstrating its recalcitrance to ozone/BAF treatment. These data also confirmed the lack of ozone-reactive NMOR precursors in the influent water, as shown by a previous study (T. Zeng et al. 2016b). Nevertheless, both NDMA and NMOR may be removed by downstream UV photolysis, which is a typical barrier in any potable reuse treatment train (Plumlee et al. 2008; Roback, Ishida, and Plumlee 2019).

Other OBPs such as acetaldehydes, formaldehydes, and glyoxals were also observed in several studies. As discussed for NDMA above, the concentrations of these compounds increased following ozonation but further decreased to the same or even lower level as the influent concentrations after BAF treatment. As previously reported, PFAS were also shown to increase after ozonation, especially the smaller MW compounds (Dickenson et al. 2015; Glover, Quiñones, and Dickenson 2018; Pisarenko et al. 2015). In this study, only one out of ten projects that evaluated PFOA showed a significant increase in PFOA after ozonation (Project K, full-scale study), indicating degradation of perfluoroalkyl acid (PFAA) precursors following ozonation. The concentrations of PFOA observed in the rest of the studies generally did not significantly change across ozone/BAF systems, thus confirmed the resistant nature of PFOA to ozone/BAF treatment (Dickenson et al. 2015; Glover, Quiñones, and Dickenson 2018; Pisarenko et al. 2015). Figure 1-15 provides a plot with changes in PFOA concentration across ozone/BAF systems among surveyed projects. Note that only one PFOA measurement in each treatment step was taken in Project B and E, and thus further investigation is needed to elucidate the fate of PFOA across ozone/BAF in these projects.

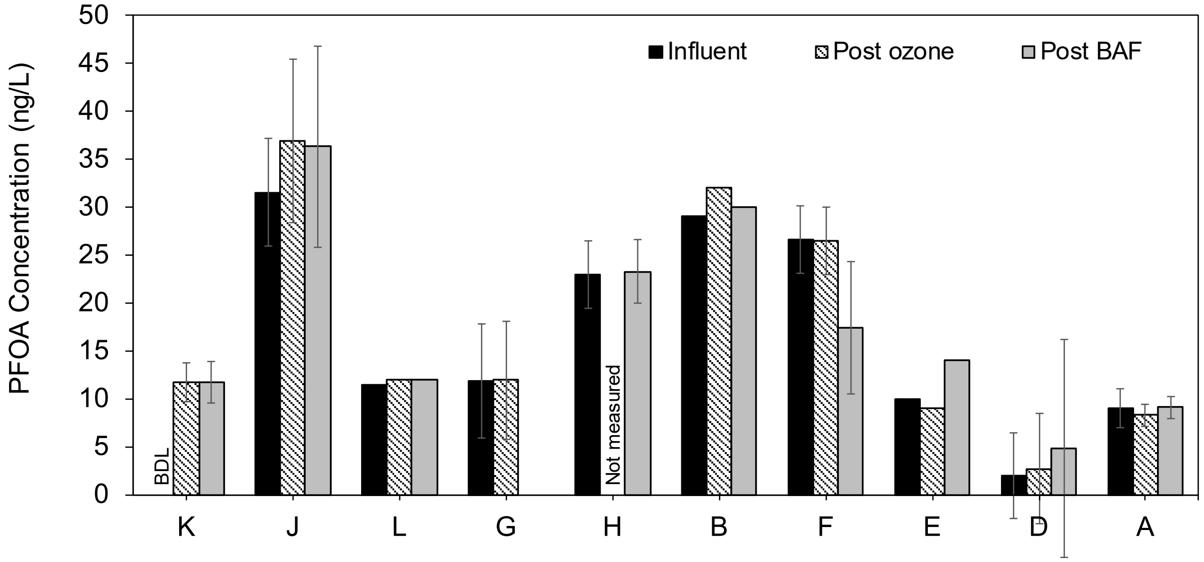


Figure 1-15. Concentrations of PFOA across Ozone/BAF Systems Observed in Ten Reviewed Projects. Projects K, J, L are full-scale studies, whereas the rest are demo-/pilot-scale studies. The error bars denote standard deviation.

1.5 BAF System Design and Operation for CEC Removal

The following sections discuss various BAF design and operational considerations within the context of CEC removal.

1.5.1 Overview of Implemented BAF System Designs and Configurations

The inclusion of BAF following ozonation is beneficial for the removal of persistent trace organic contaminants through biological degradation or potentially media adsorption, depending on the available adsorption capacity. Almost half of the studies assessed through the questionnaire and literature review utilized GAC as their sole filtration media, while an equal number of studies utilized combinations of two or three media types such as GAC + sand, GAC + anthracite, GAC + sand + anthracite, etc. (Figure 1-16[a]). As expected, most studies employed gravity-based filters with downward flow (Figure 1-16[b] and [c]). A nozzle-based underdrain system was mentioned in four questionnaire responses; however, it is possible that other types of underdrains may be used in other facilities.

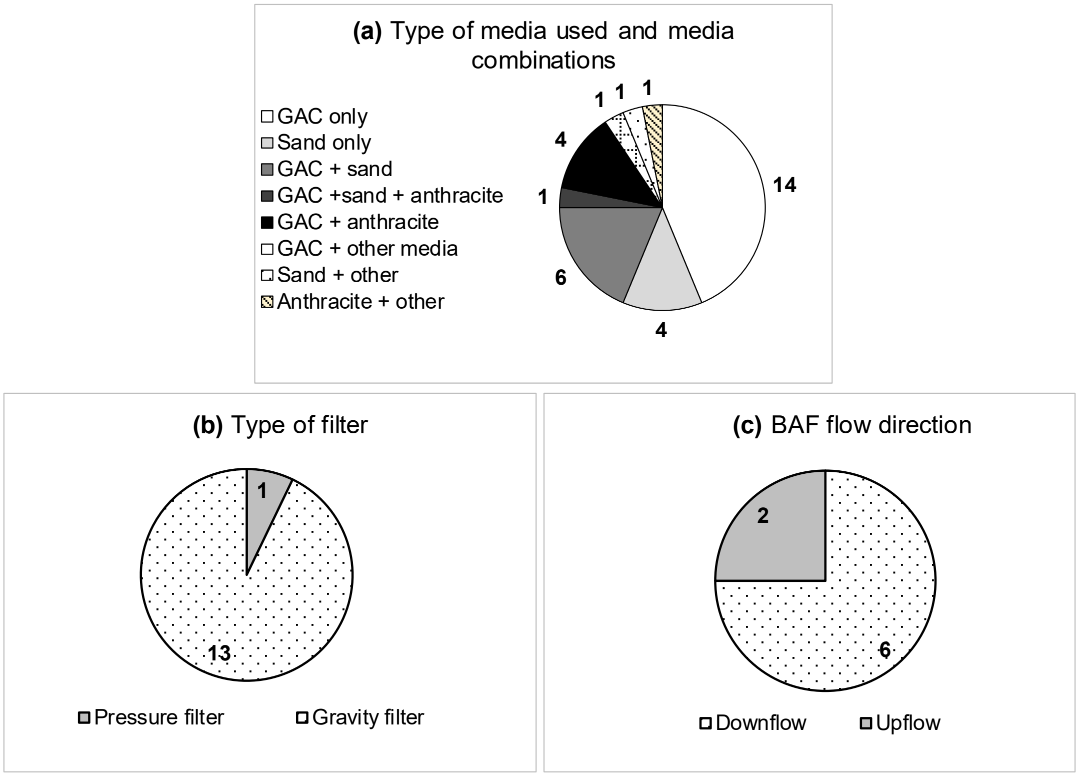


Figure 1-16. (a) Types of Media, (b) Filter, and (c) Flow Directions Utilized in the Reviewed Studies.

Selection of filtration media is important as it can have an impact on the microbial growth and activity. A recent study evaluating two biofilter medias (BAC and anthracite) for potable reuse application empirically demonstrated similar first-order biodegradation rate constants between anthracite and BAC, although TOC removal was generally higher using BAC (Gifford, Selvy, and Gerrity 2018). Relatively higher removal of TOC by BAC was also observed by other studies (Arnold et al. 2018; Thiel et al. 2006). Based on the insignificant differences in the adenosine triphosphate (ATP) analysis between BAC and anthracite, Arnold et al. (2018) suggested that the superior performance of BAC may not be due to microbial abundance, but most likely due to the dynamics of adsorption/desorption and/or the differences in the microbial community structure (Gerrity et al. 2018). For studies that employed GAC, a multitude of GAC products were selected. The different types of GAC employed and their characteristics are presented in Table 1-2.

Table 1-2. Various GAC Products Utilized in Reviewed Studies.

Project ID	GAC Depth (inches)	Product Name	Manufacturer	Raw Material	Mesh Size	Iodine Number (min)	Moisture by Weight (%)	Effective Size (mm)	Uniformity Coefficient (max)	Abrasion Number (min)	Apparent Density (g/cc)	Ash Content (%)	Specific Surface Area (m^2/g)	Initial Media Condition	Acclimation Period
A	62	Filtrasorb 820	Calgon Carbon	Bituminous coal	8 x 20	900	2	1.0-1.2	1.5	75	0.56	NA	NA	Exhausted	NA
B	66	Filtrasorb 300	Calgon Carbon	Bituminous coal	8 x 30	900	2	0.8 - 1	2.1	78	0.56	NA	NA	NA	4 months
C	54	Filtrasorb 400	Calgon Carbon	Bituminous coal	12 x 40	1000	2	0.55-0.75	1.9	75	0.54	NA	NA	Virgin	NA
D	78	Filtrasorb 820	Calgon Carbon	Bituminous coal	8 x 20	900	2	1.0-1.2	1.5	75	0.56	NA	NA	Virgin	NA
E	60	Filtrasorb 300	Calgon Carbon	Bituminous coal	8 x 30	900	2	0.8 - 1	2.1	78	0.56	NA	NA	Exhausted	12 weeks
F	31	Filtrasorb 400	Calgon Carbon	Bituminous coal	12 x 40	1000	2	0.55-0.75	1.9	75	0.54	NA	NA	NA	NA
G	48	Filtrasorb 400	Calgon Carbon	Bituminous coal	12 x 40	1000	2	0.55-0.75	1.9	75	0.54	NA	NA	Virgin	NA
		Norit 400	Cabot	Bituminous coal	12 x 40	1030		0.7	1.6			NA	NA	Virgin	
H	120	Filtrasorb 300	Calgon Carbon	Bituminous coal	8 x 30	900	2	0.8 - 1	2.1	78	0.56	NA	NA	Regenerated and Exhausted	Varied
I		DSR-A 8x40, Calgon Carbon	Calgon Carbon	Bituminous coal	8 x 40	750	2	NA	NA	NA	0.6	NA	NA	Regenerated	14 days seeding with MBR effluent
K	144	Filtrasorb 820	Calgon Carbon	Bituminous coal	8 x 20	900	2	1.0-1.2	1.5	75	0.56	NA	NA	Virgin	NA
		Norit 820	Cabot	Bituminous coal	8 x 20	970	NA	1.1	1.4	NA	NA	NA	NA	Virgin	
L	48	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	Virgin	NA
M	47	Cyclecarb 401, Chemviron Jacobi	Chemviron Jacobi	Coal based		900	NA	NA	NA	NA	0.45		900	Virgin	NA
		Norit 830	Cabot	Bituminous coal	8 x 30	950	5	0.9-1.1	1.7	NA	0.5	12	1150	Exhausted	112 days with secondary effluent (9000 BV), followed by 292 days of effluent diluted with groundwater
N	42	Filtrasorb 816	Calgon Carbon	Bituminous coal	8 x 16	900	2	1.3-1.5	1.4	75	0.5	NA	NA	Virgin	NA
O	59	Carbsob 30	Chemviron Jacobi	Bituminous coal	8 x 30	900	2	0.9	1.8	NA	NA	NA	900	Exhausted	NA
T	90	Hydrodarco 3000, Cabot	Cabot	Lignite coal	8 x 30	500	8	0.7-0.9	2.1	70	0.38	0.3	NA	Virgin	NA

1.5.2 Effects of BAF Process Parameters and Process Control

EBCT is a major design parameter for BAF systems and should be carefully selected to ensure sufficient removal of a wide range of CECs and their degradation products, especially for compounds that are recalcitrant and could potentially cause health effects when present in the finished water. The typical EBCT values in the reviewed studies, as presented in Figure 1-17, ranged from 2 to 50 minutes, with an average of 17 minutes. Numerous studies have shown that EBCT substantially impacts the removal of bulk organic compounds, as assessed by UVA and TOC (Arnold et al. 2018; Gerrity et al. 2011; Vaidya et al. 2019), and known recalcitrant trace organic compounds such as NDMA and PFAS (D. Li et al. 2017; Sundaram et al. 2020). Factors such as media type (sand, anthracite, GAC) and initial media condition (virgin versus exhausted) may also impact the performance of BAF in removing CECs.

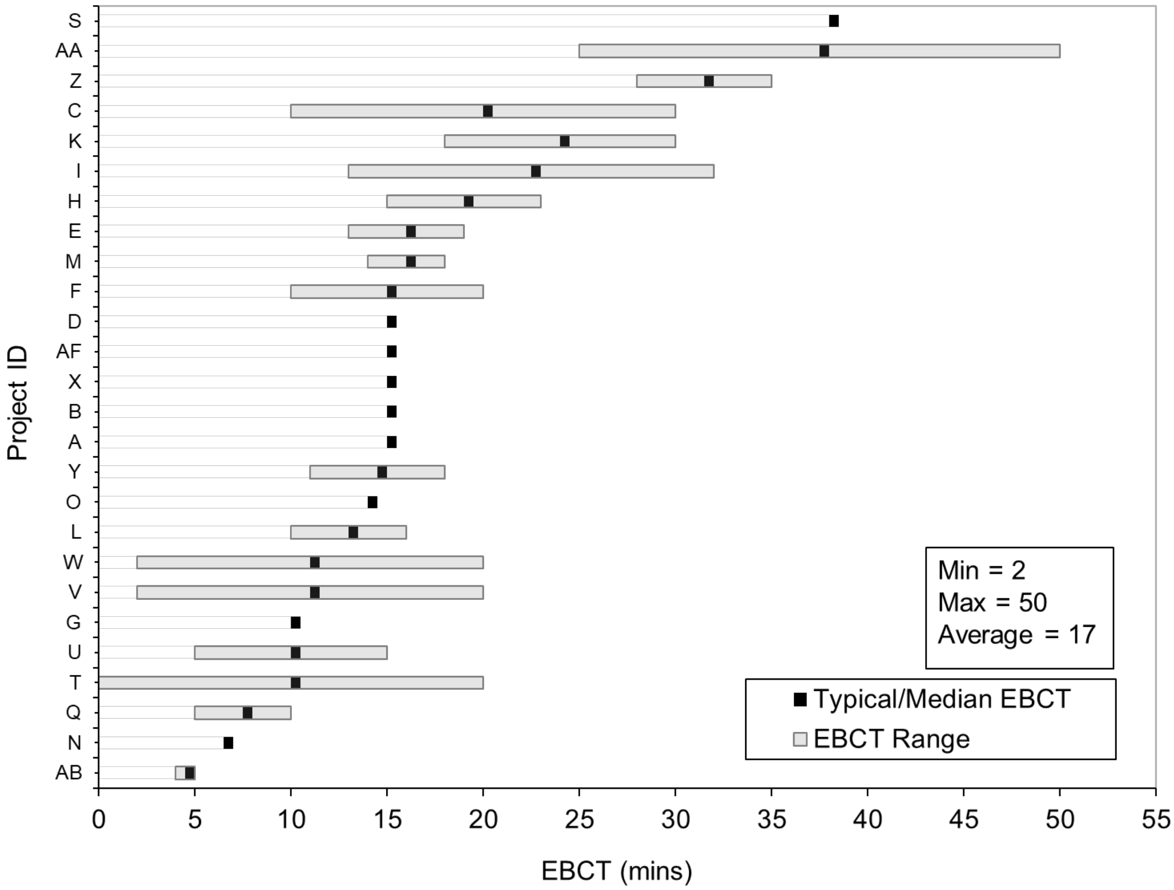


Figure 1-17. Typical EBCTs Employed across Multiple Projects.

1.5.2.1 Influence of EBCT on CEC Removal

A previous study showed there was no clear correlation between EBCT and DBP precursor removal (Arnold et al. 2018), although higher EBCTs tend to remove bulk organic compounds (Arnold et al. 2018; Reungoat et al. 2012; Sundaram et al. 2020). Nevertheless, TOC removal was shown to plateau after reaching a certain EBCT, suggesting the presence of an optimum EBCT (at constant O_3:TOC ratio) (Bacaro et al. 2019). In order to better understand the effect of EBCT on CEC removal, comparisons were first made among facilities with similar EBCTs and O_3:TOC ratios as a baseline for analysis (Figure 1-18). All selected facilities applied an O_3:TOC range between 0.7 – 1.3 mg O_3/mg TOC for ozonation and used an EBCT of 15 minutes for GAC-based BAF. As shown in Figure 1-18, compounds highly reactive with molecular ozone or hydroxyl radicals—including gemfibrozil, triclosan, carbamazepine, trimethoprim, atenolol, and sulfamethoxazole—were removed to a greater extent (above 90%) following ozonation alone. Note that the removal of triclosan by ozonation in Project B was lower at >61.5% (compared to Projects A and D) because the influent concentration was too close to the analytical detection limit. In most cases, these compounds were removed to below detection limit before BAF treatment (thus, those compounds were marked as "BDL" in Figure 1-18). In the cases where these compounds were not completely removed by ozonation, BAF seemed to be able to further remove these compounds (greater than 50% removal).

Lower removals by ozonation were observed for moderately reactive compounds such as fluoxetine, primidone, meprobamate, and DEET. The removals of these four compounds are:

- 77.8 ± 10.0% to 90.8 ± 2.30% for fluoxetine
- 66.9 ± 6.36% to 95.1 ± 2.97% for primidone
- 39.0 ± 15.6% to 71.8 ± 6.06% for meprobamate
- 68% to 90.9 ± 5.70% for DEET

The variations in the removals were most likely due to the differences in the water matrix and initial concentrations. In most cases ozonation was able to remove these compounds to near detection limits; thus, BAF performance could not be clearly elucidated when the concentrations were very low. When sufficient concentration in the ozonated effluent was present (e.g., meprobamate in Project A), BAF seemed to be able to provide additional removal. Note that the low meprobamate removal by BAF in Project D was because the concentration was near detection limit following ozonation.

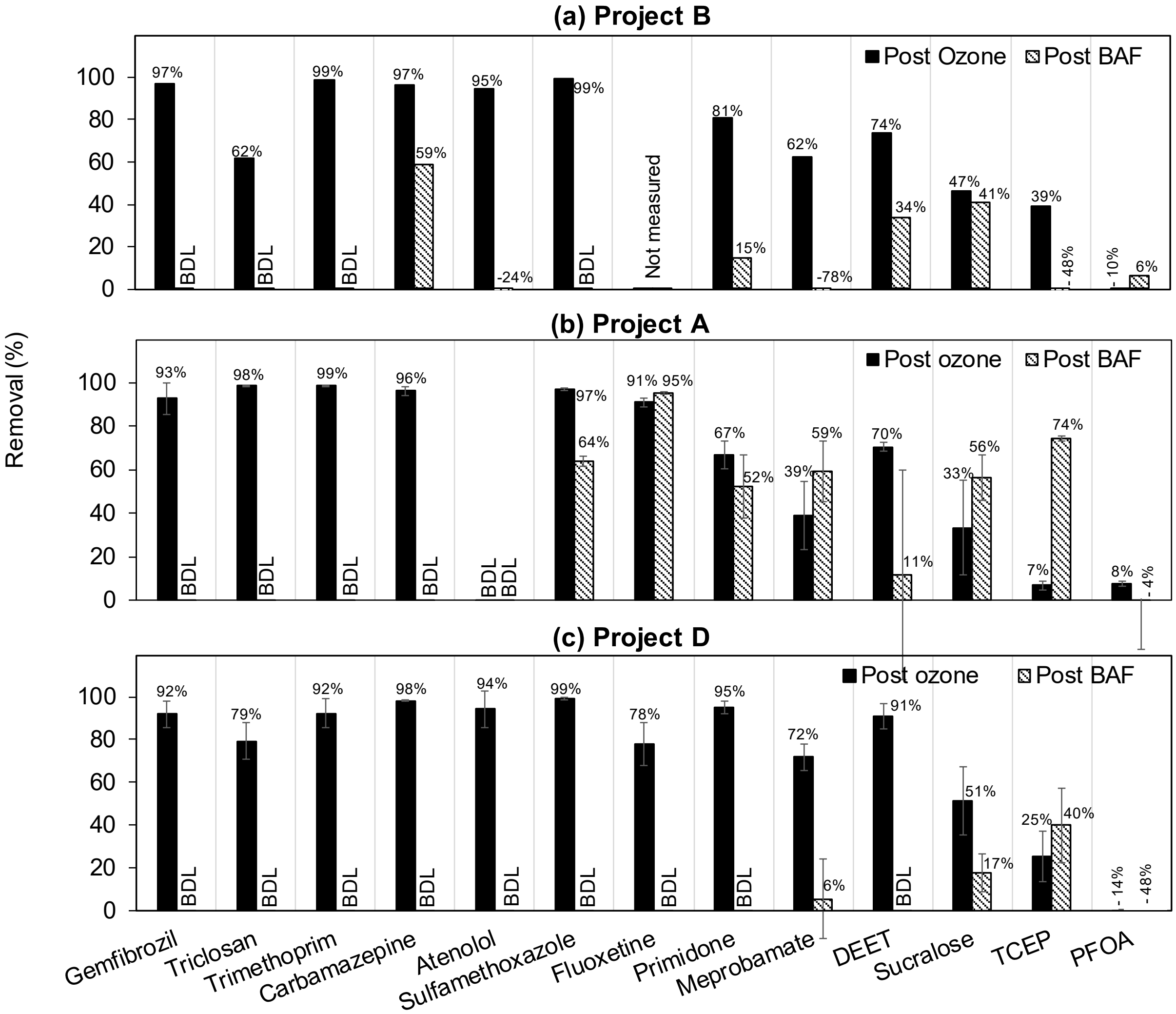


Figure 1-18. Removal of Selected CECs at Three Facilities.

Removals were calculated for ozone and BAF individually (i.e., they are not cumulative). Note that BDL appears when the ozone effluent was below or near detection limit, thus BAF removal could not be established. Percent removal after ozonation and BAF treatments are provided on top of the bars. The error bars denote standard deviation. Facilities employ a similar range of O_3:TOC/O_3:DOC (0.7-1.3) and an EBCT of 15 minutes.

Poorly-ozonated compounds such as sucralose were consistently low in removal through the ozonation process (removal range between 33.3 ± 21.6% to 51.1 ± 15.9%, across these studies). As expected, BAF did not provide significant improvement in the removal in the finished water in almost all cases. TCEP was not well removed by ozonation, but as shown in Projects A and D, additional removal was achieved by BAF. In the case of TCEP in Project B, the concentrations of TCEP in the influent water, ozonated effluent, and BAF effluent were already close to the detection limit; thus, the negative removal by BAF was most likely due to the slight variation in the concentration. PFOA, as expected, was also not removed well by ozonation and BAF. While it seems that PFOA were negatively removed in following ozonation (Projects B and D) and BAF (Projects A and D), the concentrations in the influent, post-ozone, and post-BAF were statistically similar (refer to Figure 1-15), and thus the negative removal was most likely just due to analytical/sampling variability.

The removals of compounds that were resistant to ozone/BAF treatment and insensitive to initial ozone concentrations in these three facilities were further compared to the removals in one facility employing similar ozone dose with two different EBCTs (Project F, O_3:DOC of 0.9 mg O_3/mg DOC and EBCT of 10 and 20 minutes). Compounds that were recalcitrant to BAF treatment at EBCT of 15 minutes (Figure 1-18) were removed at slightly higher extent in Project F at EBCT of 10 mins (Figure 1-19). Nevertheless, the slightly higher removal was most likely due to the remaining adsorption capacity of the media employed in Project F. Higher removal of the same compounds was even observed at Project F when extending the EBCT to 20 minutes. The increase in removal in this facility, however, may not be solely attributed to the small increase in EBCT but also due to potential remaining adsorption capacity of the GAC media at this facility. Indeed, compounds such as PFAS are not biodegradable, and thus, the enhanced removal at higher EBCT was most likely due to adsorption/desorption dynamics. This indicates the importance of understanding the remaining adsorption capacity of media in addition to EBCT, which is discussed further in the following Section.

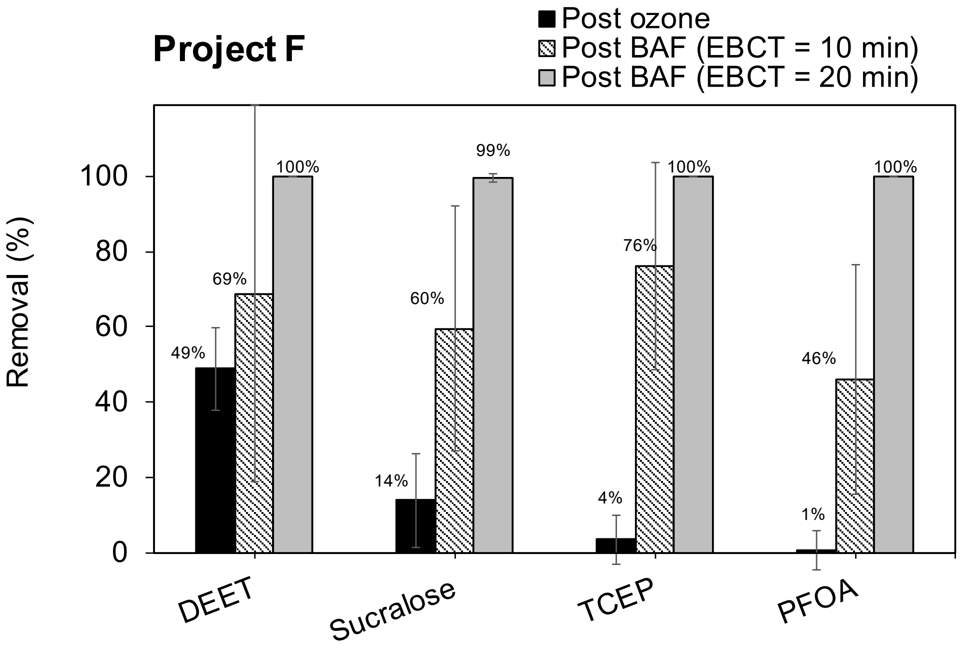


Figure 1-19. Persistent CEC Removals along the Treatment Train at Project F with O_3:DOC of 0.9 and an EBCT of 10 and 20 Minutes.

Removals were calculated for ozone and BAF individually (i.e., they are not cumulative). Percent removal after ozonation and BAF treatments are provided on top of the bars. The error bars denote standard deviation.

1.5.2.2 Effect of Media Type and Initial Media Condition on CEC Removal

Most of the evaluated studies utilized GAC in their biological filters although several facilities also employed other medias such as sand and anthracite. Previous studies have shown that vastly different microbial populations develop in different medias, with carbon-based media exhibiting greater microbial diversity, potentially impacting BAF performance (Gerrity et al. 2018; Greenstein et al. 2018; Vignola et al. 2018). The impact of media type on CEC removals in this study was assessed through comparison of selected CECs along the treatment train of two full-scale facilities utilizing different media types, but similar O_3:TOC ratios (0.5 – 0.65 mg O_3/mg

TOC). The Project J facility employs anthracite in their BAF system while the Project K facility utilizes GAC.

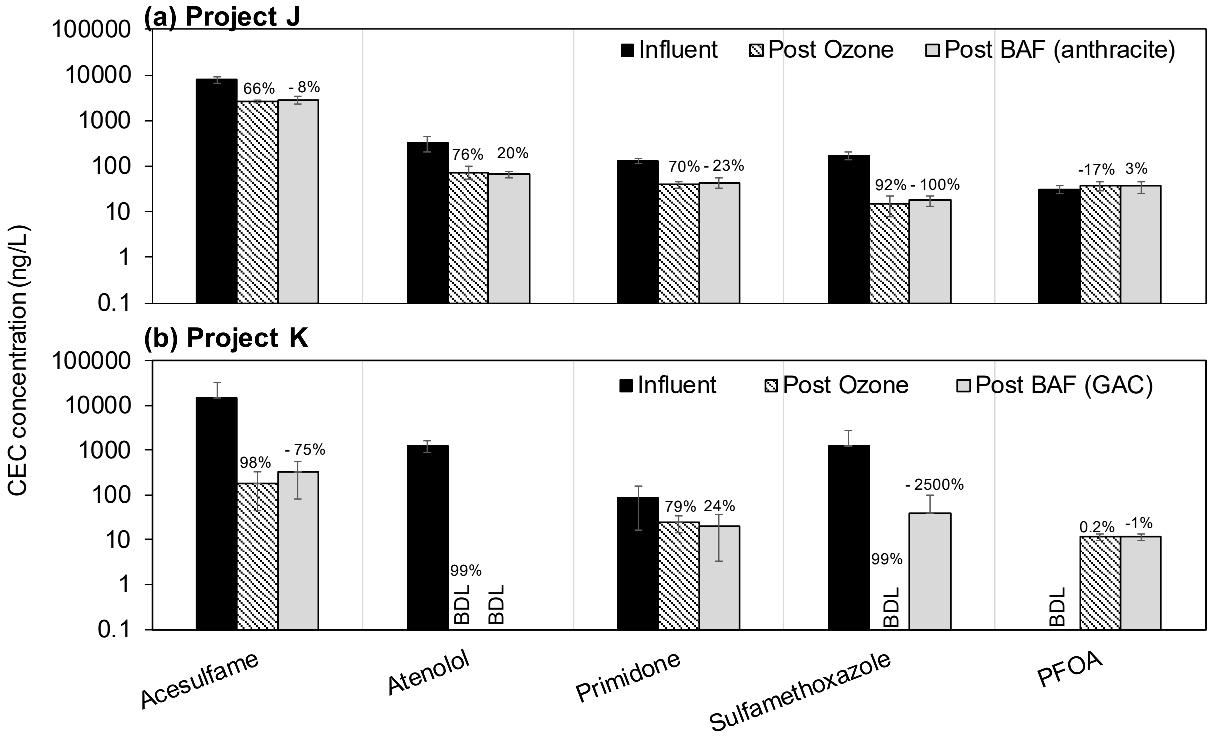


Figure 1-20. Comparison of CEC Concentrations in two Facilities Employing Different Media Filtration. (a) anthracite in Project J and (b) GAC in Project K. Both facilities utilized O_3:TOC between 0.5 to 0.65. Percent removal after ozonation and BAF treatments are provided on top of the bars. The error bars denote standard deviation.

As shown in Figure 1-20, the concentrations of some compounds such as acesulfame, atenolol, and sulfamethoxazole, were better reduced following ozonation in Facility K despite the similar O_3:TOC ratio applied. The better removal might be attributed to the varying wastewater characteristics such as the organic content and composition, presence of scavengers, etc. Nevertheless, the media configurations at both projects do not appear to provide additional removal of these compounds, as demonstrated by the similar concentrations in the ozone and BAF effluents. Both projects demonstrate that either ozone removes some CECs to a concentration that is too low to evaluate removals in the BAF or the BAF effluent causes slight addition of the CEC. It is important to note, however, that performance of BAF is also dependent on the media age, remaining adsorption capacity, and backwashing frequency (Gerrity et al. 2018).

A similar analysis was also performed by comparing two facilities that systematically evaluated medias (GAC in both cases) with different initial conditions: virgin or regenerated and exhausted. Virgin media is generally high in adsorption capacity but will provide limited removal via biodegradation at the beginning of operation. Regenerated media is a used media that has been thermally treated to restore its adsorptive capacity to a level similar to that of virgin media. Exhausted media on the other hand, has lost most of its adsorption capacity, which means that its contaminant removal capability largely depends on the biodegradability of the contaminants and the biological activity in the media (Servais, Billen, and Bouillot 1994). Nevertheless, exhausted GAC was also shown to retain its adsorption capacity after years of operation (Persson et al. 2007). Operational experience in South Africa with the ozone/BAC system in the 1980s showed benefits of leaving some 20% of spent GAC in the columns when recharging with virgin or regenerated GAC (Water Research Commission 1982).

Figure 1-21 shows the concentrations of selected CECs in two facilities that employ medias with different initial conditions (virgin/regenerated versus exhausted). Trimethoprim was removed to a high extent (>90%) by ozonation to below detection limit in both studies. Similarly, compounds such as azithromycin, diclofenac, atenolol, and carbamazepine were also removed to a high extent in Project H. Thus, low ozonated effluent concentrations of these compounds make it difficult to discern differences in BAF removal efficiencies. While BAF removal could be evaluated for the same compounds in Project M, there was no significant difference between virgin and exhausted media in this project. Sulfamethoxazole and primidone, however, seemed to be better removed by virgin/regenerated media in both projects, although sulfamethoxazole removal in Project M varied more. Lastly, sucralose and acesulfame, as expected, were poorly removed by GAC treatment due to their polar nature thereby hindering adsorption and their lack of biodegradability. In both projects, sucralose seemed to be better removed by virgin or regenerated media. Acesulfame's removal by BAF varied more, especially in Project M, but the exhausted medias used in both projects seem to cause some spikes of acesulfame in the BAF effluents. Contaminant breaching may potentially occur when there is biomass sloughing in the biofilter which can be caused by backwashing, blending, and other factors that might shift the biomass population (Lauderdale et al. 2011; Lauderdale et al. 2014). Soluble microbial products (SMPs) from the biofilter were shown to be released into the ozone/BAF effluent, causing an increase in TOC and fluorescence (Bacaro et al. 2019). Desorption and minor fluctuations in the concentration in the influent when the compounds are close to the reporting limit might also contribute to the minor spikes in the BAF effluents.

It is also important to note that in addition to the factors mentioned above, BAF performance is also influenced by media age and backwashing frequency and intensity (Arnold et al. 2018; Sundaram et al. 2020). The effect of media age is especially important when utilizing GAC as the contaminant removal mechanism will transition from carbon-based to mixed carbon to non-carbon-based (e.g. biodegradation, adsorption to biofilms) and finally to full biodegradation at approximately 20,000 bed volumes (BV) (Sundaram et al. 2020). While the adsorption capacity is expected to be the highest at lowest BV, exhausted media still retains some adsorption capacity (Reungoat et al. 2011). For example, Bourgin et al. (2018) showed that GAC can still be effective in removing CECs by adsorption even after 50,000 BVs. Thus, to gain a better understanding of the removal mechanisms during ozone/BAF treatment, extended field testing around this issue is warranted.

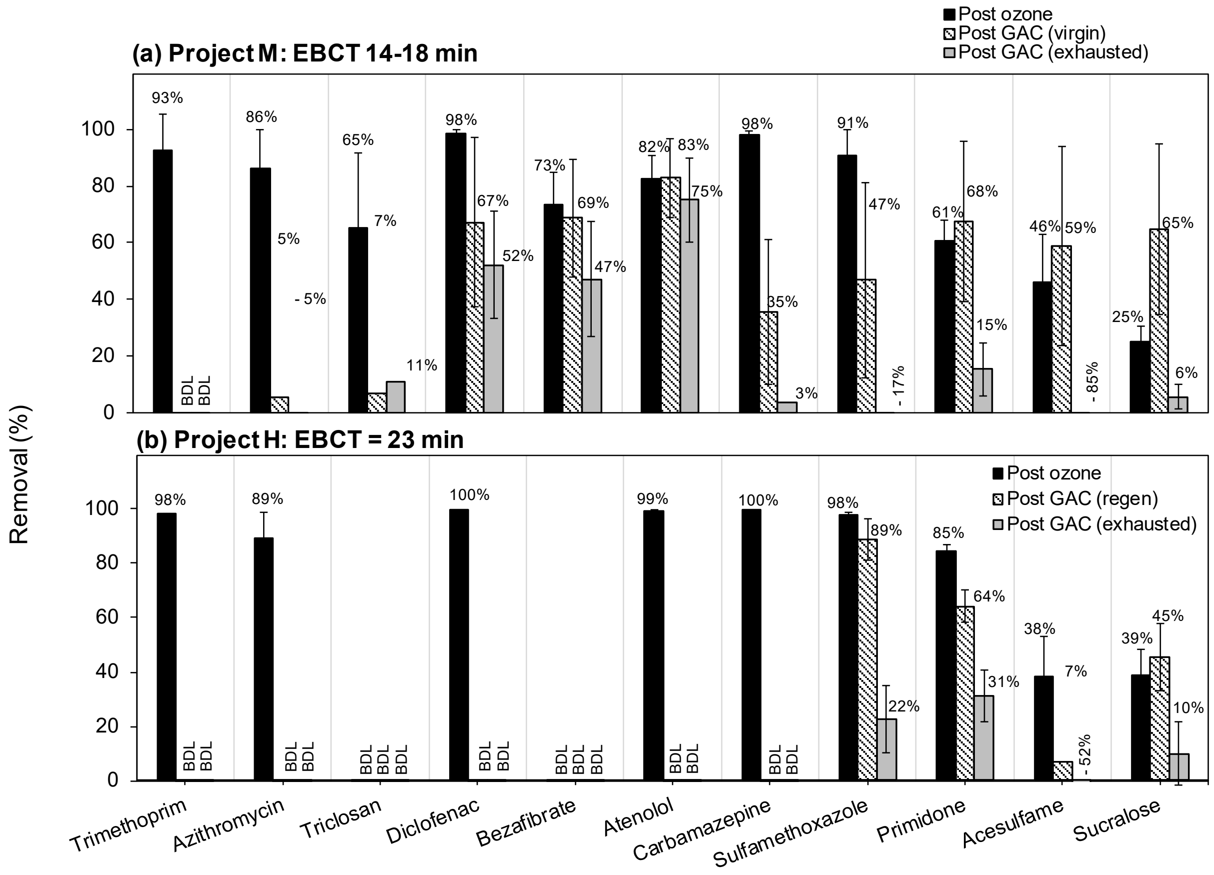


Figure 1-21. Comparison of Two Projects Employing GAC with Different Initial Conditions. (a) Project M employing O_3:TOC of 0.5 mg/mg and EBCT of 14 and 18 minutes for virgin and exhausted media, respectively; (b) Project H employing O_3:TOC of 0.65 mg/mg and EBCT of 23 minutes for both types of media (regenerated and exhausted). Percent removal after ozonation and BAF treatments are provided on top of the bars. The error bars denote standard deviation.

1.5.3 Effect of Backwashing Strategies

Filter backwashing regime is an important variable that may impact the performance of an engineered biofiltration system as it can affect the stability of the microbial community within the filters (Gerrity et al. 2018). When there is a shift in biomass population, die-off and biomass sloughing can occur, as demonstrated by an increase in the fluorescence in the filter effluent, indicating a release of SMPs (Bacaro et al. 2019). A study by Gerrity et al. (2018) investigating the change in the microbial community as affected by backwashing regime showed that infrequent backwashing may result in the colonization of *Bradyrhizobium*, a known ammonifier and secretor of EPS. Release of SMPs in the filter effluent may be problematic for plants that target significant TOC removal. The sloughing events may also cause a breach of other contaminants, including CECs, into the filter effluent, although more systematic studies are needed to better understand this phenomenon.

Based on the questionnaire responses, very limited information was obtained regarding backwashing regime during ozone/BAF operations. Based on the responses from six studies, backwashing was generally performed weekly (1-2 times), although it can be stretched to once every two weeks or once a month (Figure 1-22). The backwashing rate ranged from 5 to 20 gpm/sf, using mainly non-chlorinated water sourced either from tertiary effluent, filtered secondary effluent, or BAF filtrate. Most of the studies also indicated that air scouring was performed as part of the backwashing regime. The sequence for backwashing, based on two studies, generally started by air scouring, followed by high and then low flow rate backwashing. Further study on the effect of different backwashing regimes on BAF performance in relation to CEC removal is still currently warranted.

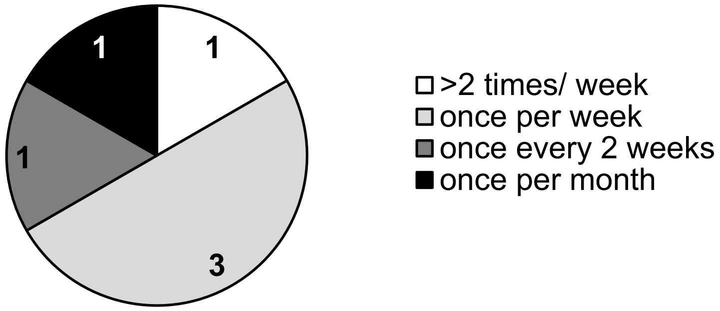


Figure 1-22. Backwashing Frequency Employed in some of the Projects Reviewed.

1.5.4 Common Issues with BAF Systems and Mitigation Strategies

As previously mentioned, detachment and particle breakthrough in the BAF filtrate is one major issue in the operation of an ozone/BAF system targeting bulk organic removal. Biomass sloughing may be attributed to the disruption in the microbial community causing biomass overgrowth and/or die-off. When excessive biomass occurs as bulk and trace contaminants are removed by the filter, the pore spaces become congested, resulting in higher shear forces within those spaces and eventually leading to head buildup, contaminant breakthrough, and operational difficulties (Hijnen and Medema 2010). Optimization of filter backwashing then becomes important not only to curb excessive accumulation of solids and/or biological growth, but also to ensure that there is sufficient biological activity for contaminant degradation. Including hydraulic bumps (i.e. bump cycle) during the backwashing period can also remove air accumulation in the biofilters (Aquino 2017). This is particularly important for ozone/BAF systems as oxygen is added during ozonation. Gas binding accumulation in the filter media can hinder water flow through the filter, potentially leading to a decrease in filter efficiency. A hydraulic bump cycle every four hours was shown to be beneficial in eliminating gas binding in the biofilters following ozonation (Trussell et al. 2016).

1.6 Fate and Transport of CECs in Ozone/BAF Systems

Systematic analysis of selected CEC removals across multiple studies as shown in the previous discussions were expanded for a wide range of CECs to create a database that could be linked to the design and operational data. In this study, approximately 400 compounds were identified and their removals following ozonation and BAF treatments were calculated and analyzed. One hundred forty-seven of those approximately 400 compounds were then selected for prioritization based on their percent removal during ozonation process and the number of available data points. Seventy-one of these compounds with greater than two data points were first categorized for prioritization based on their removal by ozone oxidation and their sensitivity to O_3:TOC ratio (Table 1-3). The same compounds were then further categorized based on their removal by BAF (after ozonation) and media condition (Table 1-5). As the remaining 77 compounds only have ozonation removal frequency less than two, meaning that removal was only based on one measurement, these compounds were categorized as compounds that require further investigation (Table 1-4 and Table 1-6).

1.6.1 CEC Removal During Ozonation Treatment

Approximately 30% of the 70 analyzed compounds exhibited removals greater than 90% by ozone oxidation (Table 1-3). Compounds with known k_{O3} values in this category such as estrone, carbamazepine, diclofenac, sulfamethoxazole, etc. exhibit high values ($k_{O3} > 10^3 M^{-1}s^{-1}$), indicating their high susceptibility to molecular ozone oxidation. However, compounds with relatively low to moderate k_{O3} values but high k_{OH} values, could also demonstrate high removal via hydroxyl radical oxidation. Very high removal (without peroxide) could also be achieved when the compound structure contains active reaction sites for oxidation. For example, ibuprofen was considered a readily oxidizable compound most likely due to its high k_{OH} value and the presence of an aromatic group in its structure. Some of these compounds, as previously discussed, showed some dependency on O_3:TOC ratio such as sulfamethoxazole, fluoxetine, triclosan, and dilantin, while the majority showed high removal independent of O_3:TOC ratio (e.g., triclocarban, gemfibrozil, trimethoprim, etc.). A number of the compounds with number of data points less than two (thus not included in the 70 main compounds) were also identified as potentially highly oxidizable (23 compounds), as shown in Table 1-4. Indeed, this category contains compounds with potentially high oxidation rates and are commonly used such as antibiotics (amoxicillin, roxithromycin, etc.), anti-inflammatories (acetaminophen), and other personal care products (parabens). Therefore, further investigation is required to confirm their level of removal and sensitivity to O_3:TOC ratio.

About 38% of the 70 compounds demonstrated moderate sensitivity to ozonation, with removals varying between 50 to 90%. Based on this study, only a few compounds showed susceptibility to O_3:TOC ratio, namely atenolol, DEET, meprobamate, and primidone. Compounds such as diuron, azithromycin, mecoprop, caffeine, and citalopram showed consistent levels of removal (at least in more than two separate measurements), suggesting that they are less sensitive to O_3:TOC ratio. The removal of azithromycin, however, was close to 90%, suggesting that it lies somewhere between the highly and moderately oxidized categories. The remaining compounds in this category (18 compounds) require further investigation regarding sensitivity to O_3:TOC ratio. Thirty-six compounds with removal occurrence frequency less than two were also categorized as moderately oxidizable, although further study is needed to confirm the level of removal and their sensitivity to O_3:TOC ratio (Table 1-4).

The last category (32% out of 70 compounds) shows the compounds with low removal by ozonation (<50%). Most of the compounds categorized in this group showed less sensitivity to O_3:TOC ratio, suggesting that they tend to be recalcitrant to ozone. Some of these compounds even increased during ozonation, such as NDMA, suggesting the presence of precursor compounds in the influents. Sucralose, interestingly, while showing poor removal by oxidation as the removals across multiple facilities were consistently below 50%, still showed slight susceptibility to O_3:TOC ratio. Based on the removal level and the occurrence frequency, compounds such as acesulfame, candesartan, hydrochlorotiazide, irbesartan, lopressor, and iopamidol were also categorized as poorly oxidized and their susceptibility to O_3:TOC ratio is still unknown. However, their removals significantly varied and there is a potential that they are on the cusp between moderately and poorly oxidized categories. These compounds, in addition to the 19 compounds with low occurrence frequency (Table 1-4) require further investigation.

It is important to note that while some compounds were shown to be dependent on O_3:TOC ratio such as sulfamethoxazole and sucralose in a number of discrete systematic studies, comparing the results with other studies at similar O_3:TOC ratio yielded mixed results. This suggests that the relationship between CEC removal and O_3:TOC ratio may be impacted by confounding factors such as the wastewater matrix components might also play a role. For example, as previously discussed, initial concentrations might play a role in determining the removals of several compounds, but the trend was inconsistently demonstrated. Other factors such as pH, dissolved organic matter content and composition potentially affecting hydroxyl radical formation as well as the presence of scavengers such as alkalinity, ammonia and nitrite might also impact the ozone stability (Bourgin et al. 2018; Chys et al. 2018b). Therefore, there is still a need for systematic evaluations of these issues.

Table 1-3. Characterization of CECs based on their Removal by Oxidation and Sensitivity to O_3:TOC Ratio.

	Readily Oxidized (Avg. removal >90%)					Moderately Oxidized (Avg. Removal 50–90%)					Marginally Oxidized (Avg. Removal <50%)				
Less Sensitive to O_3:TOC	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**
	Estrone	Hormones	6.2 x 10^{3} –2.1 x 10^{7}	1.1 x 10^{9} –7 x 10^{10}	4	Diuron	Herbicides	14.8	4.6 x 10^{9}	4	TCPP	Flame retardants	--	--	10
	Triclocarban	Personal care products	--	--	6	Mecoprop	Pesticides	--	--	3	TDCPP	Flame retardants	--	--	4
	Carbamazepine	Pharmaceuticals	3 x 10^{5}	8.8 x 10^{9}	18	Azithromycin[b]	Pharmaceuticals	--	--	5	TCEP	Flame retardants	1	6 x 10^{8}	11
	Gemfibrozil	Pharmaceuticals	--	--	12	Caffeine	Pharmaceuticals	650	5.9–6.9 x 10^{9}	6	Iopromide	Medical contrast agents	0.8	3.3 x 10^{9}	3
	Trimethoprim	Pharmaceuticals	3 x 10^{5}	8.92 × 10^{9}	11	Citalopram	Pharmaceuticals	--	--	3	NMOR	Nitrosamines	--	--	3
	Naproxen	Pharmaceuticals	2 x 10^{5}	9.6 × 10^{9}	10						NDMA[a]	Nitrosamines	--	--	5
	Diclofenac	Pharmaceuticals	1 x 10^{6}	7.5 × 10^{9}	9						Simazine	Pesticides	4.3 (pH 5)	2.9 x 10^{9}	4
	Diltiazem	Pharmaceuticals	--	--	4						PFOS[a]	PFAS	--	--	4
	Ibuprofen	Pharmaceuticals	9.1	7.4 × 10^{9}	4						PFOA	PFAS	<1	<1 x 10^{9}	10
	Diphenhydramine	Pharmaceuticals	--	--	2						PFHxA[a]	PFAS	--	--	8
	Lidocaine	Pharmaceuticals	7.3 × 10^{4}	1 x 10^{10}	2						PFHpA[a]	PFAS	--	--	5
	Lincomycin	Pharmaceuticals	--	--	2						PFDA[a]	PFAS	--	--	4
	Sulfadiazine	Pharmaceuticals	--	--	2						PFPeA[a]	PFAS	--	--	4
	Sulfadimethoxine	Pharmaceuticals	--	--	2						PFNA[a]	PFAS	--	--	3
	Tramadol	Pharmaceuticals	4 × 10^{3}	6.3 × 10^{9}	2						PFBS[a]	PFAS	--	--	2
	Venlafaxine	Pharmaceuticals	8.5 x 10^{3}	1 x 10^{10}	2						Cotinine	Pharmaceuticals	--	--	5
More Sensitive to O_3:TOC	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**
	Triclosan	Personal care products	4 × 10^{7}	1 x 10^{10}	13	DEET	Pesticides	10	4.95 x 10^{9}	16	Sucralose	Artificial sweeteners	<0.1	1.6 x 10^{9}	14
	Dilantin	Pharmaceuticals	--	-	3	Atenolol	Pharmaceuticals	1.7 × 10^{3}	7.05 x 10^{9}	14					
	Fluoxetine	Pharmaceuticals	--	-	6	Meprobamate	Pharmaceuticals	1	4 x 10^{9}	10					
	Sulfamethoxazole	Pharmaceuticals	2.6 × 10^{6}	5.5 × 10^{9}	16	Primidone	Pharmaceuticals	1	7 x 10^{9}	13					
Sensitivity to O_3:TOC Needs Further Evaluation						**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**
						Iohexol	Medical contrast agents	–	3.21 x 10^{9}	3	Acesulfame[b]	Artificial sweeteners	88	4.5 x 10^{9}	9
						NPYR	Nitrosamines	--	--	2	Candesartan[b]	Pharmaceuticals	563	0	2
						Benzotriazole	Industrial chemicals	20	6.2 x 10^{9}	5	Hydrochlorothiazide[b]	Pharmaceuticals	1.64 × 10^{4} (pH 9)	5.7 x 10^{9}	2
						Bisphenol A	Endocrine disruptors	7 x 10^{5}	1 x 10^{10}	3	Irbesartan[b]	Pharmaceuticals	23	0	2
						2,4-D	Herbicides	5.3 (pH 2)	3.21 x 10^{9}	2	Lopressor[b]	Pharmaceuticals	--	--	2
						Atrazine	Pesticides	6–7.9	2.4–3.0 x 10^{9}	2	Iopamidol[b]	Medical contrast agents	--	--	2
						Amisulpride	Pharmaceuticals	1.5 x 10^{5}	0	2					
						Antipyrine	Pharmaceuticals	--	--	2					
						Bezafibrate	Pharmaceuticals	590	7.4 x 10^{9}	2					
						Clarithromycin	Pharmaceuticals	4 × 10^{4}	7.5 x 10^{9}	2					
						Erythromycin	Pharmaceuticals	--	--	2					
						Gabapentin	Pharmaceuticals	2.2 × 10^{4}	9.1 x 10^{9}	3					
						Metoprolol	Pharmaceuticals	2 × 10^{3}	8.39 x 10^{9}	4					
						Oxazepam	Pharmaceuticals	1	9.1 x 10^{9}	2					
						Paraxanthine	Pharmaceuticals	--	--	2					
						Ranitidine	Pharmaceuticals	4.1 × 10^{6}	1 x 10^{10}	2					
						Salicylic Acid	Pharmaceuticals	--	--	2					
						Theophylline	Pharmaceuticals	--	--	2					

[a] Formed during ozonation

[b] Removals were at the highest limit of the category

Table 1-4. Additional Compounds Requiring Further Investigation during Ozonation.

Readily oxidized (Avg. Removal >90%)					Moderately oxidized (Avg. Removal 50–90%)					Marginally oxidized (Avg. Removal <50%)				
Compound	**Category**	k_{O3}	k_{OH}	**Count**	**Compound**	**Category**	k_{O3}	k_{OH}	**Count**	**Compound**	**Category**	k_{O3}	k_{OH}	**Count**
4-nonylphenol - semi quantitative	Nonylphenols	--	--	1	Testosterone	Hormones	--	--	1	4-androstene-3,17-dione	Hormones	--	--	1
4-tert-Octylphenol	Nonylphenols	--	--	1	Ethylparaben	Personal care products	--	7.7×10^9	1	Triethyl phosphate	Industrial chemicals	--	--	1
Methylparaben	Personal care products	4.1×10^5 (pH 6)	6.8×10^9	1	Galaxolide	Personal care products	--	--	1	Tris(chloroethyl) phosphate	Flame retardants	--	--	1
Propylparaben	Personal care products	2.5×10^5 (pH 2)	8.6×10^9	1	Tonalid	Personal care products	--	--	1	Tris(chloropropyl) phosphate isomers	Flame retardants	--	--	1
Di(2-Ethylhexyl)phthalate	Pesticides	--	--	1	3,4-Dichloroaniline	Pesticides	--	--	1	1,4-Dioxane	Industrial chemicals	--	--	1
Acetaminophen	Pharmaceuticals	--	--	1	Bromoxynil	Pesticides	--	--	1	Triclopyr	Pesticides	--	--	1
Aliskiren	Pharmaceuticals	--	--	1	Carbendazim	Pesticides	--	--	1	PFHxS	PFAS	--	--	1
Amoxicillin	Pharmaceuticals	--	--	1	Dicamba	Pesticides	--	--	1	Lamotrigine	Pharmaceuticals	--	7.7×10^9	1
Atorvastatin	Pharmaceuticals	--	--	1	Fluroxypyr	Pesticides	--	--	1	Nicotine	Pharmaceuticals	--	--	1
Cephalexin	Pharmaceuticals	--	--	1	Hexazinone	Pesticides	--	--	1	Bromate[a]	DBP	--	--	1
Cetirizine	Pharmaceuticals	--	--	1	MCPA	Pesticides	--	--	1	N-Nitrosodibutylamine (NDBA)[a]	Nitrosamines	--	--	1
Diethylphthalate	Pharmaceuticals	--	--	1	Metalaxyl	Fungicides	--	--	1	Acetaldehyde[a]	Personal care products	--	--	1
Frusemide	Pharmaceuticals	--	--	1	Metolachlor	Pesticides	--	--	1	Acetone[a]	Personal care products	--	--	1
Indomethacin	Pharmaceuticals	--	--	1	Tebuconazole	Pesticides	--	--	1	Formaldehyde[a]	Personal care products	--	--	1
Losartan	Pharmaceuticals	5.3 x 10^4	--	1	Terbutryn	Pesticides	--	--	1	2,3,7,8-TCDD[a]	Pesticides	--	--	1
Phenazone	Pharmaceuticals	1×10^5	5.3 x 10^9	1	Butalbital	Pharmaceuticals	--	--	1	Desisopropyl Atrazine[a]	Pesticides	--	--	1
Propranolol	Pharmaceuticals	7×10^4	1 x 10^{10}	1	Carisoprodol	Pharmaceuticals	--	--	1	PFBA[a]	PFAS	--	--	1
Roxithromycin	Pharmaceuticals	--	--	1	Cimetidine	Pharmaceuticals	--	--	1	PFDoA[a]	PFAS	--	--	1
Sulfasalazine	Pharmaceuticals	--	--	1	Dehydronifedipine	Pharmaceuticals	--	--	1	Dichloromethane[a]	VOCs	3.4×10^5 (pH 6)	--	1
Theophylline (semi-quantitative)	Pharmaceuticals	--	--	1	Doxylamine	Pharmaceuticals	--	--	1					
Carbon disulfide	VOCs	--	--	1	Eprosartan	Pharmaceuticals	--	--	1					
Toluene	VOCs	--	--	1	Fexofenadine	Pharmaceuticals	1	--	1					
					Levetiracetam	Pharmaceuticals	--	3.8×10^9	1					
					Meclofenamic Acid	Pharmaceuticals	--	--	1					
					Nifedipine	Pharmaceuticals	--	--	1					
					Norfloxacin	Pharmaceuticals	--	--	1					
					Oxycodone	Pharmaceuticals	10	--	1					
					Phenytoin	Pharmaceuticals	--	5×10^9	1					
					Sertraline	Pharmaceuticals	--	--	1					
					Telmisartan	Pharmaceuticals	--	--	1					
					Temazepam	Pharmaceuticals	38	--	1					
					Valsartan	Pharmaceuticals	--	6.7×10^9	1					
					Warfarin	Pharmaceuticals	--	--	1					
					2-Butanone	VOCs	--	--	1					
					p-Dichlorobenzene (1,4-DCB)	VOCs	4	--	1					

[a] Formed during ozonation

1.6.2 CEC Removal During BAF Treatment

The 70 CECs were further categorized in terms of their removals by BAF and filtration media condition, and in some cases their sensitivity to the change in EBCT. As shown in Table 1-5, CECs were first categorized into two major groups to identify whether BAF treatment provided an additional 50% removal following ozonation. Fifty-two percent of these compounds could not be additionally removed to a higher extent by BAF. However, about 30% of this category showed sensitivity to initial media condition, especially for virgin/regenerated media. Some compounds such as sucralose, acesulfame, sulfamethoxazole, primidone, and azithromycin were also shown to be sensitive to change in EBCT although a more systematic study is warranted to confirm these results. While 8% of the compounds in this category also showed insensitivity to media condition (iopromide, DEET, and clarithromycin), approximately 62% of the remaining compounds require further investigation to determine the impact of media condition and change in EBCT on their removal.

BAF was considered ineffective for removal of many trace organic contaminants (such as those without deprotonated amines that are amenable to biological treatment) as the expected primary degradation pathway is via cometabolism rather than degradation as is the case for a primary substrate like bulk organic matter (Gifford, Selvy, and Gerrity 2018; Bacaro et al. 2019). However, BAF treatment was also able to provide >50% additional removal following ozonation for approximately 48% of the 70 compounds analyzed, as long as ozonation did not reduce the concentrations below the analytical detection limit. Several of these compounds (about 18%) also demonstrated dependency on initial media condition. One notable example is flame retardants such as TCEP and Tris(1-chloro-2-propyl) phosphate (TCPP) which are recalcitrant to ozone but are better removed by virgin GAC compared to exhausted GAC, which indicates the importance of adsorption in their removal (Sundaram, Emerick, and Shumaker 2014). BAF was also able to provide >50% additional removal for 32% of the compounds in this category, regardless of the media condition. Two of the compounds in this sub-category (trimethoprim and atenolol) even demonstrated sensitivity to a change in EBCT, although more evidence is warranted. Further investigation is needed for the remaining compounds (50%) in this category to assess the impact of media condition and the change in EBCT on their removal.

The remaining 77 compounds (out of 147 compounds) were not categorized in the main BAF removal bin (Table 1-6) as they also require further investigation to: i) confirm the capability of BAF to provide additional removal due to the lack of data points in these studies and ii) assess their sensitivity to media condition and the change in EBCT during BAF operation.

Table 1-5. Characterization of CECs based on their Additional Removal by BAF and Dependency on Initial Media Condition.

	>50% Additional Removal by BAF			**<50% or no Additional Removal by BAF**		
Actual Removal not Influenced by Initial Media Condition (Virgin/Regenerated or Exhausted)	**Compound**	**Category**	**Count**	**Compound**	**Category**	**Count**
	Benzotriazole	Industrial chemicals	6	Iopromide	Medical contrast agents	4
	Diuron	Herbicides	5	DEET[a]	Pesticides	17
	Carbamazepine	Pharmaceuticals	12	Clarithromycin	Pharmaceuticals	3
	Trimethoprim[a]	Pharmaceuticals	2			
	Tramadol	Pharmaceuticals	3			
	Atenolol[a]	Pharmaceuticals	13			
	Citalopram	Pharmaceuticals	4			
	Amisulpride	Pharmaceuticals	3			
	Candesartan	Pharmaceuticals	3			
	Hydrochlorothiazide	Pharmaceuticals	3			
	Irbesartan	Pharmaceuticals	3			
Actual Removal Influenced by Initial Media Condition (Virgin/Regenerated or Exhausted)	**Compound**	**Category**	**Count**	**Compound**	**Category**	**Count**
	Triclosan[a]	Personal care products	6	Sucralose[a]	Artificial sweeteners	21
	Diclofenac[a]	Pharmaceuticals	5	Acesulfame[a]	Artificial sweeteners	13
	Bezafibrate[a]	Pharmaceuticals	4	Mecoprop	Pesticides	2
	Metoprolol	Pharmaceuticals	4	Perfluorooctanesulfonic acid	PFAS	6
	TCPP[a]	Flame retardants	17	Perfluorononanoic acid	PFAS	8
	TCEP[a]	Flame retardants	21	Sulfamethoxazole[a]	Pharmaceuticals	19
				Venlafaxine	Pharmaceuticals	3
				Primidone[a]	Pharmaceuticals	17
				Azithromycin[a]	Pharmaceuticals	4
				Gabapentin	Pharmaceuticals	3
				Meprobamate	Pharmaceuticals	15
Effect of Initial Media Condition not Systematically Evaluated	**Compound**	**Category**	**Count**	**Compound**	**Category**	**Count**
	TDCPP	Flame retardants	8	Estrone	Hormones	0 (BDL)
	Iopamidol	Medical contrast agents	3	Iohexol	Medical contrast agents	3
	NPYR	Nitrosamines	4	NMOR	Nitrosamines	6
	NDMA	Nitrosamines	10	Bisphenol A	Endocrine disruptors	1
	Triclocarban	Personal care products	3	2,4-D	Herbicides	2
	Fluoxetine	Pharmaceuticals	3	Simazine	Pesticides	4
	Diltiazem	Pharmaceuticals	3	Atrazine	Pesticides	1
	Gemfibrozil	Pharmaceuticals	5	PFOA	PFAS	17
	Naproxen	Pharmaceuticals	4	PFHpA	PFAS	10
	Ibuprofen	Pharmaceuticals	2	PFDA	PFAS	5
	Lincomycin	Pharmaceuticals	2	PFBS	PFAS	8
	Compound	Category	Count	Compound	Category	Count
	Sulfadiazine	Pharmaceuticals	2	PFHxA	PFAS	8

	>50% Additional Removal by BAF			<50% or no Additional Removal by BAF		
Effect of Initial Media Condition not Systematically Evaluated (Continued)	Sulfadimethoxine	Pharmaceuticals	2	PFPA	PFAS	5
	Caffeine	Pharmaceuticals	4	Lidocaine	Pharmaceuticals	1
	Antipyrine	Pharmaceuticals	2	Oxazepam	Pharmaceuticals	3
	Lopressor	Pharmaceuticals	1	Salicylic Acid	Pharmaceuticals	1
				Cotinine	Pharmaceuticals	8
				Dilantin	Pharmaceuticals	5
				Diphenhydramine	Pharmaceuticals	0 (BDL)
				Erythromycin	Pharmaceuticals	0 (BDL)
				Paraxanthine	Pharmaceuticals	5
				Theophylline	Pharmaceuticals	3
				Ranitidine	Pharmaceuticals	0 (BDL)

[a] Might be affected by changes in EBCT

Table 1-6. Additional Compounds Requiring Further Investigation during BAF Treatment.

Compound	Category	Count
Bromate	DBP	2
4-androstene-3,17-dione	Hormones	0 (BDL)
Testosterone	Hormones	0 (BDL)
N-Nitrosodibutylamine	Nitrosamines	2
4-nonylphenol (semi-quantitative)	Nonylphenols	0 (BDL)
4-tert-Octylphenol	Nonylphenols	0 (BDL)
1,4-Dioxane	Industrial chemicals	4
Diethylphthalate	Pharmaceuticals	0 (BDL)
Triethyl phosphate	Industrial chemicals	1
Tris(chloroethyl) phosphate	Flame retardants	1
Tris(chloropropyl) phosphate isomers	Flame retardants	1
Acetaldehyde	Personal care products	1
Acetone	Personal care products	1
Ethylparaben	Personal care products	0 (BDL)
Formaldehyde	Personal care products	1
Galaxolide	Personal care products	1
Methylparaben	Personal care products	0 (BDL)
Propylparaben	Personal care products	0 (BDL)
Tonalid	Personal care products	0 (BDL)
2,3,7,8-TCDD	Pesticides	0 (BDL)
3,4-Dichloroaniline	Pesticides	0 (BDL)
Bromoxynil	Pesticides	0 (BDL)
Carbendazim	Pesticides	2
Desisopropyl Atrazine	Pesticides	1
Di(2-Ethylhexyl)phthalate	Pesticides	0 (BDL)
Dicamba	Pesticides	1
Fluroxypyr	Pesticides	0 (BDL)
Hexazinone	Pesticides	0 (BDL)
MCPA	Pesticides	1
Metalaxyl	Fungicides	0 (BDL)
Metolachlor	Pesticides	1
Tebuconazole	Pesticides	0 (BDL)
Terbutryn	Pesticides	0 (BDL)
Diuron	Pesticides	1
Triclopyr	Pesticides	1
PFBA	PFAS	1
PFDoA	PFAS	1
PFHxS	PFAS	1
Acetaminophen	Pharmaceuticals	2
Aliskiren	Pharmaceuticals	2
Amoxicillin	Pharmaceuticals	0 (BDL)
Atorvastatin	Pharmaceuticals	0 (BDL)
Butalbital	Pharmaceuticals	0 (BDL)
Carisoprodol	Pharmaceuticals	0 (BDL)
Cephalexin	Pharmaceuticals	0 (BDL)
Cetirizine	Pharmaceuticals	2
Cimetidine	Pharmaceuticals	0 (BDL)
Dehydronifedipine	Pharmaceuticals	1

Compound	Category	Count
Doxylamine	Pharmaceuticals	0 (BDL)
Eprosartan	Pharmaceuticals	2
Fexofenadine	Pharmaceuticals	2
Frusemide	Pharmaceuticals	0 (BDL)
Indomethacin	Pharmaceuticals	0 (BDL)
Lamotrigine	Pharmaceuticals	2
Levetiracetam	Pharmaceuticals	2
Losartan	Pharmaceuticals	2
Meclofenamic Acid	Pharmaceuticals	0 (BDL)
Nicotine	Pharmaceuticals	3
Nifedipine	Pharmaceuticals	0 (BDL)
Norfloxacin	Pharmaceuticals	0 (BDL)
Oxycodone	Pharmaceuticals	0 (BDL)
Phenazone	Pharmaceuticals	2
Phenytoin	Pharmaceuticals	0 (BDL)
Propranolol	Pharmaceuticals	0 (BDL)
Roxithromycin	Pharmaceuticals	0 (BDL)
Sertraline	Pharmaceuticals	0 (BDL)
Sulfasalazine	Pharmaceuticals	1
Telmisartan	Pharmaceuticals	2
Temazepam	Pharmaceuticals	1
Theophylline (semi-quantitative)	Pharmaceuticals	0 (BDL)
Valsartan	Pharmaceuticals	2
Warfarin	Pharmaceuticals	0 (BDL)
2-Butanone	VOCs	0 (BDL)
Carbon disulfide	VOCs	0 (BDL)
Dichloromethane	VOCs	0 (BDL)
p-Dichlorobenzene (1,4-DCB)	VOCs	0 (BDL)
Toluene	VOCs	0 (BDL)

1.6.3 Presence of Recalcitrant CECs and Transformation Products in Ozone/BAF Effluent

Based on the discussions above, there are presently some compounds that demonstrate insensitivity to either ozone treatment alone or ozone in combination with BAF treatment. These compounds are categorized as shown in Table 1-7. BAF does provide >50% additional removal for ten of the compounds not effectively removed by ozone. These include flame retardants, PFAS, and nitrosamines. Some compounds (e.g., NDMA, acetaldehyde, and formaldehyde) were even formed during ozonation, but BAF was able to remove these compounds to a large extent. These results demonstrate the benefit of BAF in providing an additional barrier preventing passage of these ozone-recalcitrant compounds to the finished water. In some cases, BAF also provided additional removal for compounds that are not removed well by membrane-based treatment (e.g., aldehydes and glyoxals). Note that TCEP was shown to be negatively removed; however, TCEP was not formed during ozonation. The negative removal was due to the slight variation in the concentrations in the influents, ozone effluents, and BAF effluents, which were generally at very similar levels.

The remaining 26 compounds that were marginally removed by ozonation or formed during ozonation were not well removed by BAF. Notable examples are PFOA and sucralose, which show consistently low removals after ozone/BAF treatment in all cases. Some shorter chain PFAS were also shown to increase after ozonation, suggesting chain breaking may be occurring during ozonation (Glover, Quiñones, and Dickenson 2018). These same shorter chain PFAS were not well removed by BAF.

Table 1-7. Recalcitrant Compounds in Ozone/BAF Systems.

	>50% Additional Removal by BAF					<50% or no Additional Removal by BAF				
	Compound	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**
Marginally Oxidized (Avg. Removal <50%)	TCPP	Flame retardants	--	--	10	Simazine	Pesticides	4.3 (pH 5)	2.9 x 10^9	4
	TDCPP	Flame retardants	--	--	4	Cotinine	Pharmaceuticals	--	--	5
	Lamotrigine	Pharmaceuticals	--	7.7×10^9	1	PFOS	PFAS	--	--	4
						Iopromide	Medical contrast agent	0.8	3.3 x 10^9	3
						NMOR	Nitrosamines	--	--	3
						1,4-Dioxane	Industrial chemicals	--	--	1
						Triethyl phosphate	Industrial chemicals	--	--	1
						Tris(chloropropyl) phosphate isomers	Flame retardants	--	--	1
						Triclopyr	Pesticides	--	--	1
						PFHxS	PFAS	--	--	1
						Nicotine	Pharmaceuticals	--	--	1
						4-androstene-3,17-dione	Hormones	--	--	1
						Tris(chloroethyl) phosphate	Other CECs	--	--	1
						Sucralose	Artificial sweeteners	<0.1	1.6 x 10^9	14
Negatively Removed during Ozonation	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**	**Compound**	**Category**	**k_{O3}**	**k_{OH}**	**Count**
	TCEP	Flame retardants	1	6 x 10^8	11	PFOA[a]	PFAS	<1	<1 x 10^9	10
	NDMA[a]	Nitrosamines	--	--	5	Bromate[a]	DBP	--	--	1
	Acetaldehyde[a]	Personal care products	--	--	1	NDBA	Nitrosamines	--	--	1
	Acetone	Personal care products	--	--	1	PFHxA	PFAS	--	--	8
	Formaldehyde[a]	Personal care products	--	--	1	PFHpA	PFAS	--	--	5
	PFDoA	PFAS	--	--	1	PFDA	PFAS	--	--	4
						PFPA	PFAS	--	--	4
						PFNA	PFAS	--	--	3
						PFBS	PFAS	--	--	2
						PFBA	PFAS	--	--	1
						2,3,7,8-TCDD	Pesticides	--	--	1
						Desisopropyl Atrazine	Transformation products (atrazine)	--	--	1
						Dichloromethane	VOCs	3.4×10^5 (pH 6)	--	1

[a] Formed during ozonation

1.6.4 Performance Surrogates and Indicators for Ozone/BAF CEC Removal

1.6.4.1 Ozone/BAF Performance Surrogates

A surrogate parameter is defined as quantifiable change of a bulk parameter that can be used to measure the performance of a unit process in removing trace organic compounds (Drewes et al. 2008). TOC and UVA were the most monitored surrogates for process control followed by fluorescence and COD, as shown in Figure 1-23. Other surrogates monitored in the review studies included DBPs, effluent organic matter (EfOM), and nutrients. Most of the studies indicated no nitrite control strategies implemented; however, there are two studies that included nitrite for ozone dose normalization (Projects A and B).

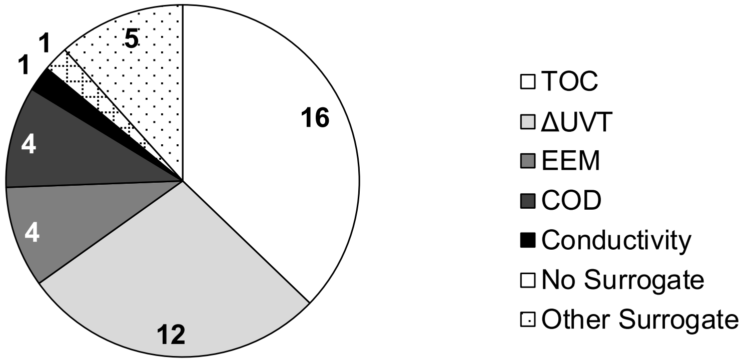


Figure 1-23. Various Process Control Surrogates used in the Reviewed Studies.

Previous studies have shown that UVA removal was higher with the combined ozone/BAF process compared to BAF alone, suggesting that ozone removed unsaturated and/or aromatic carbons (Ibn Abdul Hamid et al. 2019; Im et al. 2019; G. Li et al. 2018). This also suggests that UVA removal might be a good performance surrogate for ozonation. Indeed, a study showed that the change in UVA removal correlated with removal of trace organic compounds with a broad range of ozone reactivity (Gerrity et al. 2012; Chys et al. 2018a). However, it is recommended that a reliable online ultraviolet-visible spectroscopy (UV-VIS) sensor equipped with cleaning mechanism be installed to better estimate removal of trace organic compounds. Total fluorescence (TF) may also be a reliable performance indicator, with slightly better reproducibility compared to UVA. A study of the UV/AOP process also confirmed that both UVA and TF had the highest linear correlation with removal of trace organic compounds, demonstrating their potential as strong surrogates (Miklos et al. 2019).

In contrast, TOC removal may not correlate well with the removal of trace organic compounds during ozonation due to minimal TOC reduction by ozonation alone. While TOC reduction was minimal, there was a clear transformation of bulk organic matter, as demonstrated by the change in UVA and EEM (Bacaro et al. 2019). Thus, TOC may be a more suitable performance surrogate during biofiltration. A study by Tackaert et al. showed that online TOC monitoring provided a powerful tool to detect and respond to chemical pulses during ozone/BAF treatment (i.e. detecting potential operational/water quality upsets) (Tackaert et al. 2019). Nevertheless, data obtained by Bacaro et al., suggested that TOC removal was not a reliable surrogate for

NDMA removal during biofiltration (Bacaro et al. 2019), as it is not a universal surrogate that can be applied for all treatment objectives.

ATP can be used as a potential surrogate to better understand the biomass density in the BAF system (Bacaro et al. 2019). However, a study showed that ATP was insufficient to distinguish the performance of GAC and anthracite filters when GAC was shown to be superior in performance (Aquino 2017).

1.6.4.2 Prioritizing CECs for Potential Chemical Indicators

In addition to using performance surrogates, using chemical indicators is also beneficial to determine the optimum operational conditions for ozone/BAF, particularly for potential direct potable reuse (DPR). Selection of chemical indicators depends on the ozone/BAF treatment goals. Based on the current literature, chemical indicators employed for assessing ozone/BAF performance mostly include recalcitrant compounds such as NDMA, PFAS, TCEP, TCPP and Tris(1,3-dichloroisopropyl) phosphate (TDCPP) (Sundaram et al. 2020). By targeting recalcitrant compounds, the system can be expected to also remove the less recalcitrant ones, which may be more abundant; thus, covering the removal of a wider array of contaminants.

Predicting the performance of ozone/BAF, however, cannot solely rely on the most recalcitrant indicators. Potential indicators should be selected as representatives of different groups of contaminants based on their expected removals through the ozone/BAF process. For example, Table 1-8 shows a shortlist of potential indicators established by Swiss Federal Office for the Environment (FOEN) which are binned into three categories based on their expected removals (<50%, 50%-80%, >80%). The 12 indicators were selected because they are not easily biodegraded therefore are not well removed by conventional wastewater treatment processes. Note that the removal limits should be determined based on the project goals. The compounds included in FOEN’s list are also mostly used in Europe and may not be applicable in regions outside of Europe. As such, identification of universal potential indicators is warranted. A previous study has been conducted to identify potential indicators for bench- and full-scale ozonation and GAC (Drewes et al. 2008). The CEC prioritization results obtained in this study can then be used to expand the already established list to identify potential performance indicators for ozone/BAF systems.

Table 1-8. Twelve Indicators Established by the FOEN for Assessing Ozone/BAF Performance.

Data Source: Bourgin et al. 2018.

Category	Compound	Application	K_{O3}, pH 7 ($M^{-1} s^{-1}$)
Group I (>80% abatement)	Amisulpride	Pharmaceutical—Antipsychotics	1.5×10^5
	Carbamazepine	Pharmaceutical—Antiepileptic	3.0×10^5
	Citalopram	Pharmaceutical—Antidepressant	--
	Clarithromycin	Pharmaceutical—Antibacterial	4.0×10^4
	Diclofenac	Pharmaceutical—Anti-inflammatory	6.8×10^5
	Hydrochlorothiazide	Pharmaceutical—Diuretic	8.4×10^4
	Metoprolol	Pharmaceutical—Beta-blocker	2.0×10^3
	Venlafaxine	Pharmaceutical—Antidepressant	--
Group II (50-80% abatement)	Benzotriazole	Industrial chemical—corrosion inhibitor	140
	Methylbenzotriazole	Industrial chemical—corrosion inhibitor	460

Category	Compound	Application	K_{O3}, pH 7 ($M^{-1} s^{-1}$)
Group II (50-80% abatement) (continued)	Candesartan	Pharmaceutical—antihypertensive, angiotensin II antagonist	563
	Irbesartan	Pharmaceutical—antihypertensive, angiotensin II antagonist	23
Group III (<50% abatement)	Acesulfame	Food additive—sweetener	88
	Sucralose	Food additive—sweetener	<0.1

1.7 Summary and Conclusions

There are currently numerous studies investigating the use of ozone/BAF for water reuse. While there is an increasing interest in implementing ozone/BAF to act as a CEC barrier, the majority of ozone/BAF pilot- and full-scale facilities have so far focused on specific project goals and thus may not capture the full range of design and operational conditions and configurations. In this study, we collected design, operational, and water quality data from several demo-, pilot-, and full-scale ozone/BAF studies/projects around the world (United States, Australia, Namibia, Germany, Switzerland, and Austria) through a curated questionnaire and interviews and then compiled the data into a comprehensive database. We also integrated assessment of CEC performance data obtained from multiple facilities to identify the most relevant and challenging CECs from which to develop performance criteria for ozone/BAF treatment trains. One hundred and forty-seven compounds in multiple categories along the ozone/BAF treatment train were compared across multiple studies and benchmarked by common treatment variables such as O_3:TOC ratio, initial media condition, and EBCT. Through prioritization of a wide array of CECs, this study provides a shortlist of CEC data that can be utilized to identify potential performance-based indicators for ozone and BAF treatments.

To bring ozone/BAF into the mainstream for potable reuse application, technological challenges and knowledge gaps related to design and operation of ozone/BAF systems, need to be addressed. Some of the technology application boundaries identified include:

- Ozone/BAF performance in removing CECs is highly dependent on the influent water quality from the upstream secondary and tertiary treatment steps. Particularly, the type and effectiveness of the secondary biological treatment process seem to affect the water quality needed to improve performance of downstream ozone/BAF. The presence of radical scavengers such as TOC, alkalinity, and nitrite (to a lesser extent) in the influent water will impact ozone demand and dose, leading to higher costs and potentially reduced ozone/BAF performance if variations in those parameters are not properly accounted for through real-time monitoring and control. Thus, a highly treated influent with sufficient nutrient reduction (i.e., fully nitrifying plant) is needed for ozone/BAF systems. Higher SRT in the secondary treatment has also been shown to be beneficial in nutrient reduction with added benefit of CEC removal (Kim, Snoeyink, and Saunders 1976; Oppenheimer et al. 2007).
- TOC removal by ozone/BAF in most studies was less than 50% whereas a higher removal of TOC could be achieved by RO-based treatment (>90%). Thus, a polishing step such as GAC filtration following ozone/BAF treatment is often installed to increase TOC removal and/or minimize DBP formation potential.

- Ozone/BAF does not remove nitrate. To meet the primary MCL of 10 mg/L, nitrate would need to be addressed through upstream wastewater processes, additional advanced treatment technology, or side stream treatment. An effective nitrification and denitrification process should be capable of reducing effluent total nitrogen, majority of which is nitrate, to around 10 mg/L. Of the facilities reviewed, higher nitrate concentration was observed in facilities that achieved only partial denitrification. Other downstream or side stream treatment options for nitrate removal include IX or electrodialysis.
- While ozone/BAF removed trace organic contaminants including CECs comparably to RO-based treatment, ozone/BAF alone does not provide removal of salinity. Thus, blending with low TDS water (e.g., as at Windhoek, Namibia), a polishing step, or side stream treatment, such as RO, IX, or EDR, could be considered in some cases to address high TDS and comply with the secondary MCL and/or local limit requirements.

In addition to the technological issues listed above, some of the knowledge gaps identified in this review include:

- CEC removal in the facilities reviewed in this study was mostly evaluated for limited design and operational parameters. However, data interpretation becomes complicated due to the differences in water matrix (i.e., presence of scavengers, pH, organic matter, etc.) in addition to the lack of completeness in the dataset including operation parameters such as filtration rate, media age, etc. Thus, more systematic studies and side-by-side comparisons may be needed to fully evaluate a wider range of design and operational parameters. More extended field testing may also be beneficial to fully understand how and when the media condition changes (i.e., dynamic adsorption/desorption of certain compounds with exhausted GAC) with increasing bed volumes and the impact to ozone/BAF performance in reducing CECs.
- Many compounds were well removed by ozonation alone. Therefore, it was difficult to determine the performance of BAF in removing these compounds, especially as affected by different operational parameters (EBCT, type of media, etc.).
- Because the study had limited information regarding backwashing regimes in the studied facilities, additional studies are required to better understand how backwashing regime impacts BAF performance, particularly in terms of CEC removal. There is also a need to understand any change to incoming water quality parameters with the frequency of BAF backwashing.
- Selection of appropriate indicators based on recalcitrant compounds that can be universally applied needs to be further investigated. This review provides a short list of compounds that can be candidates for performance surrogates and CEC indicators.
- The impact of upstream secondary treatment on biomass characteristics in the BAF that may affect its performance and stability needs to be evaluated. For example, comparison of biomass characteristics for systems fed by high and low total suspended solids (TSS) influent is needed to understand the biomass during seeding and steady-state operation.

1.7.1 Public Outreach

While there is a definite interest in the application of potable reuse in many parts of the world to combat water scarcity, there is still a stigma associated with reusing water from sewage water, especially for non-environmental buffer application (i.e., DPR). Thus, there is a need for continuous outreach efforts to build public acceptance of potable reuse. In addition, the success of potable reuse programs is also highly dependent on the ability of the government and the surrounding community in understanding of the potable reuse concept and the impacts to health, safety, and environment (WHO 2017). Studies funded by The Water Research Foundation (WRF) (previously WateReuse Research Foundation) focusing on fostering the acceptance of potable reuse have been conducted in the last decade, providing guidelines and framework for public outreach through the development of both state- and community-level communication plans (Macpherson and Snyder 2013; Millan, Tennyson, and Snyder 2015). Using the correct terminology with clear and direct language to encourage positive mindset about potable reuse and avoid confusion which can instill fear is also important for the public to easily grasp the potable reuse concept (Macpherson and Snyder 2013; WHO 2017). Some of the key findings in achieving successful public outreach for potable reuse programs include:

- Familiarizing the public with the actual reuse systems implemented such as via a plant tour can be a great trust-building activity;
- Consistency in terminology and messaging throughout the outreach effort is important to avoid confusion;
- Information transparency is crucial to forge trust and build relationships, especially when faced with difficult questions associated with health, safety, and environment;
- Information should be made readily available and easily accessible to public. The use of social media may be beneficial in continuously engaging public interest, and so on.

CHAPTER 2

Health-Based Water Quality Goals for CECs

2.1 Introduction

Microbial and chemical contaminants in recycled water may have adverse effects on human health depending on their concentration (as a function of the effectiveness and reliability of the treatment system), route (i.e., skin, inhalation, and consumption), frequency, and duration of exposure. Maintaining a water quality that is protective of both human health and the environment is paramount to the success of all indirect potable reuse (IPR) projects. This requires that pathogens and chemicals in municipal wastewater are attenuated to safe levels before potable reuse and discharge to the environment. Generally, low concentrations of non-pathogenic microorganisms and chemicals are not harmful; therefore, a public health goal (PHG) is not to eliminate all chemicals and microorganisms, but rather to limit human exposure to concentrations of those chemicals and pathogens that may be harmful to human health.

The chemical universe is evolving at a rate that is challenging to identify harmful chemicals for traditional risk assessment paradigms where the focus has been to assess chemical by chemical. This constitutes a challenge for potable water reuse where many thousands of chemicals can be present in recycled water. As noted above, it is important to regulate constituents that may result in adverse human health impacts, but the question is how to identify the most potent and relevant chemicals for setting appropriate health standards for IPR projects. Thus, generally applicable and comprehensive approaches are needed to capture the risks associated with any remaining chemicals—known or unknown—in the product water of IPR projects.

The State of California (CA) has specified in its Recycled Water Policy to incorporate the most current scientific knowledge on constituents of emerging concern (CECs) into regulatory policies for use by California state agencies (SWRCB 2009). To facilitate this process the State has initiated a process to engage an independent Scientific Advisory Panel to provide recommendations regarding ‘Monitoring Strategies for Constituents of Emerging Concern in Recycled Water’. In early 2010, this Panel developed a risk-based framework for prioritizing and selecting CECs for recycled water monitoring programs (Anderson et al. 2010) (Figure 2-1). The framework was then used to develop a short list of recommended monitoring parameters, including both health-based CECs, performance-based indicator chemicals, and surrogate parameters. Health-based CECs are defined as CECs that have toxicological relevance to human health. Performance-based indicator CECs do not necessarily have human health relevance but can be used to monitor the efficacy of recycled water treatment processes. These indicator chemicals are individual chemicals representing a larger family of chemicals with similar structures or reactivity that are suitable to assess the removal efficiency of a unit process or operation for CECs. Some health-based CECs may also serve as performance indicator CECs. Finally, a surrogate parameter is a measurable physical or chemical property that can be used to measure the effectiveness of a process and correlates with the removal of CECs by this process.

The list also incorporated CECs from multiple source classes (e.g., pharmaceuticals, personal care products, food additives, household chemicals, hormones, and disinfection byproducts). To evaluate the toxicological relevance of CECs, predicted no effect concentrations (PNEC) for subchronic and chronic exposure to these chemicals are calculated considering known ‘no observed adverse effect levels’ (NOAELs) or a ‘benchmark dose lower confidence level of 10%’ (BMDL10), which are commonly derived in controlled exposure studies. Depending on the degree of certainty in these studies, different safety factors (10 -1,000) are applied in calculating a PNEC value. These PNEC values represent a safe level where no adverse effect through exposure to a given chemical can be expected and serve as an interim monitoring trigger levels (MTLs) in the assessment of CECs. In addition, occurrence data of CECs in secondary or tertiary treated effluents (defined as measured effluent concentrations [MECs]) are compiled. From the distribution of all occurrence data, a 90th percentile concentration of a specific chemical can be derived (MEC 90th). Chemicals exhibiting MTLs exceeding the 90th percentile concentration observed in secondary or tertiary treated effluents were considered for the selection of health-based indicator CECs (Figure 2-1). For CECs that did not exceed the ratio of MEC to MTL of 1, it is very unlikely that any of the CECs have the potential to pose a risk to public health.

The original Panel’s final report in December 2010 considered the state-of-the-science regarding CEC monitoring in recycled water applications at the time. As a result, in 2013 the State Water Board adopted the Panel’s recommendation of a risk-based framework to identify relevant CECs for inclusion in monitoring programs as an important concept. This is specified in Attachment A of the Recycled Water Policy (SWRCB 2013).

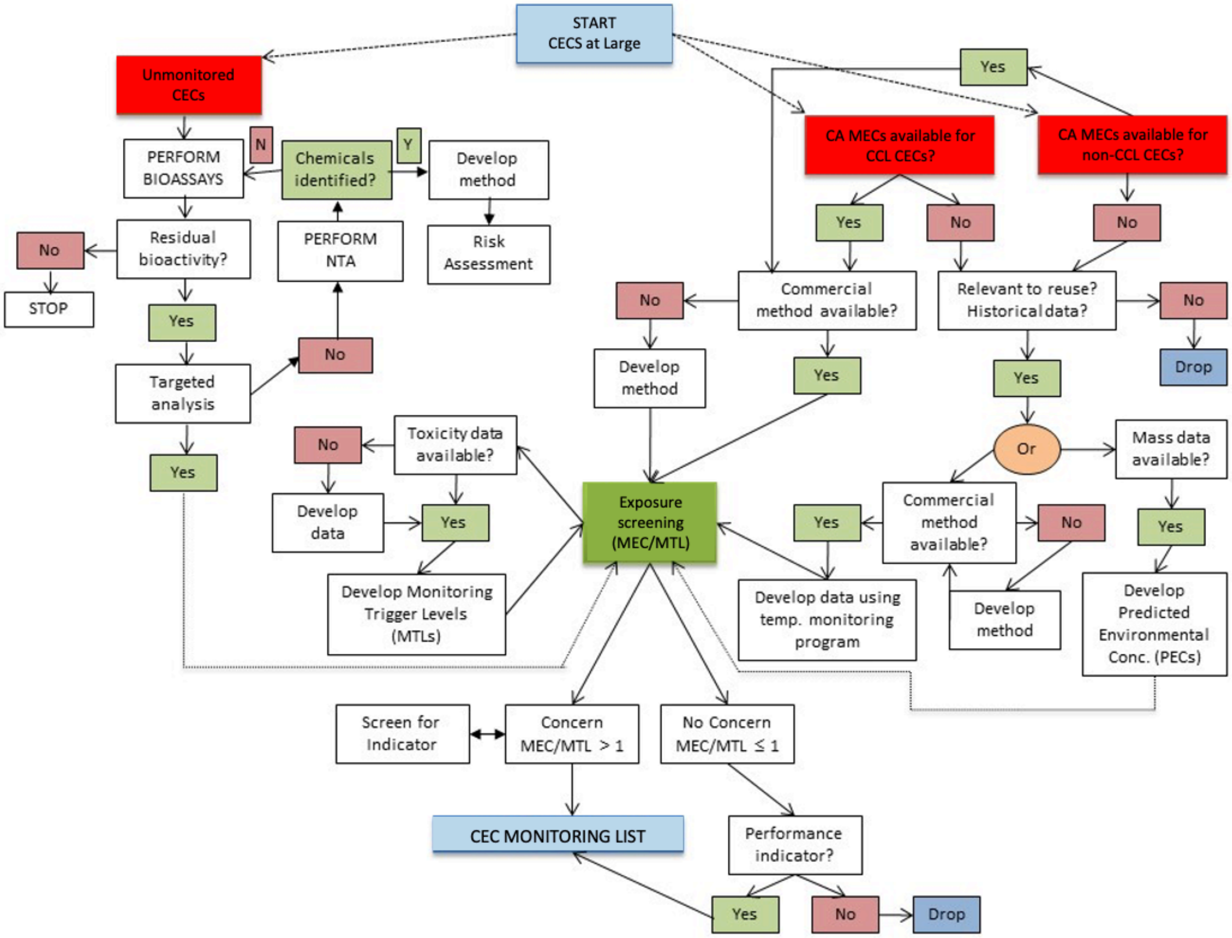


Figure 2-1. Risk-Based CEC Selection Framework Recommended by the Expert Panel on CECs in Recycled Water.
Source: Drewes et al. 2018.

Due to the uncertainty that is inherently associated with the universe of chemicals that might occur in recycled water, the need to establish a more responsive review and updating process that addresses rapidly developing CEC issues is critical. Identifying and incorporating new information on occurrence and toxicity provides the basis for adding new CECs to the framework (i.e., an on-ramp) and for removing CECs that do not (or no longer) pose a risk to human health (i.e., an off-ramp). Thus, the risk-based framework was reviewed and updated by the same Expert Panel in 2018. As a result of this review, the Panel recommended to enhance screening for yet unmonitored CECs by applying two additional approaches, namely bioanalytical tools (broadly referred to as “bioassays”) and non-target analytical (NTA) methods.

As opposed to targeted chemical methods that quantify individual chemicals, bioanalytical tools are non- or semi-targeted methods that utilize *in vitro* (cell or protein-based) and *in vivo* (whole animal) test systems. Such test systems can detect a wide spectrum of CECs and may also provide some indication of adverse effect (Figure 2-2). While targeted methods focus on known compounds, bioanalytical methods include the ability to integrate unknown compounds that have the same mode of action or that interact with each other in mixtures within complex environmental matrices. Toxicity evaluations of single chemicals will generally miss the synergistic, additive, or antagonistic potential found in mixtures, thus providing a false sense of security or false indication of a potential risk. The Expert Panel suggested to consider two *in vitro* bioassays that can screen for CECs by two actions: feminization and impaired reproduction using the endpoint estrogen receptor alpha (ER-α) and cancer and impaired reproduction using the endpoint Aryl hydrocarbon receptor (AhR). While the ER-α activity can capture CECs like estradiol, bisphenol A, or nonylphenol, the AhR endpoint would be responsive to the presence of dioxin-like chemicals, polycyclic aromatic hydrocarbons, and pesticides. These two bioassays were chosen because both threshold levels of responses correlate directly with an adverse outcome and both bioassays could be performed by commercial laboratories. These two bioanalytical methods do not represent all possible and relevant adverse endpoints.

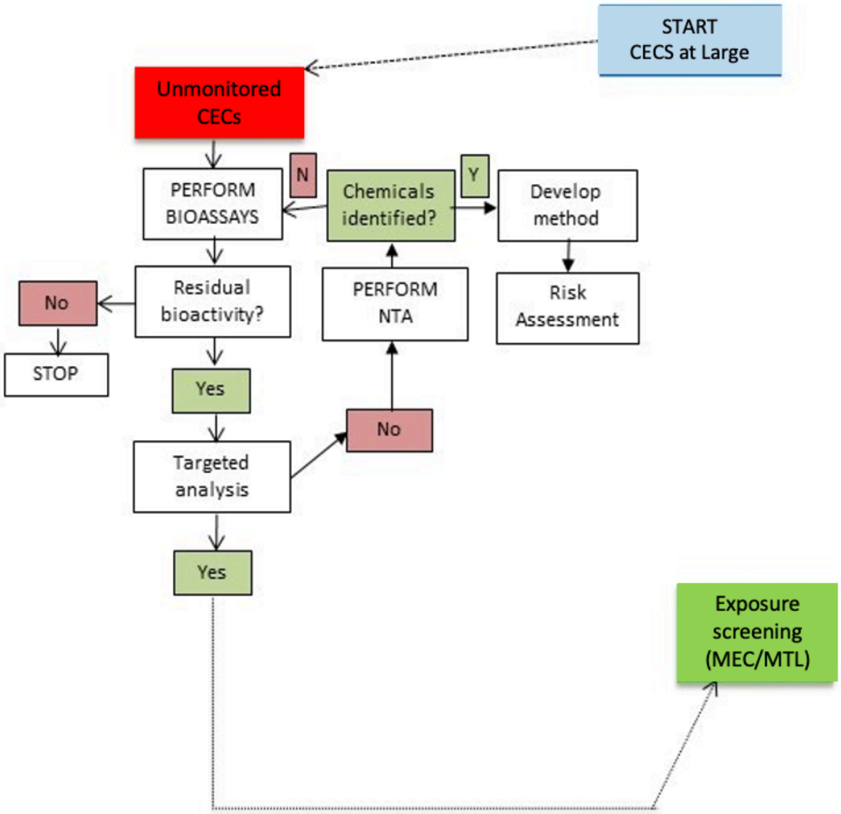


Figure 2-2. **Screening Approach for Unmonitored CECs using Bioanalytical Tools and Non-Targeted Chemical Analysis in Recycled Water.**
Source: Drewes et al. 2018**.**

In case of positive results in a bioassay or as an additional screening effort, NTA evaluations could be performed that might give indications of not yet identified chemicals of relevance. NTA methods hold great promise for the identification of previously unknown substances in recycled water. However, it is important to understand the limitations, complexities, and costs of performing NTA methods. Thus, the Expert Panel recommended that NTA is not suitable as a separate regular monitoring approach for monitoring of recycled water but might assist in identifying compounds that are biologically active in water (e.g., measurable responses above or near screening trigger levels during bioanalytical investigations) or, similar to bioanalytical tools, to assess overall treatment efficiency of recycled water during special studies.

These additional recommendations and updates were considered in the most recent amendment of the Recycled Water Policy in the State of California specifying monitoring requirements for CECs in recycled water used for groundwater recharge and reservoir water augmentation (SWRCB 2018b). For the specified IPR practices, treatment processes involve soil aquifer treatment (SAT) and reverse osmosis/advanced oxidation process (RO/AOP). Building upon this framework, in this chapter we identified suitable monitoring approaches that comprehensively assess CEC removal by ozone coupled with biologically active filtration (ozone/BAF) systems as part of IPR applications.

2.2 Prioritizing CECs for Proper Design of Ozone/BAF Systems

2.2.1 Demonstrating Removal of Regulated Contaminants and Health-based CEC Indicators

In the State of California, any IPR project must comply with the limits for health-based indicator CECs specified in Attachment A of the Recycled Water Policy, irrespective of the treatment processes applied (SWRCB 2018b). Thus, if ozone coupled with biologically activated carbon

(ozone/BAC) treatment processes are integrated in an IPR scheme in lieu of using high-pressure membranes, such as RO, the MTLs specified in Table 2-1 must be met in the product water. Very recently, due to new toxicological evidence for per- and polyfluoroalkyl substance (PFAS) published by the Office of Environmental Health Hazard Assessment (OEHHA), lower notification levels (NLs) for Perfluorooctanesulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA) have been published for drinking water (SWRCB 2019a). Thus, for IPR projects in California, the new limits of 0.0065 and 0.0051 μg/L for PFOS and PFOA, respectively, must be considered as health-based CECs.

A unique side effect of using ozonation in water treatment is the formation of oxidation by-products and transformation products (TPs) of which some might be of toxicological concern. In this report, the term TPs refers to products from the oxidation of CECs whereas oxidation byproducts (OBPs) are formed from (untargeted) reactions of ozone with the water matrix and also include chemicals known as disinfection byproducts (DBPs) (e.g., bromate) from other applications. Thus, where conditions prevail to favor the formation of these byproducts, proper monitoring for these chemicals is warranted. Studies have also reported formation of the health-based CEC N-Nitrosodimethylamine (NDMA) during ozonation (Pisarenko et al 2012; Sgroi et al. 2014), particularly in the presence of elevated levels of relevant precursors like dimethylsulfamide (DMS) (von Gunten et al. 2010). Combining ozone with BAF can result in attenuating NDMA, provided proper operating conditions (i.e., empty bed contact time [EBCT] and pre-conditioning the microbial community) are established (Bacaro et al. 2019). Thus, frequent monitoring of NDMA in ozone/biofiltration processes is critical.

Elevated levels of bromide in the feed water can result in the formation of increased levels of bromate, for which a maximum drinking water level exists at the federal and state level. Although already a regulated chemical, it is recommended to add bromate as an additional health-based indicator chemical for ozone/BAC applications given its relevance for ozonation processes. Formation of other regulated by-products typically known from disinfection processes (e.g., trihalomethanes [THMs]), is of minor importance during ozonation (von Gunten 2003b) but can become relevant in ozone/BAF based reuse concepts upon final chlorination. However, several studies indicate a good removal of by-product precursors by ozone (Arnold et al. 2018; Vatankhah et al. 2019b).

Table 2-1. Relevant Drinking Water Standards, Health-Based Chemical Indicators, Monitoring Trigger Level, and Reporting Limits.

Source: SWRCB 2018b.

Constituent	Relevance/Indicator Type	Monitoring Trigger Levels (µg/L)	Reporting Limit (µg/L)
According to Recycled Water Policy, Attachment A (SWRCB 2018b)			
1,4-Dioxane	Industrial chemical/ Health-based indicator	1	0.1
N-Nitrosodimethylamine	Disinfection byproduct/ Health-based indicator	0.010	0.002
N-Nitrosomorpholine (NMOR)	Industrial chemical/ Health-based indicator	0.012	0.002
Perfluorooctane sulfonate (PFOS)	Consumer/industrial chemical/ Health-based indicator	(0.013) 0.0065[a]	0.0065
Perfluorooctanoic acid (PFOA)	Consumer/industrial chemical/ Health-based indicator	(0.014) 0.0051[a]	0.007
For Ozone/BAC Applications			
Bromate	Oxidation byproduct/ Health-based indicator	10	1

[a] According to revised notification levels based on new toxicological evidence (SWRCB 2019a)

2.3 Specifying Performance-Based CEC Indicators

Performance-based indicators are individual chemicals representing a larger family of chemicals with similar structures or reactivity that are suitable to assess the removal efficiency of a unit process or operation for CECs. Performance indicators for different processes including biological wastewater treatment, adsorption to activated carbon, ozonation, and managed aquifer recharge have been proposed before (Dickenson et al. 2009; Dickenson and Drewes 2010; Jekel et al. 2015). These indicator chemicals should i) be detectable in the feedwater of an ozonation unit at concentrations of 10 x method reporting limit (MRL), ii) represent different amenabilities to removal during ozone/BAF, and iii) be able to quantify with commercially available analytical methods.

Adapting previous concepts (Hübner, Keller, and Jekel 2013; Y. Lee et al. 2014), indicators for CEC removal during ozonation can be categorized in 5 different groups based on the reactivity of CECs with ozone and hydroxyl radicals (Table 2-2). CECs with limited reactivity to ozone (group I) can be categorized by their removal through hydroxyl radical reactions. Compounds with $k_{OH} < 10^9$ $M^{-1}s^{-1}$ (group Ia) mostly persist during ozonation whereas CECs with $k_{OH} > 10^9$ $M^{-1}s^{-1}$ (group Ib) often show considerable removal (approximately 30-70%, depending on water quality) at applied ozone to total organic carbon (TOC) ratio (O_3:TOC) of 0.5 mg/mg (Hübner, Keller, and Jekel 2013; Lee and von Gunten 2016). CECs from this group should be monitored to indicate radical formation efficiency during ozonation. Moderately ozone reactive compounds ($10\ M^{-1}s^{-1} < k_{O3} < 10^3\ M^{-1}s^{-1}$, group II) are characterized by partial reaction with both, ozone and hydroxyl radicals. The third group of CECs with $10^3\ M^{-1}s^{-1} < k_{O3} < 10^5\ M^{-1}s^{-1}$ is also efficiently removed by direct reaction with ozone but can be constantly detected in ozonated water to indicate changes of system performance. CECs with second order rate constants $k_{O3} > 10^5\ M^{-1}s^{-1}$ (group IV) should be removed to levels close to or below detection limits in any ozone application. Elevated concentrations in ozonation effluent indicate failures or short circuiting during ozonation.

Table 2-2. Performance Indicators for Ozonation based on Reactivity to Ozone (Groups II-IV) and Ozone and Hydroxyl Radicals (Group I).

Group	Second Order Rate Constants (pH 7)	Example Performance Indicators[a]
Group Ia: Low removal during ozonation	$k_{O3} < 10\ M^{-1}s^{-1}$ $k_{OH} < 10^9\ M^{-1}s^{-1}$	PFOA, PFOS, TCEP[b], TCPP[b], sucralose[f]
Group Ib: Significant removal by radicals	$k_{O3} < 10\ M^{-1}s^{-1}$ $k_{OH} > 10^9\ M^{-1}s^{-1}$	primidone[c], iopromide, ibuprofen, 1,4-dioxane
Group II: Reaction with ozone and hydroxyl radicals	$10\ M^{-1}s^{-1} < k_{O3} < 10^3\ M^{-1}s^{-1}$	benzotriazole, acesulfame[d], gabapentin[e]
Group III. Fast reaction with ozone	$10^3\ M^{-1}s^{-1} < k_{O3} < 10^5\ M^{-1}s^{-1}$	atenolol, tramadol
Group IV: Instantaneous/complete reaction with ozone	$k_{O3} > 10^5\ M^{-1}s^{-1}$	carbamazepine, diclofenac

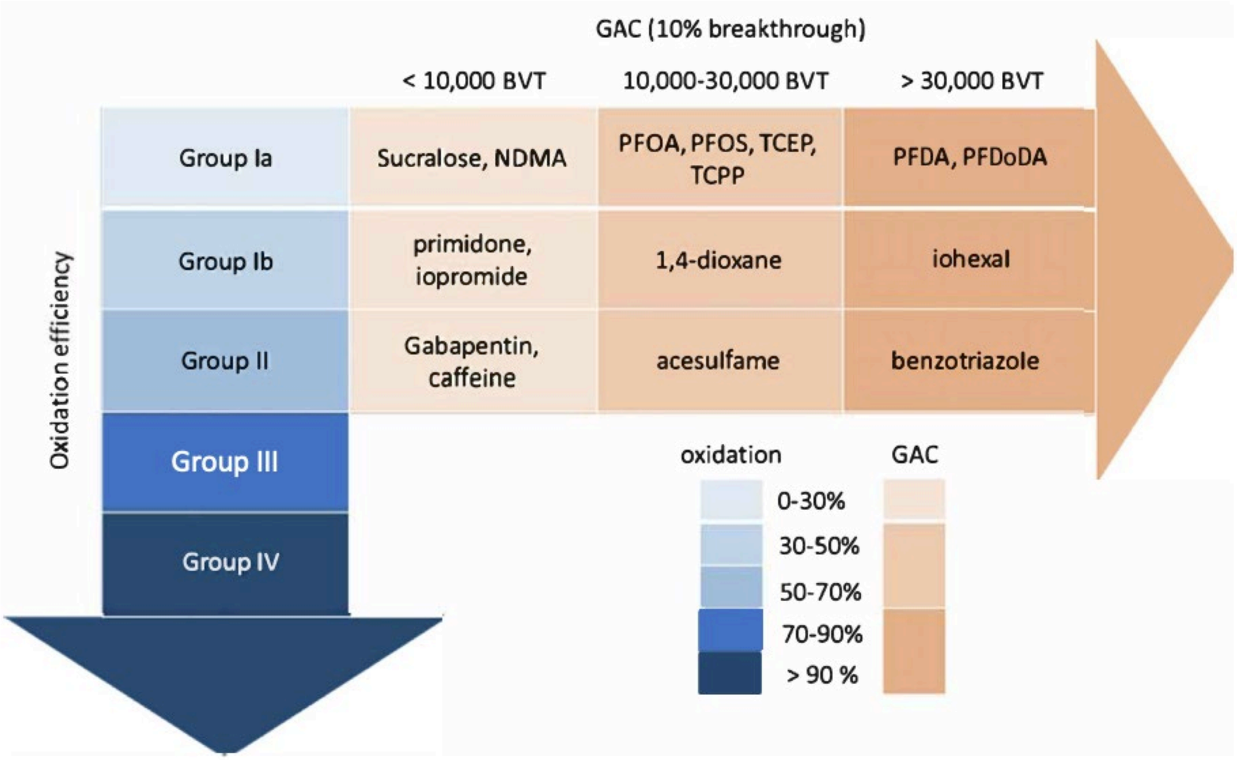
[a] Majority of k_{O3} and k_{OH} taken from von Sonntag and von Gunten (2012) and references therein
[b] Watts and Linden (2009)
[c] Real et al. (2009)
[d] Scheurer et al. (2012)
[e] Lee et al. (2014)
[f] Bourgin et al. (2017), observed removal defined from Sundaram et al. 2020

The assessment of removal efficiencies of CECs during (bio)filtration is dependent on multiple operational parameters. These include media type and filter operation (e.g., EBCT, backwash frequencies, and regeneration of activated carbon). In this chapter, BAF_{inert} refers to filtration processes with inert filter material (e.g., sand and anthracite), whereas BAC filtration describes filtration with granular activated carbon (GAC) operated with higher bed volumes treated (BVT) than common GAC filtration to take advantage of combined sorption and biodegradation processes. Different utilization rates of the activated carbon can result in very different adsorption efficiencies for CECs. Thus, to address different potential engineering practices, the following pragmatic approach is proposed that considers the degree of carbon utilization. Performance indicators are provided for three different scenarios:

- Operation of GAC filters with the objective to remove individual CECs by sorption. These filters are not primarily designed as a biological treatment step and carbon is regenerated after breakthrough of target CECs.
- BAC filters, which are operated with higher BVT (approximately 30,000-80,000 BVT) but still provide residual sorption for CECs.
- BAF_{inert} or BAC with exhausted adsorptive capacity (> approximately 80,000 BVT).

It should be noted that this operationally defined categorization is based on a limited number of long-term studies to evaluate the breakthrough of CECs in BAC and can therefore only provide estimations (Müller, Drewes, and Hübner 2019; Sundaram et al. 2020; Zhiteneva, Drewes, and Hübner 2021). Breakthrough of CECs in GAC filters and full exhaustion of adsorptive capacity depend on site-specific factors like carbon type, filter design and operation (e.g., EBCT, filtration rate), and water quality. Pilot studies are recommended to better understand breakthrough behavior of CECs in carbon filters after ozonation and to adjust proposed categories to site-specific conditions.

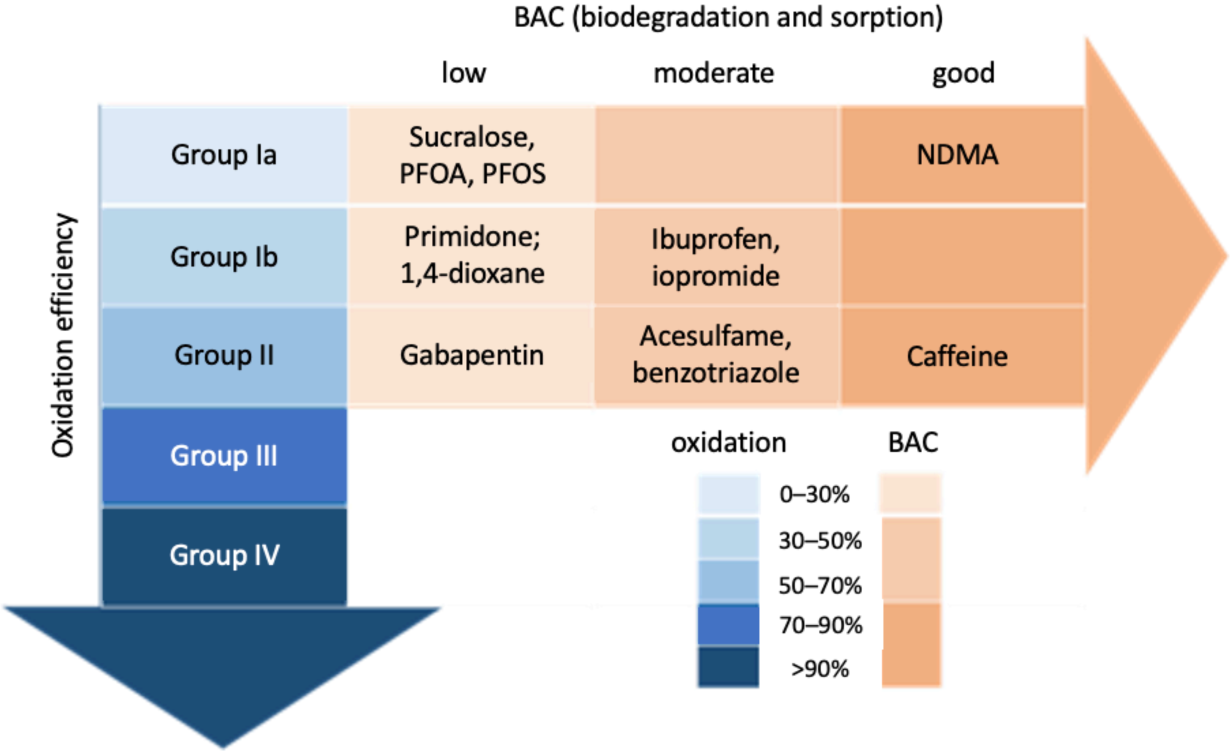
From the 5 groups of performance indicators for ozonation, only poorly and moderately ozone-reactive CECs can be regularly monitored after oxidation and used as indicators for GAC/BAF. Suggested performance indicators for the combination of ozonation with GAC are illustrated in Figure 2-3. In contrast to biofiltration, GAC performance for CEC removal is characterized by a continuous breakthrough as a function of BVT. Therefore, performance indicators are categorized based on their breakthrough at 10% of initial concentration estimated as poor (< 10,000 BVT), moderately (10,000-30,000 BVT), and well adsorbable (> 30,000 BVT). Selection is mainly based on results from rapid small-scale column test (RSSCT) experiments with ozonated wastewater treatment plant (WWTP) effluent (Müller, Drewes, and Hübner 2019), but also suggested performance indicators for powdered activated carbon (PAC) were adapted for the concept (Jekel et al. 2015). Well adsorbable PFAS and CEC indicators were based on the results from two recent studies (Park et al. 2020; Vaidya et al. 2020). It should be noted that breakthrough of CECs is highly site-specific depending on EBCT, carbon type, and water quality. More data is needed to better specify performance indicators for GAC after ozonation.



	< 10,000 BVT	10,000-30,000 BVT	> 30,000 BVT
Group Ia	Sucralose, NDMA	PFOA, PFOS, TCEP, TCPP	PFDA, PFDoDA
Group Ib	primidone, iopromide	1,4-dioxane	iohexal
Group II	Gabapentin, caffeine	acesulfame	benzotriazole
Group III			
Group IV			

Figure 2-3. Suggested Performance Indicators for Ozone/GAC Treatment.
GAC regenerated after breakthrough of target CECs, estimated as approximately 30,000 BVT

The performance indicators for ozone/BAC (approximately 30,000-80,000 BVT) are shown in Figure 2-4. Removal of BAC is based on a combination of biological and sorptive processes. Ideally, the final list of performance indicators should contain compounds which are only removed by adsorption (e.g., PFOA, PFOS, 1,4-dioxane) or only by biodegradation (e.g., NDMA, caffeine). However, as adsorption capacity is mainly exhausted at this stage, removal of > 70% by residual sorption is limited to very few very well sorbing CECs (Zhiteneva, Drewes, and Hübner 2021). On the other hand, biodegradable CECs like caffeine, ibuprofen and acesulfame are effectively removed in well-operated biological nutrient removal (BNR) facilities and consequently often not present at elevated concentrations in the influent of biofilters (after ozonation). Therefore, NDMA or other ozonation products (e.g., formaldehyde, acetaldehyde) represent better performance indicators for BAF.



	low	moderate	good
Group Ia	Sucralose, PFOA, PFOS		NDMA
Group Ib	Primidone; 1,4-dioxane	Ibuprofen, iopromide	
Group II	Gabapentin	Acesulfame, benzotriazole	Caffeine
Group III			
Group IV			

Figure 2-4. **Suggested Performance Indicators for Ozone/BAC Treatment.**
BAC operated for approximately 30,000-80,000 BVT.

Different removal categories of indicators in an ozone/BAF_{inert} system are illustrated in Figure 2-5. Classification of indicators during biofiltration is based on reported removal efficiency from Chapter 1 and literature results (Dickenson et al. 2009; Jekel et al. 2015; Sari et al. 2020; Tackaert et al. 2019). However, it should be noted that, especially in literature, data are largely based on biofiltration systems without pre-ozonation, and the accuracy of performance indicators could be significantly improved with results from a larger database including ozone/BAF_{inert} applications.

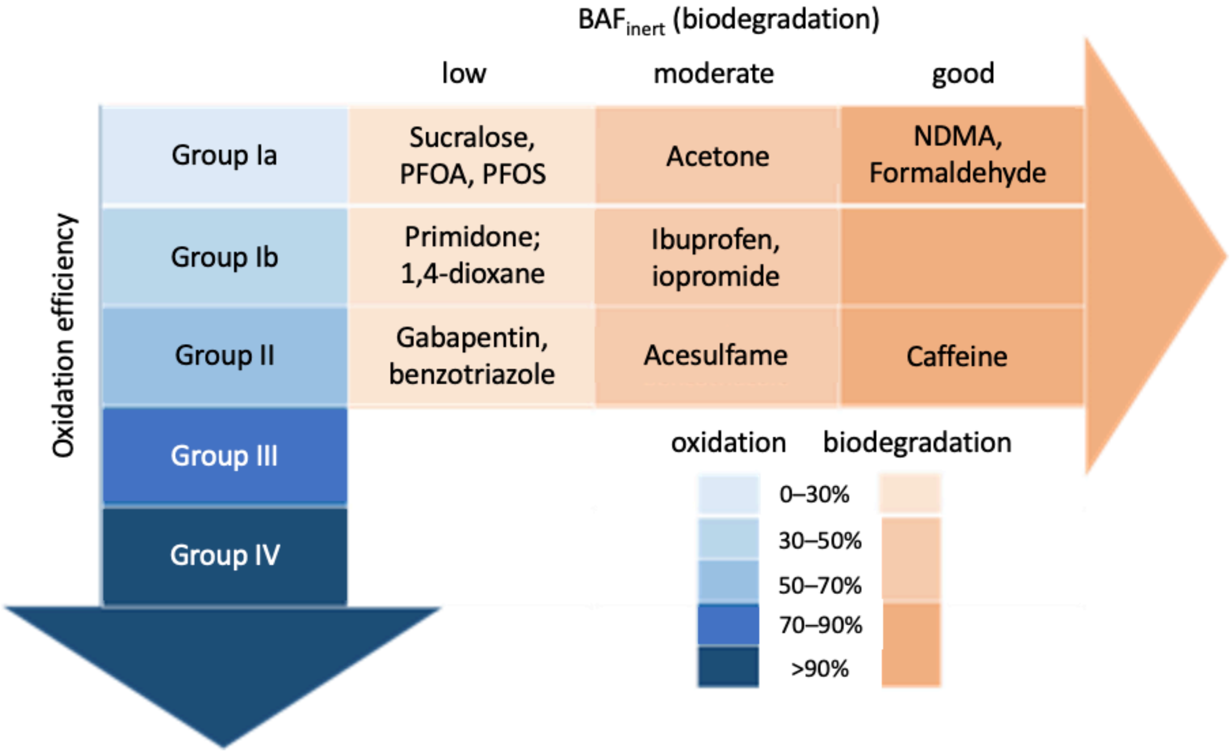


Figure 2-5. Suggested Performance Indicators for Ozone/$\text{BAF}_{\text{inert}}$ Treatment.
$\text{BAF}_{\text{inert}}$ = Biofiltration with BAC operated after full exhaustion of sorptive capacity, approximately > 80,000 BVT, or other non-sorptive media.

2.4 Specifying Control and Monitoring Strategies for Ozonation

Utilities apply different strategies to operate and control ozone/BAF systems. The most frequently used strategies for ozonation identified in Chapter 1 include volume proportional (as g O_3/m^3) and load proportional (as O_3:TOC or O_3:TOC ratio) ozone dosing. These strategies are often complemented with an online nitrite analyzer to compensate ozone decay by nitrite peaks. In addition, performance of unit processes can be monitored using surrogate parameters. These performance surrogates should i) enable routine monitoring, ideally through online measurements, and ii) provide good indication on performance efficiency through validation of water quality changes. If possible, these surrogates should be selected based on available correlations with target CEC removal. Besides solely monitoring, surrogates can also be used for process control purposes. This following Section is divided into two parts—first existing and potential control strategies are discussed before suitable surrogates for performance monitoring are proposed.

2.4.1 Control Strategies for Ozonation

Commonly applied control strategies for ozonation processes have considered volume-based or load-based dosing of ozone. These operational strategies were also mostly employed by utilities surveyed during Chapter 1 (Table 2-3). Volume-based ozone dosing (i.e., adjusting the ozone dose to flow measurements) provides a very simple and robust approach. Changes in water quality, for example during wet weather events, however, are not compensated by this concept, which can result in overdosing. It is therefore recommended to accompany this approach with continuous monitoring of surrogate parameters for proper performance assessment.

Ozone decomposition in secondary or tertiary effluents is mainly driven by the presence of effluent organic matter (EfOM), nitrite, and pH (Y. Lee and von Gunten 2016). Consequently, a more consistent removal of target CECs can be achieved by using load-based ozone dosing expressed as O_3:TOC, O_3 to dissolved organic carbon (O_3:DOC), or O_3 to chemical oxygen demand (O_3:COD) ratios. Several studies demonstrate good reproducibility of CEC removal, when constant O_3:TOC ratios are applied, and even showed good comparability of CEC removal in different WWTPs with the same O_3:TOC ratios (Y. Lee et al. 2013). Due to its rapid reaction with ozone, elevated nitrite concentrations can strongly decrease ozone availability for CEC oxidation. Some utilities therefore combine the O_3:TOC concept with online sensors for nitrite measurement. Although this concept does not provide any analytical feedback on performance efficiency like in classical surrogate concepts, it is considered a sophisticated control system which can be operated safely without additional surrogate measurements.

When ozonation is applied for disinfection, concentration multiplied by contact time (CT)-values are mostly used for process control. This is usually achieved by analyses of residual ozone concentration at the outlet of the reactor. Based on hydraulic retention time (HRT) and ozone decay in the reactor, ozone exposure (CT-value) can be estimated. Also, for ozonation of secondary/tertiary effluent the knowledge of ozone (and hydroxyl radical) exposure would provide highest accuracy of CEC and pathogen mitigation (Lee and von Gunten 2016). However, rapid ozone decay in wastewater often limits the reliable analysis and adjustment of residual dissolved ozone (Hübner, Keller, and Jekel 2013; Nöthe, Fahlenkamp, and von Sonntag 2009). In addition, accurate calculation of ozone exposure from residual ozone is challenging due to the multi-phasic ozone depletion in wastewaters (Nöthe, Fahlenkamp, and von Sonntag 2009; Zucker et al. 2016). Consequently, traditional CT concepts based on one or two dissolved ozone analyzers do not represent an accurate option to determine ozone exposure in ozone/BAF systems for advanced wastewater treatment. Online analysis of ozone decay in the treated water, e.g., by discontinuous measurement in small reaction cells, could provide additional benefits, especially when disinfection targets need to be met.

Another promising option, which is currently tested at full-scale (e.g., WWTP Neugut, Switzerland and WWTP Weißenburg, Germany), is to use the surrogate parameter change UV absorbance (ΔUV_{254}) determined from continuous UV sensors in reactor influent and effluent (see details in Section 2.4.2) for process control. As the differential UV absorbance (UVA) can be directly correlated to CEC removal, this concept can compensate for any water quality changes (TOC, nitrite). However, reliable measurement of UV sensors in reactor influent and effluent needs to be ensured, which includes consideration of UVA by residual dissolved ozone and the use of redundant UVA sensors. Operation also needs to consider the lag-time between actual treatment and the availability of a signal from effluent UVA measurements. Detailed implications from practical application can be found in literature (Stapf, Miehe, and Jekel 2016).

Table 2-3. Applied Control Strategies for Ozonation (from Chapter 1).

Control Strategy	Advantages/Limitations	References
Volume-based dosing [as mg/L]	• Easy operation and maintenance • Changes of water quality (e.g., at rain events) not compensated • Effects of nitrite peaks directly affect removal of CECs and pathogens • Additional surrogates recommended to monitor performance	9 utilities from Chapter 1
Load-based dosing [as O_3:DOC/TOC/COD ratio]	• Maintenance, redundancy of DOC/TOC sensors • Compensation of changing water quality • Can be combined with online nitrite sensor to account for ozone decomposition by nitrite peaks	13 utilities from Chapter 1
ΔUVA_{254} absorbance	• Integration of surrogate signal compensates for water quality changes (including nitrite peaks) • For advantages and challenges of ΔUVA_{254} absorbance as a surrogate see Section 2.4.2 • Short feedback loop needed to avoid lag times	2 utilities from Chapter 1
CT (based on residual ozone analysis)	• Sensors available, but often not reliable • Careful placing of sensor needed • Accurate information on flow rate and contact time essential • CT estimation (at high dosages) • Allows prediction of CEC and pathogen removal • Indirect compensation for water quality changes • No direct information on water quality changes	1 utility from Chapter 1

2.4.2 Identify Suitable Surrogate Parameters for Ozonation

Potential surrogates for ozonation are listed in Table 2-4 along with analytical considerations, advantages, and drawbacks. Although it is often used as a parameter to control load-based ozone dosage for oxidation (see Section 3.1), DOC/TOC and respective O_3:TOC or O_3:DOC ratios are not ideal surrogates for performance of ozonation as they are not significantly changing during oxidation. COD is not recommended as a surrogate because of limited sensitivity during ozonation. Color (measured as absorbance at 436 nm) is highly sensitive to ozone. Due to its fast elimination by ozone, however, it could only serve as a surrogate for fast reacting compounds and is therefore not included in Table 2-4.

Table 2-4. List of Possible Surrogate Parameters for Ozonation.

Surrogate	Analytical Considerations	Advantages/Limitations
ΔUV absorbance at 254 nm	• Robust and reliable sensor technology • Monitoring in ozonation influent and effluent • Redundant sensors recommended to compensate drift, or frequent verification/calibration	• UVA of organics effectively reduced by ozone oxidation • Good correlation to CEC removal • Well-established for monitoring and control at full-scale (see Chapter 1) • Compensates for water quality changes (i.e., enhanced nitrite concentrations) • Additional research needed to determine applicability for pathogen removal

Surrogate	Analytical Considerations	Advantages/Limitations
	• Need to avoid interference with residual ozone and oxygen/ozone gas bubbles	
ΔUV absorbance at 254 nm (continued)	• Sensors with multiple wavelengths can improve robustness of measurement, e.g., by compensating for turbidity	• See previous page
ΔExcitation-emission matrix (EEM) (total fluorescence, individual wavelength)	• Sensor technology available • Sensors expensive • Online meters available for certain excitation/emission wavelength pairs (2-D)	• Effective reduction by ozone • Good correlation to CEC removal • Compensates for water quality changes • Limited applicability for pathogen removal

Selection of suitable surrogates should be based on treatment targets for ozonation. Differential measurements of UVA at 254 nm, total fluorescence (TF) or individual excitation/emission wavelength are promising surrogates to indicate removal of CECs, good correlations between reduction of these parameters and CEC mitigation have been reported in different studies.

Correlations between reduction of UVA and mitigation of primidone from literature and own experiments are exemplarily shown in Figure 2-6. Results show acceptable correlations, even between studies conducted in different wastewater, but also indicate that site-specific determination of UVA-CEC correlations are needed to optimize accuracy. It should also be noted that most correlations reported in literature result from lab-scale experiments with one wastewater sample at different ozone dosages. Higher variability can be expected from pilot- and full-scale ozonation with changing water quality and stable applied ozone dosage.

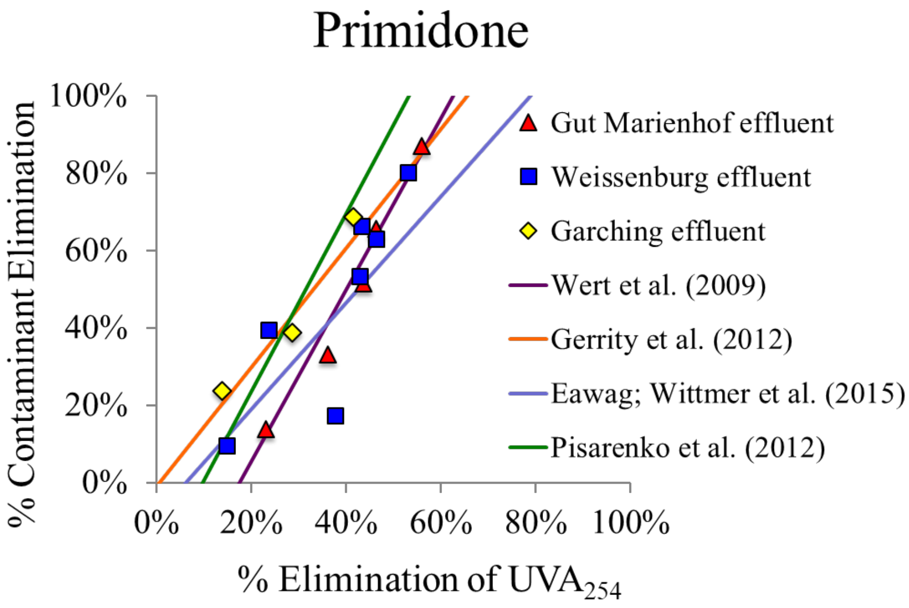


Figure 2-6. Correlation Between UV Absorbance and Contaminant Elimination during Ozonation.
Comparison of Literature Correlations with Own Experimental Data.
Source: Reproduced from Tackaert et al. 2015 with permission.

A relevant factor for the establishment of surrogate concepts is the analytical accuracy of the sensors. Especially ozonated water contains significant amount of assimilable organic carbon (AOC), which can induce biofilm growth on online monitoring sensors and thereby adversely affect readings. In addition, residual ozone might affect results by interferences. UVA by ozone peaks at approximately 260 nm. An option to avoid these interferences might be the monitoring of water quality in the effluent of the biofilter. Following this approach, however, significantly increased monitoring intervals need to be accepted (Stapf, Miehe, and Jekel 2016).

In contrast to CECs, suitability of spectrophotometric surrogates to indicate efficiency of disinfection is less documented. While removal of CECs usually targets efficiency of > 90% removal, > 99.9% are mostly needed for efficient disinfection. Therefore, disinfection efficiency during ozonation can already be compromised by suboptimal conditions allowing little amounts of short circuiting. Spectroscopic sensors are likely not sensitive enough to detect such issues.

2.5 Specifying Control and Monitoring Strategies for Biofiltration or Ozone/BAF Systems

2.5.1 Control Strategies for Biofiltration

Operation, control, and monitoring of biofilters as post-treatment for ozonation processes strongly depends on specific objectives for treatment which may include:

- Removal of biodegradable or assimilable organic carbon (e.g., aldehyde and keto functional groups) formed from reactions of ozone in the water matrix.
- Biodegradation of target CECs which are not efficiently removed by ozone or adsorption (i.e., the carcinogen NDMA).
- Additional removal of health-relevant CECs, which are not efficiently removed by ozonation (e.g., PFAS) through adsorption onto BAC/GAC.

Ammonia concentrations and nitrification are not considered relevant objectives for biofiltration because water reclamation facilities for intended water reuse applications usually provide fully nitrified/denitrified effluent. Current control strategies for BAF systems are mostly limited to operating the system within its design parameters (i.e., loading rate, flow rate, fixed bed volume) and control strategies from standard tertiary filtration systems, which mainly trigger backwashing through headloss or turbidity measurements. The most relevant design parameter with respect to efficiency of biological processes is the EBCT. Previous studies reported fast removal of biodegradable DOC already with short EBCT whereas longer contact time is needed to provide consistent removal of CECs (Müller, Drewes, and Hübner 2017). Most advanced water treatment (AWT) facilities run at a relatively constant flow (and EBCT) compared to WWTPs which handle the hydraulic swings from rain events. EBCT can be calculated in real-time for a control system, but it is being monitored rather than actively controlled for biodegradable dissolved organic carbon (BDOC) or CEC removal. If activated carbon is used to achieve treatment targets for specific health-based indicators, information on breakthrough of these substances is needed to trigger regeneration or replacement of the carbon.

2.5.2 Identify Suitable Surrogate Parameters for Biofiltration

To the best of our knowledge, surrogate concepts are not applied at full-scale biofiltration systems yet. Typical surrogates to monitor standard filtration processes include filter effluent turbidity and pressure headloss. These surrogates are not relevant for ozone/BAF systems as they do not indicate water quality changes due to biodegradation and/or sorption in BAC filters. Potential surrogates for biofiltration (or the combination of ozone/BAF) are listed in Table 2-5.

Changes in DOC or TOC can be monitored to indicate biotransformation of easy degradable products from ozonation. Since DOC concentration remains mostly stable during ozonation, initial DOC/TOC can also be monitored before the ozonation system to avoid potential biofilm growth from easy degradable carbon on sensors and analytical interferences with residual ozone. Measurement of differential DOC can be applied as a good indicator for biological processes especially during acclimation process. More work is needed to establish correlation with biotransformation of NDMA, since that too is dependent on reaching steady-state conditions and affected by upstream treatment (Sundaram et al. 2020). Removal of DOC by biological activity does not seem to correlate with removal of other CECs by sorption in activated carbon filters (Zhiteneva et al. 2020). UVA is strongly reduced by ozone, depending on applied ozone dose conditions. This transforms most of the bulk organic matter to be non-absorbent of UV radiation, limiting the use of differential UVA to correlation to the performance of biological filter performance.

Other potential surrogate concepts mainly address the indication of biological activity in the filters. Depletion of dissolved oxygen (DO) is easy to monitor, but influent concentration needs to be evaluated carefully as oversaturation in the filter inlet after ozonation can be expected, which may lead to degassing of oxygen and inaccurate analysis of influent concentrations. Besides differential measurements, however, effluent DO sensors can also be used to confirm oxic conditions (> 1-2 mg/L) throughout the filter. Other parameters to determine biological activity in biofilter (e.g., the analysis of adenosine triphosphate [ATP] or flow cytometry) have not been investigated as surrogates for biofiltration yet.

Until now, surrogate concepts for biofiltration after ozonation are widely underexplored with current pilot- and full-scale systems operating within their design parameters without additional monitoring or control. Available online sensors for DOC/TOC or DO can provide information on biological activity, but concepts to reliably monitor biodegradation of NDMA or sorption of CECs in BAC filters are missing.

Table 2-5. List of Potential Surrogates for Biofiltration of Full Ozone/BAF Treatment.

Surrogate	Analytical Considerations	Advantages/Limitations
TOC/DOC	• Continuous sensor available • Drift of sensors problematic, especially in ozonated water	• Efficient removal during BAF, directly indicates removal of biodegradable products from ozonation (e.g., aldehydes) • Not a good indicator for CEC removal in BAC filters
DO	• Sensors available • Potentially limited accuracy at DO > 100% after ozonation	• Surrogate for biological activity • Not tested at pilot- or full-scale

2.6 Assessing Oxidation Byproducts and Transformation Products

2.6.1 Oxidation Byproducts

A unique aspect of any ozonation process in water treatment is the formation of OBPs. OBPs with toxicological relevance include NDMA and bromate. As already discussed in Section 2.1 these two chemicals should be closely monitored as health-based indicators for ozone/biofiltration systems.

Typical OBPs of ozonation are aldehydes and ketones. These usually do not persist very long in the environment and are also amendable to biodegradation during subsequent biofiltration treatment (provided EBCTs are sufficiently long). The formation of these OBPs is one main reason to combine an ozonation process with a subsequent biofiltration step. A relevant aldehyde that might occur during ozonation is formaldehyde. California has specified a NL for formaldehyde of 100 μg/L (SWRCB 2021b). Since formaldehyde is well degradable under aerobic conditions during subsequent biofiltration, this chemical may be used as an indicator for biotransformation performance in ozone/BAF treatment.

2.6.2 Transformation Products

Considering typically applied dosages during ozonation, chemicals including CECs are not completely mineralized. Depending on the specific reactivity of a chemical with ozone and hydroxyl radicals, different TPs are formed. In general, specific activity and/or toxicity, such as antibiotic activity or endocrine disruption, of CECs and their TPs is efficiently reduced during ozonation (Carbajo et al. 2015; Escher et al. 2008; Escher, Bramaz, and Ort 2009; Macova et al. 2010; Reungoat et al. 2010; Tawk et al. 2017). However, some studies showed increased toxicity of individual TPs in unspecific bioassays such as *Vibrio fisheri* (Illes et al. 2014; K. Li et al. 2008; Rehman et al. 2019; Stalter, Magdeburg, and Oehlmann 2010; Stalter et al. 2010). Many TPs contain aldehyde and ketone functional groups that are well biodegradable (Hübner et al. 2014; Hübner, von Gunten, and Jekel 2015). However, there are some exceptions. For instance, nitro-groups, N-oxides, and sulfoxides that form during ozonation and are expected to persist after treatment by BAF (Hübner, von Gunten, and Jekel 2015).

Several relevant TPs from individual CECs are well characterized in literature including compounds with nitro groups (Goi, Trapido, and Tuhkanen 2004; C. Lee, Yoon, and von Gunten 2007), N-oxides (Zimmermann et al. 2012; Zucker et al. 2016), sulfoxides (Dodd et al. 2010; Hübner, von Gunten, and Jekel 2015), and TPs from ozonation of olefinic compounds (Hübner et al. 2014; Hübner, von Gunten, and Jekel 2015; von Sonntag and von Gunten 2012). Health-based PNEC values and analytical standards are needed to include these chemicals into concepts defined in Section 2.2.1. In addition, the formation during ozonation makes TPs suitable performance indicators for BAF post-treatment.

2.7 Assessing the Toxicological Relevance of Any Remaining CECs and Oxidation Byproducts

2.7.1 Assessing the Toxicity of Unknown CECS

As recommended by the Expert Panel and adopted in the most recent revision of the Recycled Water Policy (Drewes et al. 2018; SWRCB 2018b), IPR projects in California are required to perform regular bioassays monitoring including two relevant endpoints: the ER-α and the aryl hydrocarbon receptor. The MTLs in the Recycled Water Policy have been defined as E2-bioanaltycial equivalent concentrations of 3.5 ng E2/L and 2,3,7,8-tetrachlorodibenzo-p-dioxin BEQ (TCDD-BEQ) concentrations of 0.5 ng TCDD/L. For both targeted chemistry and bioanalytical screening tools, the response actions for exceeding the MTLs are to further investigate what is responsible for the exceedance if the magnitude of the exceedance is greater than a factor of 10 higher than the MTL. The Recycled Water Policy does not require further investigation if the magnitude of an exceedance is less than 10 times the MTLs because the purpose of the CEC monitoring requirements is to investigate the occurrence and magnitude of CECs in recycled water, and the MTLs are relatively conservative values.

For these two bioassays standard operation procedures were subsequently developed for monitoring programs of potable recycled water projects in California (NWRI 2020).

While other endpoints were also considered relevant to IPR projects, these two endpoints were selected due to the maturity of the tests available. Other *in vitro* assays that are suitable to screen for CECs by different mode of action were also considered by the Expert Panel (see Table 2-6) but were not recommended due to their current stage of development (Drewes et al. 2018).

Table 2-6. *In Vitro* Assays that Screen for CECs by Mode of Biological Action.
Source: SWRCB 2018b**.**

Endpoint Activity	Relevant CECs	Adverse Effect	Development Stage[a]
Endocrine Disrupting Chemicals (EDCs)			
ER-α	Estradiol, bisphenol A, nonylphenol	Feminization, impaired reproduction, cancer	4
Anti-estrogen receptor (ER-)	Pyrethroids	Disrupted reproductive development, impaired reproduction	2
Anti-androgen receptor (AR-)	Musks, phthalates, pesticides	Androgen insensitivity, impaired reproduction, cancer	2
Glucocorticoid receptor (GR)	Anti-inflammatory steroids	Development, immune diseases, diabetes	3
Progesterone receptor (PR)	Progestins	Cancer, hormone resistance syndrome, impaired reproduction	2
Carcinogenic Chemicals			
AhR	Dioxin-like chemicals, polycyclic aromatic hydrocarbons, pesticides	Cancer, impaired reproduction	3
Tumor suppressor protein Response Element (p53RE)	Dioxin-like chemicals, PAH metabolites	Oxidative stress, tissue and DNA damage, cancer	1
Immunosuppressants, Neurotoxins and Other Chemicals of Concern			
Thyroid receptor (TR)	Pesticides, bisphenol A	Impaired metabolism, auto-immune diseases	1

Endpoint Activity	Relevant CECs	Adverse Effect	Development Stage[a]
Immunosuppressants, Neurotoxins and Other Chemicals of Concern (Continued)			
Peroxisome proliferator activated receptor (PPAR)	Pharmaceuticals, phthalates	Metabolic disorders, impaired immune function, cancer	1
Acetylcholine receptor	Neonicotinoid and other pesticides	Neurotoxicity, behavior	1

[a] Development stage:

Stage 1 (Exploratory): adaptation for water quality measurement
Stage 2 (Optimization): demonstration of performance consistent with monitoring goals
Stage 3 (Standardization): documentation of standard operating procedure (including QA/QC)
Stage 4 (Pilot Evaluation): establishment of initial trigger level and trial data collection
Stage 5 (Implementation): validation and certification of method

2.7.2 Assessing the Toxicity of TPs and OBPs

While the bioassays selected by the expert panel are suitable to assess specific toxicity caused by CECs (i.e., ER-α, AhR) and its reduction in ozone/BAF systems, they are not specifically targeted to potential adverse effects caused by TPs formed during ozonation. To assess TPs from ozonation, standardized tests are required, which can indicate specific effects of TPs formed during ozonation (e.g., effects induced by aldehyde or ketone functional groups). These bioassay responses serve as a diagnostic tool to trigger targeted investigations to better understand the cause and degree of TP formation.

Völker et al. (2019) reviewed recent literature on toxicity testing after ozonation of secondary and tertiary effluents. They identified two assays, the umuC assay and the Ames test using strain YG7108. These two assays may be used to assess potential for an increased toxicity caused by TPs and by-products formed during ozonation. However, more research is needed since the specificity of these tests to individual chemicals is largely unknown. It should also be noted, that reported effects are usually (partly) removed during subsequent biofiltration. More research is needed to understand how different filter design, media properties, and EBCT may affect relative reduction of overall toxicity and correlating that to the removal of any specific TPs.

2.8 Meeting Pathogen Inactivation and Drinking Water Quality Goals

2.8.1 Water Quality Goals for Potable Reuse Schemes

There are currently no federal regulations specific for potable water reuse in the United States, although there are several potable reuse projects currently in operation (EPA 2017e). Multiple states have addressed potable reuse schemes in specific regulations or guidance frameworks for indirect or direct potable reuse (DPR). IPR projects in California are regulated by a 12/10/10 rule in which there is a 12-log reduction for viruses, 10-log reduction of *Cryptosporidium*, and 10-log reduction of *Giardia* based on the maximum organism density in raw sewage. Arizona, Florida, Hawaii, Texas, Colorado, North Carolina, Oklahoma, Virginia, and Washington are among a number of states with policies that address potable reuse schemes. Despite this, potable water reuse schemes follow established regulations regarding disinfection and pathogens outlined for drinking water including the Safe Drinking Water Act (1974), the Clean

Water Act (1972), the Surface Water Treatment Rule (SWTR) (1989), and any additional state requirements that may exist to address aspects of potable water reuse.

Two guidance documents released by the World Health Organization (WHO) are applicable to potable reuse schemes worldwide: Guidelines for Drinking-Water Quality and Potable Reuse: Guidance for Producing Safe Drinking Water Guidelines. Both documents are intended for use by health regulators, drinking water suppliers, and policymakers. In these documents, it is recommended to set log reduction values (LRVs) for enteric bacteria, viruses, and protozoa based on the concentration of pathogens in the source water and the pathogen concentrations equivalent to 10^{-6} disability-adjusted life years per person per year. Drinking water suppliers are encouraged to set performance targets with data specific to their system and communities. Potable water reuse schemes are not directly regulated by European Union (EU) legislation, although the first European wide regulation on minimum requirements for water reuse for agricultural irrigation have been established as of May 2020 (Regulation EU 2020/741) (EU Parliament 2020). Drinking water standards across the EU are promulgated under the EU Drinking Water Directive (Council Directive 98/83).

2.8.2 Pathogen Crediting for Ozone/BAF Systems

To meet the log reduction targets for reference pathogens outlined in different water reuse guidance documents and regulations, multiple treatment processes can be implemented in series to achieve pathogen removal. Treatment processes such as filtration, biological treatment, and disinfection that achieve effective pathogen removal are given pathogen credits based on pathogen crediting frameworks outlined in different documents. For drinking water treatment, inactivation or disinfection credits are often determined by adequately maintained CT values. In contrast to ozonation of drinking water, ozone decay in treated wastewater is usually very fast which limits the applicability of the CT-concept in ozone/BAF systems for potable reuse. Furthermore, disinfection efficiency of ozonation in wastewater seems to depend on level of pre-treatment, especially with respect to turbidity. Current concepts for pathogen removal crediting are often based on general assumptions.

Research is needed to identify major drivers for pathogen inactivation during ozonation of either secondary or tertiary treated effluents. These efforts should address correlation of pathogens with specific water quality parameters (e.g., TOC, turbidity, nitrite), but also identify powerful surrogate-pathogen correlations for future operation and control of ozonation systems with respect to disinfection.

2.8.3 Drinking Water Quality Goals for Regulated DBPs for Ozone/BAF Treatment Trains

DBPs are formed in water treatment by the reaction of inorganic and organic constituents in the influent and the disinfectant applied. There have been hundreds (>600) of DBPs that have been identified in drinking water, however only the following are regulated by the U.S. Environmental Protection Agency (EPA): four THMs, five haloacetic acids, bromate, and chlorite. Standards for these DBPs are outlined in the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rule (1998, 2006)

Stage 1 Disinfectants and Disinfection Byproducts Rule has maximum residual disinfectant levels and maximum contaminant levels (MCLs) for all community water systems and nontransient noncommunity water systems that add chemical disinfectant to their water. The maximum residual disinfectant levels pertain to chlorine, chloramines, and chlorine dioxide, and MCLs pertain to total THMs (TTHMs), the sum of five haloacetic acids (HAA5), bromate, and chlorite. Stage 2 Disinfectants and Disinfection Byproducts Rule cover community water systems and nontransient noncommunity water systems that add disinfectants, other than UV, with the aim of requiring reduced levels of DBPs in distribution systems. The MCLs remain the same, but compliance is determined based on a location running average, not a system wide running average.

2.8.4 Additional Design Considerations for Pathogen Inactivation and Drinking Water Quality Goals

A multiple-barrier treatment strategy is an essential aspect to implementing potable reuse schemes. The EPA defines the multiple barrier approach as risk prevention, risk management, monitoring, and compliance, and individual action which can take on the form of technical, operational, and managerial barriers. For enhanced pathogen removal and DBP mitigation, multiple treatment barriers and system redundancy must be considered from source water control to tertiary treatment. Technical barriers occur in series, with constituent removal occurring in multiple treatment steps. The objective of this approach is to increase system reliability and resilience while reducing risk. Previous studies on potable reuse (WHO 1975) have reported that multiple-barrier treatment steps should ensure that pollutants should be reduced in concentration by at least two, but preferably three or more, treatment processes. California regulations stipulate that there must be at least three separate treatment processes for each pathogen for IPR schemes.

Constituents from primary wastewater sources are regulated by coupling the regulations outlined in the National Pretreatment Program and implementing source control programs. Wastewater can originate from several difference sources including discharges from industry, commercial facilities, and private residences. As a result, the composition of any given wastewater matrix can be highly variable. Source wastewaters can often be of very poor quality and contain high concentrations of pathogens and a variable range of chemical constituents. The purpose of the National Pretreatment Program and Federal Pretreatment Standards are to reduce the possible introduction of harmful constituents to a public treatment facility, which would otherwise be difficult to remove and potentially interfere with treatment operations. The purpose of implementing a source control program in conjunction with the National Pretreatment Program is to eliminate these pollutant loadings from specific wastewater sources as a preventative approach. The use of a source control program when planning a potable reuse treatment train can be the most cost-effective strategy to eliminate or control the presence and discharge of potentially harmful constituents and to enhance the performance of AWT processes.

In addition to source control, pretreatment steps such as biological processes in secondary treatment and filtration can enhance disinfection through microbial pathogen removal. Effective pretreatment can also enhance disinfection by ozonation through the removal of influent suspended solids (or biological flocs) and other colloidal materials. The presence of suspended solids would otherwise result in a heightened ozone consumption while reducing effective ozonation of target organic pollutants and pathogens. Studies have shown that pretreatment could reduce the ozone consumption as high as 25% (C. Wu et al. 2018). High suspended solid concentrations have also shown to often lead to frequent blockage of BAF and shorten the backwash cycle. An effective pretreatment step could also minimize the presence of DBP precursors (such as TOC concentrations) and in turn reduce the formation of harmful DBP. High concentrations of organic constituents in the source wastewater can lead to elevated concentrations of DBPs by reactions between disinfectants and organic constituents. The formation of DBPs also depends on the type of disinfectant used. In the case of ozone/BAF treatment, the oxidation of bromide and iodide can lead to bromate and brominated and iodinated DBPs. An effective pretreatment step could remove organic compounds prior to the disinfection step. In addition to pretreatment, DBPs can be removed by subsequent treatment steps after disinfection by means of tertiary treatment or an environmental buffer for IPR.

For risk mitigation and enhanced treatment, multi-barrier treatment should be considered with treatment steps and treatment train design based on the specific water matrix entering the potable reuse scheme and ozone/BAF system.

CHAPTER 3

Synthesis of Results and Additional Testing

3.1 Introduction and Objectives

Existing water supply systems have become increasingly stressed as global populations continue to rise. In response, water providers are enhancing the urban water cycle to include potable reuse as a source of local, sustainable, and safe drinking water. Full advanced treatment (FAT), consisting of reverse osmosis (RO) systems, has become the workhorse of many potable reuse projects throughout the world, but the associated costs and environmental footprint associated with energy use and brine disposal costs have led researchers and water providers to seek alternative treatment strategies. Ozone and biologically active filtration (BAF) and carbon-based advanced treatment (CBAT) represent a promising new frontier for potable reuse due to their ability to produce high quality purified effluents with reduced capital and operational costs compared to FAT. However, many questions remain related to recalcitrant constituents of emerging concern (CECs), appropriate performance surrogates, operational and design parameters for optimized performance, and necessary upstream and downstream treatment processes to create a reliable CBAT treatment train capable of exceeding regulatory requirements for potable reuse. Chapter 3 of this project addresses these key questions through use of the Chapter 1 literature review and survey data, insights provided by the Chapter 2 report, and other existing literature and project experience. Any remaining knowledge gaps are also identified for further research.

The four main objectives of Chapter 3 are as follows:

- Synthesize the results from Chapter 1 to test existing correlations between CEC and surrogate removals and identify recalcitrant CECs. Evaluate performance surrogates and indicators for ozone and BAF systems.
- Compare observed concentrations of recalcitrant CECs to the health-based water-quality parameters established in Chapter 2 and identify additional pre-treatment and post-treatment requirements for CECs and regulated compounds with public health concerns.
- Discuss operational and design considerations for ozone/BAF systems, including upstream water quality and treatment. Identify key design and operational parameters for ozone/BAF systems by leveraging survey data, literature, and industry knowledge that will inform Chapter 4.
- Identify any remaining knowledge gaps with respect to the above objectives.

The sections are organized according to the objectives listed above.

3.2 Performance Surrogates and Indicators

As part of Objective A of this chapter, data compiled from Chapter 1 were used to evaluate available models from past studies and identify performance surrogates to predict CEC removals by ozonation and BAF. For this chapter, a surrogate is defined as a quantifiable, online parameter that can serve as a performance measure of a treatment process by being correlated with the removal of specific constituents. Additionally, it should be able to indicate that there were changes in water quality.

Different indicators of BAF biological acclimation (i.e., transition from adsorption-dominated removal to biology-dominated removal) were also investigated. These parameters were referred to as indicators rather than surrogates because they are not being used as performance measures for a treatment process. Rather, they are being used to indicate that biological acclimation has occurred and BAF is performing adequately at steady state.

3.2.1 Ozone Performance Surrogates

The following sections discuss potential surrogates for performance of an ozone system. The ozone to total organic carbon (TOC) ratio (O_3:TOC) is a ratio of the ozone dose (mg/L) to the TOC concentration in the influent of the ozone system (mg/L). It can be used to indirectly target a specific CEC removal. Other surrogate parameters, including differential UV_{254} absorbance (ΔUV_{254}) and differential total fluorescence (TF), can be directly correlated with the elimination of CECs during ozonation (S. Snyder et al. 2014).

3.2.1.1 O_3:TOC Ratio

Generally, O_3:TOC ratio is used as both a design parameter and operational control strategy for the ozonation process. The O_3:TOC ratio can be an effective way to account for varying ozone demand and indirectly ensure that an adequate ozone dose was applied for a target level of CEC removal. As a design parameter, a target O_3:TOC ratio to achieve a performance objective allows for the estimation of a range of ozone doses for sizing the ozone system based on a range of anticipated influent TOC concentrations. As an operational control strategy, the ozone dose can be varied in real time based on changes in the TOC concentration. This can be thought of as a surrogate for ozone demand of the influent water to achieve a constant O_3:TOC ratio and achieve stable ozone exposure as long as other parameters such as nitrite, alkalinity and pH do not vary significantly. This is especially useful in a wastewater matrix when operating below the full ozone demand threshold (i.e., lack of significant ozone residual is generated), when ozone decay is very rapid, or when there may be operational reasons for not using dissolved ozone analyzers. Nitrite, in particular, must be considered in addition to TOC when applying O_3:TOC ratio as either a design parameter or operational control strategy. Ozone reacts moderately fast (reported reaction rate constants of $k = 1.8 \times 10^5\ M^{-1}\ s^{-1}$ and $5.83 \times 10^5\ M^{-1}\ s^{-1}$) with nitrite at a 1:1 molar stoichiometry without generating hydroxyl radicals (Naumov et al. 2010), so the target ozone dose should take the nitrite concentration into account. Notably, the O_3:TOC ratio does not directly validate that ozone reacted with TOC as the organics are typically transformed in the ozonation process and not removed. The use of O_3:TOC ratio as an operational control strategy may be further validated by considering the use of oxidized water quality changes to the organics (e.g., absorbance, fluorescence, biodegradable organic carbon/assimilable organic carbon [AOC]).

If the transferred ozone dose is determined in the receiving water by monitoring transfer efficiency (e.g., monitoring of ozone in the off-gas and accounting for that loss), then the O_3:TOC ratio can become a reliable predictor of CEC removal (Y. Lee et al. 2013, 2016). The first step is to determine the specific design criteria that will consistently achieve the treatment goals. One of these criteria will be a certain O_3:TOC ratio. If the influent water quality changes during operation (e.g., TOC increases), the control system for the ozone process will compensate by modifying the ozone dose, thereby maintaining a constant O_3:TOC ratio with the overall goal of consistent CEC removal. Previous studies have developed graphs relating the O_3:TOC ratio or specific ozone dose to percent reductions in ΔUV_{254} and TF (Gerrity et al. 2012; Park et al. 2017). If correlations between the percent reductions in CECs and ΔUV_{254} or TF have been developed for the particular wastewater matrix at a treatment facility, then the CEC removal can be predicted indirectly.

Several past studies have shown that a higher applied ozone dose and thus higher O_3:TOC ratio results in greater CEC removal (Huber et al. 2005; Y. Lee 2014; Pisarenko et al. 2012; Sundaram et al. 2020). Additionally, increasing the O_3:TOC ratio increases the hydroxyl radical exposure, ozone concentration multiplied by contact time (CT), and ozone residual (Gerrity et al. 2014). Typically, the consumption of ozone in water can be described as a two-stage process: initially, there is a rapid consumption of ozone due to reactions with organic compounds, and then a secondary, relatively slow decay occurs (EPA 2010, 11-16). The rapid decomposition of ozone during water treatment generates hydroxyl free radicals, which are primarily responsible for oxidative processes during the secondary phase. Ensuring the presence of an ozone residual should increase CEC removal because instantaneous ozone demand was satisfied, and a higher concentration of hydroxyl radicals were generated. This should be particularly effective for CECs that are susceptible to attack by ozone (e.g., triclosan, diclofenac, and naproxen). Regardless, CECs with relatively high ozone reaction rate constants (i.e., $K_{O3} \geq 10^5$ M^{-1} s^{-1}) can be significantly removed even when the ozone dose is less than the instantaneous ozone demand, causing ozone CT to not be measurable (Wert, Rosario-Ortiz, and Snyder 2009a).

3.2.1.2 ΔUV_{254} and ΔUVT

ΔUV_{254} has been shown to correlate well with CEC removal for advanced oxidation processes (AOPs) since ozone preferentially destroys aromatic carbon and UV_{254} represents the aromatic portion of organic matter (Gerrity et al. 2010; Nanaboina and Korshin 2010; Pisarenko et al. 2012; Rosario-Ortiz, Wert, and Snyder 2010; Wert, Rosario-Ortiz, and Snyder 2009b). As a water quality parameter, it indicates a decrease in the concentration of and/or transformation of the organics in the water. In other words, ΔUV_{254} can be used to confirm that there were changes in water quality corresponding to the degradation of CECs, so it may function as a performance surrogate. An additional benefit of ΔUV_{254} is that compounds with similar molecular structures or ozone and hydroxyl radical reaction rate constants can be grouped together because it has been shown they have similar removal efficiencies (Dickenson et al. 2009; Y. Lee et al. 2013; Y. Lee et al. 2014). Thus, a ΔUV_{254} correlation for a certain compound could be used to estimate percent removals of other similar compounds for which there are no data (Gerrity et al. 2012; Pisarenko et al. 2012). Gamage et al. (2013) found that ΔUV_{254} approached a horizontal asymptote of approximately 65% at O_3:TOC ratios above approximately 1.25. As ozone dose is increased absorbance diminishes and reaches a small value (e.g., <0.01 cm^{-1}) that becomes more difficult to measure accurately. Therefore, one potential limitation for ΔUV_{254} would be differentiating the impacts of O_3:TOC ratios greater than 1.25 that achieve ΔUV_{254} near 65% or higher. ΔUV_{254} data were available for six of the Chapter 1 facilities with an average of 40% and maximum of 52%, which would indicate that generally lower O_3:TOC ratios are used.

Measuring the change of absorbance at only a wavelength of 254 nm may not be sufficient to characterize all organic matter in wastewater (Nanaboina and Korshin 2010). Indeed, UV_{254} primarily assesses the aromatic component of organic matter (Wert, Rosario-Ortiz, and Snyder 2009b). Additionally, other wavelengths in different parts of the electromagnetic spectrum (e.g., visible light) may better capture the effects of oxidation on organic matter (Dickenson et al. 2009). However, it can be difficult to differentiate between varying ozone doses based on changes in visible light absorption (S. Snyder et al. 2012). Also, the relative differential absorbance in the visible spectrum may be high, but the actual magnitudes of the absorbance values are significantly lower compared with UV absorbance (UVA), possibly resulting in analytical limitations (S. Snyder et al. 2014). Therefore, ΔUV_{254} was chosen as the appropriate performance surrogate.

Gerrity et al. (2012) separated CECs into five groups based on second-order reaction rate constants with ozone and hydroxyl radicals (Table 3-1). Linear regression parameters were then developed by Gerrity et al. (2012) for CECs within each group that relate the ΔUV_{254} absorbance through the ozone process with CEC removal. For Groups 1–4, parameters were also developed for a representative "indicator," which was based on the values of all CECs studied within a specific group.

Table 3-1. Ozone and Hydroxyl Radical Rate Constants for Example Compounds in each CEC Group.

Data Source: Gerrity et al. 2012.

Compound	K_{O3} (M^{-1} s^{-1})	K_{OH} (M^{-1} s^{-1})
Group 1—High Reactivity with Ozone and •OH		
Bisphenol A	7×10^5	1×10^{10}
Carbamazepine	3×10^5	9×10^9
Group 2—Moderate Reactivity with Ozone and High Reactivity with •OH		
Atenolol	2×10^3	8×10^9
Gemfibrozil	5×10^4	1×10^{10}
Group 3—Moderate Reactivity with Ozone and •OH		
Ibuprofen	10	7×10^9
Primidone	1	7×10^9
Group 4—Low Reactivity with Ozone and Moderate Reactivity with •OH		
Atrazine	6	3×10^9
1, 4-Dioxane	<1	3×10^9
Group 5—Low Reactivity with Ozone and •OH		
Musk Ketone	<1	2×10^8
TCEP	<1	6×10^8

Linear regression parameters for Groups 4 and 5 were used to predict the percent removal of sucralose to determine the accuracy of the models. Sucralose was chosen because it was recommended by the 2018 Recycled Water CEC Science Advisory Panel as a performance-based indicator CEC for potable and non-potable reuse practices (Drewes et al. 2018). Ozone and hydroxyl radical reaction rate constants for sucralose are <0.1 and 1.6×10^9 M^{-1} s^{-1}, respectively (Bourgin et al. 2017). Based on these rate constants, sucralose likely belongs in either Groups 4 or 5. Therefore, parameters for the "indicator" were used for Group 4; for Group 5, parameters for Tris(2-carboxyethyl) phosphine (TCEP) were used because it was the only Group 5 CEC studied. Additional linear correlations for ΔUV_{254} have been developed (Pisarenko et al. 2012; S. Snyder et al. 2012), but sucralose was not studied. The sucralose removals predicted by the

ΔUV_{254} regression parameters, actual sucralose removals, and ozone dose ratios for five facilities are graphed in Figure 3-1 below.

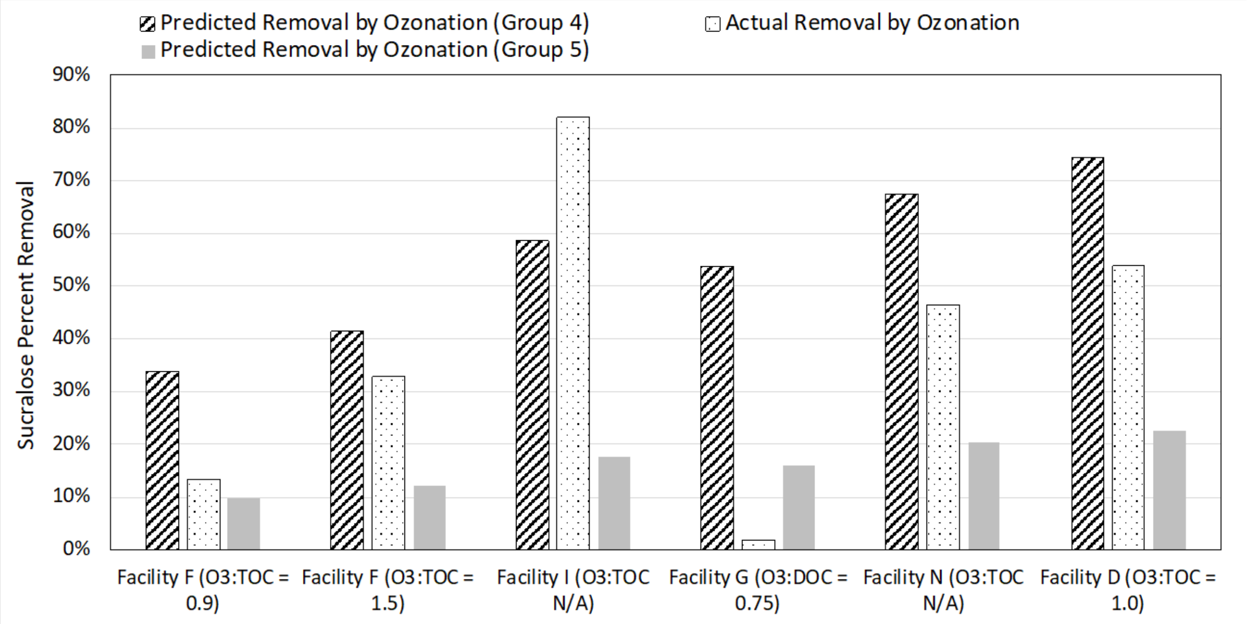


Figure 3-1. Predicted and Actual Sucralose Removals by Ozonation as a Function of O_3:TOC or O_3:DOC Ratios.

The actual removal is typically between the predicted removals from Gerrity et al. (2012). Particularly, the Group 4 predicted values—represented by the columns with diagonal lines—are usually higher than the actual removals while the Group 5 predicted values—represented by solid gray columns—are usually below the actual removals. The Group 4 "indicator" may not provide a reliable correlation for sucralose, so a specific correlation may need to be developed. Facility G is an outlier: the actual removal was only 2%, which is substantially lower than the predicted values. A similar analysis completed for meprobamate as a Group 4 CEC using specific regression parameters from Gerrity et al. (2012) also resulted in a predicted removal that was much higher than actual removal (19% versus 59%). One possible explanation is that the ozone dose was too low and hydroxyl radicals were scavenged away by the sample matrix. Facility I is also an outlier because the actual removal of 82% is substantially higher than the predicted values. Hydrogen peroxide (H_2O_2) is added at Facility I as part of the ozonation process, which accelerates ozone decay and thus the formation rate of hydroxyl radicals (von Gunten 2003a). Oxidation by hydroxyl radicals could thus be a potential explanation given sucralose's moderate reactivity. However, previous research has shown that H_2O_2 addition during wastewater ozonation only increased the elimination efficiency of ozone-resistant CECs such as sucralose by less than 10% (Y. Lee et al. 2013).

3.2.1.3 Sucralose

Sucralose was recommended by the 2018 Recycled Water CEC Science Advisory Panel as a performance-based indicator CEC for potable and non-potable reuse practices (Drewes et al. 2018) because it was found to be a ubiquitous, persistent compound. To assess the suitability of sucralose as a performance surrogate for ozone, percent removals of sucralose were compared with those of meprobamate and TCEP in Figure 3-2. These CECs were chosen for the following reasons: i) Data from several facilities were available, ii) They are not easily oxidized by ozone, and iii) They have similar ozone and hydroxyl radical reaction rate constants compared to sucralose (Table 3-2).

Table 3-2. Ozone and Hydroxyl Radical Reaction Rate Constants for Sucralose, Meprobamate, and TCEP.

CEC	k_{O3} (M^{-1} s^{-1})	k_{OH} (M^{-1} s^{-1})
Sucralose[a]	<0.1	1.6×10^9
Meprobamate[b]	<1	4×10^9
TCEP[c]	<1	6×10^8

[a] Source: Bourgin et al. 2017.

[b] Source: Y. Lee and von Gunten 2012.

[c] Source: Watts and Linden 2009.

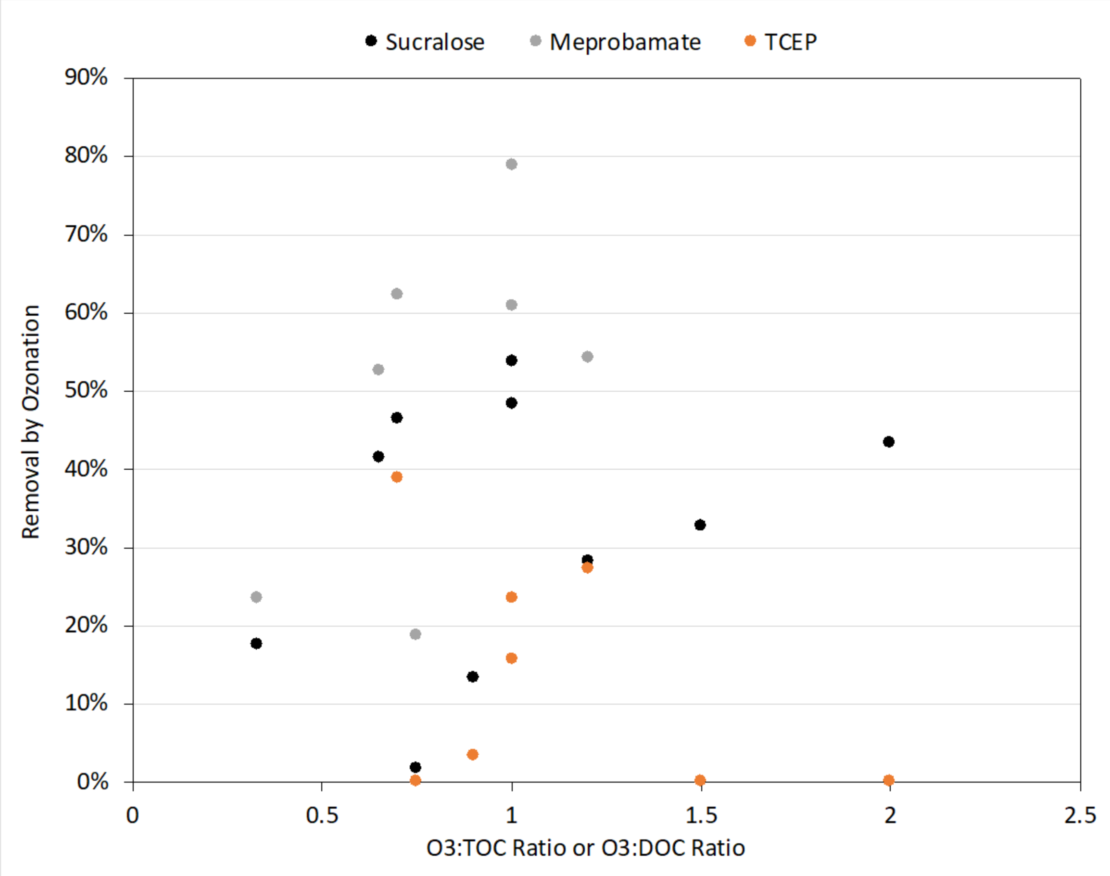


Figure 3-2. Percent Removals of Sucralose, Meprobamate, and TCEP from Chapter 1 Facilities as a Function of O_3:TOC or O_3:DOC Ratios.

The sucralose data are clustered in two groups: i) Steep relationship with O_3:TOC ratio that is similar to meprobamate and ii) A flatter relationship with O_3:TOC. For TCEP, removals were set to zero if the calculated values based on the provided data were negative. Generally, there is a lot of scatter, and it is not readily apparent that a higher ozone to organic carbon ratio results in greater removal of these CECs. One possible explanation is the lack of site specificity in Figure 3-2. Sucralose removal was between removals of meprobamate and TCEP for each facility with data for all CECs. Water matrices of varying quality can have different instantaneous ozone demands and thus dissimilar ozone oxidation efficiencies. Therefore, it is preferable to develop

CEC removal correlations for a specific water matrix. Past research studies have shown that increasing the O_3:TOC ratio for a particular water matrix generally results in higher CEC removal (Gerrity et al. 2012; Y. Lee et al. 2013, 2016; Pisarenko et al. 2012). Site-specific testing is necessary to determine the correlations between the removal of an indicator compound and CECs.

Indicators that are poorly removed under normal operating conditions provide little insight into system performance (Dickenson et al. 2009). In principle, if it is demonstrated for a particular water matrix that a certain level of removal of an indicator compound achieves a target performance removal (e.g., ≥90%) of CECs of interest, then those correlations should consistently hold assuming the characteristics of that water do not change significantly. By this logic, poorly removed CECs such as TCEP and sucralose should not be used as indicators for the ozonation process. The selection of meprobamate would be better suited as an indicator for the ozone process because its removals are consistently higher than TCEP and that of sucralose, yet it is not easily removed such that partial failures of the ozonation process would not go undetected.

3.2.1.4 Differential Total Fluorescence

Fluorescence spectroscopy has shown promise in predicting the removal of CECs during advanced water treatment (AWT) (Anumol et al. 2015; Gerrity et al. 2012; Pisarenko et al. 2012; Sgroi et al. 2017). For example, Anumol et al. (2015) found good linear correlations when comparing differential total fluorescence (ΔTF) with the removals of different CECs including atenolol, meprobamate, gemfibrozil, and triclocarban. Gerrity et al. (2012) also developed linear regression parameters for differential fluorescence. It was concluded that ΔTF can be used as a surrogate for target compound elimination, and full-scale application of empirical equations is feasible because automated online analyzers are available. Pisarenko et al. (2012) and Anumol et al. (2015) found that the correlations for ΔTF were better than those of ΔUV_{254}, although both surrogates performed sufficiently well.

Fluorescence data are presented as three-dimensional excitation-emission matrices where fluorescence intensities are a function of excitation and emission wavelengths (Sgroi et al. 2017). There are a variety of methods used to interpret excitation-emission matrices (EEMs). Fluorescence regional integration (FRI) involves the division of EEMs into five regions and subsequent integration of the volumes under the five regional EEM surfaces (Sgroi et al. 2017). TF is the sum of the integration for all regions. The five regions were operationally defined by Chen et al. (2003) based on the locations of EEM peaks determined by past research for a variety of substances. These five regions indicate the presence of specific organic fractions, including aromatic proteins, soluble microbial products (SMPs), fulvic-like substances, and humic-like substances. Generally, peaks at shorter excitation (<250 nm) and emission (<350 nm) wavelengths are related to aromatic proteins while peaks at longer excitation (>280 nm) and emission (>380 nm) wavelengths are related to humic-like substances. Peaks at intermediate excitation (250–280 nm) and shorter emission (<380 nm) wavelengths are related to SMPs. Peaks at shorter excitation (<250 nm) and longer emission (>380 nm) wavelengths are related to fulvic-like substances. Bench-scale ozonation experiments for five U.S. secondary effluents indicated the organic fractions associated with aromatic proteins and SMPs were transformed extensively and at a particularly rapid rate, although there was significant transformation in all regions (S. Snyder et al. 2012). Additionally, it was found that the regional fluorescence intensity for humic acids decreased at the slowest rate out of all the regions, but its contribution to the TF was the lowest at 15% (S. Snyder et al. 2012).

A modified FRI method described elsewhere (Gerrity et al. 2011; Stanford et al. 2011) was used to create a graph of the ΔTF versus estimated O_3:TOC ratio for data from Facility D (Figure 3-3).

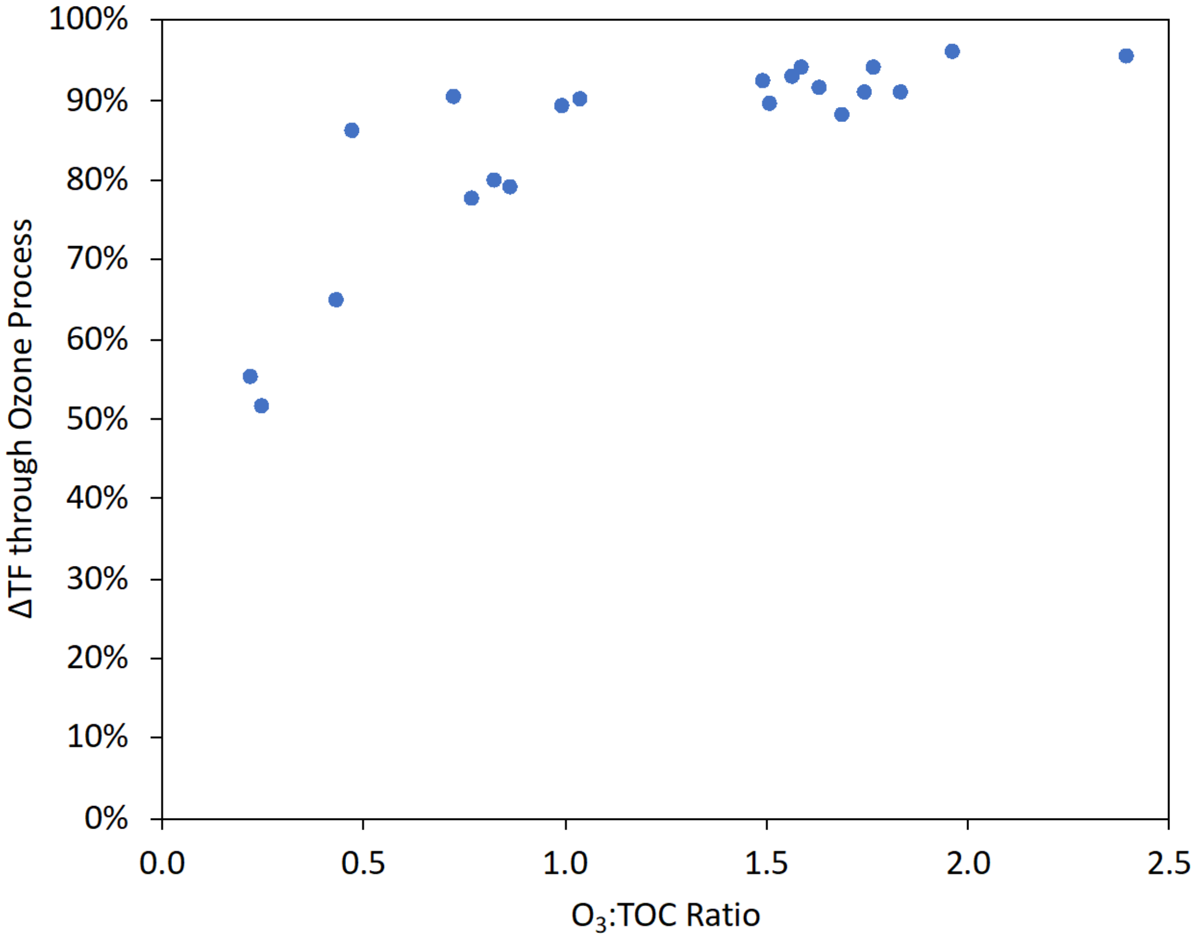


Figure 3-3. ΔTF through Ozonation as a Function of O_3:TOC Ratio at Facility D.

ΔTF can indicate that organics were oxidized via addition of ozone. Increasing O_3:TOC ratio beyond approximately 1.5 does not significantly impact ΔTF, as maximum decrease in ΔTF is observed. There are no fluorescence data for the other 15 facilities from Chapter 1. Generally, fluorescence is not regularly monitored at full-scale treatment facilities. Complex analyses are necessary to transform EEM information into useful data; UV_{254} analyses are relatively simple. An integrated online system is necessary for continuously monitoring process performance. Online fluorescence meters are not as available, and there is a substantial cost associated with a benchtop unit. Overall, there is currently no substantial incentive to use it as a surrogate over ΔUV_{254}. However, there is still potential for ΔTF to be used at full-scale facilities in the future as online fluorescence meters become more widely available. As mentioned previously, ΔTF correlations to CEC removal have been found to be better than those of ΔUV_{254}.

3.2.1.5 Ozone CT

Ozone CT is another parameter that could serve as a performance surrogate for CEC removal when ozone demand has been overcome, meaning the organics that readily react with ozone will likely be destroyed, and hydroxyl radicals will be generated. It requires measurement of the ozone residual and contact time. Ozone residual can be challenging to measure in wastewater, but it is done when seeking disinfection credit. There are guidance manuals available from the United States Environmental Protection Agency (EPA) concerning the calculation of ozone CT and inactivation of pathogens depending on the water temperature and CT value (e.g., Long Term 2 Enhanced Surface Water Treatment Rule [LT2ESWTR] Toolbox Guidance Manual, 2010). Ozone CT is a viable option for facilities looking to obtain additional log removal credits for viruses, *Giardia,* and even *Cryptosporidium*, which requires a higher CT compared to the other two pathogens. Recent studies, however, suggest that significant microbial inactivation is possible when the applied ozone dose is less than the instantaneous ozone demand, which corresponds to an apparent CT of 0 mg-min/L (Gamage et al. 2013; S. Snyder et al. 2014). No studies were found where ozone CT and CEC removal were directly correlated. Ozone CT could be used to indirectly predict CEC removal by developing a relationship with the O_3:TOC ratio. Gamage et al. (2013) developed a linear relationship between these two parameters based on bench-scale ozonation experiments of five U.S. secondary effluents with O_3:TOC ratios of 0.5 to 1.3. It was found that the O_3:TOC ratio provides an accurate estimate of ozone CT at ratios less than 1.5 (Gamage et al. 2013). Snyder et al. (2014) developed a power relationship between O_3:TOC ratio and ozone CT through bench scale experiments of U.S. and international secondary effluents. Finally, Gerrity et al. (2014) developed a relationship that also included the TOC concentration, instantaneous ozone demand, and ozone decay rate constant. For some dosing conditions (O_3:TOC = 0.3 and 0.5), it was not possible to develop regressions because the dissolved ozone residual decreased too rapidly (Gerrity et al. 2014). These relationships could be used to estimate the O_3:TOC ratio based on measured ozone CT, which could in turn be used to predict CEC removal.

Ozone CT is not an appropriate surrogate under low-dosing conditions. Ozone exposures are generally not quantifiable until the O_3:TOC ratio increases beyond 0.35 (S. Snyder et al. 2014). If ozone CT were to be used for the prediction of CEC removal, then it is suggested that it be used in conjunction with hydroxyl radical exposure as discussed in the following Section.

3.2.1.6 Chemical Kinetics and R_{ct}

An approach based on chemical kinetics can be used to predict the removal of CECs if the rate constants and exposures associated with ozone and hydroxyl radicals are known. The R_{ct} concept developed by Elovitz and von Gunten (1999) is a ratio of hydroxyl radical exposure and ozone exposure. R_{ct} was shown to be constant over variable ozone dosing conditions for several natural waters (Elovitz and von Gunten 1999). Once R_{ct} value is known, hydroxyl radical exposure can be directly correlated to ozone exposure and used dynamically. Currently, a few hundred K_{O3} values and more than a thousand K_{OH} values are known for various organic compounds and contaminants in water (Y. Lee and von Gunten 2016). Ozone exposure can be determined by integrating ozone decay curves over time, and hydroxyl radical exposure can be calculated by integrating the hydroxyl radical concentration over the reaction time (Y. Lee and von Gunten 2016). The change in concentration of an ozone-resistant compound such as *para-*

chlorobenzoic acid can also be used to experimentally determine the hydroxyl radical exposure at a given ozone dose and ozone exposure (Elovitz and von Gunten 1999). Lee et al. (2013) validated this approach by finding that CEC elimination was consistent in different wastewater effluents when the applied ozone dose was normalized to the concentration of dissolved organic carbon (DOC). Additionally, CEC elimination strongly correlated with the specific reaction rate constants, so CEC groups based on those constants had characteristic elimination patterns. Lee et al. (2014) further validated this approach by using it to reasonably predict the elimination of CECs for a membrane bioreactor (MBR)-treated hospital wastewater effluent.

Integrating ozone decay curves over time to obtain the ozone exposure can be problematic in wastewater effluents due to relatively high concentrations of organic matter, especially for nitrite-corrected specific ozone doses less than approximately 0.3 g O_3/g DOC (Y. Lee and von Gunten 2016). These organics react instantaneously with ozone, making it difficult to accurately determine the ozone exposure without advanced methods (Hübner, Keller, and Jekel 2013). An alternative approach that could be utilized for continuous performance monitoring at a full-scale facility would be to select a CEC that is reactive with ozone (e.g., carbamazepine) and an ozone-resistant CEC that is susceptible to hydroxyl radicals (e.g., iopromide or meprobamate). Tracking the removals of these CECs by ozonation would allow for the indirect measurements of ozone exposure and hydroxyl radical exposure. It would then be possible to estimate the removals of other CECs if the specific reaction rate constants are known. Prior studies have demonstrated that this approach is possible and that the use of an ozone-resistant CEC to predict the hydroxyl radical exposure works reasonably well (Elovitz and von Gunten 1999; Huber et al. 2005; Hübner, Keller, and Jekel 2013; Y. Lee et al. 2014). However, there are substantial uncertainties in the estimation of the ozone exposure due to the complex ozone chemistry and the non-linear relationship between the ozone exposure and specific ozone dose (Y. Lee and von Gunten 2016).

3.2.1.7 Summary of Ozone Performance Surrogates

The O_3:TOC ratio can be used as both a design parameter and operational control strategy for the ozonation process. O_3:TOC ratio can be an effective way to account for varying ozone demand and indirectly ensure adequate ozone dose was applied for a target level of CEC removal. If the transferred ozone dose in the receiving water is determined by monitoring transfer efficiency, then the O_3:TOC ratio can become a reliable predictor of CEC removal (Y. Lee et al. 2013; Y. Lee and von Gunten 2016). If the influent water quality changes during operation (e.g., TOC increases), the ozone dose can be modified to maintain a constant O_3:TOC ratio with the overall goal of consistent CEC removal.

Both ΔUV_{254} and ΔTF have been shown to correlate fairly well with CEC removal for AOPs (Anumol et al. 2015; Gerrity et al. 2010; Gerrity et al. 2012; Nanaboina and Korshin 2010; Pisarenko et al. 2012; Rosario-Ortiz, Wert, and Snyder 2010; Sgroi et al 2017; Wert, Rosario-Ortiz, and Snyder 2009b). However, complex analyses are necessary to transform EEM information into useful data, while UV_{254} analyses are relatively simple. Online fluorescence meters for continuously monitoring process performance are not as available, and there is a substantial cost associated with a benchtop unit. Overall, there is currently no substantial incentive to use ΔTF as a surrogate over ΔUV_{254}. There is still potential for ΔTF to be used at full-scale facilities in the future as online fluorescence meters become more widely available because ΔTF correlations to CEC removal have been found to be better than those of ΔUV_{254} (Anumol et al. 2015; Pisarenko et al. 2012). Sucralose was used to test the correlations determined by Gerrity et al. (2012) and also investigated as a performance surrogate. The actual sucralose removal was typically between the removals predicted by compounds associated with Groups 4 and 5 (Table 3-1). Sucralose was determined to not be a suitable performance surrogate specifically for the ozonation process because its removal levels are too low.

Ozone CT is a viable option for facilities looking to obtain additional log removal credits for pathogens. If ozone CT were to be used for the prediction of CEC removal, then it is suggested that it be used in conjunction with hydroxyl radical exposure as part of the R_{ct} method. R_{ct} is a ratio of hydroxyl radical exposure and ozone exposure. This approach involves the use of chemical kinetics, specifically the ozone and hydroxyl radical rate constants and exposures, to predict the removal of CECs. This approach has been validated, and it is known that CEC groups based on reaction rate constants had characteristic elimination patterns (Y. Lee et al. 2013, 2014). Generally, a more practical and simpler approach would be to use the O_3:TOC ratio in combination with ΔUV_{254}.

3.2.2 BAF Performance Surrogates and Indicators

The following sections discuss potential performance surrogates and biological acclimation indicators for BAF. ΔTOC is a simple and reliable performance surrogate for the biological degradation of organics through the BAF. ΔUV_{254} can also be used as a performance surrogate for the change in organics, but precise measurements are required. Different indicators of acclimation can be used, including TOC, Perfluorooctanoic acid (PFOA), and N-Nitrosodimethylamine (NDMA). Adenosine triphosphate (ATP) can serve as an indicator of biological activity.

3.2.2.1 ΔTOC

TOC removal is the main performance surrogate for BAF. For potable reuse, control of organic matter is critical, due to either the potential toxicity of complex mixtures of residual trace organic compounds, disinfection byproduct (DBP) formation after chloramination or chlorination, or biological regrowth in distribution systems (Gifford, Selvy, and Gerrity 2018). Pre-ozonation transforms recalcitrant bulk organic matter into more biodegradable fractions, so BAF efficiently removes TOC. Ozonation has been shown to increase the biodegradable fractions from 20% to 30% and the amount of AOC from 3% to 9% (Terry and Summers 2018). This increase in AOC increases median TOC removal during biofiltration from 10% for non-ozonated water to 15% for ozonated water (Terry and Summers 2018). TOC percent removals for facilities from Chapter 1 were calculated based on the provided data for ozone and BAF effluents (Table 3-3).

Table 3-3. Provided Ozone Effluent and BAF Effluent TOC Data for Several Facilities from Chapter 1 and the Calculated TOC Removal.

Facility	EBCT (min)	O_3:TOC or O_3:DOC Ratio	TOC (mg/L)		Calculated Removal
			Ozone Effluent	BAF Effluent	
Facility F	10	0.9	8.8	6.5	26%
Facility F	20	0.9	8.8	3.3	62%
Facility F	10	1.5	7.6	6.4	16%
Facility F	20	1.5	7.6	4.0	47%
Facility F	10	2.0	7.4	5.8	22%
Facility F	20	2.0	7.4	3.8	48%
Facility C	20	N/A	5.9	2.1	64%
Facility A	15	1.2	6.3	4.6	27%
Facility P	9–28	0.1	4.7	3.8	19%
Facility G	10	0.5–1	0.4	0.1	70%
Facility K	18–30	0.35–0.65	5.1	3.7	27%
Facility H	15–23	0.0–1.1	4.5	3.3	28%
Facility D	15	0.8–1.2	7.4	5.0	32%

TOC removals ranged from 16% to 70%. The data provided for the relatively high percent removals may have been from the period where carbon-based adsorption was still significantly contributing to bulk organics removal. Regardless, a well-designed BAF with a healthy biological community should consistently remove at least 15–20% of TOC. A median TOC removal of 28% was observed from the pool of facilities surveyed in Chapter 1. This will likely reduce the formation of total trihalomethanes (TTHMs) by downstream chlorination as a positive correlation between TTHM formation and effluent TOC concentration was identified in a previous study (Arnold et al. 2018).

3.2.2.2 ΔUV_{254} and ΔUV

ΔUV_{254} may also be used as a BAF performance surrogate. This could be attractive from an operational standpoint if ΔUV_{254} is already being used as a performance surrogate for the ozone system because it would simplify monitoring. However, the relative change in UV_{254} by BAF is expected to be much less than that of ozonation since most of the aromatic portion of natural organic matter (NOM) would have been removed by ozonation prior to BAF. The change in UV transmittance (ΔUVT) for several facilities from Chapter 1 is given below in Table 3-4.

Table 4-1. UV Transmittance Values for Ozone Effluent and BAF Effluent from Several Chapter 1 Facilities.

Facility from Chapter 1	Ozone Effluent		BAF Effluent		UV_{254} Difference (cm^{-1})	UVT Difference
	UVT(%)	UV_{254} (cm^{-1})	UVT(%)	UV_{254} (cm^{-1})		
Facility F	76.4	0.117	80.5	0.094	0.023	4.1
	76.4	0.117	92.8	0.032	0.085	16.4
Facility C	81.5	0.089	86.3	0.064	0.025	4.8
Facility I	84.5	0.073	91.6	0.038	0.035	7.1
Facility G	99.1	0.004	99.3	0.003	0.001	0.2
Facility J	91.4	0.039	95.5	0.020	0.019	4.1
Facility D	84.7	0.072	90.7	0.042	0.030	6.0

A typical increase in UVT by BAF is 4 to 7% based on Table 3-4. The median UV_{254} difference is 0.025 cm^{-1}. Therefore, accurate and precise measurements would be required for this surrogate to be reliable. A UVT analyzer with a relatively long path length may be needed for the BAF effluent. These analyzers are available, but there are limited data showing that ΔUVT consistently correlates well with BAF performance surrogates and indicators such as NDMA or TOC removal. ΔTOC would be preferred over ΔUV_{254} as a BAF performance surrogate because there is a greater margin for measurement error with ΔUV_{254}.

3.2.2.3 Indicators for BAF Acclimation and Healthy Biomass

TOC is the easiest way to show that most of the adsorptive capacity of the granular activated carbon (GAC) has been exhausted. Refer to Section 3.5.3.7 (Acclimation Period) for additional information. Initially, TOC is well adsorbed by virgin GAC, but the removal steadily decreases due to a reduction in the number of available adsorption sites. Eventually, TOC removal plateaus, indicating that a form of steady state has been reached (i.e., the dominant bulk organic removal mechanism has shifted from adsorption to biodegradation). However, CEC removal by adsorption may still occur even after this transition. Bourgin et al. (2018) found that removal of several CECs (e.g., benzotriazole, diclofenac, and metoprolol) was still about 40–50% for exhausted GAC after 50,000 bed volumes were treated. Desorption of adsorbed CECs can also occur due to displacement by compounds that adsorb more strongly or when the concentration gradient between the liquid and solid phases in an adsorber reverses, resulting in back diffusion to the water phase (Corwin and Summers 2011). Past studies have indicated that CEC desorption from GAC can occur under certain conditions (Bacaro et al. 2019; Sun et al. 2018; Sundaram et al. 2020). For example, Greenstein et al. (2018) found that multiple CECs—including caffeine, N, N-diethyl-meta-toluamide (DEET), gemfibrozil, and trimethoprim—continued desorbing 30 days after influent contaminant dosing was terminated. Generally, BAF is not relied upon for the removal of most recalcitrant CECs and primarily is used for biological removal of NDMA, bulk organic matter, and low molecular weight (MW) transformation products (TPs) resulting from the ozonation process. However, CEC desorption from BAF should still be considered as it cannot be controlled. If the CEC concentration in the BAF effluent is of concern due to lack of removal by BAF or due to desorption, then downstream GAC would be the recommended resolution.

Besides TOC, there are two different types of compounds that could be used as indicators for steady-state operation of BAF: i) Compounds that are well adsorbed by GAC but do not biodegrade easily, and ii) Compounds that are biodegradable but are not well removed by GAC. Example compounds for the first type are the surfactants PFOA and Perfluorooctanesulfonic acid (PFOS), artificial sweeteners such as sucralose and flame retardants such as TCEP. Acetone and NDMA are examples of the second type of compounds as potential indicators of biological health and performance.

GAC effectively removes the first type of compounds (e.g., PFOA/PFOS) via adsorption (Appleman et al. 2013; Du et al. 2014; Kucharzyk et al. 2017). Additionally, their characteristic fluorine-saturated carbon chain element of per- and polyfluoroalkyl substances (PFAS) compounds provides resistance to utilization by microorganisms as carbon and energy sources (Kucharzyk et al. 2017). The limited number of studies testing biodegradation of PFOA/PFAS obtained conflicting results, suggesting that more research is needed to understand the process (Kucharzyk et al. 2017). Artificial sweeteners such as sucralose and flame retardants such as

TCEP can also be well-removed by GAC but are not easily biodegradable. For Facility F, there were reductions in sucralose concentrations of up to 99% when the empty bed contact time (EBCT) was increased from 10 min to 20 min (Table 3-5). The difference in percent removals is likely due to the filter with the 20-min EBCT having a greater adsorptive capacity due to fewer bed volumes treated (BVT), which is shown in Table 3-5, as opposed to the increased EBCT resulting in greater biodegradation. Sucralose removal was demonstrated to be a function of BVT at Facility F as adsorptive capacity decreased; for an O_3:TOC ratio of 0.9, percent removal in the 10-min EBCT filter was near 100% at 2,743 BVT but eventually decreased to less than 10% at 57,682 BVT (Sundaram et al. 2020).

Table 3-5. Sucralose Concentrations in the Ozone Influent, Ozone Effluent, and BAF Effluent for Facility F at Different EBCTs and O_3:TOC Ratios.

EBCT (min)	O_3:TOC Ratio	BVT	Ozone Influent (ng/L)	Ozone Effluent (ng/L)	BAF Effluent (ng/L)	Percent Removal by BAF
10	0.9	16,325[a]	74,154	64,234	21,496	71%
20	0.9	8,322[a]			521	99%
10	1.5	61,725	58,000	39,000	33,000	43%
20	1.5	31,981			1,900	97%
10	2.0	62,880	53,000	30,000	37,000	30%
20	2.0	32,559			2,000	96%

[a] Denotes average of all BVT values associated with each individual data point.

The removal of the second type compounds, such as acetone and NDMA could be tracked over time to estimate the beginning of substantial biological activity and the general health of the microbial community. A compound with a larger log K_{OW} (octanol-water partition coefficient) is more hydrophobic and more likely to partition out of the bulk water phase. With a log K_{ow} of -0.57, NDMA is hydrophilic, so it adsorbs poorly to activated carbon (Mitch et al. 2003). Acetone also has a negative log K_{ow} of -0.23 (Cumming and Rücker 2017). Sundaram et al. (2020) found that NDMA data from Facility F show a transition between carbon-based and non-carbon-based mechanisms during the test duration and a BAF acclimation time of around 140 days or 20,000 BVTs. While virgin GAC might initially be able to remove NDMA effectively, the removal percentages in the aforementioned study decreased steadily over the first 70 days or 10,000 BVTs to as low as ~30%. Additionally, multiple studies have found activated carbon adsorption to be an ineffective water treatment process for NDMA removal (Dai et al. 2009; Fleming et al. 1996; Ho et al. 2011; Krasner et al. 2013; Mitch et al. 2003). Removal of NDMA by BAF is primarily due to biodegradation, not carbon-based adsorption. As with acetone, formaldehyde is also formed during ozonation but effectively removed by BAF (Tackaert et al. 2018). As such both acetone and formaldehyde may be more economical than NDMA to serve as indicators of biological removal of trace organic compounds.

ATP can be used as an indicator of biological activity. A review of biofilm processes in GAC found that ATP correlates well with the number of living, viable biofilm cells and oxygen uptake rate (Simpson 2008), so the quantity of ATP present in a biofilm provides an indication of overall bacterial activity (i.e., biomass growth rate, substrate removal rate, and physiological state of the bacteria). One study of pilot-scale GAC filters was not able to detect ATP, but this was attributed to the relatively high detection limit associated with the chromatography method used (Gibert et al. 2013).

Velten et al. (2007) developed a method to estimate the active biomass on GAC particles by combining a direct ATP measurement on GAC particles with the determination of case-specific ATP value per cell. For the ATP measurement, the luminescence of a sample was measured in relative light units using a luminometer, and the result was then converted to an ATP concentration using a calibration curve constructed with a pure ATP standard solution. Determination of the case-specific ATP concentration per cell was determined using a combination of ATP analysis and flow cytometry. Testing of GAC from full-scale and pilot-scale reactors indicated the method produced realistic values for biomass concentration when compared with those of alternative methods (Velten et al. 2007). Additionally, a measurement uncertainty of 15% was calculated for the method, indicating the results are reproducible; furthermore, the method was able to capture the rapid changes in biomass concentration during the start-up phase of a GAC reactor (Velten et al. 2007). This method was further validated during six-month testing of a pilot-scale GAC filter by Velten et al. (2011). However, an important issue with this method is that it is not appropriate for online continuous process monitoring because sample analysis takes approximately 45 minutes (Velten et al. 2007).

de Vera and Wert (2019) determined the active microbial biomass of water samples taken from two full-scale treatment facilities using both a discrete offline method and an online automated method. The offline method was similar to the one used by Velten et al. (2007) in that it was luminescence-based. The online ATP method had a sampling interval of six hours and was based on the chemiluminescent reaction involving luciferin and luciferase. Sample analysis and data processing for the online method took seven minutes. Results of the online ATP analyses agreed well with the results obtained from discrete ATP measurements. Particularly, the online method was able to differentiate between four different water samples, which are listed in order of highest to lowest ATP concentrations: i) raw water and acetate, ii) ozonated water, iii) raw water, and iv) final chlorinated water. Furthermore, the online method was able to capture rapid changes in ATP when samples were spiked with acetate. Generally, it was found that the online method was useful for rapid assessment of viable biomass.

In summary, ATP analysis can be used as an indicator of biological activity for BAF. Furthermore, it can capture rapid changes in biomass during dynamic periods of BAF operation (e.g., start-up), and it can differentiate between water samples taken from different points of a treatment train. Therefore, it can be useful for tracking the growth of biomass and determining if there is enough biomass for the removal of biodegradable compounds such as NDMA. However, its applicability is limited as no correlations were found between ATP and CEC removal in the literature. While the results of de Vera and Wert (2019) do serve as a proof-of-concept, it is still an emerging online technology and thus not practical for daily operations of a full-scale facility.

3.2.2.4 Summary of Indicators for BAF Acclimation and Healthy Biomass

Online TOC meters provide the most direct metric for assessing BAF process performance, from start-up with virgin GAC, to exhaustion, and steady-state operations. NDMA, acetone, formaldehyde are examples of ozone byproducts and can be used as indicators of biological degradation of trace organic compounds. The use of ATP for assessing the relative health of BAF needs to be further evaluated to become a viable indicator of process performance.

3.3 Recalcitrant CECs

A key part of this project is understanding which CECs are recalcitrant through the ozone/BAF process, and to what degree project planners should be concerned with these compounds in terms of public health. The following Section includes an analysis of the CEC water quality data collected in the Chapter 1 facility survey and identifies the CECs that were detected in BAF effluent. The detected CEC concentrations were compared to established health-based water quality objectives, including those identified in Chapter 2. Chemical properties of the detected CECs are also discussed in the context of identifying additional treatment options for CECs with potential concerns for public health.

Water quality data from 16 of the participating utilities was used to develop a matrix of detected CECs in BAF effluent. For this analysis, CECs were defined as compounds which are not currently regulated by the EPA's drinking water Maximum Contaminant Levels (MCLs). This approach is consistent with the California (CA) State Water Resources Control Board (SWRCB) Monitoring Strategies for CECs in Recycled Water Science Advisory Panel Report (Drewes et al. 2018). The methodology for examining recalcitrant CECs was performed as follows:

- Any CECs that were measured above the detection limit were tabulated for each of the 16 facilities that provided water quality datasets. The 90th percentile BAF effluent concentrations (BAF_{eff}) were calculated for each facility and the largest BAF_{eff} values were reported and compared to health-based concentration limits and/or benchmarks[2]. Other CECs that are recognized in the literature to be recalcitrant through ozone and BAF, but were lacking data from participating utilities, were also discussed.
- Concentration limits and/or benchmarks were tabulated for each of the CECs that were detected. These limits and benchmarks were included from the following sources:
    - EPA drinking water Notification Levels (NLs) (EPA 2020a)
    - California Toxics Rule (CTR) Human Health Criteria (EPA 2000)
    - SWRCB Monitoring Strategies for CECs in Recycled Water (Science Advisory Panel Report) and Water Quality Control Policy for Recycled Water monitoring trigger levels (MTLs) (Drewes et al. 2018; SWRCB 2018b)
    - California EPA Office of Environmental Health Hazard Assessment (OEHHA) Public Health Goals (PHGs) (OEHHA 2020a; OEHHA 2020b)
    - Risk-based concentrations for DBPs, as calculated by Evans, Campbell, and Naidenko (2020).
    - California 10^{-6} Lifetime Excess Cancer Risk (LECR), as calculated by T. Zeng, Plewa, and Mitch (2016a).

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[2] In the 2018 Science Advisory Panel report, measured environmental (or effluent) concentrations (MECs) are used to describe observed CEC concentrations in secondary/tertiary effluent. BAC_{eff} is used in this report to avoid confusion: the use of MEC may imply that the concentration was measured in secondary/tertiary effluent.

  - Minnesota Department of Health (MDH) human health-based guidance values: Concentration benchmarks based on acute, subchronic, or chronic chemical exposures (MDH 2020a; MDH 2020b)
  - Texas Commission on Environmental Quality (TCEQ) oral reference doses (RfDs) for PFAS (TCEQ 2016).
- Any detected CECs that exceeded any of the above listed limits or benchmarks were highlighted for further inspection.
- Because some CECs have no established concentration limits or benchmarks, toxicological parameters were used in order to gain information about the relevance of the observed concentrations to public health in comparison to compounds with concentration limits (e.g., NLs and MTLs). The following toxicological information was obtained from the EPA CompTox Chemicals Dashboard database:
  - Lowest Observed Adverse Effect Level (LOAEL): The lowest chemical dose in a study which is observed to cause an adverse health impact based on acute, subchronic, or chronic exposure
  - No Observed Adverse Effect Level (NOAEL): A chemical dose in a study which is not observed to cause an adverse health impact based on acute, subchronic, or chronic exposure
  - Lethal Dose 50 (LD_{50}): A metric of acute toxicity which measures the dose at which 50% of a sample population is killed

The following sections provide a breakdown of the observed detected CECs by different groups of compounds and potential treatment options.

3.3.1 Detected Disinfection Byproducts—Sources, Prevention, and Treatment

DBPs are formed when a disinfectant (e.g., free chlorine, chloramines, ozone) reacts with organic precursors in the water. While many DBPs are currently regulated under the EPA Stage 1 and Stage 2 Disinfection Byproducts Rules, there are several compounds which do not currently have regulatory limits and can therefore be classified as CECs.

3.3.1.1 Observed Detections of DBP CECs

Table 3-6 includes the non-nitrosamine DBP species that were detected in the BAF effluent of the participating facilities which provided CEC water quality data. These include haloacetic acids (HAAs), trihalomethanes (THMs), and chlorate. It should be noted that the HAAs monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid are regulated collectively as a sum of the five haloacetic acids (HAA5) but are not regulated as individual compounds. The MCL for HAA5 is 60 µg/L as a sum of all compounds. Similarly, the trihalomethanes (THMs) bromodichloromethane, dibromochloromethane, bromoform, and chloroform are regulated as TTHM. The MCL for TTHM is 60 µg/L as a sum of all compounds.

The italicized compounds shown in Table 3-6 are compounds which had a maximum facility BAF_{eff} that exceeded any of the listed thresholds (NL, CTR limit, MTL, or PHG). Every HAA besides monochloroacetic acid and every THM had a maximum facility BAF_{eff} exceeding the California EPA PHG. Though no PHG exists for bromochloroacetic acid, a recent paper calculated cancer risk-based concentrations for DBPs using a similar methodology to OEHHA

(Evans, Campbell, and Naidenko 2020). The maximum facility BAF_{eff} for bromochloroacetic acid was higher than the benchmark established in Evans, Campbell, and Naidenko (2020). The PHGs and Evans, Campbell, and Naidenko (2020) benchmarks are more conservative than the current MCLs for HAA5 and TTHM and are based on recent cancer risk assessments using the most current literature and practices (OEHHA 2020a; OEHHA 2020b; Evans, Campbell, and Naidenko 2020). PHGs are not enforceable but become the basis for the formulation of California EPA MCLs. The exceedances in Table 3-6 are not unique to ozone/BAF systems and potable reuse: many drinking water systems in California that are currently in compliance would have to provide additional treatment to ensure future compliance if the PHGs were authorized as MCLs. In addition to the PHGs, dichloroacetic acid was observed in exceedance of the 1.5 µg/L MTL. As for the THMs, dibromochloromethane was observed in exceedance of the 0.401 µg/L CTR limit and 0.87 µg/L MTL, and bromodichloromethane was observed in exceedance of the 0.56 µg/L CTR limit.

Table 3-6. Detected DBP CECs from the Survey Data.

DBP	# of Facilities with Detects	Max Facility BAF_{eff} (µg/L)	CTR (µg/L)	MTL (µg/L)	CA OEHHA PHG (µg/L)	Evans et al. (2020) Benchmark (µg/L)
Dibromoacetic Acid[c]	1	2.1	--	--	0.03	0.04
Bromochloroacetic Acid[c]	1	3.0	--	--	--	0.02
Monochloroacetic Acid[c]	1	2.6	--	--	53	--
Dichloroacetic Acid[c]	1	3.0	--	1.5	0.2	--
Trichloroacetic Acid[c]	1	1.6	--	60	0.1	--
Bromoform[c]	1	1.8	--	--	0.5	--
Chloroform[c]	3	3.3	[a]	--	0.4	--
Dibromochloromethane[c]	2	4.84	0.401	0.87	0.1	--
Bromodichloromethane[c]	2	4.5	0.56	--	0.06	--
Chlorate[b]	1	160	--	210	--	--

[a] A criterion was not promulgated in the final rule but has been reserved for future assessment

[b] The detection of chlorate at this single facility is hypothesized to be the result of hydraulic conditions which intermittently allowed chlorinated tertiary effluent to be fed into the ozone feed. Under normal conditions, non-chlorinated tertiary effluent is fed to the ozone system. The chlorine dose is also high to achieve non-potable recycled water disinfection requirements.

[c] This compound had a maximum facility BAF_{eff} that exceeded any of the listed thresholds.

Table 3-7 includes the nitrosamine species that were detected in the BAF effluent of the participating facilities which provided CEC water quality data. Of these nitrosamine species, N-Nitrosodimethylamine had a maximum facility BAF_{eff} in exceedance of the CTR limit of 0.69 ng/L, the California EPA 10^{-6} LECR concentration of 3 ng/L, and the NL and MTL of 10 ng/L. N-Nitrosodiethylamine had a maximum facility BAF_{eff} in exceedance of the California EPA 10^{-6} LECR concentration of 1 ng/L, but the BAF_{eff} was not in exceedance of the NL and MTL of 10 ng/L.N-Nitrosomorpholine and had a maximum facility BAF_{eff} in exceedance of the MTL of 12 ng/L and California EPA 10^{-6} LECR concentration of 5 ng/L.

Table 3-7. Detected Nitrosamine CECs from the Survey Data.

DBP (Nitrosamine)	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	CTR (ng/L)	MTL (ng/L)	CA EPA 10^{-6} LECR (ng/L)[a]
N-Nitrosodimethylamine (NDMA)	4	25	10	0.69	10	3
N-Nitrosodibutylamine (NDBA)	2	2.0	--	--	--	3
N-Nitrosodiethylamine (NDEA)	2	2.3	10	--	10	1
N-Nitrosodipropylamine (NDPA)	1	1.0	10	5	10	5
N-Nitrosomethylethylamine (NMEA)	1	1.0	--	--	--	1.5
N-Nitrosomorpholine (NMOR)	3	578	--	--	12	5
N-Nitrosopiperidine (NPIP)	1	1.0	--	--	--	3.5
N-Nitrosopyrrolidine (NPYR)	2	2.3	--	--	20	15

[a] 10^{-6} LECT concentration (ng/L) was calculated by T. Zeng, Plewa, and Mitch (2016a)

3.3.1.2 HAAs, THMs, Chlorate, and Perchlorate

HAAs and THMs are formed when organic precursors react with chlorine during disinfection therefore these compounds are not formed during ozonation or BAF. Chlorate is a byproduct of sodium hypochlorite solution (either from manufacturing or by degradation during storage) and is also independent from the ozone and BAF processes (Black and Veatch 2010). Low levels of HAAs, THMs, and chlorate may also be persistent in the disinfected drinking water that ultimately ends up in sewersheds. It is worth noting that bromate, which is formed during ozone disinfection, is a regulated compound with an MCL of 10 µg/L and will be discussed in more detail in Section 3.4.1. Ozone and BAF are typically evaluated for their effectiveness at reducing HAA and THM formation potential by removing the organic precursors that lead to these compounds upon reaction with chlorine (Arnold et al. 2018; Chuang and Mitch 2017; Wert and Rosario-Ortiz 2011). However, these processes are not commonly evaluated as a barrier for the removal of THMs and HAAs when these compounds are already present in the source water since chlorine disinfection typically occurs after ozonation and BAF.

HAA5 species have been shown to be marginally removed by ozone, with typical removal efficiencies in the range of 5%-20% (Ratasuk, Kositanont, and Ratanatamskul 2008). Of these, monochloroacetic acid and bromoacetic acid were most effectively removed with the other HAA species remaining relatively unchanged. Increasing ozone dose from 0.5 mg O_3/mg C to 2 mg O_3/mg C or contact time from 5 to 20 min also did not have a significant impact on removal. On the other hand, HAAs have been shown to be effectively removed by BAF, with removals ranging from 80%-100% (Ratasuk, Kositanont, and Ratanatamskul 2008; Xie and Zhou 2002). These studies showed that higher EBCTs produced improved HAA removal, with the highest removals observed at and EBCT of 20 min or higher. The exceedance in Table 3-6 occurred at a facility with an EBCT of 15-20 min, which should also be adequate for HAA removal. While some studies have shown high removal efficiencies with virgin media, GAC has been shown to have a low adsorption capacity for HAAs due to their hydrophilic and ionized nature at typical pH levels (Ratasuk, Kositanont, and Ratanatamskul 2008; Tung, Unz, and Xie 2006; Xie and Zhou 2002). Larger log K_{OC} (organic carbon-water partition coefficient) values mean that the compound has a higher affinity for adsorption to organic carbon. The log K_{OW} and log K_{OC} values for the HAAs in Table 3-8 are on the lower end, but some adsorption would be expected. HAAs however, have low Henry's Law constants and are not volatilized via stripping.

As with HAAs, ozonation is not effective at reducing THMs once they have already been formed in the source water (Rice 1980). Bromoform is a THM that has also been recognized as an oxidation byproduct (OBP) through ozonation (Westerhoff et al. 2010). However, bromoform was not consistently observed in the survey data, and, for the one facility where it was detected, the concentration was low. Furthermore, no thresholds besides the TTHM MCL exist for bromoform. There are mixed conclusions from the body of research on THM removal through BAF, with some studies demonstrating minimal biodegradation (Tung, Unz, and Xie 2006), and others demonstrating that biological degradation of THMs and THM formation potential in BAF results in significant removal efficiencies (Selbes et al. 2017; Wobma et al. 2000; Zainudin, Abu Hasan, and Abdullah 2017). A more recent study that evaluated transport of DBPs through an advanced treatment train used in potable reuse showed minimal removal of chloroform, bromodichloromethane, dibromochloromethane and tribromoform (T. Zeng, Plewa, and Mitch 2016a). The same study showed some removal of dichloroacetonitrile, trichloroacetaldehyde, and dichloracetamide by biologically activated carbon (BAC), examples of non-regulated DBPs. Removals of DBPs in the Zeng et al. study were over two separate sampling events. Both the literature and Chapter 1 survey data from this study (as shown in Table 3-6) indicate that BAF is not a reliable treatment barrier for these compounds, and additional treatment barriers may be necessary if these compounds are present in source waters. More widely used and effective technologies for the removal of THMs include air stripping and carbon adsorption processes like GAC (Black and Veatch 2010; Stanford et al. 2019; Symons et al. 2002). The Henry's Law constants, log $K_{OW,}$ and log K_{OC} values for the THMs in Table 3-8 indicate that either stripping or GAC would be effective treatment technologies for these compounds.

Chlorate and perchlorate are also not well removed by ozone and BAF processes but, like bromate, are well rejected by RO. Studies have shown that GAC exhibits some partial removal of chlorate through adsorption, but it has also been noted that desorption is a major concern. Ion exchange (IX) is another option; however, the presence of several other competing anions will impact the efficacy of this technology (Alfredo et al. 2015). In general, it is more common to control addition of chlorate and perchlorate by preventing formation in delivered and stored sodium hypochlorite by specifying maximum impurity percentages and controlling factors such as storage temperature (preference towards lower temperatures), pH (11.86-13), dilution (lower concentrations degrade slower), and storage time (longer storage times equate to more degradation) (Black and Veatch 2010; Gordon, Adam, and Bubnis 1995; S. Snyder et al. 2009).

Table 3-8. Summary of Henry's Law Constants, Log KOW, and Log KOC Values for the Detected DBPs.

DBP	Henry's Law Constant (atm-m^3/mol)	Log K_{OW}	Log K_{OC}	Source
Dibromoacetic Acid	4.29×10^{-9} – 4.49×10^{-9}	0.7	1.59	OEHHA 2020a; EPA n.d
Bromochloroacetic Acid	7.01×10^{-9}	0.61 – 1.18	1.09	EPA n.d
Monochloroacetic Acid	8.97×10^{-9} – 1.12×10^{-8}	0.22 – 0.34	0.27 – 0.66	OEHHA 2020a; EPA n.d
Dichloroacetic Acid	8.22×10^{-9} – 2.53×10^{-8}	0.92 – 0.94	0.41 – 0.66	OEHHA 2020a; EPA n.d
Trichloroacetic Acid	1.35×10^{-8}	1.33 – 1.70	0.30 – 0.89	OEHHA 2020a; EPA n.d
Bromoform	5.35×10^{-4}	2.4	2.06	OEHHA 2020b
Chloroform	3.67×10^{-3}	1.97	1.44	OEHHA 2020b
Dibromochloromethane	7.83×10^{-4}	2.24	1.92	OEHHA 2020b
Bromodichloromethane	2.12×10^{-3}	2.0	1.73 – 1.78	OEHHA 2020b; EPA n.d
Chlorate	--	-4.63	--	EPA n.d
Perchlorate	--	-4.63	--	EPA n.d

In summary, HAAs, THMs, and chlorate are formed primarily via disinfection with free chlorine and may be problematic when present in the feedwater to the ozone and BAF processes. While HAA removal through BAF has been observed, ozone exhibits poor removal of HAAs and THMs and BAF exhibits poor removal of THMs. The best strategy for avoiding HAA and THM issues in an ozone/BAF treatment train would be to optimize the use of chlorine prior to these treatment processes, where reactive DBP precursors are abundant. One such strategy is preformed chloramines which limits the reaction of organic precursors and free chlorine by creating a chloramines sidestream with a carrier water that has reduced organics. When upstream chlorination cannot be avoided, air stripping (THMs) or GAC (HAAs and THMs) are viable options for further removal of these compounds. Introduction of chlorate into the treatment train can be avoided by proper specification of sodium hypochlorite chemical and proper onsite storage. Ozone/BAF is also effective at reducing DBP precursors such that downstream chlorination of the treated effluent has less potential to form DBPs. The role of ozone/BAF in the removal of DBP precursors and reduction of DBP formation potential (DBPFP) is discussed in detail in Section 3.4.1. A summary of the fate of these DBPs through ozone and BAF, the prevention of their formation, and additional downstream non-RO treatment considerations is provided in Table 3-9. As defined in Chapter 1, the fate through ozone is assigned to 1 of 3 bins: readily oxidized (>90% removal), moderately oxidized (removal between 50% and 90%), and poorly oxidized or formed (removal less than 50% or negative removal). For BAF, 2 bins exist: <50% removal and >50% removal.

Table 3-9. Summary of Fate, Prevention, and Treatment for Observed Detected DBPs.

DBP	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
HAAs	Poorly oxidized	> 50% removal at EBCT of 15-20 min or higher	• Optimize use of upstream chlorination • Removal of precursors	GAC
THMs	Poorly oxidized	< 50% removal	• Restrict use of upstream chlorination • Removal of precursors	• GAC • Air stripping
Chlorate and Perchlorate	Poorly oxidized	< 50% removal	• Sodium hypochlorite impurity specifications • Proper sodium hypochlorite storage	None

3.3.1.3 Nitrosamines

Nitrosamines are found in wastewater effluents with industrial sources but are also linked to two disinfection processes: chloramination and ozonation. The use of chloramines and ozone results in reactions with amine-based precursors to form nitrosamines, the most significant of which is NDMA as it is the most detected nitrosamine species and is subject to strict NL and CTR thresholds in California (Glover et al. 2019; Pisarenko et al. 2015; Schreiber and Mitch 2006). Amine precursors can be come from various sources in domestic wastewater, industrial wastewater, and certain wastewater polymers (T. Zeng and Mitch 2015).

NDMA concentrations have been observed to increase with ozone dose but may plateau at a maximum NDMA formation above 0.5 mg O_3/mg C (Bacaro et al. 2019; Gerrity et al. 2015; Pisarenko et al. 2015; Sgroi et al. 2014). However, other nitrosamine species including NMEA, NDEA, NDPA, NMOR, NDBA, and N-nitrosodiphenylamine (NDPhA) do not exhibit significant formation due to ozonation (Gerrity et al. 2015; Pisarenko et al. 2015). For these reasons, NDMA has received the most scrutiny of the nitrosamine species in the context of ozonation for potable reuse. However, in more recent years NMOR has gained increased attention due to consistent detection in wastewater. A previous study which included sampling from eleven wastewater treatment trains showed that, after NDMA, NMOR was the second most prevalent species in untreated wastewater (Gerrity et al. 2015). In the same study, NMEA and NDEA were detected at one facility each. The findings from this study align with the current summary shown in Table 3-7, where the highest number of facilities with detects occurred with NDMA and NMOR, showing that these compounds are not only present, but recalcitrant through ozone and BAF. The removal technologies and efficiencies discussed below will focus mainly on the three nitrosamines that exceeded concentration benchmarks in Table 3-7: NDMA, NMOR, and NDEA.

As noted in Chapter 1, NDMA removal through ozonation is limited due to its low ozone reaction rate constant, $k_{O3,}$ of 0.052 M^{-1} s^{-1} and low susceptibility to hydroxyl radical oxidation with a k_{OH} of 4.5 x 10^8 M^{-1} s^{-1} (C. Lee, Yoon, and von Gunten 2007; Pisarenko et al. 2012). In Chapter 1, NDMA was observed to either remain constant through ozone, or in most cases, increase due to reaction with amine precursors (Figure 3-4). NMOR, on the other hand, was observed to remain relatively constant through ozonation and is neither removed nor formed with any significance. This aligns with previous studies which concluded that NMOR formation via ozonation is insignificant, likely due to lack of NMOR precursors in the treated wastewater (Gerrity et al. 2015; Glover et al. 2019; Pisarenko et al. 2015; T. Zeng et al. 2016b). The Chapter 1 survey data show minimal changes in NDEA concentration through ozonation, however the Water Research Foundation (WRF) 11-08 study led by Dickenson et al. (2015) did show slight formation of NDEA with the ozonation of wastewater.

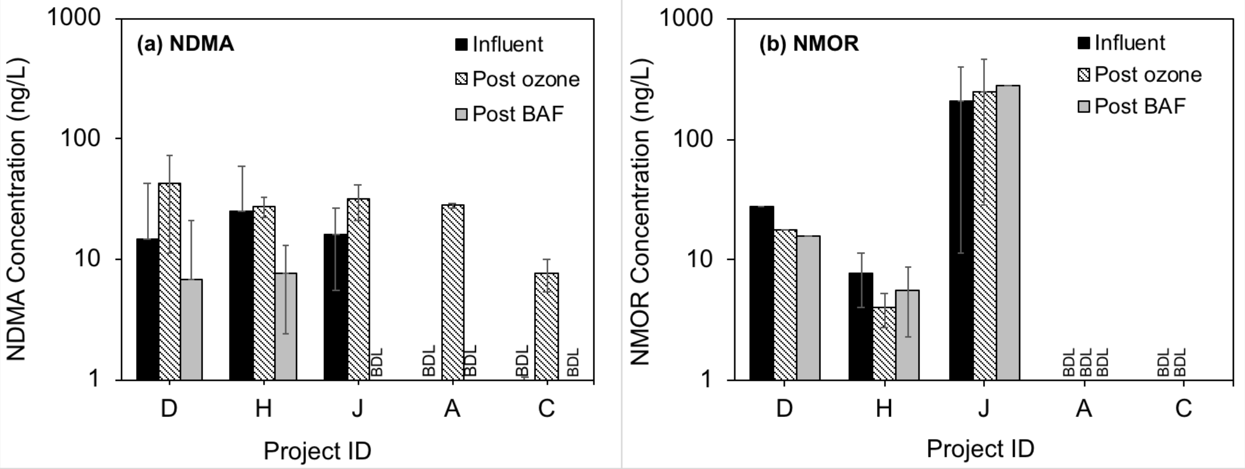

Figure 3-4. NDMA and NMOR Concentrations along the Treatment Train from the Chapter 1 Survey Data.
The error bars denote standard deviation.

Experimental results and real-world pilot- and full-scale data have demonstrated that BAC can effectively reduce existing NDMA concentrations. Several studies from reuse industry show that BAF systems can achieve 50%-90% removal of NDMA. Data summarized in Chapter 1 showed that, after NDMA formation via ozonation, BAF was able to reduce NDMA concentrations below the original influent concentrations and removals were consistently above 50%. At a constant O_3:TOC ratio of 1, NDMA removal increases greatly by increasing the EBCT up to about 10 min where greater than 90% removal is achieved (Bacaro et al. 2019). Past 10 min there are diminishing returns, but these small increases in performance with higher EBCTs upwards of 95% removal may be necessary in potable reuse applications where there are strict effluent requirements such as the CTR limit for surface water augmentation (SWA) in California. The study by Bacaro et al. (2019) also demonstrated equivalent performance for NDMA removal between BAC and anthracite. The mechanism for NDMA removal through BAF is biodegradation, as indicated by low K_{OW} and K_{OC} values in Table 3-10 which suggest that sorption alone would not be effective.

Table 3-10. Log K_{OW} and Log K_{OC} for NDMA and NMOR.

Nitrosamine	Log K_{OW}	Log K_{OC}	Source
NDMA	-0.57	1.07	EPA 2014
NDEA	0.34 – 0.49	1.1 – 1.6	B. Xu et al. 2008; EPA n.d.
NMOR	-0.44	0.78 - 1.34	Hansch, Leo, and Hoekman 1995; EPA 2012

It is also worth noting that ozonation is an important pre-treatment step for the removal of NDMA, as the Bacaro et al. (2019) study also demonstrated reduced NDMA removals with BAF alone possibly due to increased levels of biodegradable dissolved organic carbon (BDOC) and dissolved oxygen (DO). The study by Gerrity et al. (2015) also demonstrated that BAF consistently reduced NDMA levels below the method reporting limit (MRL) (Gerrity et al. 2015).

In contrast, BAF demonstrates marginal degradation of NMOR, both with and without upstream ozone (Gerrity et al. 2015; Glover et al. 2019). It should be noted that the Gerrity et al. (2015) study also detected NMEA at one facility tested and found that the compound was also more biologically recalcitrant than NDMA. The Chapter 1 survey data does not show significant removal of NDEA through BAF, and the NDEA detection in the WRF 11-08 study occurred at a facility without biological filtration therefore biological removal was not measured (Dickenson et al. 2015). However, NDEA does exhibit higher log K_{OW} and log K_{OC} values (Table 3-10) than NDMA and NMOR, which indicate that it may be more conducive to adsorption via GAC.

To meet strict effluent requirements such as California's CTR or NL thresholds, additional nitrosamine treatment would be necessary. NDMA is amenable to ultraviolet photolysis, which is a large driver for the inclusion of ultraviolet light-based advanced oxidation process (UV/AOP) in advanced treatment trains for potable reuse. In a study investigating the photolysis of nitrosamines, the quantum yields (the efficiency of photolysis for a given compound) of nitrosamines were found to be 10-100 times greater than other photosensitive contaminants (Plumlee and Reinhard 2007). In that same study, NDMA was actually found to have the lowest quantum yield of the 7 nitrosamine species tested, meaning that designing around NDMA removal ensures high removal of other nitrosamines. In a recent photolysis study conducted by Glover et al. (2019), 1-log removal of NMOR was achieved with a UV dose of approximately 325 $mJ/cm^2 \pm 10\ mJ/cm^2$, which is well below the requirement for the same level of NDMA removal. Within the potable reuse industry, UV/AOP reactor designs are typically based on a log reduction target for NDMA and AOP performance criteria with a target UV dose in mJ/cm^2. Depending on the water matrix, the UV dose per log of NDMA removal can be as high as 1000-1100 mJ/cm^2 (Hokanson, Li, and Trussell 2016). The presence or absence of other UV absorbers in the water, which is often parameterized by UVT or UVA, may drive this UV dose higher or lower. As with HAAs and THMs, downstream NDMA formation can be attenuated through the removal of amine precursors via ozone and BAF, which is discussed in Section 3.4.1.

In summary, nitrosamines are not readily oxidized via ozonation and, in the case of NDMA, can be formed in significant quantities when ozone reacts with amine precursors. Chloramination can also contribute to nitrosamine formation. NDMA is well removed through BAF at EBCTs above 10 min, and exhibits the best removals when ozone is used upstream of the BAF process. Like NDMA, NMOR is commonly detected in treated wastewater but is not typically formed during ozonation. NDEA is less commonly detected but can also form to a lesser degree via ozonation. Additionally, NMOR and NMEA have exhibited poor degradation through BAF compared to NDMA. To meet low effluent limits, additional nitrosamine treatment via UV photolysis may be required. Nitrosamines have high quantum yields and are readily photolyzed in UV reactors at doses higher than those typically used for disinfection. Designing a UV dose around NDMA removal should provide adequate removal of other target nitrosamine species. A summary of the fate of nitrosamines through ozone and BAF, their prevention, and additional downstream non-RO treatment is provided in Table 3-11.

Table 3-11. Summary of Fate, Prevention, and Treatment for Observed Detected Nitrosamines.

Nitrosamine	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
NDMA	Poorly oxidized/high levels of formation	> 50% removal at EBCT of 10 min or higher	• Restrict use of upstream chloramination • Removal of precursors • Optimization of ozone dose (less than 0.5 mg O_3/mgC)	UV photolysis
NDEA	Poorly oxidized/low levels of formation for some matrices	< 50% removal	• Restrict use of upstream chloramination • Removal of precursors • Optimization of ozone dose (less than 0.5 mg O_3/mgC)	UV photolysis
NMOR	Poorly oxidized	< 50% removal	• Restrict use of upstream chloramination • Removal of precursors	UV photolysis

3.3.2 Detected Pharmaceuticals and Personal Care Products—Sources, Prevention, and Treatment

Table 3-12 shows the pharmaceutical and personal care products (PPCPs) which were detected at the various surveyed facilities with available water quality data in Chapter 1. Overall, the detected concentrations of PPCPs were well below the established thresholds for these compounds. Most of these compounds have solely MTLs as a concentration threshold. The one exception is formaldehyde, which also has a California NL. Acetaldehyde was the only compound which exceeded a listed threshold. The maximum facility BAF_{eff} for acetaldehyde was 4,900 ng/L which exceeded the Science Advisory Panel Report MTL of 2,600 ng/L. Of the 56 recalcitrant compounds in Table 3-12, 19 had no concentration threshold (e.g., NL or MTL). Therefore, toxicological data was used to establish a basis for public health comparisons.

There are limitations when using toxicological data for this purpose including the quality of data, study-to-study variability, and differences between target organisms. To minimize these differences, toxicological data was retrieved from EPA's CompTox Chemicals Dashboard database and chronic, oral doses on rats were chosen for consistency when available. Three types of toxicity measures were used: NOAEL, LOAEL, and LD50. The NOAEL and LOAEL are more typical starting points for establishing human health thresholds and were prioritized in the database search (E. Snyder et al. 2008). However, NOAELs and LOAELs were not tabulated for every compound, therefore the acute LD50 measurement was recorded as an alternative in those cases. As a result, LD50 values were recorded for every compound when available to be able to make general comparisons on chemical toxicity.

The tabulated NOAELs, LOAELs, and LD50s in Table 3-12 were used to determine if any of the compounds without MTLs appear to be toxicologically significant. Therefore, the list of detected compounds was analyzed for any compound that had no MTL, a significantly low NOAEL, LOAEL, or LD50, and a significantly high observed maximum facility BAF_{eff} in comparison with other compounds in the table with MTLs. Nicotine had the lowest NOAEL and LD50 of the detected compounds, however the maximum facility BAF_{eff} was relatively low at 43 ng/L. This max facility BAF_{eff} was well below the MTLs of other compounds listed which range from 350 ng/L to 3 x 10^6 ng/L. The same conclusion can be made for theophylline which has a relatively low NOAEL and LD50, but also was observed with a low maximum facility BAF_{eff}. Ethyl and methyl glyoxal have NOAEL/LOAELs and LD50s that are average in comparison to the other compounds, however high maximum facility BAF_{eff} values of 7.6 x 10^4 and 8.6 x 10^3 were observed. Further efforts to characterize MTLs (or another form of health-based threshold concentrations) for these compounds may be warranted. Overall, the remaining compounds in Table 3-12 do not appear to be present a significant threat to public health at the concentrations observed. In general, the industry would benefit from an expanded library of MTLs to ensure that observed concentrations of detected compounds are not toxicologically relevant.

Table 3-12. Detected PPCPs from the Survey Data.

PPCP	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	MTL (ng/L)	LOAEL or NOAEL (mg/kg-d)	LD_{50} (mg/kg)
Acetaldehyde	2	4900	--	2600	125	661
Formaldehyde	2	7100	$1.0x10^5$	$1.0x10^5$	15	100
Galaxolide	1	341	--	$1.8x10^6$	500	5000
Triclosan	3	103	--	350	15	3700
Triclocarban	1	1	--	$1.4x10^5$	75	2000
Acetaminophen	1	3	--	$1.4x10^5$	30	1944
Albuterol	1	10	--	$2.0x10^4$	50	2500
Amisulpride	1	16	--	--	200	2000
Atenolol	7	80	--	4000	160	2000
Azithromycin	2	21	--	3900	10	2000
Bezafibrate	1	10	--	$3.0x10^5$		1082
Caffeine	4	80	--	350	40	367.7
Candesartan	2	193	--	300		2000
Carbamazepine	7	165	--	1000	250	1957
Cetirizine	1	4.6	--	--	225	703
Citalopram	2	18	--	1000	32	800
Clarithromycin	1	27	--	$6.0x10^4$		1270
Clofibric Acid	1	0.59	--	$3.0x10^4$	200	897
Cotinine	4	56	--	1000		1604
Diclofenac	3	40	--	1800	20	53
Dilantin	3	60	--	2000	50	1530
Doxylamine	1	19	--	--		600
Eprosartan	1	8.8	--	--	100	

PPCP	# of Facilities with Detects	Max Facility BAF$_{eff}$ (ng/L)	NL (ng/L)	MTL (ng/L)	LOAEL or NOAEL (mg/kg-d)	LD$_{50}$ (mg/kg)
Fexofenadine	1	45	--	--		5146
Flumeqine	1	11	--	--	100	1340
Frusemide	1	55	--	--	30	2600
Gabapentin	2	1211	--	3.0x10^{6}	250	5000
Gemfibrozil	2	29	--	4.5x10^{4}	92	1414
Hydrochlorothiazide	2	164	--	400	300	2750
Ibuprofen	2	10	--	5.0x10^{4}	25	636
Irbesartan	2	269	--	--		2000
Lamotrigine	1	251	--	3.5x10^{5}		205
Levetiracetam	1	90	--	--	50	5000
Lidocaine	1	10	--	--		317
Meclofenamic Acid	1	12	--	--		100
Meprobamate	8	174	--	1.0x10^{5}	75	794
Metformin	1	16	--	4.0x10^{4}	200	1000
Metoprolol	3	88	--	2.5x10^{4}	200	3470
Oxazepam	2	217	--	--	630	8000
Primidone	8	177	--	1.0x10^{4}	25	1500
Phenazone	2	2.9	--	1.3x10^{5}	160	1705
Salicylic Acid	2	151	--	1.1x10^{5}	150	891
Sulfamethoxazole	7	568	--	3.5x10^{4}	512	6200
Sulfasalazine	1	33	--	5x10^{5}	337.5	15600
Telmisartan	1	27	--	--	50	2750
Temazepam	1	156	--	800	30	2000
Tramadol	2	148	--	7x10^{4}	25	228
Theobromine	2	83	--	--	99	950
Theophylline	2	71	--	--	7.5	225
Trimethoprim	1	5.1	--	4x10^{4}	192	5300
Valsartan	1	349	--	9x10^{4}	200	2000
Venlafaxine	2	167	--	--	100	350
Nicotine	1	43	--	--	2.5	50
Paraxanthine	1	144	--	700		
Ethyl Glyoxal	1	7.6 x 10^{4}	--	--	100	2000
Methyl Glyoxal	1	8648	--	--		1165

3.3.2.1 Aldehydes

Most of the compounds listed in Table 3-12 are ubiquitous in secondary and tertiary treated municipal wastewater. However, acetaldehyde, formaldehyde, ethyl glyoxal, and methyl glyoxal are recalcitrant compounds which are also known to be OBPs through ozonation (Westerhoff et al. 2010). Despite the risk of forming these compounds via ozonation, all these readily biodegradable compounds were observed at concentrations several magnitudes lower than any listed thresholds in the BAF effluent.

Acetaldehyde, formaldehyde, ethyl glyoxal, and methyl glyoxal are aldehydes which are well-established byproducts of the reaction between ozone and organic precursors (Nawrocki et al. 2003; Schechter and Singer 1995; Weinberg et al. 1993; Westerhoff et al. 2010). Studies have shown that contact time has a minimal impact on aldehyde formation and the more important factor to consider is ozone dose: higher doses have been shown to correlate linearly with aldehyde concentration with a maximum aldehyde formation occurring around 1.0-1.1 mg O_3/mg C (Nawrocki et al. 2003; Schechter and Singer 1995). However, there is some evidence that suggests that acetaldehyde and formaldehyde have a stronger dose-dependence than the glyoxal compounds (Nawrocki et al. 2003). In a 1993 study which surveyed various pilot-scale and full-scale drinking water plants around North America, acetaldehyde, formaldehyde, glyoxal, and methyl glyoxal were formed in the ozone effluent of every plant surveyed (Weinberg et al. 1993). Concentrations observed in that study ranged from $1x10^4$ to $1.5x10^5$ ng/L for the sum of aldehydes, with formaldehyde comprising most of the total followed by acetaldehyde and the glyoxal compounds at approximately the same levels.

The reason why these aldehyde compounds are observed at such low levels in BAF effluent is because they are readily biodegraded through the BAF process. In the aforementioned study which surveyed aldehyde formation at several plants, BAF was observed as the main aldehyde removal process. In that study, acclimated filters with no upstream or backwash disinfectant achieved up to 100% removal of formaldehyde and acetaldehyde, while filters with applied disinfectant exhibited little to no removal (and in some cases, increases) (Weinberg et al. 1993). The same study showed that the glyoxals were slightly less biodegradable than formaldehyde and acetaldehyde, but that plants with lower filtration rates resulted in higher removals upwards of 75%-100%. Historical survey data indicate formaldehyde removal stabilizes after BAC is acclimated. Facility D formaldehyde removal from 2014 to 2021 stabilized on average greater than 90%. Other studies support the relationship of higher EBCTs resulting in higher aldehyde removals, with the largest benefit occurring for the removal of glyoxals (Krasner, Sclimenti, and Coffey 1993). EBCTs less than 5 min have been demonstrated to be sufficient for aldehyde removal in drinking water, and GAC has been shown to offer superior performance over anthracite (Krasner, Sclimenti, and Coffey 1993).

Survey data from the participating facilities in this study are plotted in Figure 3-5, Figure 3-6, and Figure 3-7 below. These data align with the conclusions discussed above: high levels of aldehyde formation via ozonation, excellent removal of acetaldehyde and formaldehyde through BAF, and slightly lower removals of glyoxals through BAF (compared to acetaldehyde and formaldehyde). All of the facilities shown in Figure 3-5, Figure 3-6, and Figure 3-7 below were operating at an EBCT of at least 15 minutes which is well above the EBCTs tested for adequate removal of aldehydes in drinking water. Biodegradation is the main mechanism for removal through BAF, as indicated by the low K_{OW} and K_{OC} values in Table 3-13: sorption is not a major removal mechanism for these aldehyde compounds.

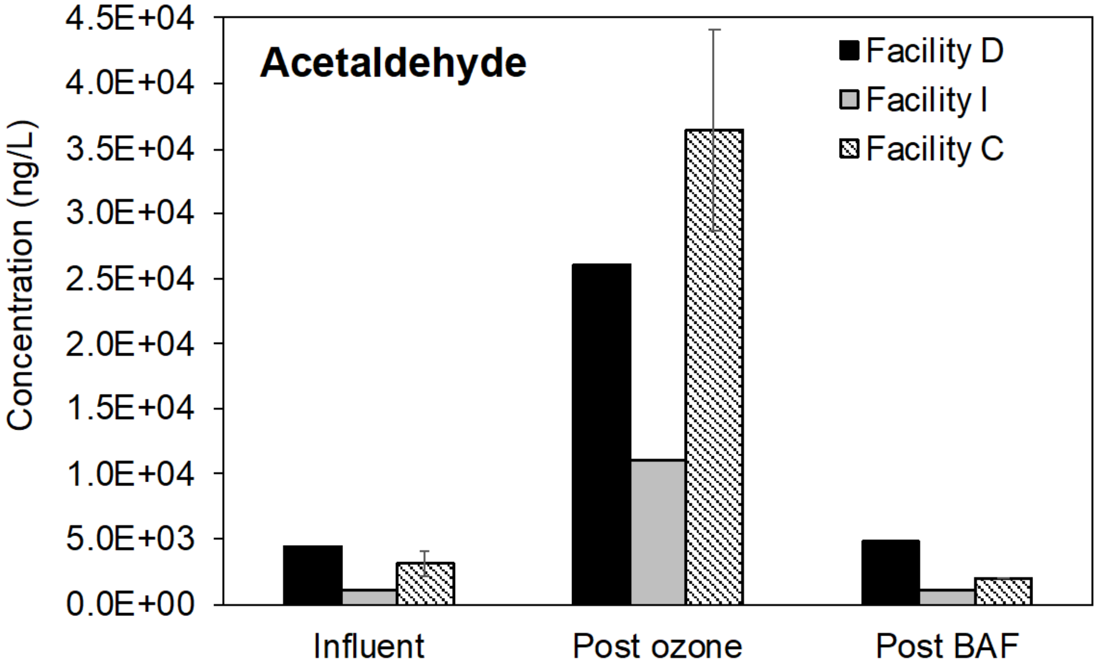

Figure 3-5. Acetaldehyde (MTL = 2.6 x 10^3 ng/L) Concentrations along the Treatment Train of the Participating Facilities with Available Data.

The error bars denote standard deviation

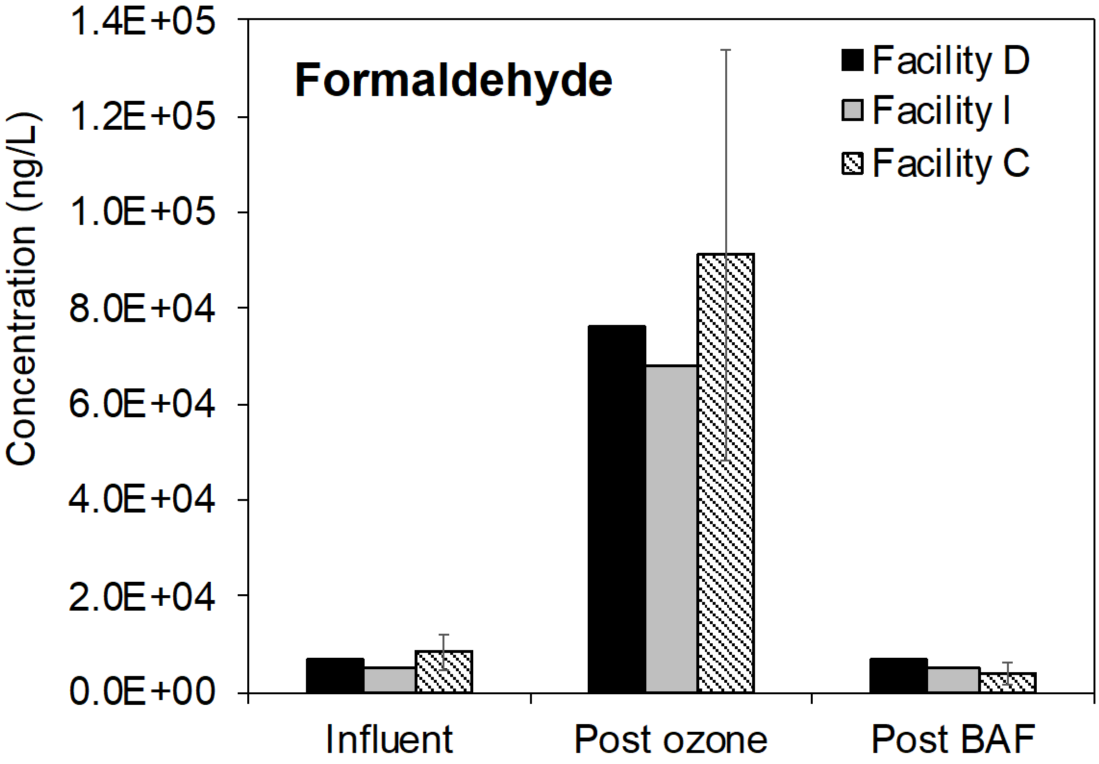

Figure 3-6. Formaldehyde (MTL & NL = 1.0 x 10^5 ng/L) Concentrations along the Treatment Train of the Participating Facilities with Available Data.

The error bars denote standard deviation

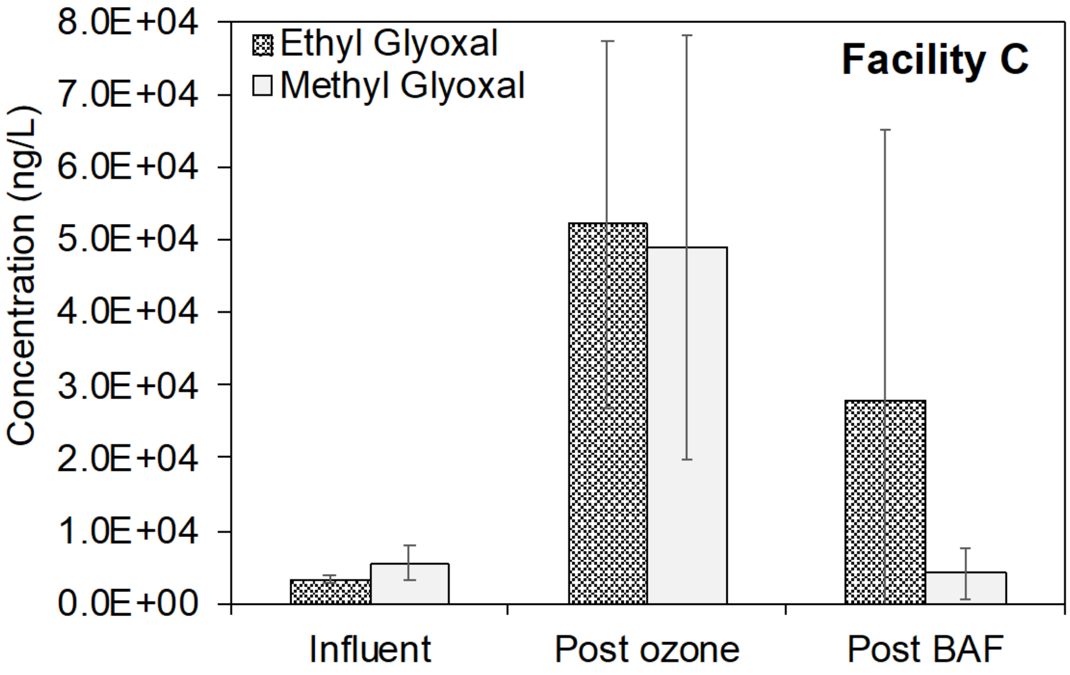

Figure 3-7. Ethyl and Methyl Glyoxal (No Thresholds Currently) Concentrations along the Treatment Train of one Participating Facility with Available Data.

The error bars denote standard deviation

Table 3-13. Log K_{OW} and Log K_{OC} for Detected Aldehydes.

Aldehyde	Log K_{OW}	Log K_{OC}	Source
Acetaldehyde	-0.34	1.0	EPA 2002; EPA 2012
Formaldehyde	0.35	0.9	Hansch, Leo, and Hoekman 1995; EPA 2012
Ethyl Glyoxal	-1.66	1.0	Meylan and Howard 1995; Meylan, Howard, and Boethling 1992
Methyl Glyoxal	-1.50	1.0	Meylan and Howard 1995; Meylan, Howard, and Boethling 1992

Table 3-14. Summary of Fate, Prevention, and Treatment for Observed Detected Aldehydes.

Aldehyde	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Acetaldehyde	Poorly oxidized/high levels of formation	> 50% removal (even at low EBCTs)	• Removal of precursors • Optimization of ozone dose (less than 1 mg O_3/mgC)	-Treatment should be optimized through BAF
Formaldehyde	Poorly oxidized/high levels of formation	> 50% removal (even at low EBCTs)	• Removal of precursors • Optimization of ozone dose (less than 1 mg O_3/mgC)	Treatment should be optimized through BAF

Aldehyde	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Ethyl Glyoxal	Poorly oxidized/high levels of formation	> 50% removal (increases with EBCT)	• Removal of precursors • Optimization of ozone dose (less than 1 mg O_3/mgC)	Treatment should be optimized through BAF
Methyl Glyoxal	Poorly oxidized/high levels of formation	> 50% removal (increases with EBCT)	• Removal of precursors • Optimization of ozone dose (less than 1 mg O_3/mgC)	Treatment should be optimized through BAF

3.3.2.2 Other PPCPs

The remainder of the PPCPs shown in Table 3-12, which are not byproducts of ozonation, are present in municipal wastewater from various sources ranging from cigarettes and soft drinks to over the counter and prescription medications. Except for diatrizoate sodium, none of the detected compounds were measured near the listed Science Advisory Panel MTLs. The majority of these PPCPs were observed at concentrations several orders of magnitude lower than the corresponding MTLs. This indicates that, although current analytical methods can detect these CECs, the concentrations at which they are recalcitrant are not significant in terms of public health protection.

3.3.3 Detected Pesticides, Herbicides, and Fungicides—Sources, Prevention, and Treatment

Table 3-15 lists the recalcitrant pesticides, herbicides, and fungicides from the surveyed facilities in Chapter 1. None of the measured BAF_{eff} values were in exceedance of any listed thresholds, indicating that the ozone/BAF processes are an effective barrier for degrading these compounds to concentrations that are acceptable for public health. It is worth noting that three herbicides were observed in BAF effluent that have MCLs and are therefore not CECs by definition and were excluded from Table 3-15. 2,4-D has a federal MCL of 7×10^4 ng/L and had an observed BAF_{eff} of 582 ng/L. Atrazine has an MCL of 3,000 ng/L and had an observed BAF_{eff} of 238 ng/L. Simazine has an MCL of 4,000 ng/L and had an observed BAF_{eff} of 376 ng/L. As with the CECs in Table 3-15, the survey data demonstrates that these regulated compounds are indeed present in ozone/BAF effluent, however at concentrations that should be acceptable to public health.

Of the 12 compounds in Table 3-15, 8 do not have MTLs. The MDH developed drinking water guidance values for a variety of chemicals including pesticides (MDH 2020b). There were 3 compounds in Table 3-15 that had neither MTLs nor MDH guidance values; therefore, toxicological data in the form of LOAELs and LD50s (see Section 3.3.2 for a description on the use of these toxicological data) was added for comparison with other compounds. For compounds without MTLs but with MDH guidance values, no compounds were observed in exceedance of a listed guidance value. For the 3 compounds without MTLs or MDH guidance values, the listed LOAELs and LD50s are not significantly low and the observed maximum facility

BAF_{eff} values are not significantly high in comparison to the other compounds. As such, this group of chemicals, though recalcitrant at low levels through ozone/BAF, does not appear to pose a significant public health threat, however this cannot be ensured in the absence of concentration thresholds related to public health. An expansion of MTLs and/or guidance values to include a wider net of pesticides, herbicides, and fungicides would help confirm this finding.

Table 3-15. Detected Pesticides, Herbicides, and Fungicides from the Survey Data.

Pesticides/Herbicides/ Fungicides	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	MTL (ng/L)	MDH Guidance Value (ng/L)	LOAEL (mg/kg-day)	LD50 (mg/kg)
Carbendazim	1	2.2	1×10^5	16×10^3	20	5050
DEET	10	97	2500	2×10^5	25	1950
Desethyl Atrazine	1	49	--	--	25	--
Desisopropyl Atrazine (DIA)	2	152	--	--	25	--
Dicamba	1	42	--	2×10^5	122	1039
Diuron	3	30	1800	5000	1.6	1017
Fluroxypyr	1	18	--	--	500	2405
Hexazinone	1	18	--	2×10^5	50	1690
MCPA	1	239	--	3000	5.7	700
Mecoprop (MCPP)	3	164	--	7000	9	650
Metolachlor	1	110	7×10^5	3×10^5	75.8	2200
Triclopyr	1	128	--	3×10^5	20	630

Pesticides, herbicides, and fungicides are present in source water from industrial and private uses within sewersheds. The analysis conducted in Chapter 1 showed that most pesticides, herbicides, and fungicides in this chemical group were at least moderately oxidized with average removals between 50-90%. Mixed results were observed for BAF, with only diuron with observed removals greater than 50%. Only simazine, triclopyr, and desisopropyl atrazine were categorized as poorly oxidized and poorly removed by BAF. Table 3-16 shows that the compounds with tabulated values have relatively low k_{O3} values but high k_{OH} values which suggests that the reaction throughout the ozone process is hydroxyl radical-dependent. However, it should be noted that none of these compounds were observed at concentrations that pose a risk to public health. As such, this group of compounds is not a significant driver for the design of additional treatment processes. However, GAC is widely accepted as a Best Available Technology for pesticides, herbicides, and fungicides and additional removal may be achieved when GAC is included for the removal of other target compounds (SWRCB 2019b). This is also apparent with the relatively high log K_{OW} and log K_{OC} values for these compounds which indicate a high affinity for sorption. Other AOPs (e.g., ozone with peroxide, UV/AOP) would also be expected to achieve good removal due to the overall high k_{OH} values observed for these compounds.

Table 3-16. k_{O3}, k_{OH}, log K_{OW}, and log K_{OC} Values for the Detected Pesticide/Herbicide/Fungicide CECs in the Chapter 1 Survey Data.

Compound	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Log K_{OC}	Source
Carbendazim	--	--	1.52	2.09 – 3.45	Hansch, Leo, and Hoekman 1995; Gawlik et al. 1998; Nemeth-Konda et al. 2002
DEET	10	4.95 x 10^9	2.02	2.1	Song et al. 2009; Gerrity et al. 2012; Hansch, Leo, and Hoekman 1995; EPA 2012
Desethyl Atrazine (DEA)	--	1.14 x 10^9	1.51	1.4 – 3.3	Khan et al. 2017; Finizio et al. 1991; Donati et al. 1994; Gerritse, Beltran, and Hernandez 1996
Desisopropyl Atrazine (DIA)	--	2.22 x 10^9	1.15	1.8 – 2.1	Khan et al. 2017; Guo et al 2016
Dicamba	0.1	--	2.21	0.5 – 1.5	Gupta and Basant 2016; Hansch, Leo, and Hoekman 1995; USDA 2017; Oliveira Jr., Koskinen, and Ferreira 2001
Diuron	14.8	4.6 x 10^9	2.68	1.7 – 3.0	Bourgin et al. 2017; Hansch, Leo, and Hoekman 1995; Rao and Davidson 1982; Nkedi-Kizza, Rao, and Johnson 1983; Madhun et al. 1986; Bouchard and Wood 1988; Kenaga 1980; Liyanage et al. 2006
Fluroxypyr	--	--	-1.24	1.7 –2.0	Tomlin 2004; Lehmann, Miller, and Laskowski 1990
Hexazinone	--	--	1.85	1.0 – 1.7	BioByte 1995; Bouchard and Wood 1998; Helling and Turner 1968; Schüürmann, Ebert, and Kühne 2006
MCPA	47.7	6.6 x 10^9	3.25	1.7 – 1.8	Benitez et al. 2004; Ilchmann et al. 1993; Helweg 1987
Mecoprop	--	--	3.20	0.7 – 1.6	Tomlin 2010; Kah and Brown 2006
Metolachlor	1.1 – 3.0	5.1 – 6.7 x 10^9	3.13	1.3 – 3.4	Acero et al. 2003; Hansch, Leo, and Hoekman 1995; Laabs and Amelung 2005; Ahrens and Edwards 1994; Krutz et al. 2004
Triclopyr	--	1.73 x 10^9	-0.45	1.1 – 2.1	Solís et al. 2016; MacBean 2010; USDA 2017

Table 3-17. Summary of Fate, Prevention, and Treatment for Pesticides/Herbicides/Fungicides.

Compound	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Pesticides/ herbicides/ fungicides	Readily oxidized	< 50% removal	Source control	• GAC • UV/AOP • Additional treatment is not a priority for these compounds due to observed low concentrations

3.3.4 Detected Perfluoroalkyl Substances—Sources, Prevention, and Treatment

Perfluoroalkyl substances have received recent scrutiny due to new regulatory limits in several states across the country. As such, PFAS have become an important recalcitrant chemical group in the context of the ozone/BAF treatment process. Table 3-18 lists the recalcitrant PFAS observed from the Chapter 1 survey data along with relevant public health concentration thresholds. PFOS and PFOA have California NLs and MTLs of 6.5 and 5.1 ng/L, respectively. PFOS and PFOA were observed in BAF effluent most consistently among the surveyed facilities and had BAF_{eff} values of 30 ng/L and 49 ng/L which were both in exceedance of these established NLs and MTLs. The presence and persistence of PFOS and PFOA as shown in these data is consistent with the recent rise in concern over these PFAS contaminants in drinking water sources, as evidenced by the approval of tighter NLs for these compounds in by the California SWRCB in August of 2019.

The remaining 8 recalcitrant PFAS that were observed in the Chapter 1 survey data did not have California NLs or MTLs, so MDH guidance values were tabulated for the portion of these compounds. TCEQ oral RfDs were also tabulated to gain information on the remaining 5 compounds without MTLs or MDH guidance values. RfDs are either LOAELs or NOAELs that are translated to human health doses by including several uncertainty factors to account for impacts such as data quality, study duration, and study species (TCEQ 2016). The shorter-chained perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS) exhibited the highest MDH guidance values and TCEQ RfDs indicating that these compounds are less toxic than other recalcitrant PFAS observed in the study. Maximum observed facility BAF_{eff} values did not exceed MDH guidance values for these compounds. Perfluorohexanesulfonic acid (PFHxS) has an MDH value of 47 ng/L which was also not exceeded by the maximum facility BAF_{eff}. The remaining 5 PFAS in Table 3-18 without MTLs or MDH guidance values have RfDs that are similar to those listed for PFOS, PFOA, and PFHxS which have MDH values of 15 ng/l, 35 ng/L and 47 ng/L, respectively. Therefore, guidance values for these compounds would be expected to be most similar to these compounds. Perfluoroheptanoic acid (PFHpA), Perfluorohexanoic acid (PFHxA), and perfluoropentanoic acid (PFPeA) exhibited the highest maximum facility BAF_{eff} values of these 5 PFAS and may be close to MTLs or guidance values if these were to be calculated for these compounds. Therefore, formulation of MTLs or guidance values for the full suite of PFAS compounds is warranted and would greatly benefit the industry. The sources, fate through ozone/BAF, and additional treatment for PFAS is discussed in the subsequent discussion.

Table 3-18. Detected Perfluoroalkyl Substances from the Survey Data.

PFAS	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	MTL (ng/L)	MDH Guidance Value (ng/L)	TCEQ RfD (mg/kg-d)
Perfluorooctanesulfonic acid (PFOS)	6	30	6.5	6.5[a]	15	2.3×10^{-5}
Perfluorooctanoic acid (PFOA)	10	49	5.1	5.1[a]	35	1.2×10^{-5}
Perfluorobutanoic acid (PFBA)	3	25	--	--	7000	2.9×10^{-3}
Perfluorobutanesulfonic acid (PFBS)	4	45	--	--	2000	1.4×10^{-3}
Perfluorohexanesulfonic acid (PFHxS)	2	10	--	--	47	3.8×10^{-6}
Perfluorodecanoic acid (PFDA)	4	5	--	--	--	1.5×10^{-5}
Perfluoroheptanoic acid (PFHpA)	5	34	--	--	--	2.3×10^{-5}
Perfluorohexanoic acid (PFHxA)	5	36	--	--	--	3.8×10^{-6}
Perfluorononanoic acid (PFNA)	3	8.9	--	--	--	1.2×10^{-5}
Perfluoropentanoic acid (PFPeA)	4	61	--	--	--	3.8×10^{-6}

[a] PFOS and PFOA have MTLs of 70 ng/L in the 2018 Science Advisory Panel Report. The MTLs have since been revised due to new toxicological evidence that led to lower California NLs, as discussed in Chapter 2.

PFAS are a group of synthetic industrial chemicals that were manufactured for a variety of goods ranging from food packaging to paint and cleaning products. PFOS and PFOA are the two PFAS that were produced in the largest quantities in the United States but have since been voluntarily phased out of production by major manufacturers (EPA 2017c). PFOS and PFOA are highly stable due to strong carbon-fluorine bonds which also give the compounds hydrophobic and lipophobic properties. These properties are leveraged for the manufacturing of nonstick cookware, clothing, electrical manufacturing, and cleaning products (EPA 2017c). These same properties make these compounds environmentally persistent and highly mobile in water systems (Dickenson et al. 2015).

Although production of PFOA and PFOS has virtually ceased, these chemicals are still present in the environment and, in the case of other PFAS, are even increasing in concentration. Larger precursor compounds can biodegrade into smaller, more stable PFAS. Known precursors include fluorotelomer alcohols, perfluoroalkyl phosphonates, and fluorotelomer sulfonate. The WRF 11-08 study led by Dickenson et al. (2015) documented the biodegradation of these larger precursor molecules to PFAS in biological wastewater treatment processes, including conventional activated sludge (CAS), trickling filters, and MBRs (Dickenson et al. 2015). In that study, which surveyed pilot and full-scale wastewater treatment plants (WWTPs), PFHxA, PFPeA, and PFOA were the most observed compounds to increase with secondary treatment.

PFAS have been shown to increase through ozonation, but the specific compounds that are formed are highly dependent on the wastewater matrix tested. The same WRF 11-08 study discussed above tested several wastewater effluent matrices for the formation of PFAS with varied ozone doses. PFHxA, PFBS, PFPeA, and PFOA were the PFAS that were most formed after ozone was applied to the different wastewater matrices but were not always formed depending on the matrix (Dickenson et al. 2015). In that study, formation of PFAS was observed to generally increase as a function of ozone dose. The WRF 11-08 study also looked at data from 8 pilot-and full-scale wastewater treatment trains with ozone. In that survey, PFHxA, PFBS, and PFOA showed the highest prevalence of increased concentrations after ozonation, which aligned well with the benchtop testing data. One observation made in this study was that shorter chain PFAS (less than 10 carbon atoms) were most prevalently formed. Benchtop testing has concluded that the formation of PFAS through ozonation is more likely caused by reactions with molecular ozone than hydroxyl radicals (Pisarenko et al. 2015).

BAF is also not a reliable barrier for PFAS removal and has been observed to cause a slight increase in PFAS concentrations for specific matrices and compounds. The WRF 11-08 pilot-and full-scale plant survey discussed above also included data from three facilities with BAF (Dickenson et al. 2015). At all three facilities, the suite of seven PFAS tested were observed to either remain the same, or slightly increase after BAC treatment. Concentration increases were observed for PFHxA, PFOA, PFPeA, and PFBS which aligned with those formed via ozonation. Other studies have shown that lower MW (e.g., smaller carbon chain) PFAS can increase through BAF (Glover, Quiñones, and Dickenson 2018; McCleaf et al. 2017; Thompson et al. 2011). Figure 3-8 and Figure 3-9 below show average PFOA and PFOS concentrations in ozone influent, post-ozone, and post-BAC from the Chapter 1 survey data. Projects K and N showed the most significant increase in average PFOA concentration through ozonation, with Projects J, L, B, and D exhibiting less significant increases through ozonation. Decreases in PFOA concentration after BAF were observed at Project F and Project G, however the observed removals are likely from adsorption as both projects were utilizing GAC media. This is further supported by the fact that in Project F, TCEP removal through BAF was 100% and for Project G, TCEP and sucralose removals were 98% and 88%, respectively. These compounds are also not well biodegraded but well removed by GAC which indicates that these projects were using media with remaining adsorption capacity during the time of testing. The remainder of the projects did not exhibit any removal of PFOA which is expected for acclimated media operating in a biological filtration mode. In Figure 3-9, PFOS was neither observed to be formed nor removed by a significant amount, except for Project K which showed lower average concentrations after ozonation. However, the influent data exhibited a high degree of variability in comparison to the ozone effluent data. PFAS removal is not expected through ozone, which is consistent with observations in the literature (Dickenson et al. 2015; Pisarenko et al. 2015). Except for Project G, no significant changes in average PFOS concentration were observed through BAF. As discussed with PFOA, the PFOS removal in Project G is caused by adsorption to the GAC media with remaining adsorption capacity.

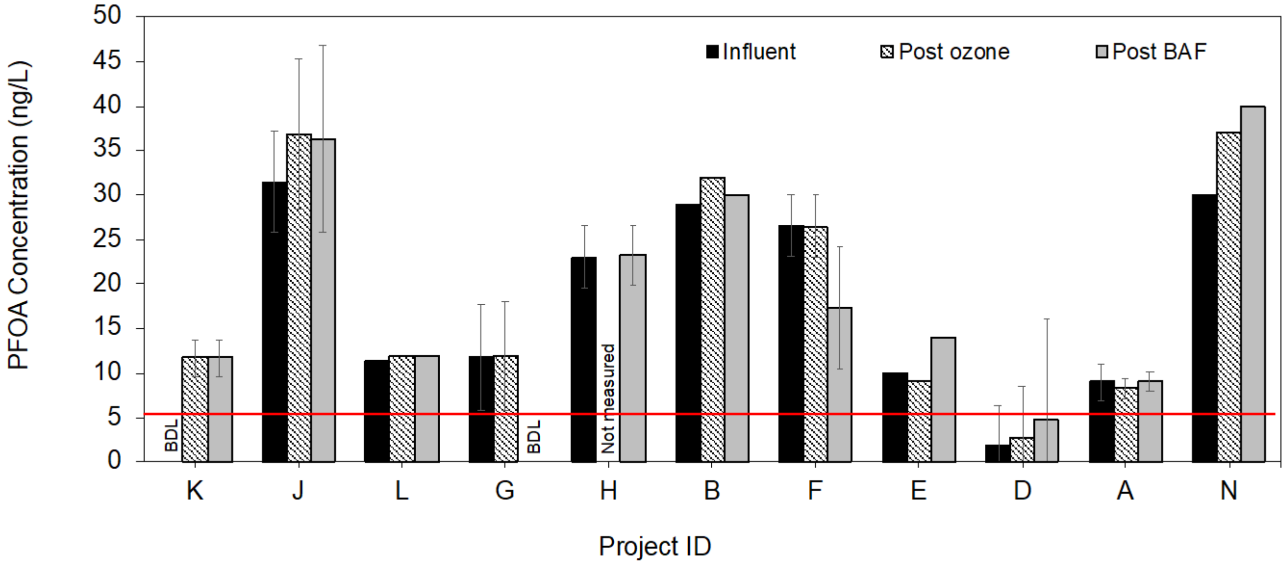

Figure 3-8. PFOA Concentrations along the Treatment Train from the Chapter 1 Survey Data.
The red line denotes the MTL concentration. The error bars denote standard deviation.

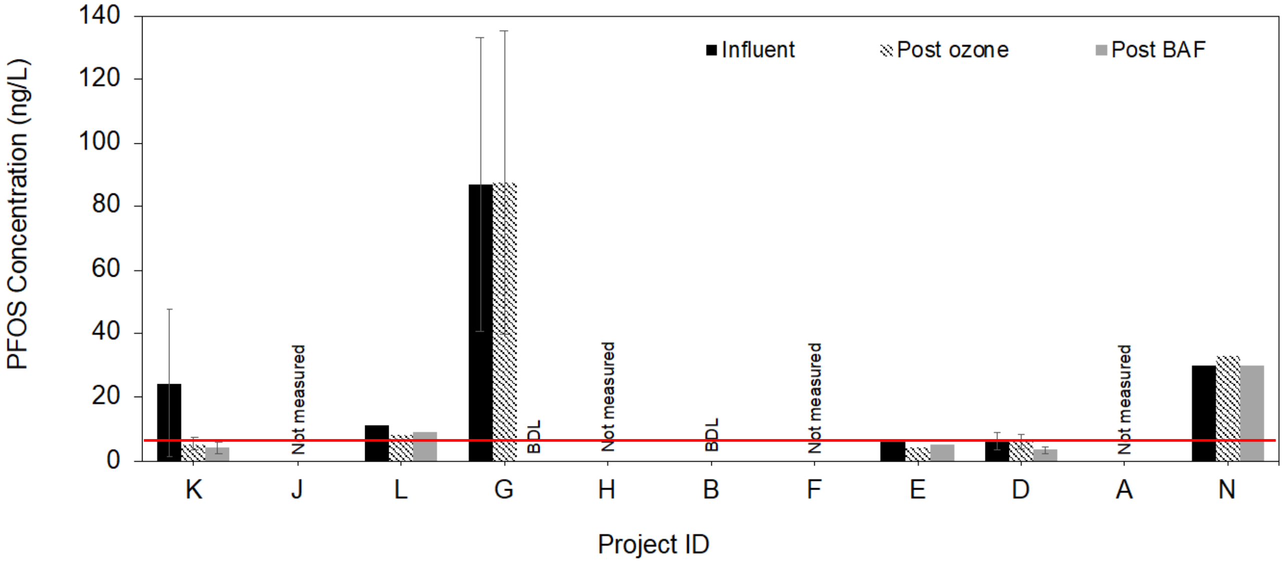

Figure 3-9. PFOS Concentrations along the Treatment Train from the Chapter 1 Survey Data.
The red line denotes the MTL concentration. The error bars denote standard deviation.

In Chapter 1, PFAS removals through BAF were observed to be highly dependent on initial media condition (e.g., virgin, exhausted, regenerated), with lower removals observed with exhausted media. In Project H, PFOA and PFOS removal through exhausted media was compared to the removal through regenerated media as shown in Figure 3-10 and Figure 3-11. The regenerated media showed greatly improved average removals in comparison to the exhausted media, supporting the fact that sorption is a main removal mechanism for the PFAS compounds.

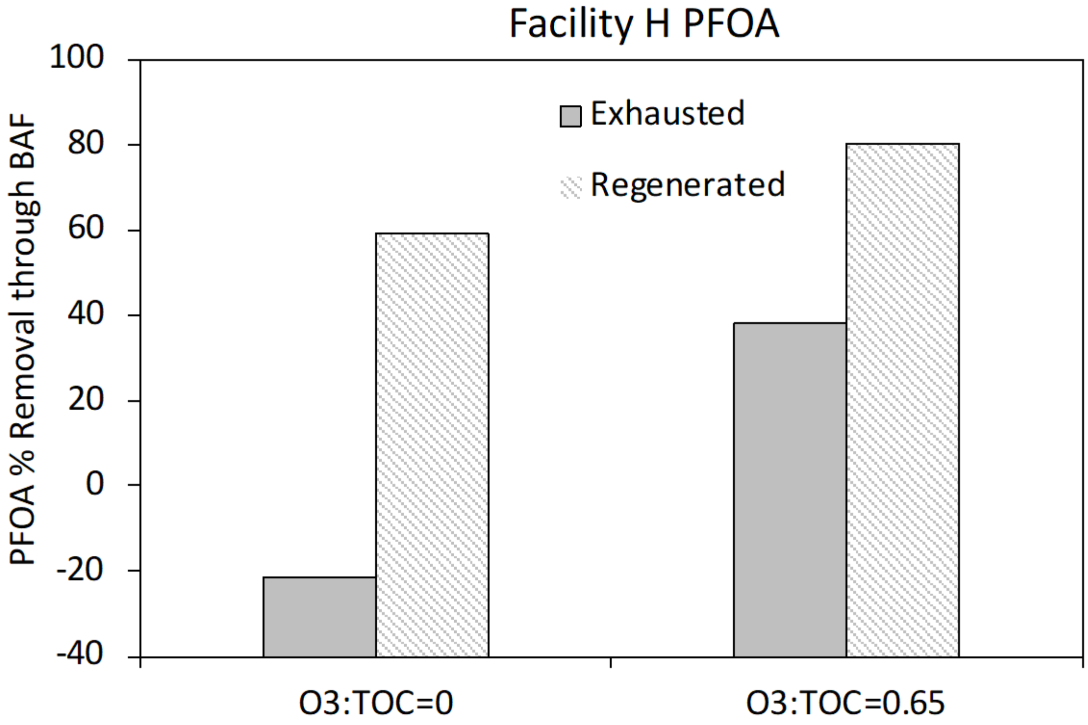

Figure 3-10. Impact of Media Condition (Exhausted Versus Regenerated) on PFOA Removal for Facility H.

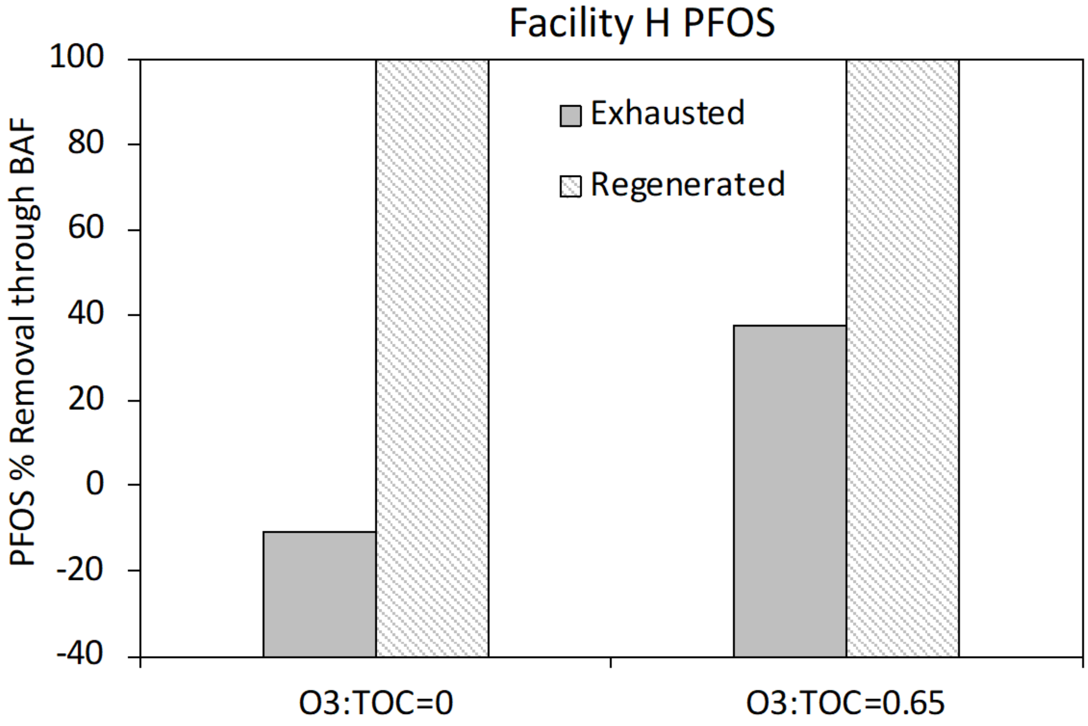

Figure 3-11. Impact of Media Condition (Exhausted Versus Regenerated) on PFOS Removal for Facility H.

Aside from high pressure membrane treatment, mitigation of recalcitrant PFAS can be accomplished through sorption processes. The two most effective sorption technologies are anion exchange and GAC; however, their effectiveness depends on the specific PFAS compounds and process design (Dickenson et al. 2015). IX and GAC have been observed to preferentially adsorb longer chain PFAS and perfluorinated sulfonates (versus perfluoroalkyl acids), and organic matter can reduce effectiveness by outcompeting PFAS, particularly those with smaller carbon chains (Dickenson et al. 2015; McCleaf et al. 2017; EPA 2020b). This trend of adsorption for larger compounds and sulfonates can be observed with log K_{OW} and log K_{OC} values, summarized in Table 3-19 below. Generally, Table 3-19 shows that larger compounds and sulfonates have higher log K_{OW} and log K_{OC} values. Isotherm data are available for adsorption of PFAS onto various types of GAC and anion exchange resins to predict and inform the design of these sorption processes (EPA 2020b). Both GAC and anion exchange processes can achieve greater than 99% removal of target PFAS compounds under optimal conditions (EPA 2020b).

Table 3-19. Log K_{OW} and log K_{OC} Values for the Detected PFAS in the Chapter 1 Survey Data.
Data Source: ARCADIS 2016.

PFAS	Log K_{OW}	Log K_{OC}
Perfluorobutanoic acid (PFBA)	2.82	1.88
Perfluoropentanoic acid (PFPeA)	3.43	1.37
Perfluorohexanoic acid (PFHxA)	4.06	1.91
Perfluoroheptanoic acid (PFHpA)	4.67	2.19
Perfluorooctanoic acid (PFOA)	5.30	1.31-2.35
Perfluorononanoic acid (PFNA)	5.92	2.39
Perfluorodecanoic acid (PFDA)	6.50	2.76
Perfluorobutanesulfonic acid (PFBS)	3.90	1.00
Perfluorohexanesulfonic acid (PFHxS)	5.17	1.78
Perfluorooctanesulfonic acid (PFOS)	6.43	2.5-3.1

In summary, PFAS are one of the more important recalcitrant compounds to consider for ozone/BAF systems and potable reuse. PFAS are found in ambient wastewater and can form through biological wastewater treatment from the degradation of larger precursors. Ozone/BAF is not a reliable barrier for PFAS removal; GAC and anion exchange sorption processes are the main non-RO mitigation measure for these compounds. PFOA and PFOS which are the most prevalent PFAS were observed in exceedance of NLs and MTLs in the Chapter 1 survey data and would require additional treatment by GAC or anion exchange following ozone/BAF. A summary for the fate, prevention, and additional treatment for PFAS is provided in Table 3-20.

Table 3-20. Summary of Fate, Prevention, and Treatment for PFAS.

Compound	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
PFAS	Poorly oxidized/ moderate levels of formation for select compounds (PFHxA, PFBS, PFPeA, and PFOA)	< 50% removal (No removal is expected, and some reformation or desorption may occur, particularly with smaller PFAS)	Source control	• GAC • Anion exchange

3.3.5 Detected Hormones—Sources, Prevention, and Treatment

Table 3-21 below shows the BAF_{eff} values for recalcitrant hormones from the Chapter 1 survey data along with MTLs. Only two compounds were detected in BAF effluent, estrone and testosterone, and neither compound was observed near the listed MTL indicating that hormones should not be of primary concern for ozone/BAF systems.

Table 3-21. Detected Hormones from the Survey Data.

Hormones	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	CTR (ng/L)	MTL (ng/L)
Estrone	1	0.50	--	--	350
Testosterone	1	8	--	--	7000

Estrone and testosterone are ubiquitous in municipal wastewaters as they are excreted by humans and animals (Roudbari and Rezakazemi 2018). Studies have observed high levels (>90%) of hormone removal through activated sludge treatment, with high sludge retention time (SRT) nutrient removal plants exhibiting the best hormone removals (Hamid and Eskicioglu 2012). As noted in Chapter 1, estrone is highly reactive through the ozone process with k_{OH} and k_{O3} values of $1.1 \times 10^9 – 7 \times 10^{10}$ $M^{-1} s^{-1}$ and $6.2 \times 10^3 – 2.1 \times 10^7$ $M^{-1} s^{-1}$, respectively (Nakonechny, Ikehata, and Gamal El-Din 2008). Estrone and testosterone concentrations in the ozone influent, post-ozone, and post-BAF are shown in Figure 3-12 and Figure 3-13. For both facilities, estrone removal through the ozone process is observed to be high (>90%). Testosterone removal through ozone is difficult to discern with the survey data due to non-detects. Testosterone has been reported to be more recalcitrant through ozone than estrone, but removals greater than 90% have been observed with ozone doses as low as 0.5 mg/L in RO permeate (Westlund, Isazadeh, and Yargeau 2018). Removal of estrone through BAF is hard to discern with the Chapter 1 data due to non-detects in the ozone effluent. The removal of estrone and testosterone through BAF shows mixed results. High estrone removal is observed at Facility N and negligible removal is observed for Facility C. Interestingly, testosterone concentrations are observed to increase in BAF effluent for Facility F but his could be due to the fact that this is a single data point. These compounds are readily biodegradable as evidenced by their degradation in wastewater treatment and natural systems, but more research may be needed to understand their specific behavior through BAF (Bradley et al. 2009; Hamid and Eskicioglu 2012). As shown in Table 3-22, the log K_{OW} values for estrone and testosterone are 3.16 and 3.32, respectively (Hansch, Leo, and Hoekman 1995). The log K_{OC} values are 2.66-4.26 for estrone and 3.25-3.52 for testosterone (W. Lee and Batchelor 2003; Yu et al. 2004). These relatively high log K_{OW} and log K_{OC} values indicate that these compounds should be amenable to sorption processes like GAC. Nonetheless, ozonation proves to be an effective barrier for any remaining compounds in the treated wastewater and the ozone/BAF treatment processes are observed to adequately reduce concentrations to acceptable public health levels without additional treatment.

Table 3-22. k_{O3}, k_{OH}, Log K_{OW}, and Log K_{OC} Values for the Detected Hormones in the Chapter 1 Survey Data.

Hormone	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Log K_{OC}	Source
Estrone	6.2×10^3–2.1×10^7	1.1×10^9–7×10^{10}	3.16	2.66-4.26	Nakonechny, Ikehata, and Gamal El-Din 2008; Hansch, Leo, and Hoekman 1995; Yu et al. 2004; W. Lee and Batchelor 2003
Testosterone	--	--	3.32	3.25-3.52	Hansch, Leo, and Hoekman 1995; Yu et al. 2004; W. Lee and Batchelor 2003

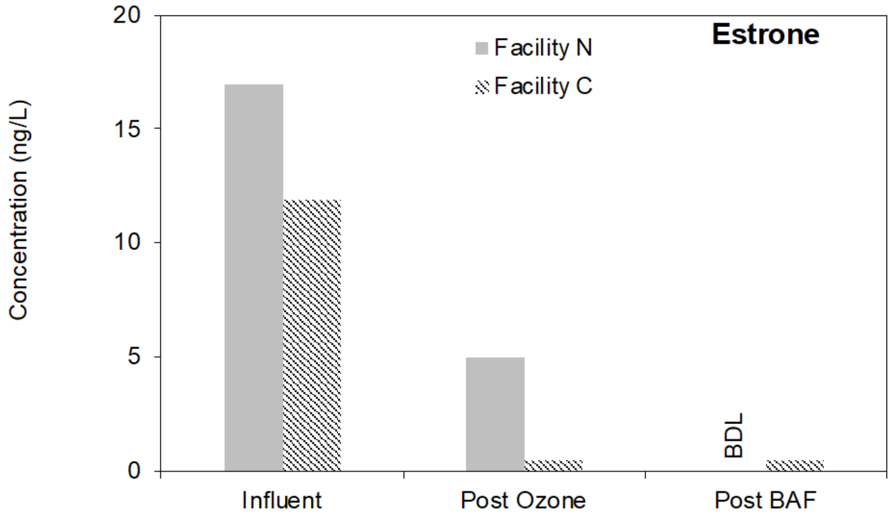

Figure 3-12. Estrone Concentrations along the Treatment Train at Facilities N and C.

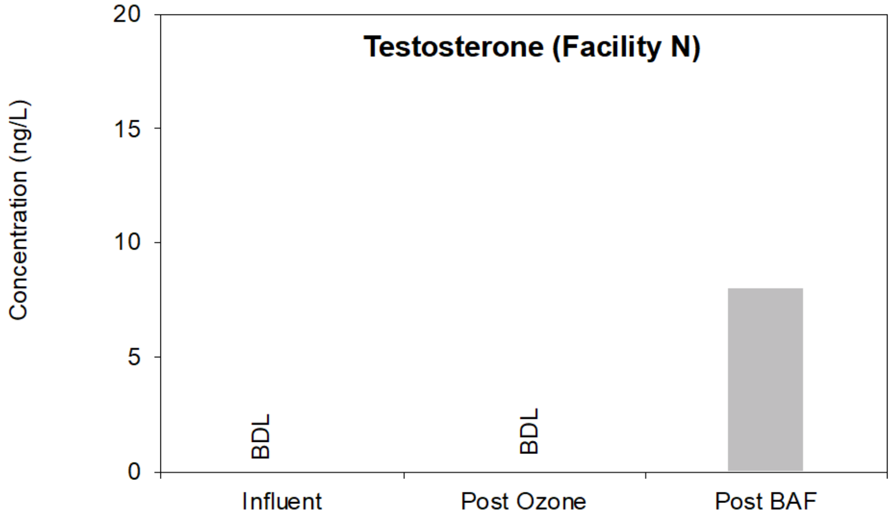

Figure 3-13. Testosterone Concentrations along the Treatment Train at Facilities N and C.

Table 3-23. Summary of Fate, Prevention, and Treatment for the Detected Hormones.

Hormone	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Estrone	Readily oxidized	Inconclusive	None	None required but GAC is effective
Testosterone	Readily oxidized	Inconclusive	None	None required but GAC is effective

3.3.6 Recalcitrant Medical Contrast Agents—Sources, Prevention, and Treatment

Medical contrast agents that were observed with concentrations above the detection limit in BAF effluent from the Chapter 1 survey data are shown in Table 3-24 below along with relevant public health concentration thresholds. Ioxehol, iopamidol, and iopromide were detected in the BAF effluent of one or more facility, however the observed BAF_{eff} values were well below their corresponding MTLs indicating that these recalcitrant compounds should be expected at safe levels with ozone/BAF treatment for potable reuse. Diatrizoate sodium was detected at a single facility where the BAF_{eff} of 4,261 ng/L exceeded the Science Advisory Panel Report MTL of 3,500 ng/L. Therefore, understanding the sources and potential treatment options for this chemical is important.

Table 3-24. Detected Medical Contrast Agents from the Survey Data.

Medical Contrast Agents	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	CTR (ng/L)	MTL (ng/L)
Iohexol	4	4830	--	--	7.2×10^5
Iopamidol	1	1.04×10^4	--	--	4×10^5
Iopromide	2	2326	--	--	7.5×10^5
Diatrizoate sodium	*1*	*4261*	--	--	*3500*

Iohexol, iopamidol, iopromide, and diatrizoate sodium are all iodinated contrast media which are used for medical X-ray visualization of human tissues and are excreted in urine and feces without being metabolized (Borowska, Felis, and Żabczyński 2015; Ning and Graham 2008). Iohexol, iopamidol, and iopromide are nonionic compounds whereas diatrizoate sodium is an ionic compound (Hartwig, Mützel, and Taenzer 1989). By design, these compounds are designed to be hydrophilic, persistent, and biologically stable to ensure their effectiveness during medical examination and prevent the formation of any undesirable degradation in the body (Ning and Graham 2008).

Table 3-25 below shows the k_{O3}, k_{OH}, and log K_{OW} values for the recalcitrant contrast agents in the survey data. The low k_{O3} and high k_{OH} values suggest that hydroxyl radicals, rather than molecular ozone, would be responsible for reactivity with these compounds in an ozone process. These high k_{OH} values also suggest that these chemicals would be highly reactive in a UV/AOP system, or in an ozone system with high hydroxyl radical exposure (either under ambient conditions or with H_2O_2 addition). The negative log K_{OW} values indicate that these compounds have a low affinity for partitioning out of solution and onto organic media. The Chapter 1 survey data showed negligible oxidation for all compounds through ozone, except for iohexol which was moderately oxidized (between 50-90%). The Chapter 1 survey data showed negligible removal of all compounds through BAF, except for iopamidol which was moderately removed around 60% at the one facility where it was detected.

Table 3-25. k_{O3}, k_{OH}, and Log K_{OW} Values for the Detected Contrast Agents in the Chapter 1 Survey Data.

Contrast Agent	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Source
Iohexol	--	3.21×10^9	--	Jeong et al. 2010
Iopamidol	18.0 ± 1.4	$2.4 \pm 0.3 \times 10^9$	-2.42	Ning and Graham 2008; BioByte 1995
Iopromide	13.5 ± 0.7	$2.2 \pm 0.7 \times 10^9$	-2.33	Ning and Graham 2008
Diatrizoate	3.67 ± 0.48	$3.0 \pm 0.5 \times 10^9$	-1.28	Ning and Graham 2008; EPA 2012

Diatrizoate sodium was the sole compound detected with a BAF_{eff} in exceedance of the MTL. This compound was detected at one facility in the survey data, Facility J, as shown in Figure 3-14. From these data, diatrizoate sodium remains approximately unchanged through the treatment processes indicating negligible reactivity with ozone and negligible biodegradation. Due to the low log K_{OW}, sorption processes are not expected to be effective for diatrizoate sodium. However, studies have shown that both UV/chlorine and UV/peroxide can effectively degrade diatrizoate sodium, which aligns with its high k_{OH} value (Velo-Gala et al. 2014; Y. Wu et al. 2019). Iohexol, iopromide, and iopamidol have also been shown to photodegrade by UV, and removals can be significantly improved when oxidant (peroxide or chlorine) is added (Borowska, Felis, and Żabczyński 2015; Falantin, Criquet, and Allard 2018; Tian et al. 2020; Wang et al. 2016). One concern with UV/oxidation of iodinated compounds and subsequent chlorination of the treated water is the risk of iodinated DBPs; however, ozone/BAF treatment is an effective barrier to organic precursor removal, as discussed in Section 3.4.1. The summary of the fate, prevention, and additional non-RO treatment for medical contrast agents is shown in Table 3-26.

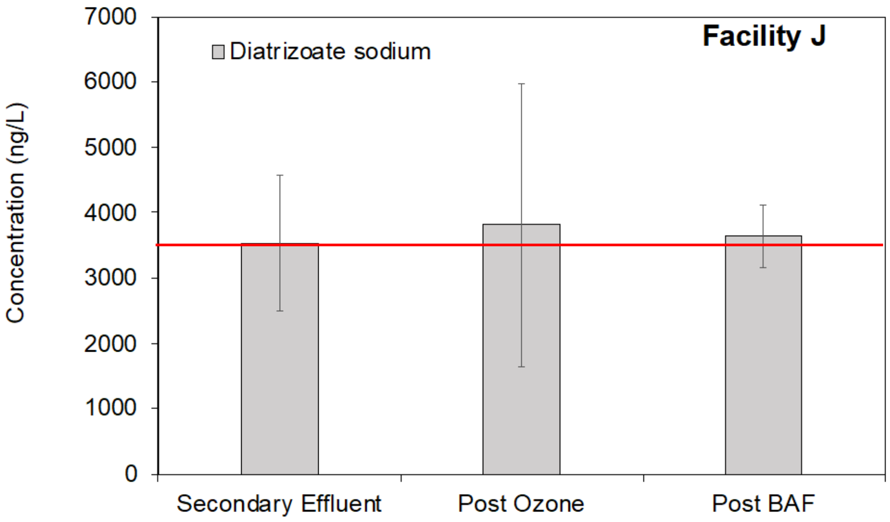

Figure 3-14. Diatrizoate Sodium Concentrations along the Treatment Train at Facility J.
The red line denotes the MTL concentration. The error bars denote standard deviation.

Table 3-26. Summary of Fate, Prevention, and Treatment for the Detected Medical Contrast Agents.

Contrast Agent	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Iohexol	Moderately oxidized	< 50% removal	None	UV/AOP
Iopamidol	Poorly oxidized	> 50% removal (60% removal with n=1 from survey data)	None	UV/AOP
Iopromide	Poorly oxidized	< 50% removal	None	UV/AOP
Diatrizoate sodium	Poorly oxidized	< 50% removal	None	UV/AOP

3.3.7 Detected Artificial Sweeteners—Sources, Prevention, and Treatment

Two types of artificial sweeteners were detected in the Chapter 1 survey data: acesulfame and sucralose. BAF_{eff} values and MTLs for these compounds are summarized in Table 3-27. The observed BAF_{eff} values for acesulfame and sucralose are both several orders of magnitude lower than the MTLs established by the Science Advisory Panel, indicating that these compounds are of minor concern for public health.

Table 3-27. Detected Artificial Sweeteners from the Survey Data.

Artificial Sweetener	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	NL (ng/L)	CTR (ng/L)	MTL (ng/L)
Acesulfame	7	6742	--	--	2.0×10^8
Sucralose	10	6.6×10^4	--	--	1.5×10^8

Acesulfame and sucralose are added to a variety of foods, drinks, personal care products, and pharmaceuticals and are commonly found in domestic wastewater (Mawhinney et al. 2011; Oppenheimer et al. 2011; Subedi and Kannan 2014). Artificial sweeteners like acesulfame and sucralose pass through the human body largely unchanged and are well-known recalcitrant compounds in water and wastewater. A summary of the k_{O3}, k_{OH}, log K_{OW}, and log K_{OC} values for acesulfame and sucralose are shown in Table 3-28. Both compounds are expected to react minimally with molecular ozone as indicated by the low k_{O3} values but do have high k_{OH} values which suggest that the compounds are amenable to oxidation through the presence of hydroxyl radicals. As such, acesulfame and sucralose were both marginally removed through ozonation in the Chapter 1 survey data, with average removals less than 50%. The Chapter 1 data also showed minimal removal of acesulfame and sucralose through BAF. Studies have observed minimal reduction of sucralose and acesulfame through biological wastewater treatment, which also suggests the biodegradability of the compounds is low (Subedi and Kannan 2014). These compounds exhibit low K_{OW} values, but higher low K_{OC} values which suggest there is some affinity for adsorption. Studies have shown that GAC and synthetic resins can effectively remove sucralose and acesulfame (S. Li et al. 2018; Mawhinney et al. 2011). Furthermore, additional studies have shown that UV/AOP processes can efficiently degrade these compounds, which aligns with the observed high k_{OH} values (Sharma, Oturan, and Kim 2014). However, due to the low levels of these compounds (without additional treatment) compared to the risk based MTLs, these compounds are of limited concern for public health.

Table 3-28. k_{O3}, k_{OH}, Log K_{OW}, and Log K_{OC} Values for the Detected Artificial Sweeteners in the Chapter 1 Survey Data.

Sweetener	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Log K_{OC}	Source
Acesulfame	88	4.55×10^9	-1.33	1.30	Kaiser et al. 2013; Subedi and Kannan 2014
Sucralose	<0.1	1.6×10^9	-1.00	1.00	Bourgin et al. 2017; Subedi and Kannan 2014

Table 3-29. Summary of Fate, Prevention, and Treatment for the Detected Artificial Sweeteners.

Sweetener	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Acesulfame	Poorly oxidized	< 50% removal	None	• GAC • UV/AOP
Sucralose	Poorly oxidized	< 50% removal	None	• GAC • UV/AOP

3.3.8 Detected Flame Retardants—Sources, Prevention, and Treatment

Three recalcitrant flame retardants were found in the Chapter 1 survey BAF effluent data: TCEP, Tris(1-chloro-2-propyl) phosphate (TCPP), and Tris(1,3-dichloroisopropyl) phosphate (TDCPP). The BAF_{eff} values and MTLs for these data are summarized in Table 3-30. TCEP, which is the only detected compound with an MTL, had an BAF_{eff} well below the MTL of 2,500 ng/L. TCPP and TDCPP did not have MTLs, therefore, MDH guidance values and toxicological metrics were used as a basis for public health relevance. TDCPP had an observed maximum facility BAF_{eff} well below the MDH guidance value of 800 ng/L. TCPP does not have a listed MDH guidance value but has a NOAEL and LD50 that are almost equivalent to TCEP. It is reasonable to assume that the corresponding MTL for TCPP would be similar to TCEP; around 2,500 ng/L. The maximum facility BAF_{eff} for TCPP was 2,300 ng/L which is lower, but close to the predicted MTL. Therefore, formulation of an MTL for TCPP is warranted to ensure that public health risks are minimized with respect to this chemical.

Table 3-30. Detected Flame Retardants from the Survey Data.

Flame Retardant	# of Facilities with Detects	Max Facility BAF_{eff} (ng/L)	MTL (ng/L)	MDH Guidance Value (ng/L)	NOAEL (mg/kg-day)	LD_{50} (mg/kg)
TCEP	10	661	2500	5000	88	1230
TCPP	9	2300	--	--	85	1500
TDCPP	3	213	--	800	5	1850

TCEP, TCPP, and TDCPP are organophosphate flame retardants found in a variety of products including clothes, furniture, building materials, and electronics. This family of organophosphate flame retardants have become more widespread in the absence of brominated flame retardants which have become phased out worldwide due to their well-documented toxicity and persistence in the environment (T. Xu et al. 2017). Like PFAS substances, these flame retardants are engineered to be extremely stable resulting in their recalcitrant nature.

A summary of the k_{O3}, $k_{OH,}$ log K_{OW}, and log K_{OC} values for TCEP, TCPP, and TDCPP are shown in Table 3-31, below. References are limited for k_{O3} values for these compounds, but reaction with molecular ozone is expected to be low, as evidenced by the small k_{O3} value for TCEP. High k_{OH}

values for TCEP and TCPP indicate that these compounds are more reactive in the presence of hydroxyl radicals. Within Chapter 1, all three compounds were categorized as “marginally oxidized” with average removals through ozone of less than 50%. As for the Chapter 1 BAF data, all three compounds exhibited >50% additional removal through the filtration process. Within the literature, TCEP, TCPP, and TDCPP have shown limited evidence of removal by biodegradation; removal through BAF is most often linked to adsorption with GAC (Sundaram and Pagilla 2019). Wastewater biological treatment studies as well as aerobic and anerobic biodegradation studies gathered by the EPA show low removal of these compounds through biodegradation pathways (EPA 2019). In Chapter 1, TCPP and TCEP removals through BAF were observed to be highly dependent on initial media condition (e.g., virgin, exhausted, regenerated), with lower removals observed with exhausted media. For example, different media conditions were tested and compared for Project H, as shown in Figure 3-15 and Figure 3-16. The regenerated media showed 2 to 3 times the average TCEP and TCPP removal versus the average removal observed for exhausted media. This further supports the hypothesis that adsorption is a main driver for removal of these compounds through BAF. This aligns with the high log K_{OW} and log K_{OC} values in Table 3-31, below.

Table 3-31. k_{O3}, k_{OH}, Log K_{OW}, and Log K_{OC} Values for the Detected Flame Retardants in the Chapter 1 Survey Data.

Flame Retardant	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Log K_{OC}	Source
TCEP	1	5.60×10^8	1.70	1.50-2.15	Watts and Linden 2009; Y. Lee and von Gunten 2012; WHO 1998;
TCPP	--	1.98×10^8	2.59	2.46	Watts and Linden 2009; WHO 1998; EPA 2012
TDCPP	--	--	3.80	3.04	WHO 1998; EPA 2012

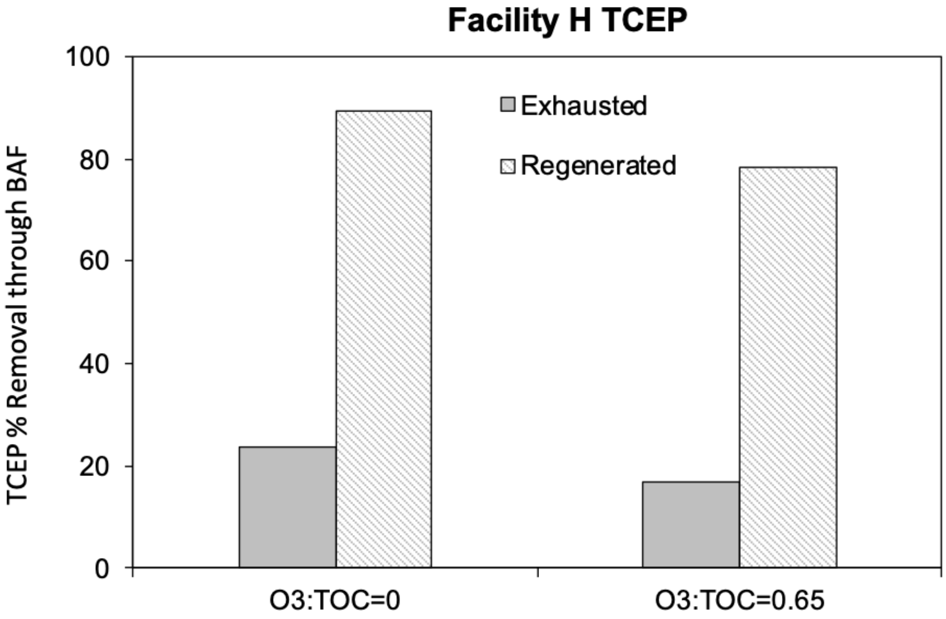

Figure 3-15. Impact of Media Condition (Exhausted Versus Regenerated) on TCEP Removal for Facility H.

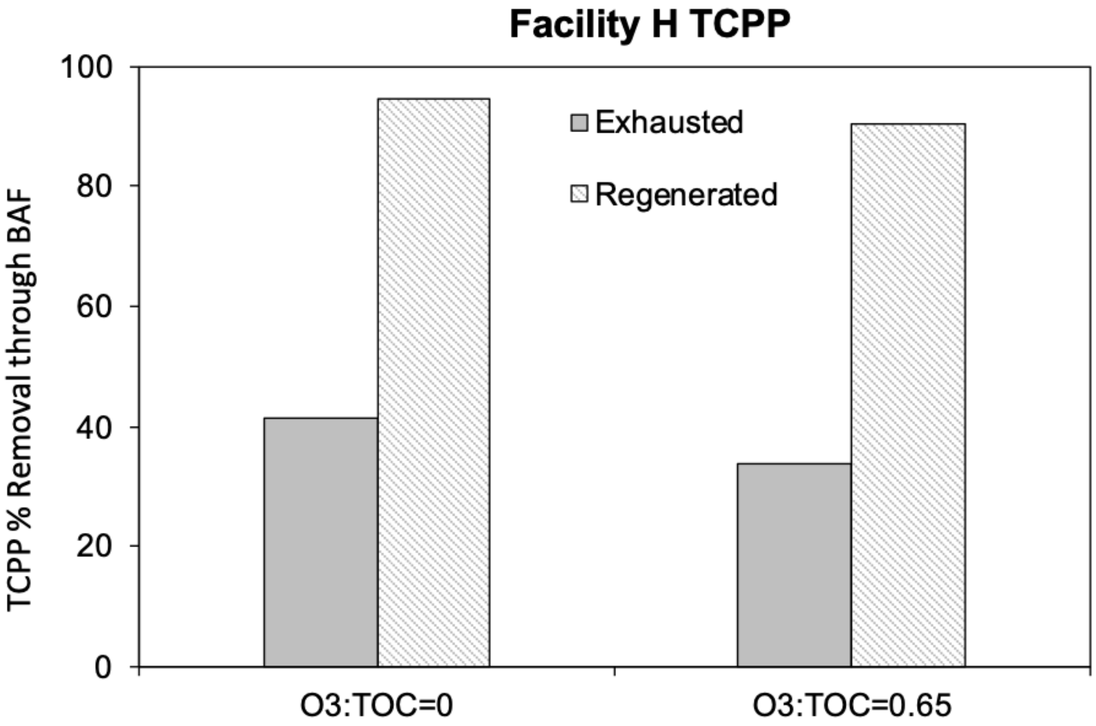

Figure 3-16. Impact of Media Condition (Exhausted Versus Regenerated) on TCPP Removal for Facility H.

Although the compounds observed in this study were not present at levels that present a threat to public health, additional treatment in the form of GAC could be used to reduce concentrations further. Studies have also shown that UV/AOP can readily degrade these flame retardant compounds, which aligns with the high k_{OH} values for TCEP and TCPP in Table 3-31 (Watts and Linden 2009). A summary of the fate, sources, and additional treatment considerations for the recalcitrant organophosphate flame retardants is provided in Table 3-32 below.

Table 3-32. Summary of Fate, Prevention, and Treatment for the Detected Flame Retardants.

Flame Retardant	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
TCEP	Poorly oxidized	< 50% removal (No removal is expected unless media is new or regenerated)	Source control (banning use in consumer products)	• GAC • UV/AOP
TCPP	Poorly oxidized	< 50% removal (No removal is expected unless media is new or regenerated)	Source control (banning use in consumer products)	• GAC • UV/AOP
TDCPP	Poorly oxidized	< 50% removal (No removal is expected unless media is new or regenerated)	Source control (banning use in consumer products)	• GAC • UV/AOP

3.3.9 Detected Miscellaneous Trace Organics—Sources, Prevention, and Treatment

The other trace organics listed in this category are other industrial chemicals which are less easily categorized by commonalities such as structure or source. Of the 6 recalcitrant trace organics listed in Table 3-33, only quinoline (detected at one facility) was observed in exceedance of the listed MTL. All the other compounds listed were several orders of magnitude below their respective MTLs, except for 1,4-dioxane. As such, the discussion in this Section will focus on quinoline and 1,4-dioxane since the other compounds pose a minimal threat to public health at the observed BAF_{eff} values.

Table 3-33. Detected Other Trace Organics from the Survey Data.

Other Trace Organic	# of Facilities with Detects	Max Facility BAC_{eff} (ng/L)	NL (ng/L)	CTR (ng/L)	MTL (ng/L)
Quinoline	1	12	--	--	10
4-nonylphenol	1	245	--	--	1.1×10^5
Benzotriazole	3	1914	--	--	1.0×10^6
Bisphenol A	1	25	--	--	3.5×10^5
1,4-Dioxane	3	842	1000	--	1000
Triethyl phosphate	1	163	--	--	2.0×10^6

3.3.9.1 Quinoline

Quinoline is an industrial chemical that is used as an intermediate in the production of various compounds and can be found in petroleum, coal processing, wood preservation, resins, and paints (EPA 2001b). Limited research exists for the investigation of oxidation rate constants for quinoline; however, it exhibits moderate log K_{OW} and log K_{OC} values indicating that sorption is a potential removal pathway. The Chapter 1 survey data, shown in Figure 3-17, show that quinoline remains unchanged through both ozone and BAF indicating that the compound is also not conducive to biological treatment. Studies have shown that both GAC and UV/AOP can effectively reduce quinoline concentrations (Zhang et al. 2003; Rameshraja et al. 2012). Therefore, these systems should be considered for additional treatment of quinoline in ozone/BAF systems.

Table 3-34. Log K_{OW} and Log K_{OC} for Quinoline.

Compound	Log K_{OW}	Log K_{OC}	Source
Quinoline	2.03	1.90-2.31	EPA 2001b

Table 3-35. Summary of Fate, Prevention, and Treatment for Quinoline.

Compound	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
Quinoline	Poorly oxidized	< 50% removal	None (potential for banning use in consumer products)	• GAC • UV/AOP

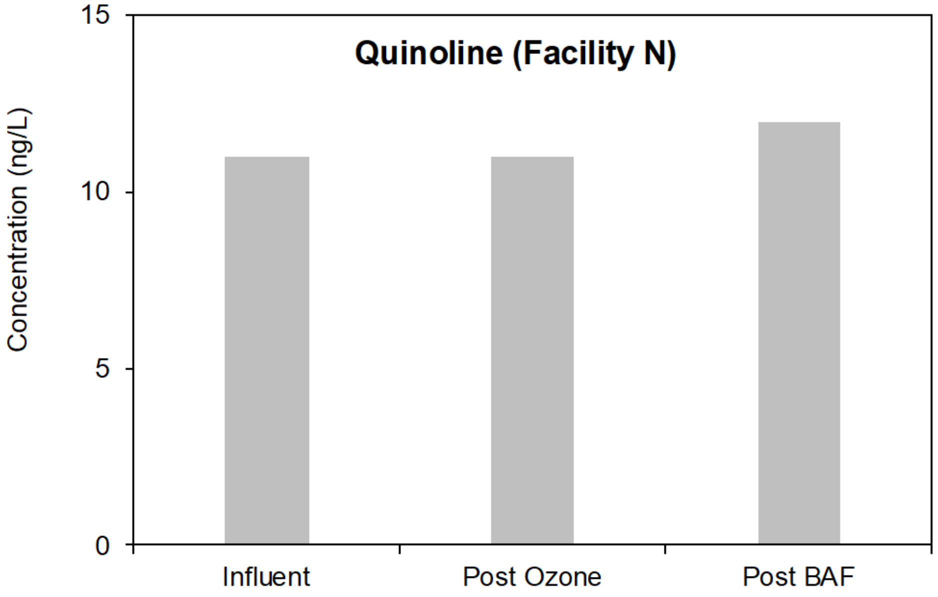

Figure 3-17. Quinoline Concentration along the Treatment Train at Facility N.

3.3.9.2 1,4-Dioxane

1,4-Dioxane is a known recalcitrant synthetic industrial chemical found in many products such as solvents, dyes, grease, automotive fluids, and is a byproduct of plastic manufacturing (EPA 2017d). A summary of the k_{O3}, $k_{OH,}$ log K_{OW}, and log K_{OC} values for 1,4-Dioxane is provided in Table 3-36. 1,4-Dioxane has a low k_{O3} which indicates that reaction with molecular ozone alone would be ineffective. However, the high k_{OH} value indicates that the compound is highly reactive with hydroxyl radicals. From the Chapter 1 survey data, 1,4-Dioxane was only marginally oxidized through ozone with an average removal of less than 50% across all the facilities. Other studies have shown upwards of 60% removal through ozone (Tackaert et al. 2019). Removal efficiency through the ozone process is likely tied to the presence of hydroxyl radicals in the specific matrix once ozonated. BAF removals observed in the Chapter 1 survey data were negligible, suggesting that biodegradation is not a major removal pathway for 1,4-Dioxane which aligns with literature findings (EPA 2017d). 1,4-Dioxane exhibits a negative log K_{OW} but a positive log K_{OC} which indicates that there may be some affinity for sorption, though it is not expected to be very high. However, recent research has indicated that both better-than-expected adsorption and biodegradation can be achieved with GAC media (Mohr 2012; Myers et al. 2018). UV/AOP is perhaps the most common treatment process for the destruction of 1,4-Dioxane, as indicated by the compound's high k_{OH} value. In the state of California specifically, projects can demonstrate proper oxidation process design by demonstrating that the process provides no less than 0.5-log (69%) reduction of 1,4-Dioxane (SWRCB 2018a). Oxidant doses to achieve this goal (paired with the necessary UV dose for NDMA removal) can vary based on the water matrix but are typically around 2-3 mg/L as Cl_2 for free chlorine or 3-5 mg/L of H_2O_2.

Table 3-36. k_{O3}, k_{OH}, Log K_{OW}, and Log K_{OC} Values for 1,4-Dioxane.

Compound	k_{O3} [$M^{-1}s^{-1}$]	k_{OH} [$M^{-1}s^{-1}$]	Log K_{OW}	Log K_{OC}	Source
1,4-Dioxane	<1	3×10^9	-0.27	1.23	Gerrity et al. 2015; EPA 2017d

A summary of the fate, prevention, and treatment for 1,4-Dioxane is provided in Table 3-37.

Table 3-37. Summary of Fate, Prevention, and Treatment for 1,4-Dioxane.

Compound	Fate through Ozone	Fate through BAF	Prevention	Additional non-RO Treatment
1,4-Dioxane	Poorly to moderately oxidized	< 50% removal	Source control	• GAC (new studies have shown better than expected removal) • UV/AOP (well proven for effective removal)

3.4 Additional Treatment Requirements

Section 3.3 above provided a detailed analysis of recalcitrant CECs by chemical type. Although CECs are the focus of this project, it is important to consider the performance of ozone and BAF systems with respect to other water quality parameters that are important in the context of potable reuse. These water quality parameters will be discussed in the following sections in terms of their relevance to potable reuse, their fate through ozone/BAF, and additional treatment requirements (as necessary).

3.4.1 Regulated DBPs and Disinfection Byproduct Formation Potential

In Section 3.3.1.1, DBPs were discussed in terms of compounds that were not yet regulated by MCLs. In terms of regulated DBPs, the major groups include TTHM, HAA5, and bromate.

3.4.1.1 Bromate

Bromate is regulated in drinking water under the Stage 1 Disinfection Byproduct Rule with an MCL of 10 µg/L. Bromate formation occurs via both direct reaction with molecular ozone and reaction with hydroxyl radicals formed via ozonation (von Gunten and Hoigné, 1994). The two main contributors to bromate concentration are: i) bromide concentration in the influent to the ozone process and ii) the applied ozone dose. Higher ozone doses can potentially provide greater removal efficiencies for CECs and pathogens, while potentially forming bromate.

Selection of a design ozone dose can be segmented by two major treatment train categories: treatment trains that include bromate mitigation and those that do not. Bromate mitigation strategies include upstream strategies such as the chlorine-ammonia process, and downstream treatment such as RO. Bromate is removed by GAC but exhibits a much shorter breakthrough than other compounds of interest. Therefore, it is economically impractical to use GAC for reliable downstream bromate mitigation. The chlorine-ammonia process works by first dosing free chlorine to oxidize bromide to hypobromous acid. Subsequent addition of ammonia prior to ozonation forms bromamines which sequesters the bromide and prevents it from forming bromate (Buffle, Galli, and von Gunten 2004). Other chemical bromate mitigation strategies include pH suppression, ammonia addition (only), chloramine addition, and H_2O_2 addition. Upstream mitigation may also include coagulation/sedimentation and tertiary filtration for enhanced TOC removal, which ultimately results in lower ozone doses. For downstream mitigation (not including RO), sorption processes such as IX and GAC has exhibited some removal, but effectiveness can vary depending on the presence of competing ions (Bao et al. 1999; Siddiqui et al. 1996; Wiśniewski and Kabsch-Korbutowicz 2010). Bromate removal has been observed through BAF under certain conditions, however removal efficiencies are typically not high enough to consistently remove high levels of formed bromate. Without bromate mitigation strategies, ozone dose should be limited to around 0.5 to 0.6 mg O_3/mg TOC to control bromate formation, but this should be determined on a site-specific basis through treatability testing prior to full-scale implementation. When bromate mitigation is in place, ozone dose limitation is less important. A more detailed discussion of the relationship between ozone dose and bromate is provided in Section 3.5.2.2.

3.4.1.2 TTHM and HAA5

TTHM and HAA5 are regulated by the Stage 1 and Stage 2 Disinfection Byproduct Rules, with MCLs of 80 μg/L and 60 μg/L, respectively. As discussed in Section 3.3.1, neither THMs nor HAAs are significantly oxidized through ozone. HAAs can be removed by BAF, whereas BAF does not provide reliable treatment of THMs. One major consideration for preventing the formation of THMs and HAAs is restricting the use of free chlorine prior to ozone/BAF.

Recent studies have shown the benefits that ozone/BAF have in reducing DBPFP via elimination of organic precursors. In a study by Arnold et al. (2018), TOC removal through ozone/BAF was well-correlated with DBPFP. Higher effluent TOC resulted in higher levels of TTHM and HAA5 formation. One major conclusion from that study was the recommendation of maximum BAF effluent TOC levels that corresponded to HAA5 and TTHM compliance: 6.2 mg/L and 3.3 mg/L, respectively. Applying a safety factor to the lower TTHM TOC threshold of 3.3 mg/L corresponds to a design goal of 2 mg/L of BAF effluent TOC for DBP compliance. Similar observations of reduced DBPFP with ozone/BAF treatment prior to chlorination have been observed in other studies as well (Chuang and Mitch 2017; Vatankhah et al. 2019b).

3.4.2 TOC/Organics

Within the United States, no universal regulation has been established for potable reuse TOC requirements. The U.S. EPA provided a recommendation that recycled water for indirect potable reuse (IPR) should contain less than 2 mg/L of TOC, however it was ultimately left to the states to develop actual regulations (Schimmoller et al. 2020). Full-scale facilities in Virginia and Georgia have chemical oxygen demand (COD) limits of 10 mg/L and 18 mg/L which equates to approximately 3-4 mg/L as TOC (Schimmoller et al. 2020). Florida’s potable reuse regulations stipulate a TOC limit of 3 mg/L. (Schimmoller et al. 2020). In the recycled water regulations that govern potable reuse in California, TOC is used as an indicator of “wastewater signature” in the recycled water effluent. For groundwater projects, the recycled water used for recharge must not exceed a TOC concentration of 0.5 mg/L divided by the recycled water contribution (RWC) credited. RWC is the amount of recycled water divided by the total amount of water to be recharged (including non-recycled water sources). For example, if a project plans to augment groundwater by using 20% recycled water and 80% imported surface water, the TOC requirement would be 0.5 mg/L divided by 0.2, or 2.5 mg/L.

For CBAT trains, the California TOC limit of 0.5 mg/L is difficult to attain efficiently. Typical TOC values in domestic wastewater effluent range from 5-15 mg/L depending on the upstream treatment. As shown in Section 3.3.2.1, TOC removal through ozone/BAF can range from around 20% to 70% (typical removal around 40%), but this is well short of the 95% or greater removal required to meet the 0.5 mg/L limit. Addition of GAC may help approach this low limit but is still not expected to be efficient in terms of carbon usage. Therefore, as currently regulated, CBAT would likely not be adequate for potable reuse projects in California other than spreading projects with high RWCs.

Recent work completed for Reuse 15-04/4771, which was created to study the characterization and control of organics under the lens of direct potable reuse (DPR), developed an alternative framework for organics (Schimmoller et al. 2020). In that study, it was concluded that absolute TOC values are not necessarily protective of public health when applied generally to all systems. Drinking water systems can have finished water TOC concentrations of less than 1 mg/L to 4 mg/L and still be deemed safe, therefore a single TOC limit is not a “one-size-fits-all” solution. As such, the study recommended the creation of a TOC alert limit for the DPR project equal to the local drinking water historical median TOC. If the DPR project regularly exceeds this level, a more in-depth analytical analysis of specific organic constituents would be required. TOC is a bulk measurement which may provide some insights to the safety of a finished water, it is the specific organic constituents that make up the TOC profile which ultimately impact public health. One of the main organic constituents linked with TOC is DBPs. As discussed in Section 3.4.1 above, the study by Arnold et al. (2018) demonstrated that TOC levels of around 3-5 mg/L would be adequate for the prevention of TTHM and HAA5. Applying a safety factor would result in a conservative TOC limit of 2 mg/L. CBAT trains with ozone, BAF, and additional GAC should be adequate to meet higher TOC limits in the range of 2-5 mg/L, which has been proven to be protective of public health.

In terms of specific organic compounds, California recycled water regulations stipulate that groundwater injection and SWA projects include an oxidation process capable of achieving adequate removal of indicator compounds from the 9 listed chemical groups. Testing conducted at Facility D’s ozone/BAC with FAT demonstration facility showed that the ozone/BAF demonstration process is capable of adequate oxidation of these compounds and therefore achieves the definition of an AOP through the lens of the California recycled water regulations. It should be noted, however, that other studies have demonstrated less than the required 0.3-log removal for the compounds in groups H and I, which is likely tied to the remaining adsorptive capacity of the BAC during testing (Gerrity et al. 2012, 2014). The 9 chemical groups and results from the Facility D study are shown in Table 3-38.

Table 3-38. Chemical Indicator Groups and Corresponding Log Removal Requirements for Meeting Advanced Oxidation Process Criteria for Potable Reuse in California Results from Facility D.

Indicator Group	Required Removal	Compounds Tested	Observed Removal
(A) Hydroxy aromatic	0.5-log	4-tert-octylphenol	> 0.97-log
		4-nonylphenol	> 1.2-log
(B) Amino/Acylamino aromatic	0.5-log	Sulfamethoxazole	> 0.56-log
(C) Nonaromatic with carbon double bonds	0.5-log	Carbamazepine	> 1.1-log
(D) Deprotonated amine	0.5-log	Diclofenac	> 1.3-log
		Trimethoprim	> 0.51-log
		Atenolol	> 1.1-log
(E) Alkoxy polyaromatic	0.5-log	--	--
(F) Alkoxy aromatic	0.5-log	Gemfibrozil	> 0.58-log
(G) Alkyl aromatic	0.5-log	--	--
(H) Saturated aliphatic	0.3-log	Meprobamate	> 0.78-log
		TCEP	> 1.06-log
		TCPP	> 1.04-log
		TDCPP	> 0.49-log
(I) Nitro aromatic	0.3-log	--	--

As an alternative to demonstration of adequate removal of these indicator groups, project sponsors may demonstrate adequate oxidation performance by showing that the process achieves at least 0.5-log (69%) reduction of 1,4-dioxane. For projects with FAT, this simpler approach is more commonly used. Within California, NDMA is also a key organic constituent in the context of ozone/BAF, which must meet the CTR limit of 0.69 ng/L for SWA and the NL of 10 ng/L for groundwater projects. Lastly the recently developed California NLs for PFOA and PFOS of 5.1 ng/L and 6.5 ng/L, respectively, must also be achieved for SWA and groundwater projects.

Based on guidance from the California's Science Advisory Panel on CECs, several health-based CECs are required to be monitored at the monitoring wells of subsurface application groundwater projects and in the purified effluent prior to discharge for injection and SWA projects (SWRCB 2018b). A summary of these required CECs for monitoring is included in Table 3-39. MECs are compared to MTLs and the magnitude of the MEC/MTL ratio is used to select appropriate follow-up actions.

Table 3-39. Health-based CECs Required for Monitoring in Potable Reuse Effluents in California.

Health-Based CEC	Monitoring Trigger Level (μg/L)
1,4-dioxane	1.000
NDMA	0.010
NMOR	0.012
PFOS	0.013[a]
PFOA	0.014[a]

[a] California recently finalized NLs for PFOS and PFOA of 0.0065 μg/L and 0.0051 μg/L, respectively

3.4.3 Nutrients

The main nutrient of concern in the context of potable reuse and public health is nitrogen. Nitrate is regulated nationally with an MCL of 10 mg/L, and in California, groundwater recharge projects are held to a total nitrogen (TN) limit of 10 mg/L (the majority of which is expected to be nitrate, with the balance comprised of ammonia, chloramines, and dissolved organic nitrogen). Florida and Washington also have state-specific potable reuse regulations that include a TN limit of 10 mg/L. For SWA in California, TN and total phosphorus (ToP) in the discharge to the reservoir are evaluated on a project-specific basis depending on the watershed's Basin Plan objectives. Facility D, a SWA project in California, must achieve TN and ToP concentrations of 2.0 mg/L and 0.025 mg/L, respectively (RWQCB 2020). These limits are more relevant from an environmental health perspective to prevent eutrophication of the receiving water.

TN and ToP remain largely unchanged through the ozone/BAF processes; therefore, removal is largely dependent on upstream and downstream processes. At the upstream WWTP, biological nutrient removal (BNR) with nitrification and denitrification (NDN) with an anaerobic selector should be optimized as the workhorse for TN and ToP removal. A well-run NDN process should be capable of achieving an effluent TN concentration of around 10 mg/L (the majority of which is nitrate). ToP levels in the effluent of a well-run biological wastewater treatment process with an anaerobic selector can be less than 1 mg/L, and further removal can be achieved with coagulant and tertiary filtration. Downstream treatment options for further nitrate removal include IX with a strong base anion resin, or electrodialysis.

3.4.4 Pathogens

As discussed in the context of TOC, there are no uniform national regulations for pathogen reduction in potable reuse projects. As such, projects are governed at the state level. Within the U.S., California has the most robust set of regulations related to pathogenic microorganism control for potable reuse. For groundwater recharge in California, projects must attain log reduction values (LRVs) equal to or greater than 12/10/10 for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts (SWRCB 2018a). Credits must be achieved through a minimum of three separate treatment processes, which can include wastewater treatment, advanced treatment, and aquifer treatment. No process may be credited with an LRV greater than 6 to ensure a multi-barrier approach. Surface spreading groundwater projects can be credited with LRVs of 6/10/10 for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts if 6 months of aquifer retention time is demonstrated via tracer study[3]. If the groundwater is injected rather than percolated by spreading, the aquifer protozoa credits are lost but the virus credit is maintained[3]. For SWA in California, baseline LRVs of 8/7/8 for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts are required prior to reservoir discharge. Additional LRVs are required depending on the modeled residence time and dilution factors of the reservoir. A minimum of two credited treatment processes are required for each pathogen and the maximum LRV of 6

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[3] The aquifer treatment LRVs for the protozoa must be demonstrated via added tracer, which will provide 1 virus LRV per month demonstrated. If an added tracer is not used to demonstrate the retention time, lower LRVs per month of retention time are credited (0.67 for intrinsic tracer, 0.5 for numerical modeling, 0.25 for academically accepted equations)

per process also applies. Draft DPR regulations in California require LRVs of 20/14/15 for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts. A total of four processes must be credited to provide at least 1 LRV for each pathogen and must include the three following mechanisms: UV disinfection, physical separation, and chemical disinfection.

Nevada's potable reuse regulations include the California pathogen framework of 12/10/10 for pathogen LRVs in groundwater augmentation projects (EPA and CDM Smith 2017). In Texas, requirements are determined on a case-by-case basis, however guidance from the Texas Water Development Board has established baseline target LRVs of 8/6/5.5 for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts (TWDB 2015). North Carolina includes *E. coli*, coliphage, and *Clostridium perfringens* LRV requirements of 6/5/4, respectively (EPA 2017a). Effluent standards for these microorganisms also exist in the form of monthly geometric mean limits of ≤ 3/100 mL for *E. coli*, ≤ 5/100 mL for coliphage, and ≤ 5/100 mL for *Clostridium perfringens*. Virginia has monthly geometric mean concentration thresholds of ≤14 colonies/100 mL for fecal coliform and ≤11 colonies/100 mL for *E. coli.* Lastly, Washington includes pathogen requirements based on whether the final effluent is Class A (higher effluent quality for direct groundwater injection and SWA) or Class B (lower effluent quality for indirect groundwater recharge and select SWA applications) (EPA 2017a). Class A requirements include disinfection for 4-log virus reduction and a 7-day median total coliform concentration of ≤2.2 most probable number (MPN)/100 mL. For Class B uses, only a 7-day median total coliform concentration limit of ≤23 MPN/100 mL exists. A summary of state-by-state pathogen regulations for potable reuse is provided in Table 3-40.

Table 3-40. Summary of Established State Regulations for Pathogen Removal in Potable Reuse Projects.

State	Type of Potable Reuse	Pathogen Removal Regulation
California	IPR: Groundwater spreading or injection	Enteric virus/*Giardia* cyst/*Cryptosporidium* oocyst LRVs of 12/10/10
	IPR: SWA	Enteric virus/*Giardia* cyst/*Cryptosporidium* oocyst LRVs of 8/7/8 (additional LRVs required based on dilution and residence time)
	DPR	Enteric virus/*Giardia* cyst/*Cryptosporidium* oocyst LRVs of 20/14/15
Nevada	IPR	Enteric virus/*Giardia* cyst/*Cryptosporidium* oocyst LRVs of 12/10/10
Texas	IPR and DPR	Determined on a case-by-case basis but baseline enteric virus/*Giardia* cyst/*Cryptosporidium* oocyst LRVs of 8/6/5.5 are recommended for DPR
North Carolina	IPR and DPR	Type 2 Reclaimed Water: *E. coli*, coliphage, and *Clostridium perfringens* LRV requirements of 6/5/4, respectively. Monthly geometric mean limits of £ 3/100 mL, £ 5/100 mL, and £ 5/100 mL, respectively
Virginia	IPR	£14 colonies/100 mL for fecal coliform (monthly geometric mean) £11 colonies/100 mL for *E. coli* (monthly geometric mean)
Washington	Class A (select SWA, indirect and direct aquifer recharge)	Virus LRV of 4

State	Type of Potable Reuse	Pathogen Removal Regulation
Washington (continued)	Class A (select SWA, indirect and direct aquifer recharge) (continued)	7-day median total coliform concentration of £2.2 MPN/100 mL
	Class B (select SWA, indirect aquifer recharge)	7-day median total coliform concentration of £23 MPN/100 mL

Due to the location-specific nature of how pathogen removal is regulated for potable reuse, there isn't a "one-size-fits-all" solution. For pathogen crediting of ozone systems, the EPA's Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) Toolbox Guidance Manual includes temperature-dependent CT values for *Cryptosporidium* inactivation by ozone. There are also equations for the log removals of *Giardia* and virus depending on the temperature and calculated CT, however the CT for the more resistant *Cryptosporidium* drives the design and results in substantial *Giardia* and virus removal (more than the 6-log maximum per process in California). Depending on CT, the *Cryptosporidium* LRV can be between 0.25 and 3.0 per these guidelines. Currently, no pathogen crediting frameworks exist for BAF alone. Therefore, for states that employ the 12/10/10 framework for pathogen LRVs, additional treatment in the form of membrane filtration and/or UV/AOP may be necessary.

3.4.5 Total Dissolved Solids

Total dissolved solids (TDS) is a measure of all the dissolved organic and inorganic constituents within a given water sample. EPA established a secondary maximum contaminant level (SMCL) of 500 mg/L for concerns associated with color, hardness/deposits, and taste. Furthermore, in California, specific watersheds with a given Basin Plan maybe be held to specific TDS requirements to preserve environmental conditions (either groundwater or surface water). Neither ozone nor BAF remove TDS so, in the context of CBAT, the TDS of the wastewater effluent is what sets the TDS of the final purified effluent for reuse. Therefore, projects which have an inherently high recycled water TDS may not be suitable for CBAT treatment trains. Partial sidestream treatment through electrodialysis or RO and blending may be viable solutions under these circumstances to achieve target TDS levels in the final effluent.

3.4.6 Bioassays

Bioassays are bioanalytical screening methods which are used to observe an adverse effect from a wide spectrum of CECs. Bioassays can be conducted *in vitro* (using cells or protein) or *in vivo* using whole organisms. The benefit of using bioassays is that they can be used as a monitoring tool to understand the potential human-health impacts of unknown CECs. This type of tool also accounts for synergistic, additive, or antagonistic impacts of chemical mixtures (Drewes et al. 2018). The outputs from bioassays are referenced to a substance (equivalency agonist) that creates a target adverse impact from the receptor to generate a bioanalytical equivalent concentration (SWCRB 2018b).

California was the first state to implement requirements for bioassay monitoring in its recycled water policy (SWRCB 2018b). Based on guidance from the State's Science Advisory Panel, two bioassays were recommended and implemented for the monitoring of potable reuse effluents in CA: the estrogen receptor alpha (ER-α) and the aryl hydrocarbon receptor (AhR) (Drewes et al 2018; SWRCB 2018b). ER-α screens for potential feminization, impaired reproduction, and cancer effects of estrogenic chemicals (e.g., estradiol, bisphenol A, nonylphenol) while AhR screens for potential cancer and impaired reproduction effects of dioxin-like chemicals (e.g., polycyclic aromatic hydrocarbons, pesticides). These two bioassays were selected by the Science Advisory Panel because they both have clear adverse outcome pathways that can be adequately standardized and implemented (Drewes et al. 2018). However, as discussed in Chapter 2, several bioassay tools are available for other endpoint responses, but are at varying levels of development.

Within California, surface application groundwater projects can conduct bioassay monitoring from groundwater monitoring wells. For groundwater injection and SWA projects, bioassay monitoring must be conducted in the purified effluent prior to injection or reservoir discharge. A summary of the required bioassays and corresponding equivalency agonists and MTLs are shown in Table 3-41. Like with targeted CEC analyses, E2-bioanaltycial equivalent (BEQ) to MTL ratios are used to determine the relative public health safety of the monitored effluent and select appropriate follow-up actions.

Table 3-41. Required Bioassays for Monitoring Potable Reuse Effluents in California.

Bioassay	Equivalency Agonist	MTL (ng/L)
Estrogen Receptor alpha	17-b-estradiol	3.5
Aryl hydrocarbon Receptor	2,3,7,8-tetrachlorodibenzo-p-dioxin	0.5

3.4.7 Additional Required Upstream Treatment Processes

The main objectives for wastewater treatment upstream of CBAT are as follows:

- Reduce nutrients to the level required for the project (or to levels low enough such that additional post-treatment can achieve effluent goals)
- Reduce TOC as much as feasibly possible in order to:
  - Reduce ozone demand
  - Reduce TOC load on BAF and downstream GAC (replenishment of downstream GAC can be costly over time)
  - Meet the effluent TOC limit pertaining to local regulations
  - Reduce the formation of DBPs in downstream disinfection processes
- Pathogen and chemical removal can provide additional reliability and redundancy but is required in some scenarios

Specific elements of a well-run upstream wastewater treatment process are discussed in the following sections.

3.4.7.1 Nutrients, Organics, and Solids

The treatment provided by an upstream WWTP (or water reclamation plant), is a key consideration for potable reuse projects. A high-quality feedwater is an essential first step for any potable reuse project and can be especially important for CBAT trains. Wastewater treatment plays an important role in the removal of four key constituents for CBAT potable reuse treatment trains: i) organics (both TOC and CECs), ii) nutrients, iii) turbidity and suspended solids, and iv) pathogens.

For both conventional activated sludge and MBR plants, SRT is one of the main parameters by which these biological processes are both designed and operated. The removal of organic matter is the primary objective in wastewater treatment. Biological oxygen demand (BOD) is the amount of oxygen utilized to microbially break down organic material present in a wastewater sample and is a common measure of treatment performance. Additional nutrient treatment can be achieved with higher SRTs, oxygen control (i.e., anoxic and aerobic ones for nitrogen and anaerobic for biological phosphorus removal), and in some cases chemical addition (e.g., carbon source, ferric coagulant). Typically, activated sludge SRTs fall into the following categories (exact SRTs may vary due to temperature and influent wastewater quality):

- SRT ≤ 2 days (with fully aerated basins): BOD removal only (not ideal due to lower effluent water quality: higher concentrations of TOC and CECs, TN and ToP)
- 2 days < SRT < 8 days (with fully aerated basins): BOD removal and partial nitrification (not ideal due to the potential to form nitrite and negative impacts on ozone)
- SRT > 8 days (with anoxic and aerobic basins): BOD removal, complete nitrification, denitrification, and phosphorus removal (ideal due to higher effluent water quality: lower concentrations of TOC and CECs, TN and ToP)

In the case of CBAT trains for potable reuse, upstream nutrient treatment can play a role in downstream CBAT process performance. Although more research is needed on the topic, changing the nutrient makeup of the BAF feedwater could impact CEC removal by affecting microbial health or changing the microbial community itself. For example, high levels of ammonia carryover from wastewater may have an adverse impact on the biological treatment provided by the BAF process. In the Water Environment and Reuse Foundation (WE&RF) Project 13-10, NDMA was formed in a pilot BAF system with feedwater sourced from a WWTP with high effluent ammonia (Stanford 2017). Nitrite, which can be formed by incomplete nitrification, is a highly reactive ozone scavenger that can impact ozone performance. When nitrite is present, ozone is used up in the oxidation of nitrite to nitrate which decreases the available ozone for oxidation of organic compounds and disinfection. Pilot work has shown that correcting ozone dose for nitrite demand can improve TOC removal by up to 10% through the ozone/BAF process (Brown and Caldwell and Trussell Technologies 2018). Therefore, complete nitrification is essential to control these potential issues.

On the nutrient compliance side, upstream wastewater treatment is the workhorse of nitrogen and phosphorus removals in a CBAT train. Neither ozone nor BAF are designed to remove nutrients. As such, nitrification with denitrification is a prerequisite biological process for projects with nitrogen limits. Denitrification can also be obtained via the use of tertiary denitrification filters. In WE&RF Project 13-12 () titled “Guidelines for Source Water Control Options and the Impact of Selected Strategies on Direct Potable Reuse”, recommendations for upstream wastewater treatment were a full nitrification (less than 0.5 mg/L of ammonia-N), denitrification (less than 10 mg/L TN), and low effluent phosphorus levels via biological or chemical removal (Rimer, DeCarolis, and Sathyamoorthy 2017). This two-step process transforms ammonia to nitrate and nitrate to nitrogen gas which is released to the atmosphere. Well-run CAS and MBR systems with NDN are capable of achieving effluent TN concentrations of less than 10 mg/L (Tchobanoglous et al. 2003; Rimer, DeCarolis, and Sathyamoorthy 2017).

More sophisticated systems with step feed and chemical addition can reach TN levels of less than 3 mg/L (Rimer, DeCarolis, and Sathyamoorthy 2017). SWA projects in California are subject to the most stringent nutrient limits depending on the reservoir. The Facility D in California has effluent limits of 2.0 mg/L and 0.025 mg/L for TN and ToP, respectively for discharge into a surface water reservoir (RWQCB 2020). For projects with similar nutrient limits, additional treatment downstream of the CBAT train, such as IX, may be required.

Though wastewater treatment is not designed to remove specific CECs, research has shown that significant biodegradation, transformation, and attenuation of certain compounds can occur (Rimer, DeCarolis, and Sathyamoorthy 2017). In Water Environment Research Foundation Project CEC4R08 (WRF Project #1347) titled “Trace Organic Compound Indicator Removal During Conventional Wastewater Treatment”, work was done to advance the knowledge of the fate of CECs through secondary wastewater treatment (Salveson et al. 2012). A summary table adapted from that report is shown in Table 3-42. Nitrosamines were not studied in that project, but research has shown that NDMA and NMOR are well removed through secondary treatment (Gerrity et al. 2015).

Table 3-42. Fate of Select CECs through Biotransformation and Sorption in Secondary Wastewater Treatment.
Data Source: Salveson et al. 2012.

	Slow Biotransformation	**Moderate Biotransformation**	**Rapid Biotransformation**
Low Sorption	Carbamazepine Meprobamate Primidone TCEP Sucralose	DEET Sulfamethoxazole Gemfribrozil Iopromide Trimethoprim	Acetaminophen Caffeine Naproxen Ibuprofen Atenolol
Moderate Sorption	TCPP	Cimetidine	Benzophenone Diphenhydramine Bisphenol A
High Sorption	Triclocarban	--	Triclosan Fluoxetine

In the WERF CEC4R08 project and others, CEC removal efficiency percentage varies greatly based on compound and the type of treatment process. SRT has been linked to removal efficiency and critical SRT values have been established to designate the minimum SRT required to obtain a certain removal (typically 80%) (Clara et al. 2005a; Oppenheimer et al. 2007; Salveson et al. 2012). While some compounds are well removed at lower SRTs (< 5 days), more recalcitrant compounds exhibit critical SRTs of 10 days or higher (Clara et al. 2005a; Oppenheimer et al. 2007; Salveson et al. 2012). Data from the Chapter 1 survey showed higher concentrations of DEET and triclosan at facilities with lower SRTs (<1-4 days). This aligns with studies that have shown that these compounds are more recalcitrant, with critical SRT values of at least 10 days (Oppenheimer et al. 2007; Salveson et al. 2012). As such, plants that operate with an SRT of 10 days or higher for nitrification would also benefit from increased CEC removals (Clara et al. 2005a; Clara et al. 2005b).

Tertiary treatment is an effluent polishing step (or combination of several steps), to further improve the effluent wastewater quality. The most commonly observed tertiary treatment processes are chemical precipitation using aluminum or iron-based coagulants, media filtration, and disinfection. Precipitation and filtration processes are effective for the removal of additional suspended solids which can improve effluent turbidity. This can improve the performance of downstream ozone/BAF. Pathogens in treated wastewater can attach to particles which can "shield" them from disinfectants such as ozone (WaterSecure 2017b). Therefore, particle removal can both decrease pathogens, and decrease the potential shielding effect in downstream disinfection processes. Particle removal can also improve BAC performance by decreasing headloss buildup and extending runtime between backwashes. Two-stage systems which include both precipitation and filtration have been proven to be effective at removing additional TOC, phosphorus (effluent concentrations as low as 0.02 mg/L) and metals such as iron and manganese (Tchobanoglous et al. 2003). Precipitation and filtration have been shown to reduce the concentration of hydrophobic CECs in wastewater effluent that are amenable to adsorption: this is particularly important for compounds that are well adsorbed but not effectively biodegraded (Salveson et al. 2012). Oppenheimer et al. (2007) analyzed CEC removal through two WWTPs with tertiary filtration: one with coagulant and one without. Overall, the plant with upstream coagulant addition exhibited slightly higher CEC removals, especially with respect to more hydrophobic compounds such as triclosan (Oppenheimer et al. 2007). However, this study concluded that tertiary filtration does not offer significant overall removal of target CECs. The Chapter 1 survey data included 11 plants with tertiary filtration and 2 plants without: no significant improvements in CEC removal were observed for plants with filtration. Therefore, tertiary treatment may offer some benefits for removing select adsorbable CECs, but the main advantages include the removal of turbidity, pathogens, TOC, phosphorus, iron, and manganese.

In recent years, municipalities have developed growing interest in enhanced coagulation, flocculation, sedimentation, and filtration as a tertiary treatment process upstream of advanced treatment for potable reuse. This series of treatment processes is more typically used in drinking water treatment and involves dosing a coagulant (typically ferric or alum) with rapid mixing, gentle mixing for flocculation, and sedimentation prior to filtration. In addition to phosphorus removal, enhanced coagulation can also result in additional TOC removal and could even be credited using the Surface Water Treatment Rule (SWTR) pathogen crediting framework for virus, *Giardia*, and *Cryptosporidium*. Research remains limited on the application of this technology on recycled wastewater; therefore, it is difficult to claim typical TOC removal ranges. The EPA Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual provide guidance for TOC removal by enhanced coagulation in drinking water treatment applications (EPA 1999b). In that document, TOC removal requirements range from 15% to 60% depending on the source water TOC and alkalinity. Under this framework, typical recycled wastewater would require 30-40% TOC removal by enhanced coagulation. The major advantages of applying enhanced coagulation as pretreatment to CBAT are the additional removal of TOC which helps reduce DBP formation potential and help achieve low effluent TOC limits in the absence of RO and the removal of solids which can help downstream ozone efficiency and BAC operation as discussed above.

MBRs combine activated sludge biological treatment with physical membrane filtration to provide integrated treatment of nutrients, organics, and suspended solids. As such, MBRs can replace CAS, secondary clarification, and tertiary filtration and can significantly reduce the footprint of a wastewater treatment facility while improving TOC and suspended solids removal. MBRs typically operate at a high SRT (≥10 days) and do so more efficiently than CAS with respect to footprint. This is because MBRs can operate with much higher mixed liquor suspended solids concentrations. Operation at an elevated SRT provides improved TOC, nutrient and CEC removals, as discussed above. In some studies, MBR systems have been shown to offer higher CEC removals in comparison to CAS systems due to their superior ability to remove suspended and colloidal particles which CECs may be associated with (USBR 2009; Salveson et al. 2012). However, the two largest water quality advantages associated with MBR systems are the removal of bulk organics (e.g., BOD and TOC) and particulates (e.g., total suspended solids [TSS] and turbidity). A comparison of key water parameters for CAS and MBR is shown in Table 3-43 below.

Table 3-43. Comparison of Key Effluent Parameters for CAS and MBR Treatment Processes.

Parameter	CAS (BOD)	CAS (Nitr.)	CAS (NDN)	CAS (NDN) + Tertiary Filtration (w/ Chemical)	MBR (NDN)
TN (mg/L)	30-40	20-30	10-15	10-15	8-12
ToP (mg/L)	1-2	1-2	1-2	0.1-0.5	1-2[b]
BOD (mg/L)	20-30	5-10	5-10	5-10[a]	2-5
TOC (mg/L)	10-15	8-12	8-10	8-10[a]	4-9
TSS (mg/L)	8-10	8-10	8-10	3-5	0.5-1
Turbidity (NTU)	2-5	2-5	2-5	0.5-2	0.1-0.5

[a] Media filtration w/ chemical addition can achieve additional organics removal, but conservative typical effluent values are shown to match the CAS-only case

[b] Typical MBR designs do not include chemical P removal. MBR systems could be designed for biological P removal, but P removal efficiency likely to suffer with emphasis on N removal

It is worth noting that, historically, WWTPs were designed for the sole purpose of treating wastewater to an effluent acceptable for discharge to a receiving water (e.g., river or ocean). Potable reuse projects demand improved water quality that existing plants cannot achieve without significant modification. For example, raising the SRT is associated with major capital and footprint expansion to accommodate more activated sludge volume. However, potable reuse flows are often a portion of the total treated wastewater flow. Therefore, municipalities may consider retrofitting portions of an existing plant to include NDN or MBR to save costs.

3.4.7.2 Pathogen Crediting

Enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts are also removed through secondary and tertiary wastewater treatment. In California, water reclamation plants operated by the Water Replenishment District of Southern California (WRD), City of Los Angeles Bureau of Sanitation (LASAN), and City of San Diego have been credited for pathogen removal through the secondary treatment process. WRD and LASAN were granted LRVs based on the analysis of literature-based pathogen concentrations, while City of San Diego conducted a site-specific study for characterization of removal through the North City Water Reclamation Plant. An additional monitoring study is underway to characterize removal through tertiary filtration and update secondary treatment credits. Orange County Water District is also conducting a study to characterize virus removal through the wastewater treatment process. Pathogen crediting of secondary and tertiary wastewater treatment processes in California is a rapidly evolving field and the creation of new data via site-specific studies has led the Division of Drinking Water (DDW) to revise the default literature based LRVs. Due to the site-specific variability of the data and rapidly evolving statistical methods to analyze it, there exists a wide range of LRVs that can be attained. Site-specific monitoring remains the best strategy to accurately characterize removal through a particular facility and demonstrate the highest possible LRVs.

LRV crediting of enhanced coagulation, flocculation, and sedimentation has also been considered by some facilities in the US, though this process has yet to be credited for potable reuse within California. A pathogen crediting framework for coagulation, flocculation, sedimentation, and filtration (conventional filtration) is included in the EPA SWTR and subsequent Long Term 1 (LT1ESWTR) and LT2ESWTR. Filtration crediting in drinking water is based on filter effluent turbidity:

- If the filter effluent turbidity is less than 95% of the time, a conventional filtration process is credited with:
    - LRV of 2 for virus
    - LRV of 2.5 for *Giardia*
    - LRV of 2 for *Cryptosporidium*
- If the filter effluent is less than 0.15 NTU 95% of the time in combined filter effluent:
    - An additional LRV of 0.5 is credited for *Cryptosporidium*
- If the filter effluent is less than 0.15 NTU 95% of the time in individual filter effluents:
    - An additional LRV of 0.5 is credited for *Cryptosporidium*

Chlorine disinfection is also commonly used for the disinfection of treated drinking water and recycled water effluents. Either free chlorine or chloramines are typically used for finished water disinfection. While free chlorine is a much more effective disinfectant for viruses and protozoa, chloramines are often used to reduce the formation of DBPs, especially THMs (Black and Veatch 2010). In California, disinfected tertiary recycled wastewater is defined as a filtered wastewater which has been subjected to a total chlorine residual of at least 450 mg-min/L with a modal contact time of 90 min or has been demonstrated to achieve 5-log reduction of bacteriophage or poliovirus (SWRCB 2018a). The disinfected wastewater must also meet specific total coliform requirements. The water the feeds an AWT facility (CBAT or FAT) need not be disinfected prior to the advanced treatment. In fact, disinfection upstream of advanced treatment is not recommended due to the risks associated with DBP formation. This is especially true for free chlorine disinfection and CBAT (non-RO) potable reuse treatment trains. As discussed in Section 3.4.1, ozone and BAF can reduce DBPFP via the removal of TOC. Addition of GAC post-treatment can also contribute to lower DBP formation potential. If upstream chlorine disinfection is unavoidable, preformed chloramines using a low-TOC carrier water would be preferred to minimize free chlorine reaction with organics and minimize DBP formation.

Pathogen crediting of the MBR process is also new and rapidly developing within California. To date, no MBR facility has been credited with LRVs for potable reuse in California. Internationally, the "gold-standard" for the demonstration of MBR pathogen credit is the Australian Membrane Bio-reactor WaterVal Validation Protocol (WaterSecure 2017a). More recently, a U.S.-based validation protocol was developed under WRF Project #4997 (Salveson, Trussell, and Linden 2021). Both the WaterVal and WRF 4997 frameworks define three tiers for MBR pathogen validation, however WRF 4997 builds upon WaterVal's protocol with additional data from U.S.-based studies. The tiered approach, as defined in WRF 4997, is described below:

- Tier 1: Based on analysis of historical MBR data, default LRVs of 1.0/2.5/2.5 are granted for enteric virus, *Giardia* cysts, and *Cryptosporidium* oocysts. The MBR filtrate turbidity must also remain below 0.2 NTU 95% of the time and never exceed 0.5 NTU at any time.
- Tier 2: If additional LRVs above the default values in Tier 1 are sought, site-specific testing must be performed to demonstrate MBR pathogen removal performance under conservative operating conditions for a given membrane product. Testing is used to demonstrate pathogen LRVs and thresholds for indicators and surrogates which will be used as ongoing verifications of system performance. The testing includes three separate phases:
    - Pre-commissioning testing to determine the specific membrane performance in terms of pathogen LRVs, indicators, and surrogates (typically pilot- or demonstration-scale)
    - Commissioning testing to confirm the performance of the pre-commissioning testing at full-scale
    - Operational testing to verify ongoing performance
- Tier 3: The Tier 3 approach is a more precise process of correlating online surrogates with pathogen removal to award LRVs for the MBR process in real-time based on operating data. WRF 4997 does not discuss this approach in detail, however WRF Project #4959 (still ongoing at the time of this report) is focused on developing a validation protocol for this approach.

3.4.8 Additional Required Downstream Treatment Processes

Downstream treatment processes such as membrane filtration, GAC, IX, ultraviolet disinfection with or without chemical addition, and soil aquifer treatment (SAT).

3.4.8.1 Membrane Filtration

For the purposes of this report, membrane filtration is defined as low pressure ultrafiltration (UF) or microfiltration (MF) and does not encompass nanofiltration (NF) or RO. Advanced treatment facilities typically use MF in the form of hollow-fiber membranes. MF systems are typically used as pre-treatment for RO in FAT trains but can also be included in CBAT when additional treatment, such a pathogen credit in California or Nevada, is required. Well-operated MF systems can achieve low effluent turbidities in the 0.01 to 0.1 NTU range. The main removal mechanism for MF is size exclusion, therefore it is effective at removing suspended solids and pathogens but does not remove a significant amount of TOC or any dissolved constituents like RO does. The tradeoff is that MF does not require as much energy as RO and does not have a brine flow to treat or dispose of (however, backwash water must be handled).

Like coagulation, flocculation, sedimentation, and filtration, pathogen crediting for MF systems is governed by the SWTR for drinking water (EPA 2005). The SWTR allows the use of MF as an alternative filtration technology to achieve elevated pathogen credits. Product-specific challenge tests are required to demonstrate the removal of target organisms and integrity monitoring is required during operation to ensure that the system is not compromised. Indirect integrity tests rely on continuous turbidity monitoring while direct integrity tests are typically conducted by pressure decay tests (PDTs). Real-time LRVs can be calculated using the results of a PDT. In California, the current maximum accepted LRVs for MF in potable reuse are 0/4/4 for V/G/C.

3.4.8.2 Granular Activated Carbon

GAC is a necessary post-treatment component of a CBAT train to provide additional TOC removal and polish recalcitrant CECs that are well-adsorbed. As discussed in Section 3.1, there are several groups of ozone/BAF-recalcitrant CECs that are amenable to post-treatment with GAC. A summary of these compounds is shown in Table 3-44 below. Based on the discussion in Section 3.1, PFAS and the flame retardants TCEP, TCPP, and TDCPP are the most important CECs to consider for GAC post-treatment since they are recalcitrant, relevant to public health, and best removed via adsorption.

Table 3-44. Summary of CECs that are Recalcitrant through Ozone/BAF but Removed by GAC.

CEC or CEC Category	Log K_{OW} Range	Log K_{OC} Range
HAAs	0.2 – 1.7	0.3 – 1.6
THMs	2.0 – 2.4	1.4 – 2.1
Pesticides/Herbicides/Fungicides	-1.2 – 3.3	0.5 – 3.5
PFAS[a]	2.8 – 6.5	1.0 – 3.1
Hormones	3.1 – 3.3	2.7 – 3.5
Artificial Sweeteners	-1.3 – -1.0	1.0 – 1.3
TCEP/TCPP/TDCPP (Flame Retardants)	1.7 – 3.8	1.5 – 3.0
Other Trace Organics (e.g., quinoline)	-0.3 – 2.0	1.2 – 2.3

[a] Italicized compounds are the most important for GAC post-treatment based on BAF_{eff} values, public health thresholds, and removal pathways

The efficiency at which GAC media can adsorb CECs is dependent on the media age, as parametrized by BVTs. GAC systems with higher BVTs begin to exhibit CEC breakthrough: this is reflected by higher effluent concentrations of CECs, a higher number of CECs detected in the effluent, and decreased CEC percent removal (Vaidya et al. 2020). The influent concentrations of the target compounds and the EBCT of the GAC filter also impact the effluent water quality profile over time. Rapid small-scale column tests (RSSCTs) are a valuable bench-scale tool to characterize the breakthrough of select compounds under specific conditions (e.g., BVT, EBCT, media type, influent water quality). The advantage of RSSCT is that it provides long-term adsorption performance data on a much shorter timescale than pilot systems.

Extensive RSSCT testing has been conducted for conventional drinking water sources such as surface water and groundwater, but limited data exists for ozone/BAF effluents for potable reuse. Drinking water studies have shown that bituminous coal is a superior carbon media for

PFAS removal when compared to alternative carbon sources such as coconut (Liu, Werner, and Bellona 2019; McNamara et al. 2018; C. Zeng et al. 2020). A long-term test on a full-scale groundwater plant with bituminous coal demonstrated BVTs of 20,000 to 30,000 at EBCTs of 10 min to 30 min when choosing a breakthrough threshold of 50 ng/L as the sum of eleven PFAS species (influent concentration as high as 250 ng/L, total) (Belkouteb et al. 2020). One RSSCT study treating spiked municipal tap water (0.92 µg/L of PFOA and 0.8 µg/L of PFOS) with an EBCT of 10 min also showed breakthrough at around 20,000 to 30,000 BVT, when choosing a threshold of 70 ng/L (the EPA health advisory level for PFOA + PFOS) (McNamara et al. 2018). Another interesting observation from this study was that reactivation of the GAC actually improves subsequent breakthrough performance by around 10,000 BVT. Reactivation greatly reduces the operational costs associated with applying GAC treatment. Another RSSCT study achieved BVTs between 40,000 to over 100,000 (threshold set at 70 ng/L for sum of PFAS) for various Arizona groundwaters at a lower EBCT of 5 min (C. Zeng et al. 2020).

A major difference between drinking water matrices and recycled wastewater is TOC concentration: bulk organics can compete for adsorption sites and accelerate breakthrough of trace organics. RSSCTs conducted on LASAN's Donald C. Tillman Advanced Water Purification Facility (DCTAWPF) ozone/BAF effluent (average TOC concentration of 6.45 mg/L) showed that TOC exhibited breakthrough before the six PFAS tested: PFOA, PFOS, PFBS, PFDA, PFHpA, and PFHxA (Trussell Technologies 2018). Data from the 20 min EBCT test in that study is shown in Table 3-45. For the water quality and conditions tested in that study (which are not atypical for an ozone/BAF design for potable reuse), TOC was the driving parameter for GAC sizing. However site-specific testing is essential, especially for ozone/BAF effluents with significantly higher TOC and PFAS concentrations. The RSSCT literature on PFAS in drinking water shows that at similar influent concentrations, PFOA will achieve breakthrough faster than PFOS (Belkouteb et al. 2020; Liu, Werner, and Bellona 2019; McNamara et al. 2018; Xiao et al. 2017). Short-chain PFAS such as PFHxA breakthrough earlier than both PFOA and PFOS (Belkouteb et al. 2020; Schaefer et al. 2020; Zhi 2017). More research is necessary to better understand: i) the breakthrough of PFOA, PFOS, and shorter-chain PFAS at varied influent concentrations in ozone/BAF effluent, ii) the breakthrough of short-chain PFAS in ozone/BAF effluent, and iii) the impact of varied TOC concentrations on PFAS breakthrough.

Table 3-45. RSSCT Results for TOC and PFAS at DCTAWPF (EBCT = 20 min).

	20 min EBCT Effluent Concentrations						
BVT	**TOC [Inf=6.18 mg/L][a]**	**PFOA [Inf=13 ng/L][a]**	**PFOS [Inf=ND][a]**	**PFBS [Inf=3.7 ng/L][a]**	**PFDA [Inf=2.1 ng/L][a]**	**PFHpA [Inf=2.3 ng/L][a]**	**PFHxA [Inf=19 ng/L][a]**
0	0.457 mg/L	ND	ND	ND	ND	ND	ND
1,905	2.09 mg/L	ND	ND	ND	ND	ND	ND
5,267	3.98 mg/L	ND	ND	ND	ND	ND	2 ng/L

[a] Influent concentration

While TOC can be well removed (>90%) by virgin media, sorption performance quickly drops off as the BVT increases. This concept is also discussed in the context of BAF acclimation in Section 3.5.3.7. The TOC breakthrough curve from the DCTAWPF is shown in Figure 3-18. From breakthrough curves such as this, GAC usage and regeneration or replacement frequency can be estimated with different EBCTs and reactor configurations. GAC filters with higher EBCTs experience breakthrough at higher BVTs (i.e., longer duration before media replacement or regeneration), but the tradeoff is higher initial capital investment associated with larger filters and more media in comparison to lower EBCTs. Assuming a conservative influent TOC concentration of 7 mg/L, a treatment goal of 2.49 mg/L, and 8 filters operated in parallel, the GAC consumption for EBCTs of 10 min, 20 min, and 30 min was compared using the DCTAWPF RSSCT data (Trussell Technologies 2018). Results from that analysis are shown in Table 3-46. At the highest EBCT, regeneration can be extended to 134 days which equates to a GAC consumption of 0.58 lbs/1000-gal treated. Regeneration costs would ultimately need to be weighed against the cost of larger filter construction to select the optimal GAC configuration for a specific project. Additionally, because the breakthrough of PFAS like PFOA and PFOS occurs at higher BVTs, GAC sizing and regeneration would be a lot more economical if designed for PFAS breakthrough rather than the TOC-based analysis discussed above.

Additional RSSCT research on various ozone/BAF effluent water qualities (e.g., TOC concentrations) and design conditions (e.g., EBCT) is warranted to understand the long-term behavior of PFAS removal efficiency. Additionally, much of the literature has focused on PFOA and PFOS, so additional data on the behavior shorter-chain PFAS such as PFHpA, PFHxA, and PFPeA (which have been shown to achieve breakthrough faster) would be beneficial.

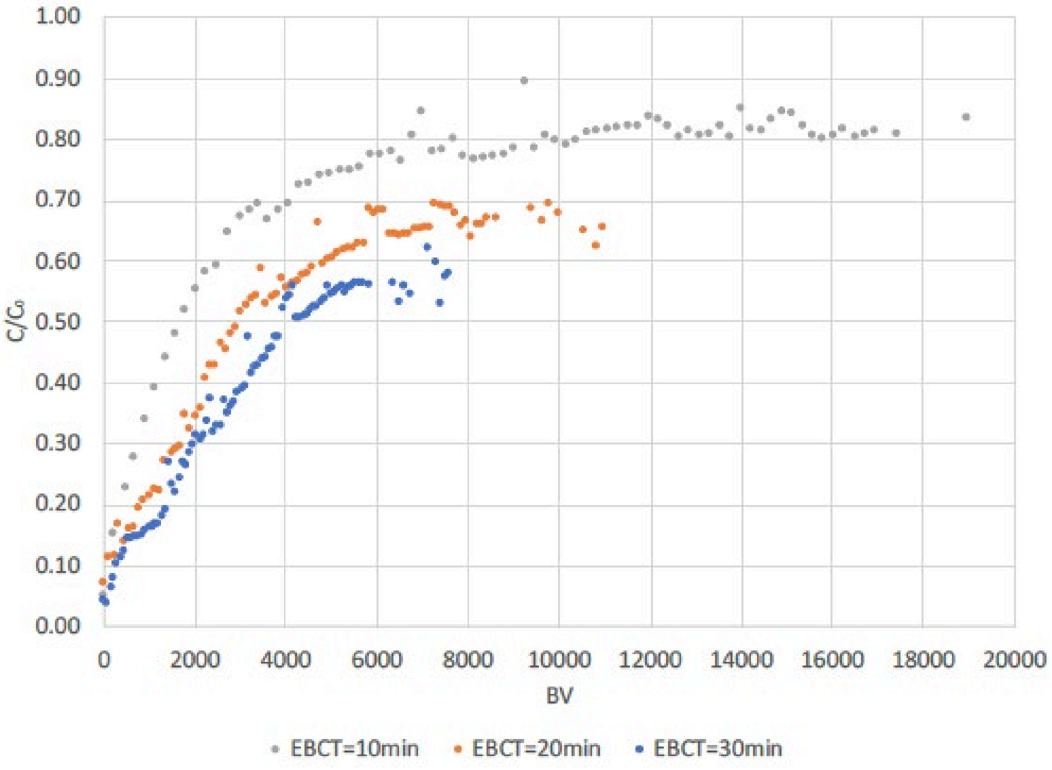

Figure 3-18. TOC Breakthrough Curve at Various EBCTs from the DCTAWPF RSCCT Study.
Average influent [TOC] = 6.4 mg/L.

Table 3-46. GAC Regeneration Requirements using the DCTAWPF RSSCT Breakthrough Curve Data.

Assumptions: Influent TOC of 7 mg/L, effluent goal of 2.49 mg/L, 8 filters operating in parallel.

EBCT (min)	Regeneration Frequency (days)	GAC Consumption (lbs/1000 gal)
10	17	4.59
20	65	1.20
30	134	0.58

3.4.8.3 Ion Exchange

Ion exchange is another sorption treatment technology which uses synthetic resin media rather than the carbon media used in GAC. IX and GAC are competing adsorption technologies, each with advantages and disadvantages depending on source water quality and effluent goals. One major distinction is that IX can be effective at removing other anionic compounds such as nitrate and bromate. Nitrate removal would benefit projects with strict effluent TN limits (e.g., SWA in California) or inadequate upstream biological treatment (i.e., no denitrification). Bromate removal through IX could replace or support upstream chemical bromate control strategies for projects with high bromate formation potential through ozone (i.e., high ozone doses for pathogen credit). The caveat is that IX resins are highly specialized for specific constituents such as nitrate, organic matter, or trace organics such as PFAS.

PFAS-specific resins are typically single-use and discarded once exhausted. However, recent research has shown that resins designed for bulk organics removal have exhibited simultaneous removal of PFAS, DOC, and nitrate (Dixit et al. 2019, 2020, 2021). The same research group also demonstrated that the organic-scavenging resin can be regenerated which is more economical and environmentally friendly than PFAS-specific single-use resins (Dixit et al. 2020, 2021). PFAS-specific resins offer better PFAS removal efficiencies (120,000 BVT versus 23,500 BVT until Gen X breakthrough), but do not exhibit as high of TOC removals as the organic-scavenging resin (15% versus 65% DOC removal) (Dixit et al. 2021). It should be noted that the applicability of these findings is highly dependent on water quality including PFAS concentrations, TOC concentration and composition, and background anion concentrations. Site-specific testing would be essential to confirm if these technologies are feasible for a given site. Unfortunately, there are scaling issues which can prohibit the use of RSSCT with IX resins. Typically, media (either GAC or IX resin) is ground in order to facilitate RSSCT. Though some recent studies have begun to establish methods for using IX resins with RSSCT (Schafer et al. 2019, 2020; C. Zeng et al. 2020), this is a rapidly developing field and further studies are required to prove out these methods and results.

IX can also achieve high removal efficiencies at lower EBCTs than GAC systems (as low as 3 min) which equates to smaller reactors (Schaefer et al. 2019, 2020; C. Zeng et al. 2020). However, operational costs are typically higher for IX due to brine disposal for resins that can be regenerated, or resin replacement for single-use systems which are typical for PFAS (Dixit et al. 2020). A summary of these advantages and disadvantages is provided in Table 3-47.

Table 3-47. Comparison of GAC and IX Technologies.

Parameter	GAC	IX
Footprint	Larger (longer EBCTs)	Smaller (shorter EBCTs)
Contaminants Removed	Organic compounds including TOC and trace organics	Anionic compounds including TOC, trace organics, and nitrate.
Challenged by	High TOC	High TDS, high TOC (when using organic-scavenging resin)
Reactor Cost	High (more reactors)	Low (less reactors)
Media Cost	Low	High
Operational Cost	Low (media regeneration an option)	High (brine for regeneration or resin replacement for single use resins[a])

[a] IX resins are typically single use for PFAS applications, but recent studies have investigated the potential for IX regeneration for PFAS treatment (Dixit et al. 2020)

In distilled water with no competing inorganic anions or organic matter, PFAS removal can exceed 99% (influent concentration of 10 µg/L) for more than 150,000 BVT with an organics-scavenging resin (Dixit et al. 2020). When the same resin is introduced to DOC concentrations of 5 mg/L, both PFOA and PFOS exceed 70 ng/L (individually) after 22,000 and 27,000 BVT, respectively (Dixit et al. 2020). DOC removal was around 65% at the point of PFAS breakthrough. The same resin can achieve 17,000 and 18,500 BVTs until breakthrough of PFOA and PFOS when treating a real wastewater effluent with a DOC of 5 mg/L and a nitrate concentration of 26 mg/L (Dixit et al. 2020). Nitrate removal was over 70% and DOC removal was around 40-50% at PFOA breakthrough. Therefore, it is evident that both DOC and ions such as nitrate compete with PFAS removal when using an organics-specific resin for simultaneous treatment of TOC and PFAS.

With a PFAS-specific resin treating groundwater, lead reactors in a lead-lag design can treat upwards of 200,000 BVT before 70 ng/L breakthrough of PFOA + PFOS (EPA health advisory level, which is much higher than he California NL) (C. Zeng et al. 2020). This study, which used novel RSSCT technology with IX resins, reported a range of breakthrough BVTs from 40,000 to well over 1,000,000 for a suite of groundwaters (not drastically different in DOC or TDS composition) which indicates that further research is needed to understand the causes of variability when using RSSCT with IX.

3.4.8.4 Ultraviolet and Ultraviolet with Advanced Oxidation

Ultraviolet radiation systems are either implemented in advanced treatment trains as simple ultraviolet disinfection systems or as more complex systems with upstream chemical dosing to create an AOP. The non-AOP systems are typically used as an alternative primary disinfectant to chlorination which can reduce the formation of DBPs. UV disinfection is a photochemical reaction which works by damaging the nucleic acid of target pathogens, avoiding chemical reaction byproducts. In addition to disinfection, UV can also photochemically transform recalcitrant organic chemicals. The most common and important group of recalcitrant organics that are photoreactive are the nitrosamines, including NDMA.

UV/AOP requires addition of a chemical oxidant to the reactor influent which reacts with the ultraviolet radiation to create hydroxyl radicals. The two most commonly applied oxidants are free chlorine and H_2O_2. The hydroxyl radicals can transform recalcitrant organic chemicals which are conducive to hydroxyl radical reaction. UV/AOP reactors also gain the benefits of UV reactors including disinfection credit and photodegradation of target compounds like NDMA. Ozone/BAF-recalcitrant photoreactive and hydroxyl radical-reactive compounds are shown in Table 3-48 below. With the exception of nitrosamines and some specific compounds within different groups, such as atrazine, iohexal, iopromide and acesulfame, most of these compounds would require U/AOP to achieve additional removal. Flame retardant compounds have relatively low reactivity with hydroxyl radicals and similar to PFAS may require a different type of post-treatment.

Table 3-48. Summary of Compounds that are Recalcitrant through Ozone/BAF but Removed by UV or UV/AOP.

Recalcitrant Group (Example Compound)	k_{UV} Range [$mJ^{-1}\,cm^2$]	k_{OH} Range [$M^{-1}s^{-1}$]
Nitrosamines (NDMA[a])	$>1x10^{-3}$	--
Pesticides/herbicides/fungicides (Atrazine[a])	$>1x10^{-4}$	$1 – 7 \times 10^9$
Medical Contrast Agents (Iohexal[b], Iopromide[c])	$>1x10^{-3}$	$2 – 3 \times 10^9$
Artificial Sweeteners (Acesulfame-K[d,e], sucralose[e])	$<1x10^{-7}$– $>1x10^{-3}$	$2 – 5 \times 10^9$
Flame Retardants (TCEP/TCPP/TDCPP)	N/A	$2 – 6 \times 10^8$
1,4-dioxane[f,g]	$<1x10^{-5}$	3×10^9

[a] Lee et al. 2016

[b] Hokanson, Li, and Trussell 2016

[c] Canonica, Meunier, and von Gunten 2008

[d] Perkola et al. 2016

[e] Scheurer et al. 2014

[f] Keen and Linden 2013

[g] Patton et al. 2017

The EPA Ultraviolet Disinfection Guidance Manual includes UV dose requirements to reach LRVs up to 4.0 for V/G/C (EPA 2006). In California, potable reuse projects have been permitted to extrapolate to maximum LRVs of 6.0/6.0/6.0 for V/G/C which can be achieved at a UV dose of 300 mJ/cm^2 (Wright et al. 2020). In UV/AOP systems, the UV dose is driven by requirements for chemical removal, such as the removal of NDMA and 1,4-dioxane. The UV doses required for the degradation of NDMA (via photolysis) and 1,4-dioxane (via formation and subsequent reaction with hydroxyl radicals) can vary based on water quality. Specific water quality such as pH, alkalinity, residual chloramines, and feed water NDMA concentrations can also impact which chemical, NDMA or 1,4-dioxane, will drive the UV dose design. In California, the treatment efficiency of the UV/AOP system may be demonstrated via challenge testing to achieve 0.5-log (69%) removal of 1,4-dioxane (SWRCB 2018a). Also in California, effluent NDMA concentrations must either meet the NL of 10 ng/L (groundwater projects) or the CTR limit of 0.69 ng/L (SWA projects). Projects with higher recalcitrant NDMA levels (e.g., higher wastewater concentrations, poor removal through BAF) would require higher UV doses to achieve compliance.

As with ozone, UVT is a key process parameter for UV/AOP. A higher UVT corresponds to better water quality and more efficient use of UV lamp power. A lower UVT corresponds to worse water quality and inefficient use of UV lamp power (i.e., UV light is being absorbed by background constituents and less is available to target pathogens and chemicals). Typically, UV/AOP processes have been used for potable reuse projects with RO-based treatment (i.e., FAT). In these applications, UV/AOP has been documented to be extremely effective due to high UVT and lower levels of background hydroxyl radical scavengers including bicarbonate ion and TOC. In lower-UVT matrices without upstream RO-treatment, for the same UV/AOP performance (e.g., 0.5-log removal of 1,4-dioxane) higher UV and/or oxidant doses may be necessary depending on treatment goals. Researchers in Gerrity et al. (2016) analyzed various wastewater effluents to develop semi-empirical models which were used to predict UV/AOP performance based on matrix characteristics such as DOC and UVT. Though UVT will be lower in CBAT projects versus RO-based projects, the ozone/BAF process is effective at decreasing organics and increasing UVT to approximately 85-90%, which should improve UV/AOP system performance and make it more cost-effective. Site-specific testing on a particular matrix is vital to ensure optimal UV/AOP system design and performance. Bench-scale collimated beam tests can be used to confirm UV dose-response curves for NDMA removal. Pilot and/or demonstration-scale tests can be used to test both UV dose and oxidant dose for 1,4-dioxane removal. Typical UV doses for simultaneous removal of NDMA and 1,4-dioxane for FAT plants in California range of 800-1200 mJ/cm^2, which is several times higher than the dose required for pathogen removal with UV alone.

There are advantages and disadvantages associated with the use of H_2O_2 or free chlorine as the oxidant for UV/AOP. Typical doses are 2-3 mg/L as Cl_2 for free chlorine and 3-4 mg/L as H_2O_2. For high-bromide waters, the use of UV/AOP with free chlorine can lead to bromate formation. Therefore, CBAT plants with high influent bromide should use upstream ammonia bromate control strategies to curb bromate formation. H_2O_2 does not have a bromate issue, but incurs higher chemical costs associated with the oxidant itself and the need to quench residual H_2O_2 in the treated water. With free chlorine, the oxidant residual can be carried in the effluent pipeline to gain additional disinfection credit. A such, free chlorine is typically more economically advantageous. Project planners must weigh these issues when deciding between a UV/AOP oxidant.

3.4.8.5 Soil Aquifer Treatment

For groundwater projects, the receiving aquifer can also play a vital role in polishing the purified effluent prior to pumping for public use. As discussed in Section 3.4.4, groundwater aquifers can be credited with LRVs of up to 10/10 for G/C for spreading projects with at least 6 months of retention time and up to 1 LRV for virus for each month of retention time demonstrated for injection projects[4]. Beyond pathogen removal, SAT can reduce TOC, nutrients, and any remaining CECs in the purified effluent. While SAT has been demonstrated in the literature to remove a suite of organic and inorganic contaminants ranging from bulk organics to trace organics such as hormones, the following discussion is limited to constituents which have known health impacts and have been shown to be recalcitrant through CBAT.

Soil column testing was conducted at the DCTAWPF to better understand the attenuation of TOC, CECs, and nutrients through SAT with a variety of feed water sources. Soil columns which were fed with CBAT-treated water (ozone/BAC/UV effluent and ozone/BAC/ozone effluent) and operated with 30-day hydraulic retention times (HRTs) averaged just over 50% removal of TOC

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[4] Credit is 1.0 LRV per month when using an added tracer, 0.67 LRV per month when using an added tracer, 0.50 LRV per month when using numerical modeling, and 0.25 LRV per month when using analytical equations (SWRCB 2018a).

(Brown and Caldwell and Trussell Technologies 2018). For the same columns, complete removal of NDMA to levels of non-detect were observed, and bromate removal was approximately 50%. 1,4-dioxane data was only available for a column fed with a blend of CBAT and MF/RO-treated water and concentrations were reduced to non-detect in those tests. For the flame retardants TCEP, approximately 40 to 50% removal was observed for the CBAT columns. The higher HRT blend column demonstrated better removal to non-detect. For TCPP, the 30-day CBAT columns showed a wide range of performance, with higher SAT effluent concentrations occurring in the ozone/BAC/UV column. The higher HRT blended column, however, showed improved performance indicating that higher retention time helps in the case of these flame retardants. PFOA removals were on the order of 20-30% for the CBAT columns and worsened with higher HRT, as shown by higher effluent concentrations in the blended 180-day column. PFOS data was only available for the 30-day CBAT columns, where concentrations were reduced to non-detect. A summary of the removal of TOC, bromate, and trace organics (e.g., constituents with health-based concerns that may still be an issue in CBAT effluents) from the DCTAWPF SAT column testing is shown in Table 3-49.

Table 3-49. Summary of DCTAWPF SAT Column Testing Results for TOC and Trace Organics.

Constituent	Concentration in SAT Feed (ng/L)	Typical % Removal	Notes
TOC	6.3 to 6.4	50	30-day columns fed with CBAT effluent
NDMA	Non-detect to 15	Non-detect	30-day columns fed with CBAT effluent; all effluent concentrations were reduced to non-detect
Bromate	8	50	30-day column fed with CBAT effluent (only ozone/BAC/ozone column had data)
1,4-Dioxane	0.25	Non-detect	180-day column with 50% CBAT and 50% MF/RO
TCEP	210 to 230	40 to 50	30-day columns fed with CBAT effluent
	72	Non-detect	180-day column with 50% CBAT and 50% MF/RO
TCPP	1,700 to 1,800	-40 to 50	30-day columns fed with CBAT effluent. Higher effluent concentrations were observed in the ozone/BAC/UV column
	740	60	180-day column with 50% CBAT and 50% MF/RO
PFOA	33	20 to 30	30-day columns fed with CBAT effluent
	10	-70	180-day column with 50% CBAT and 50% MF/RO
PFOS	2.6 to 2.8	Non-detect	30-day columns fed with CBAT effluent

3.4.9 Viable CBAT Trains for Potable Reuse

Table 3-50 includes a matrix of potentially viable potable reuse trains for a variety of different potable reuse project types. Because California has the most rigorous regulations pertaining to potable reuse (especially with respect to pathogenic microorganism control), the four types of California potable reuse project types were included as benchmarks:

- Groundwater spreading (assuming a 6-month retention time within the aquifer)
- Groundwater injection (assuming a 6-month retention time within the aquifer)
- Surface water augmentation (assuming a 100:1 dilution and a 4-month retention time within the reservoir)
- Direct potable reuse

An additional row for projects without pathogen-based requirements is included as a broad category pertaining to projects in locations where the 12/10/10 LRV credit concept for V/G/C is not in place. Color-coded checkmarks are included to illustrate which treatment processes are effective at removing select constituents (e.g., TOC, CECs, nutrients, and pathogens). For treatment processes which can be credited for pathogen removal, LRVs for V/G/C are included in parentheses. LRV totals are shown in the rightmost column, with the required LRVs for each project shown in parentheses.

Currently, groundwater injection and SWA projects in California include FAT. However, there is an alternatives clause within the regulations that provides a pathway for the use of alternative treatment (i.e., CBAT), provided that the alternative assures the same level of public health protection[5]. CBAT trains, such as the examples provided in Table 3-50, would need to be demonstrated to provide the same levels of public health protection as FAT under the current California regulations.

Ozone and BAF are included as the backbone of the each of the CBAT treatment trains presented, providing removal of CECs in all cases and additional removal of pathogens in the California-based projects with residuals adequate for CT crediting. For the groundwater spreading case, ozone disinfection is included to meet the definition of disinfected tertiary recycled water. For the SWA and DPR scenarios, a higher ozone dose is assumed to achieve a CT sufficient for a *Cryptosporidium* LRV of 1.0. These projects also include pipeline chlorine disinfection for additional virus crediting and credits provided by the drinking water treatment plant (DWTP).

Another key constituent that is rigorously regulated in California potable reuse projects is TOC. California groundwater projects can use diluent water to decrease the RWC and increase the TOC concentration that must be met in the recycled water effluent. Groundwater projects with diluent water credit and downstream GAC may be able to comply with the California regulations as currently configured. However, the current 0.5 mg/L limit makes groundwater projects without diluent water less feasible due to higher GAC usage. As discussed in Section 3.4.2, a TOC limit of 2-5 mg/L (which has been demonstrated to effectively reduce DBP formation) would make these treatment trains more feasible. One nuance that is not captured within Table 3-50 is that nutrient and TOC removal can be maximized with an MBR system, as discussed in Section 3.4.7.1 and Table 3-43, further enhancing the performance of ozone/BAC and GAC. For the spreading scenario, GAC is not included based on the assumption that TOC removal demonstrated by ozone/BAF, and SAT is adequate when combined with the RWC.

In terms of nutrients, SWA projects and DPR projects (which are discharging to small reservoirs) in California are subject to the most stringent effluent requirements for TN and ToP, depending on the receiving reservoir. ToP can be reduced to low levels with well-designed upstream treatment, but this still may or may not be sufficient to accomplish low Basin Plan nutrient restrictions. TN (in the form of nitrate) may need to be further reduced with IX, as shown in

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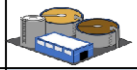
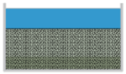
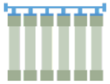
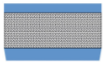
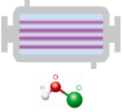
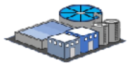
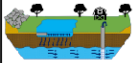
[5] The demonstration of equivalent public health protection via the alternative must be reviewed by an independent scientific advisory panel and approved by DDW (SWRCB 2018a).

Table 3-50. While possible with these additions, nutrients would be the largest challenge to implementing CBAT for SWA in California.

The treatment trains shown in Table 3-50 are included as a guidance tool to help illustrate the key water quality goals to consider and the treatment tools available to accomplish these goals under typical conditions. Feedwater quality and effluent goals can vary drastically depending on project location and may necessitate additional treatment train configurations

Table 3-50. Matrix of Viable Ozone/BAF Potable Reuse Trains for Various Potable Reuse Types.

Project Type[a]	**Biological Treatment and Filtration** 	**Ozone** 	**BAF** 	**MF** 	**GAC** 	**IX** 	**UV** 	**UV/AOP** 	**Pipeline Cl_2 + DWTP** 	**Aquifer** 	**Total Pathogen LRV (Reqd.)**
Groundwater Spreading[b]	✓ X O	X # (6/3/0)	✓ X							✓ X # (6/10/10)	*12/13/10* *(12/10/10)*
Groundwater Injection[c]	✓ X O	X # (6/3/0)	✓ X	# (0/4/4)	✓ X			X # (6/6/6)		✓ X # (6/0/0)	*18/13/10* *(12/10/10)*
Surface Water Augmentation[d]	✓ X O	X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O[g]		X # (6/6/6)	✓ X # (6/3/1 + 4/3/2)		*18/22/14* *(12/10/10)*
Direct Potable Reuse[e]	✓ X O # (1/2.5/2.5)	X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O[g]		X # (6/6/6)	✓ X # (6/3/1 + 4/3/2)		*23/24.5/16.5* *(20/14/15)*
Projects w/o Pathogen- Based Requirements[f]	✓ X O	X	✓ X		✓ X		X				N/A

✓=TOC X=CECs O=Nutrients #=Pathogen Credit: anticipated log removal values (LRV) for Virus/Giardia/Cryptosporidium

[Total pathogen LRV requirements are based on California's current and draft potable reuse regulations]

[a] These hypothetical treatment train examples are intended to illustrate the various tools that exist to achieve certain treatment goals. These alternative non-RO treatment trains need to demonstrate treatment equivalency in states such as California to comply with potable reuse regulations.

[b] Groundwater spreading scenario assumes a minimum 6-month aquifer retention time and additional organics removal via SAT which may eliminate need for GAC. Ozone dosing sufficient for CT crediting is assumed, but UV may also be used for disinfection credit. Ozone/BAF is included to help achieve TOC goals for recharge (depending on RWC).

[c] Groundwater injection scenario assumes a minimum 6-month aquifer retention time for additional virus credit. GAC is assumed to help achieve TOC goals (depending on RWC).

[d] SWA scenario assumes a higher ozone dose than the groundwater scenarios, capable of achieving a CT value adequate for 1 LRV for *Cryptosporidium*. Also assumes 100:1 dilution and a minimum 4-month retention time in the reservoir.

[e] DPR scenario assumes Tier 1 MBR LRV credits based on WRF 4997 and a higher ozone dose than the groundwater scenarios, capable of achieving a CT value adequate for 1 LRV for *Cryptosporidium.*

[f] Projects outside of California that do not have prescriptive pathogen LRV requirements.

[g] Ion exchange is also effective at removing TOC and CECs and can be used to remove these constituents in addition to nitrate (with a higher resin regeneration frequency than nitrate alone).

3.5 Ozone/BAF Design Considerations

In this Section, design and operational considerations for ozone/BAF systems, including upstream water treatment, are discussed as part of Objective C of this chapter. Potential reliability issues with ozone/BAF systems are identified by summarizing the lessons learned from the operation of Facility D. Design and operational parameters specific to ozone and BAF systems are discussed, including O_3:TOC ratio, ozone CT, EBCT, GAC media particle size, filter bed configuration, and GAC media acclimation period.

3.5.1 Mechanical Reliability Features

In this Section, mechanical failures of the ozone and BAF systems over three years of operation at Facility D are discussed. Mechanical reliability information for the other Chapter 1 facilities was not available.

3.5.1.1 Ozone System

At Facility D, a compressor supplied air to a pressure swing adsorption (PSA) system for the production of oxygen gas. The oxygen gas was stored in a tank, and a generator produced ozone from the oxygen. Ozone was introduced into the water within a serpentine contactor by an injection system. Off-gas treatment consisted of a destruct catalyst and an air blower that took air from the ozone contactor and the top of the BAF influent tank.

Various operational statistics for the ozone system at Facility D from 2014–2016 are listed in Table 3-51. There was no redundancy for the ozone system at Facility D. If there were redundancy, then the operational availability (AVO) values would likely be higher because the total downtime would decrease.

Table 3-51. Summary of Ozone System Reliability, Maintainability, and Availability at Facility D from 2014 through 2016.

Year	Frequency	Total Downtime (hours)	Portion of Time Available	MDT[a] (hours)	MTBF[b] (hours)	MTTR[c] (hours)	AVI[d]	AVO[e]
2014	5	62	99.3%	12.40	523	4	99.24%	95.69%
2015	35	391	95.5%	37.13	168	37	81.93%	92.96%
2016	42	1,410	83.9%	32.79	108	2	98.15%	78.34%

[a] Mean downtime

[b] Mean time between failures

[c] Mean time to repair

[d] Inherent availability. Equal to MTBF/(MTBF + MTTR).

[e] Measurement of actual system availability by accounting for all downtime.

In 2014, most of the downtime (~77%) was caused by electrical issues. Initially, the ozone generator was unable to attain the design dose, and the system would trip when the digital converter detected insufficient voltage to the system. The electrical issues were addressed by replacing the digital converter and high voltage board and then recalibrating the high voltage board. The discovery and replacement of a few broken dielectric rods increased the generator’s capacity to the expected value.

In 2015, there were additional causes of shutdown. Two gas leaks occurred in the off-gas system, so all the gaskets were replaced. It was discovered that the original gaskets were composed of a material not compatible with ozone. The air dryer fan and air dryer pressure switch for the air compressor failed. Most of the downtime (~64%) was associated with alarms that shut down the generator under certain conditions (e.g., supplied voltage < 430 V or > 530 V). These electrical alarms triggered frequently, indicating instability in the power source supplied to the ozone system. Finally, two failures occurred within the ozone destruct system: a communication failure shut down the destruct system when the rest of the ozone system was in operation, and the catalyst material had to be replaced.

In 2016, there were similar causes for shutdown to those in 2015. Biological upsets at the water reclamation plant upstream of Facility D necessitated the use of polymer for the tertiary filtration process. The combination of polymer and filamentous bacteria resulted in foaming events that clogged the vent valves and damaged the catalyst of the destruct system via the introduction of moisture. In response, a spray apparatus was installed in the BAF influent tank to keep foam from entering the off-gas system. Additionally, ambient ozone meters, strobe lights, and an alarm system were installed to prevent acute ozone exposure in the event of destruct system failure. Approximately 87% of the downtime was due to two failures of the water chiller that provides cool water to the generator. The condenser coil and the thermistor failed. It took approximately 1,200 hours to obtain a replacement for the condenser coil. There were three failures of the air compressor, but they were responsible for less than 1% of the total downtime in 2016. The electrical safeguard alarms continued to trigger frequently, but there was a reduction in the total downtime compared to 2015 because the improved alarm notification system resulted in shorter response times.

Several lessons were learned from operation of the ozone system for three years. A stable and sufficient power supply to the ozone generator is important to prevent shutdowns over electrical issues. The ozone destruct unit is critical for protecting personnel, so installing a redundant unit or keeping spare parts on site for fast repairs should be considered. An additional air compressor should be kept on site if air is being used as the source for oxygen gas. The upstream biological treatment process should be monitored for foaming events. Regular maintenance should be performed on the off-gas system to prevent moisture from reaching the destruct system. Finally, all material that will come into direct contact with ozone should be resistant to oxidation for the prevention of corrosion damage.

3.5.1.2 BAF System

BAF systems are less complicated technologically and have fewer components compared to ozone systems. Therefore, there should generally be fewer mechanical failures. This was observed at Facility D where there were no failures in 2014 or 2016. In 2015, the BAF system was shut down for 261 hours. Approximately 96% of the downtime was associated with repainting the filters. The original paint was inappropriate for the conditions and started rusting. The rest of the downtime was due to the replacement of valves that deformed as a result of improper placement. In response, the positioning of each valve was readjusted and verified.

3.5.2 Ozone-Specific Design and Operational Considerations

In this Section, different control strategies concerning the O_3:TOC ratio and CT for the ozonation process are discussed. Additionally, numerical recommendations for the O_3:TOC ratio are made depending on bromate formation and desired level of CEC elimination.

3.5.2.1 Control Strategies and Analyzers

Two different control strategies can be implemented depending on the treatment goals. If CEC removal is the primary purpose of ozone, then a constant O_3:TOC ratio can be targeted while considering bromate formation. Keeping the O_3:TOC ratio constant requires a TOC meter to monitor for changes in the water quality of the ozone influent. The ozone dose or residual concentration could be used to control the process. If pathogen disinfection is desired in addition to CEC removal, a constant CT can be targeted to obtain log removal credits for virus, *Giardia*, and/or *Cryptosporidium*. Both the EPA and DDW recognize the ability of ozone to inactivate pathogens. For the LT2ESWTR, EPA developed temperature-dependent CT values for *Cryptosporidium* inactivation by ozone. There are also equations for the log removals of *Giardia* and virus depending on the temperature and calculated CT. Title 22 of the California Code of Regulations requires five logs of virus removal to meet the definition of disinfected tertiary recycled water for non-potable reuses (22 CCR § 60301.230). Ozone can typically meet the five-log virus reduction requirement with a CT of 1 mg-min/L. For this strategy, the necessary CT to achieve the desired log credits for *Cryptosporidium* would drive the selection of the ozone dose because it is the most resistant to oxidation out of the aforementioned pathogens.

For both control strategies, measurement of UV_{254} to confirm sufficient ozone dose for CEC and pathogen removal is recommended. Also, facilities should consider installing a backup ozone generator for redundancy purposes and operational flexibility. Dissolved ozone analyzers will be required to measure the ozone concentration in the contact chamber(s). More than one meter may be required. Instrumentation should be provided for ozone systems to protect both personnel and the equipment because ozone is corrosive and hazardous. Gas-phase ozone detectors should be present in spaces such as generator rooms, especially if personnel are routinely present. Specific monitoring points for gas-phase ozone include the ozone generator output, contactor off-gas, ozone destruct off-gas, and the ambient air in ozone process area (EPA 1999a).

3.5.2.2 O_3:TOC Ratio

Ozone-reactive CECs ($K_{O3} > 10^5$ M^{-1} s^{-1}) such as triclosan are efficiently eliminated (typically >90%) even at a low specific ozone dose of 0.25 g O_3/g DOC (Y. Lee et al. 2013). However, this ratio is insufficient to substantially remove compounds that are more resistant to oxidation by ozone. For example, Y. Lee et al. (2013) found percent removals of atenolol ($K_{O3} = 1.7 \times 10^3$ M^{-1} s^{-1}) lower than 40% for certain secondary wastewater effluents when applying a specific ozone dose of 0.25 g O_3/g DOC. Therefore, an O_3:TOC ratio of at least 0.5 is recommended to increase removals of these CECs. The formation of bromate as an oxidation by-product should be considered when selecting a specific ozone dose. For specific ozone doses in the range of 0.25–1.45 mg O_3/mg DOC, the bromate concentration increases almost linearly with increasing specific ozone dose (Chon, Salhi, and von Gunten 2015). A relatively low bromate formation was observed for specific ozone doses less than 1.39 mg O_3/mg DOC (Chon, Salhi, and von

Gunten 2015). Another study found that bromate is only considerably formed at specific ozone doses ≥ 0.4–0.6 mg O_3/mg DOC (Soltermann et al. 2016). Based on these results, an O_3:TOC ratio of 0.6 would likely provide substantial CEC removal in addition to keeping bromate formation at inconsequential levels. If bromate formation is not a concern or if it is being mitigated, then the TOC ratio can be increased to 1.0 for additional CEC removal. However, removal of some recalcitrant CECs (e.g., TCEP) will still be fairly low.

Direct formation of NDMA by ozonation has been observed in previous studies (Gerrity et al. 2015; D. Li et al. 2017; Pisarenko et al. 2012; 2015). Additionally, NDMA concentrations have been shown to plateau at O_3:TOC > 0.5 in a variety of wastewater matrices (Gerrity et al. 2015; Pisarenko et al. 2015), so the concentration may already be maximized at the recommended O_3:TOC ratio. However, NDMA should not considered when selecting an O_3:TOC ratio because it is well removed by BAF. Also, ozonation has been shown provide significant reductions in NDMA formation potential (Pisarenko et al. 2012). Generally, CEC removal should take priority over direct NDMA formation during ozonation. In some studies, NDMA formation was found to be greater than 100 µg/L (Gerrity et al. 2015; Sgroi et al. 2014). Using these particular wastewater matrices for potable reuse may not be advisable.

3.5.2.3 Ozone CT

Using CT as a control strategy for the ozonation process is contingent on being able to measure the residual ozone residual in the contactor. Ozone is a reactive oxidant, so a variety of compounds constitute the initial ozone demand, including NOM, synthetic organics, nitrite, bromide, and bicarbonate and carbonate ions. These compounds will have to be taken into consideration when initially selecting the ozone dose, and they should be monitored regularly to ensure that ozone demand is not changing.

For the LT2ESWTR, EPA developed a table that contains *Cryptosporidium* log removal credits depending on the water temperature and CT value (EPA 2010). Facilities can be granted between 0.25 and 3.0 logs of *Cryptosporidium* inactivation credit for the addition of ozone. A site-specific study can be conducted for facility to generate a different set of CT values if approved by the state. The water temperature will have to be measured because it affects the oxidative efficiency of ozone. Different methods for calculating CT include the T10 method (which uses data collected from tracer studies) and the continuous stirred tank reactor (CSTR) method. They are thoroughly discussed in the 1991 “U.S. EPA Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources.” The 2010 U.S. EPA LT2ESWTR Toolbox Guidance Manual also discusses these methods and their corresponding extended methods. Selecting the appropriate method to use depends on the contactor configuration, availability of state-approved tracer testing results, and the level of testing and monitoring that is feasible. The U.S. EPA recommends using the CSTR method for contactors that experience significant back mixing (T10/hydraulic retention time ≤ 0.5) or when no tracer data are available (EPA 2010).

Achieving the desired CT for *Cryptosporidium* inactivation will result in substantial *Giardia* and virus inactivation because they are more susceptible to oxidation by ozone. For example, S. Snyder et al. (2014) found the average log inactivation of MS2 during ozonation is to be 5.7 ± 0.4 at an O_3:TOC ratio of 0.5 for several U.S. secondary effluents. *Cryptosporidium* inactivation has been found to trend linearly with O_3:TOC ratio. Figure 3-19 displays log removal data from the Facility D.

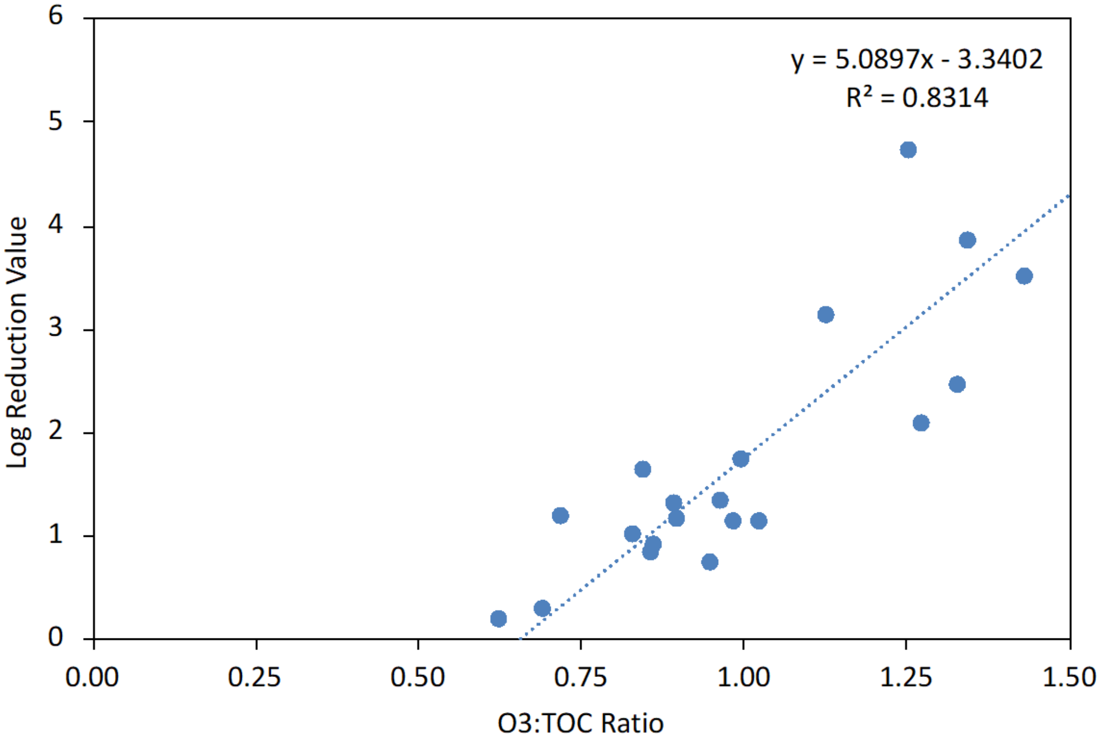


Figure 3-19. *Cryptosporidium* Log Reduction Values Versus O_3:TOC Ratio at Facility D.

3.5.2.4 Hydraulic Retention Time

The HRT for an ozone contactor is typically no greater than 15 minutes to reduce capital costs for construction and materials. Eight out of the 11 facilities that provided this information as part of the Chapter 1 survey were using an HRT of less than 15 minutes. This parameter is important because it is related to the temporal component of CT. In fact, the HRT is used in the CSTR method for estimating the contact time as part of determining pathogen log inactivation (EPA 2010).

An important design characteristic related to the HRT is baffling. Inlet, outlet, and intra-basin baffles can be installed to evenly distribute of the flow over the cross section of the contactor, reduce longitudinal mixing, and decrease the inlet and outlet flow velocities. EPA (1991) developed baffling factors corresponding to certain conditions (e.g., unbaffled, average, and superior) that allow for the estimation of T10/HRT if it is not practical to perform a tracer study. When the CT method is used for pathogen credit, the baffling factor has a significant impact on contactor size. A contactor with a baffling factor of 0.8 provides double the contact time as a contactor with a baffling factor of 0.4 and would therefore only require half the contactor volume to provide equivalent CT.

3.5.3 BAF-Specific Design and Operational Considerations

In this Section, recommendations for EBCT concerning TOC and NDMA removals are provided. Effects of various parameters such as GAC particle size and filter bed configuration on BAF treatment performance are discussed. Finally, estimates of the GAC acclimation period for a few Chapter 1 facilities were made using TOC data.

3.5.3.1 EBCT Recommendations for Removal of TOC

Gifford, Selvy, and Gerrity (2018) developed a linear equation for the optimum EBCT of GAC-based biofilters depending on the O_3:TOC ratio. It was developed by determining points of diminishing return with respect to the effect of EBCT on TOC removal. The linear equation was used to determine the optimum EBCT for the 12 facilities from Chapter 1 that provided either an O_3:TOC or O_3:DOC ratio. It was assumed that the equation could also be applied to O_3:DOC ratios. Results are included in Table 3-52. If a range of EBCT values was provided for a facility, then an average was taken.

Table 3-52. Comparison of Actual EBCT and Optimum EBCT Calculated using Gifford et al. (2018) for Several Facilities from Chapter 1.

Facility from Chapter 1	O_3:TOC or O_3:DOC Ratio	Provided EBCT from Survey (min)	Assumed Actual EBCT (min)	Optimum EBCT from Gifford, Selvy, and Gerrity (2018) (min)
Facility E	1	13 to 19	16	7
Facility O	0.18 to 0.5	14	14	4
Facility F	0.9	10	10	7
	0.9	20	20	7
	1.5	10	10	10
	1.5	20	20	10
	2.0	10	10	13
	2.0	20	20	13
Facility C	0.82	30	30	6
Facility B	0.7	15	15	6
Facility A	1.2	15	15	8
Facility M	0.35 to 0.97	14 to 14.5 (virgin); 18 (loaded)	16	5
Facility G	0.5 to 1	10	10	6
Facility K	0.35 to 0.65	18 to 30	24	5
Facility H	0 to 1.1	15 to 23	19	5
Facility D	0.8 to 1.2	15	15	7

Generally, the optimum EBCTs are substantially lower than the actual values. It is noted in Gifford, Selvy, and Gerrity (2018) that the actual EBCT may not always match the optimum EBCT because of practical considerations and/or varying treatment objectives. Additionally, the optimum EBCT may not achieve the maximum TOC removal, and various EBCTs may be tested at facilities to study the impacts on treatment performance. The minimum recommended EBCT for TOC removal is 10 minutes. TOC removal starts to plateau around this duration of time, so increasing the EBCT further provides diminishing returns (Arnold et al. 2018; Bacaro et al.

2019). An EBCT of 30 minutes or more for TOC removal would be excessive (Sundaram et al. 2020).

3.5.3.2 EBCT Recommendation for Removal of NDMA

NDMA data were available for several facilities from Chapter 1. For each facility, the NDMA percent removal by BAF were graphed against the EBCT (Figure 3-20). The method detection limit was assumed to be 2 ng/L. If there was a non-detect, it was assumed that the concentration was 50% of the method detection limit (i.e.,1 ng/L).

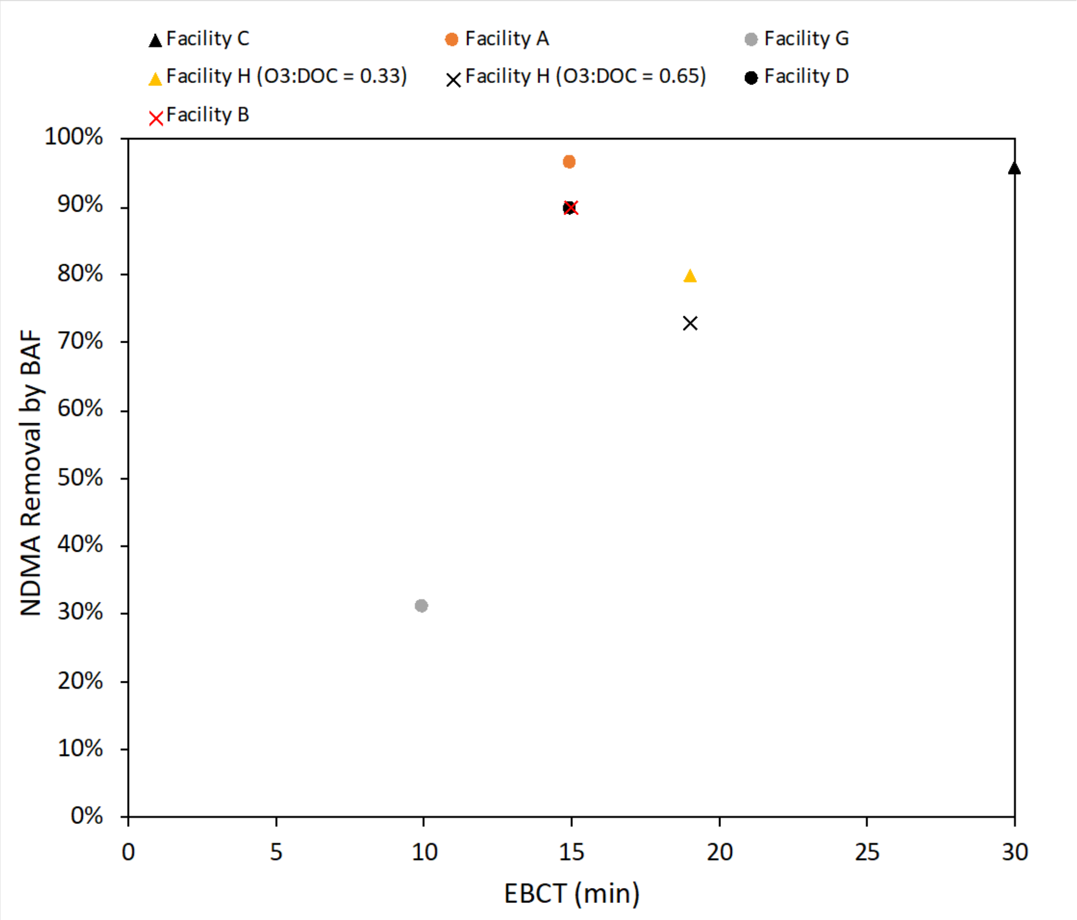


Figure 3-20. Average NDMA Percent Removal versus EBCT for Several Facilities.

BAF is consistently able to achieve more than 66% removal of NDMA. The EBCT does not appear to significantly impact the removal of NDMA, but data were not available for a wide range of EBCTs. The NDMA removal for Facility G is considered an outlier because the average NDMA concentration in the ozone effluent was only 1.47 ng/L. All facilities in Figure 3-20 indicated that at least partial nitrification is achieved. The minimum recommended EBCT for NDMA removal is 10 minutes. Bacaro et al. (2019) found there were diminishing returns for NDMA removal beyond an EBCT of 10 minutes; average NDMA removals at EBCTs of 10 and 20 minutes were ~90% and ~98%. This minor improvement might be necessary when targeting stringent potable reuse regulations (e.g., 10 ng/L NL from DDW) in systems with high concentrations of NDMA precursors (Bacaro et al. 2019).

3.5.3.3 Particle Size

Gifford, Selvy, and Gerrity (2018) developed linear equations for i) the TOC removal achieved by BAC at the optimum EBCT depending on the O_3:TOC ratio, and ii) the maximum TOC removal by BAC depending on the O_3:TOC ratio. The GAC particle size used in the study was 8 x 20. Out of the 12 facilities from Chapter 1 that provided information about the GAC particle size, two were 8 x 20; the actual TOC percent removals for these facilities were compared with the predicted maximum removal and predicted removal at optimum EBCT. Actual TOC removals for facilities with particle sizes other than 8 x 20 were also compared with the predicted TOC removals from Gifford, Selvy, and Gerrity (2018) to see how finer particle sizes compare with the linear models. It is expected that finer media are better for TOC removal while coarser media are better for longevity. The results are shown in Figure 3-21.

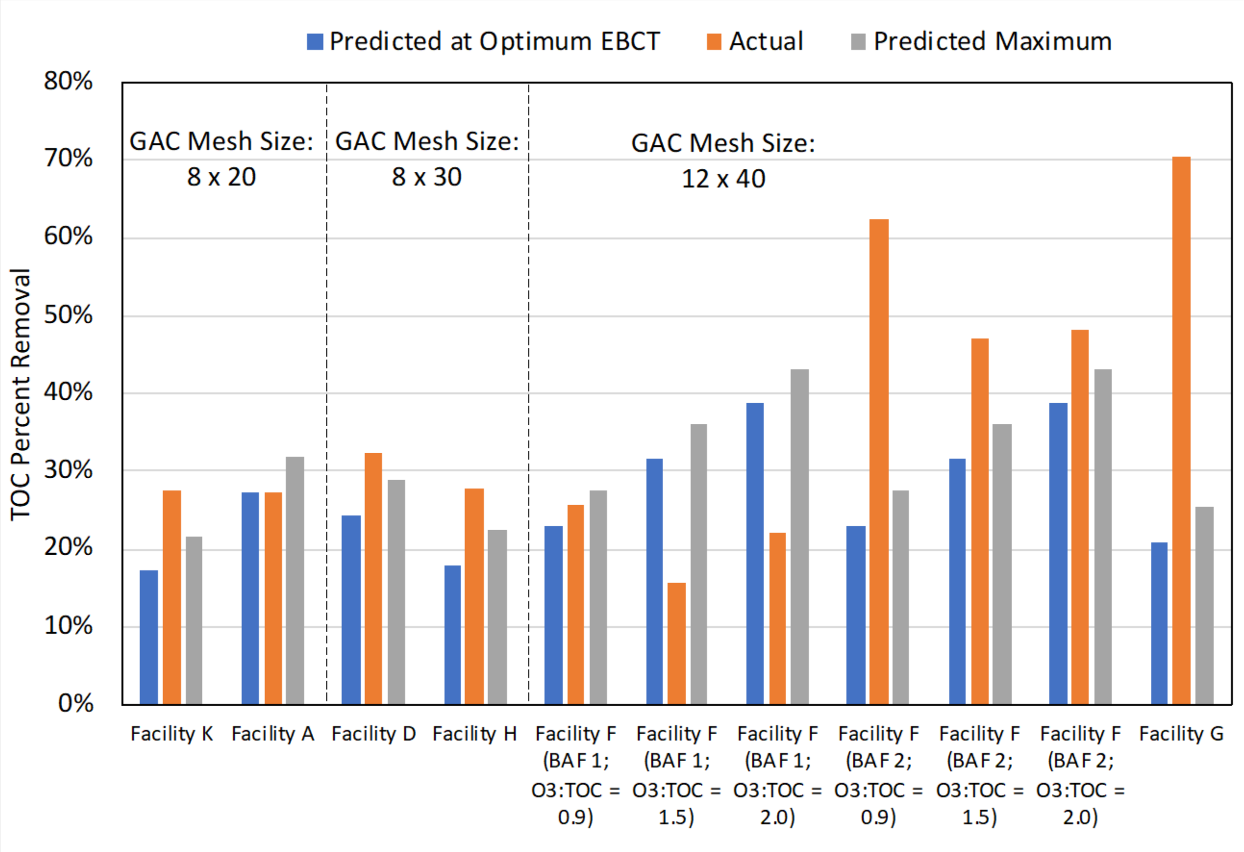


Figure 3-21. Actual and Predicted TOC Percent Removals for Facilities with BAC Filters having a Particle Size of 8 x 20, 8 x 30, and 12 x 40.

For 8 x 20 mesh, both predicted values were less than the actual value for the Facility K; for Facility A, the predicted removal at the optimum EBCT was the same as the actual removal. However, the actual EBCT of 15 minutes was almost two times higher than the optimum EBCT as shown in Table 3-52. For 8 x 30 mesh, the actual removal was slightly higher than the predicted values for the two facilities. For the 12 x 40 mesh, there were significant variations in the differences between the actual and predicted values. Finer particle sizes may result in greater TOC removal depending on the EBCT, but the data are not conclusive. No data were available for media with an effective particle size of less than approximately 0.65 mm.

Generally, the linear models from the Gifford study are conservative because the optimum EBCT is usually much lower than the actual EBCT.

3.5.3.4 Filter Bed Configuration

Previous studies have found that microbial abundance and biofilm density are higher near the surface of biological filters (Velten et al. 2011; Gibert et al. 2013; Arnold et al. 2018). A reasonable assertion from this finding is that deeper filter beds do not provide substantially increased TOC removal. Provided data from Chapter 1 concerning the height and surface of the filter bed configuration were graphed versus the TOC removal by BAF in Figure 3-22 and Figure 3-23, respectively.

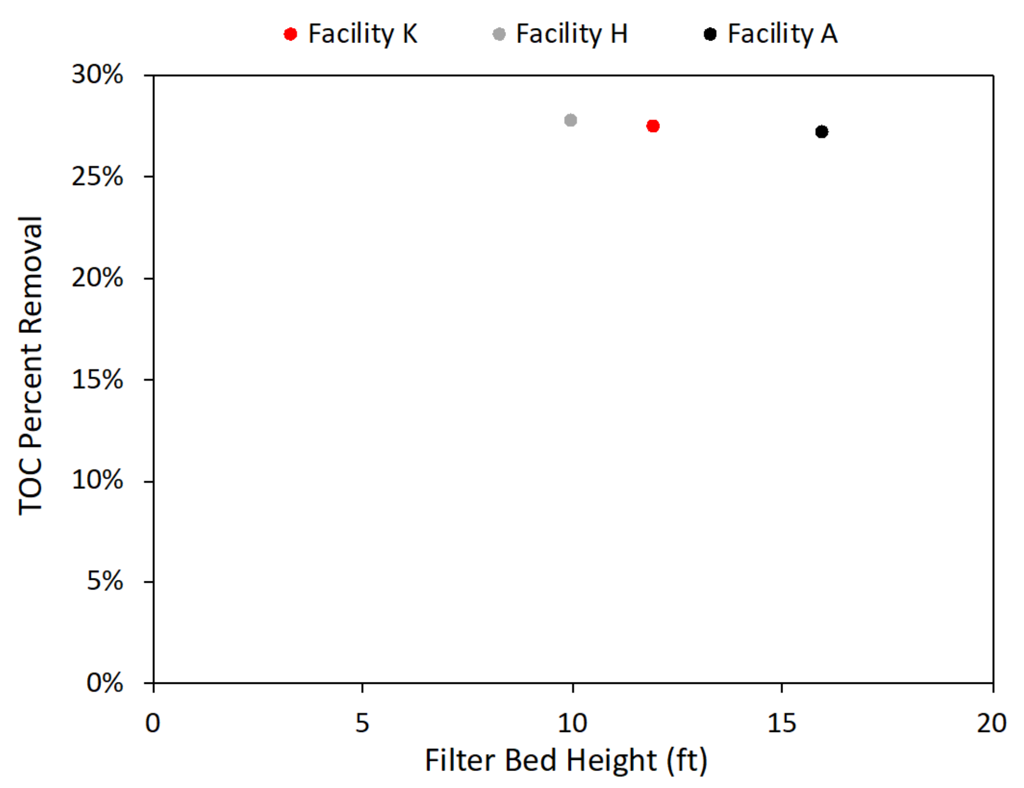


Figure 3-22. TOC Percent Removal versus Filter Bed Height for Three Facilities from Chapter 1.

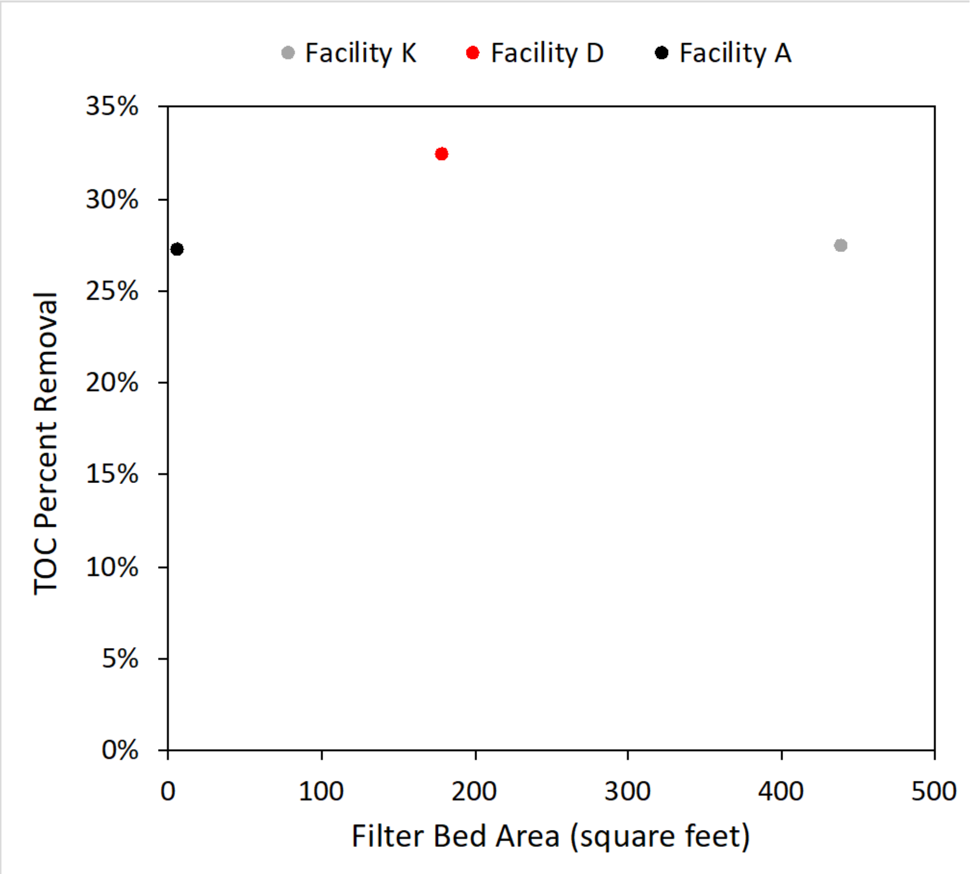


Figure 3-23. TOC Percent Removal versus Filter Bed Area for Three Facilities from Chapter 1.

The limited data suggest that filter bed area and height do not have a significant effect on TOC removal. Additional data are required to make a definitive conclusion. There is flexibility in terms of filter bed configuration. For example, deep filters can be installed to reduce the turbidity and manganese concentration in the BAF effluent without impacting TOC removal.

3.5.3.5 Hydraulic Loading Rate

The hydraulic loading rate (HLR) is a parameter with operational value because it can be used to predict run time. There were not enough data from Chapter 1 to make any definitive conclusions concerning the HLR. Filters with same EBCT can have different loading rates because of differences in the areas of the respective filter beds. If there were sufficient data, an investigation attempting to relate HLR and differences in TOC removal between facilities with the same EBCT could be conducted.

3.5.3.6 Backwashing and Headloss

Two conditions that necessitate filter backwashing are the deterioration of effluent water quality and the excessive buildup of headloss. Backwashing frequency for BAF is usually based on headloss buildup because turbidity breakthrough is not common. Additionally, focusing on headloss helps prevent air binding, which results in shortened filter runs. A media expansion of approximately 30% is typically targeted when backwashing.

During initial start-up of the ozone/BAC system at Facility D, air binding was occurring. It was effectively addressed by short, periodic pauses of 90 seconds in filter production. The filters were reprogrammed such that they rotated in and out of service every hour. This change in operation reduced the headloss over a week of operation by more than 20 inches compared to continuously operating the filters. Eventually, however, the frequency of backwashes increased over time. GAC media is brittle, so it can gradually break down from normal backwashing operations. A four-inch layer of fine media formed on the top surface of the filter bed, approximately doubling the clean-bed headloss of each filter. For immediate improvements in filter performance, scraping the surface of the filter bed to remove the fine media was found to be the optimal solution. Modifying the equipment to allow for longer backwashes at higher rates of flow would help prevent the accumulation of fines.

At Facility B, filtration was paused for 60 seconds every two hours to allow air to escape from the media to prevent excessive headloss. In contrast with Facility D, these rests were not effective in improving BAC performance or reducing headloss. Therefore, bumps (i.e., low-flow backwashes with a shorter duration) were performed instead of rests; these found to be more effective as there was no excessive headloss buildup, and the BAF was able to operate without backwashes for seven-day periods or longer. Hydraulic bumps every four hours were found to be effective at preventing gas binding for a pilot-scale BAF system receiving ozonated secondary effluent, and they became a standard operating procedure to increase duration of filter runs when there was no UF/MF system upstream (Trussell et al. 2016). It is possible that either filter rests or bumps could be effective at reducing buildup of headloss.

Using chlorinated backwash water can be a concern with respect to BAF performance. Generally, studies have shown mixed results with chlorinated backwash water, with some showing no effect and others showing significantly reduced organic carbon removal (EPA 2010). Short vigorous backwashes with a relatively low chlorine dose may be more effective in maintaining biological filtration than less vigorous backwashes at longer times with higher chlorine doses (Urfer et al. 1997). It is recommended that BAF effluent be used as the backwash water without chlorination to avoid any potential issues.

The effects of biofilter backwashing on the microbial community were studied by Gerrity et al. (2018). Backwashing increased the relative abundance of potentially pathogenic endosymbionts such as *Neochlamydia* and *Legionella*, which can be harbored within free-living amoebae. A lack of chlorine residual in the filter systems may have facilitated colonization (Gerrity et al. 2018). Infrequent backwashing (monthly or less frequent) may result in the colonization of biofiltration systems by microorganisms of the genus *Bradyrhizobium*, an ammonifier and extracellular polymeric substance (EPS) secreter, which could result in lower TOC removals and create problems for downstream chlorine disinfection via higher DBP formation potential (Gerrity et al. 2018). Therefore, a backwashing frequency of at least once a month is recommended. Most of the facilities from Chapter 1 that provided this information indicated that backwashes were performed at least weekly.

Changes in clean-bed headloss over time would indicate whether the backwashing strategy is effective or not. Not enough facilities from Chapter 1 provided clean-bed headloss or backwashing data to warrant an analysis.

3.5.3.7 Acclimation Period

Enough data were available from two facilities to graph the TOC percent removal as a function of the number of BVT (Figure 3-24).

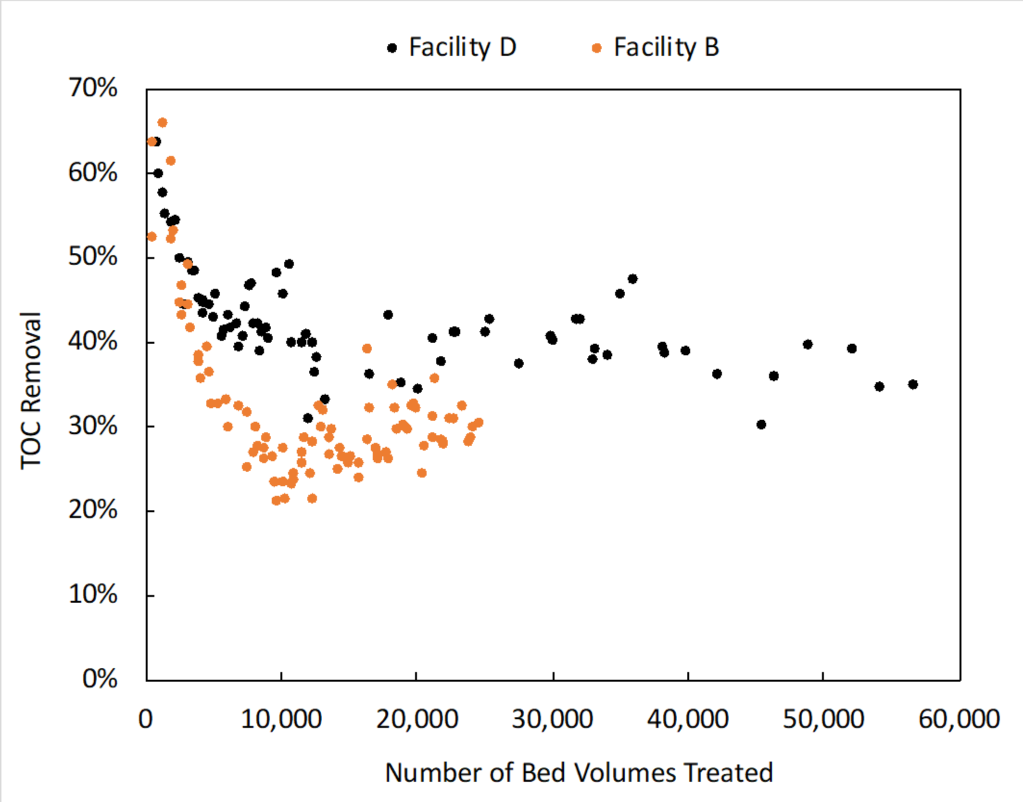


Figure 3-24. TOC Percent Removal versus the Number of Bed Volumes Treated for Two Facilities from Chapter 1.

TOC removal stabilized after approximately three and six months of operation for the Facilities D and B, respectively. Facility K indicated in the survey results from Chapter 1 that TOC removal decreased after four to six months of operation. Therefore, it can be stated that a general range for BAF acclimation is three to six months. The number of BVT for the three different facilities were calculated based on the EBCT or filter bed volume, flow rate, and number of filters (Table 3-53).

Table 3-53. Calculated Number of Bed Volumes Treated for Three Different Facilities depending on EBCT or Filter Bed Volume, Flow Rate, and Number of Filters.

Facility from Chapter 1	EBCT (min)	Filter Bed Volume (ft^3)	Flow Rate (CFM)	Number of Filters	BVT[a]	BVT[b]
Facility B	15	88	6	1	8,640	8,859
Facility K	24	5,280	3,064	27	9,000	4,642
Facility D	15	1,170	149	2	17,280	16,453

[a] Calculated based on provided EBCT value

[b] Calculated based on filter bed volume, flow rate, and number of filters

The discrepancy between the calculated BVT values for Facility K is likely because the total number of filters were provided in the response to the Chapter 1 survey. The number of duty filters is probably lower.

3.5.3.8 Media Replacement and Replenishment

Once a BAF system has acclimated and begins operating at steady state, biological performance (e.g., the removal of TOC, NDMA, and aldehydes) is expected to be sustained indefinitely, barring any major upsets to the system. Because BAF systems rely on biological degradation via the resident biomass on the media rather than the absorptive capacity of the media, breakthrough or media exhaustion is not expected as is the case with GAC systems. Therefore, addition of media is only necessary to replenish what has been lost due to mechanical attrition and losses via underdrains and/or backwashes. Replacement of large portions of the media bed is not advisable since the BAF system would lose the acclimated biology on the removed media. The system would need to undergo another acclimation period with new media to achieve steady state removals, which could either result in lost production or put the plant at risk of being out of compliance if it is kept online.

Experience from Facility L and Facility D from the Chapter 1 survey indicate that approximately 3% of the media bed must be replenished each year as a part of routine maintenance for the BAF system. Project O from the Chapter 1 survey exhibited a more frequent media replacement interval due to clogging issues with filter fines. Filter fines issues can often be managed with optimized high-rate backwashes and air scouring sequences, as discussed in Section 3.5.3.6. Both virgin and regenerated carbon can be used for these maintenance replacements, but virgin carbon typically has higher iodine values (an indicator of porosity and surface area of activated carbon).

3.5.4 Early Draft DPR Regulations in CA

In March of 2021 (and subsequently updated in August 2021), the California SWRCB released an early draft of the anticipated criteria for DPR within the state (SWRCB 2021a). The anticipated criteria for DPR includes a requirement for the following treatment processes (in this order): ozone/BAC, RO, and UV/AOP. While the provisions for RO and UV/AOP are similar to SWA (revised operational triggers are listed for RO), the ozone/BAC requirement is unique to the draft DPR regulations to ensure a high level of chemical control through the advanced treatment train. The specific requirements listed in the anticipated DPR criteria that are relevant to the design and operation of the ozone/BAC process are as follows:

- Testing must be conducted to confirm that the ozone/BAC process can reliably achieve 1.0-log removal of formaldehyde. The draft criteria also require continuous monitoring of at least one surrogate or operational parameter to indicate when the process is not operating as designed.
- The ozone process must be designed to operate with an applied O_3:TOC ratio of greater than 1.
- The BAC process must be designed to operate at an EBCT of at least 15 minutes.

The requirement for 1.0-log of formaldehyde removal ensures that the BAC system is achieving adequate levels of biodegradation. Examples of suitable surrogates for the ozone/BAC process may include ΔUV_{254} and ΔTOC to ensure both the ozone and BAC processes are operating smoothly. The O_3:TOC ratio requirement is included to ensure high levels of chemical oxidation and is reasonable in the context of downstream RO treatment. The requirement of an O_3:TOC ratio greater than 1 is higher than the recommended ratio of 0.6 discussed in Section 3.5.2.2. A ratio of 0.6 is sufficient for the control of most moderate to highly reactive CECs. In Section 3.5.2.2, the benefits and risks of higher O_3:TOC ratios are discussed. For CBAT projects without downstream RO, bromate formation is a serious concern that must be considered at O_3:TOC ratios above 1. Lastly, the EBCT requirement of 15 minutes is included to ensure adequate organics removal can be achieved through the BAC system. This requirement is greater than the recommendation for a minimum EBCT of 10 min for adequate removal of TOC and NDMA as discussed in Sections 3.5.3.1 and 3.5.3.2. The literature has shown a diminishing return at EBCTs above 10 minutes as discussed in Sections 3.5.3.1 and 3.5.3.2. Since higher EBCTs can add significant costs to a project, agencies may consider testing at lower EBCTs to demonstrate high levels of treatment (e.g., NDMA, TOC, and formaldehyde removal).

3.6 Knowledge Gaps and Further Research Needs

In this Section, identified knowledge gaps and further research needs are discussed as part of completion of Objective D of this chapter.

3.6.1 Knowledge Gaps Pertaining to the Ozone and BAF Processes

A summary of the identified knowledge gaps pertaining to the ozone and BAF processes is included in Table 3-54.

Table 3-54. Identified Knowledge Gaps and Further Research Needs for Ozone and BAF Processes.

System	Knowledge Gap Description	Importance
Ozone and BAF	Evaluate bromate control strategies for potable reuse applications	Bromate control strategies may affect ozone process efficiency and downstream BAF performance
Ozone	Comparing capital and operations and maintenance (O&M) costs of fine bubble diffusion and sidestream injection	Impact O&M of ozone systems
Ozone	Determine if O_3:TOC can be used to predict pathogen disinfection and serve as a control strategy to verify disinfection	Could simplify operation by using O_3:TOC ratio for predicting both contaminant oxidation and pathogen disinfection
BAF	Effects of filter bed configuration on TOC removal	Help inform design decisions related to dimensions of the filter bed

Practitioners of the ozone/BAF process for potable reuse must balance treatment performance in terms of contaminant oxidation and disinfection with DBP formation. One of these DBPs is bromate, which has an MCL of 10 µg/L for drinking water and is a probable human carcinogen based on sufficient evidence of carcinogenicity in animals (EPA 2001a). Practical bromate formation control strategies for wastewater matrices include the H_2O_2 addition and chlorine-ammonia process. These strategies rely on reducing the availability of free bromide ions and manipulating the formation pathways for bromate. These strategies may impact the ability of the treatment train to meet performance goals for disinfection and contaminant oxidation. Research is needed to evaluate these strategies for potable reuse of wastewater matrices by focusing on how they affect ozone process efficiency and downstream BAF performance.

The two primary methods for ozone dissolution are fine bubble diffusion and sidestream injection. For fine bubble diffusion, ceramic or stone diffusers located at the bottom of the contact chamber transfer ozone gas into water. It is simple to use, but there can be operation and maintenance concerns associated with the accessibility of diffusers and confined space entry (Wert, Lew, and Rakness 2017). Sidestream injection is a relatively new method where a Venturi device adds ozone gas to a sidestream that then rejoins the main facility flow. It offers ease of access and reduced impact of turndown compared with fine bubble diffusion. Recent advancements in ozone generation technology have made sidestream injection more economically competitive by increasing the ozone gas concentration and thus reducing the pumping costs to achieve desired gas-to-liquid ratios (Wert, Lew, and Rakness 2017). However, further research is needed to compare the capital and operating costs of sidestream injection and fine bubble diffusion. This knowledge gap was included even though it is not directly related to CEC removal by ozonation because it is generally important for operation and maintenance of ozone systems.

The O_3:TOC ratio is effective in predicting the level of CEC removal for different secondary or tertiary effluents while ozone CT is the standard framework for predicting pathogen disinfection because it is the only metric recognized by U.S. regulators. Relationships between these two parameters for secondary and tertiary wastewater effluents have been developed using regression (Gamage et al. 2013; Gerrity et al. 2014). Prior research has found that CT was not a valid dosing parameter under all ozone treatment scenarios, including low-dose applications or when the process is supplemented with H_2O_2 (Gamage et al. 2013). Furthermore, analysis of several U.S. secondary effluents for microbial inactivation relationships indicated there were similar trends for CT and O_3:TOC ratio, but the O_3:TOC ratio was still useful in predicting inactivation for dosing conditions resulting apparent CT is 0 mg-min/L (Gamage et al. 2013). Further research is required to determine if the O_3:TOC ratio can be used to accurately predict pathogen disinfection. If it were shown to be accurate under a variety of ozone dosing conditions and it were accepted by the regulatory community, then operation of the ozone process for water reuse could be simplified because the O_3:TOC ratio could be used for predicting both contaminant oxidation and pathogen disinfection.

For BAF, the effects of the filter bed configuration on TOC removal are a knowledge gap. As stated previously, prior studies have found that microbial abundance and biofilm density are higher near the surface of biological filters (Velten et al. 2011; Gibert et al. 2013; Arnold et al. 2018). Velten et al. (2011) measured attached biomass on GAC particles at four different depths of a pilot-scale filter. At steady state (i.e., average biomass growth rate of zero), the highest biomass concentration was observed at a depth of approximately 17 inches, and the lowest concentration was observed at about four feet. This vertical gradient in biomass density suggests that a relatively shallow and wide filter would perform just as well or better than a deep, narrow filter with respect to TOC removal. Interestingly, Urfer and Huck (2001) found that while biomass activity in laboratory-scale GAC filters based on oxygen consumption decreased with increasing filter depth. The biomass activity normalized to viable biomass increased with increasing filter depth, suggesting that the biomass deeper in the filter was more active with respect to substrate removal. Finally, while there were a lack of data concerning clean-bed headloss, it is not considered a knowledge gap because it is not a design parameter with a target range. Rather, it is a key performance indicator (KPI) that is monitored to determine backwashing effectiveness.

3.6.2 Knowledge Gaps Pertaining to Recalcitrant Compounds and Upstream/Downstream Processes

A summary of the identified knowledge gaps pertaining to the ozone and BAF processes is included in Table 3-55.

Table 3-55. Knowledge Gaps Pertaining to Recalcitrant Compounds and Upstream/Downstream Treatment Processes.

Recalcitrant Compounds or Treatment Process	Knowledge Gap Description	Importance
Recalcitrant compounds (PPCPs, shorter-chain PFAS, and flame retardants)	Lack of MTLs or other forms of human health-based concentration thresholds	Determine benchmark concentrations for protection of public health
Bioassays for recalcitrant compounds	Several bioassays besides ER-a and AhR are in various stages of development	Increase commercial availability of other endpoints and their range of applications, and provide insights on adverse health effects of CECs
Upstream tertiary treatment processes (coagulation, flocculation, sedimentation, filtration)	Understand treatment performance, focusing on typical TOC and CEC removals for varying wastewater quality (e.g., pH, alkalinity, TOC)	Allow for better understanding of influent water quality to ozone/BAF
Downstream treatment processes (IX resins and GAC)	RSSCT testing of IX resins and GAC studies focusing on PFAS and TOC removal from ozone/BAF effluents; EBCTs and influent TOC and PFAS concentrations should be varied	Understand physical and analytical challenges associated with scaling RSSCT; characterize breakthrough of PFAS and TOC for ozone/BAF effluents

Key objectives within Chapter 3 included: i) identification of recalcitrant compounds through ozone/BAF and ii) analysis of the public health relevance of these compounds at the concentrations observed. Many recalcitrant compounds identified currently have no NLs, CTR limits, or MTLs in place to serve as benchmarks for safe concentration in the context of human health. Local state government guidance values were also consulted, but in some cases toxicological data such as NOAELs, LOAELs, and LD50s were used in lieu of human health-based concentration thresholds. As such, the field of potable reuse as a whole would benefit from an expansion of MTLs or other forms of human health-based concentration thresholds. Examples of relevant compounds that would benefit from MTLs include PPCPs such as ethyl and methyl glyoxal, shorter-chain PFAS (such as PFHxA, PFHpA, and PFPeA), and flame retardants such as TCPP.

In addition to traditional targeted chemical analyses, bioassays allow users to monitor for adverse outcomes from a breadth of CECs, both known and unknown. The Science Advisory Panel recommended ER-α and AhR due to their clear adverse outcome pathways and commercial availability; however, several other bioassays are at various stages of development. These additional bioassays can provide insights on other classes of CECs and their adverse outcomes, but research is ongoing to better understand these tools and standardize the methods to promote more widespread application (and commercial availability) of the tools. The ER-α and AhR bioassays show favorable results through ozone/BAF, but more research is needed to evaluate the use of other endpoints which may shed more light on recalcitrant CECs through these processes.

On the upstream treatment side, coagulation, flocculation, sedimentation, and filtration as a tertiary wastewater treatment sequence has gained interest in recent years. While this treatment is common in the context of drinking water, additional research to understand treatment performance in wastewater would be beneficial. In particular, additional data are required to understand the range of typical TOC and CEC removals as a function of wastewater quality (e.g., pH, alkalinity, TOC).

With respect to downstream treatment, additional studies on GAC and IX in the context of PFAS and TOC removal are warranted. Much of the literature on PFAS and TOC removal via GAC and IX are conducted on drinking water sources, so additional studies on a variety of ozone/BAF effluents would help characterize the breakthrough of these constituents on these specific matrices. While the DCTAWPF study used RSSCT to characterize TOC breakthrough, long-term data on the breakthrough of PFAS in ozone/BAF are needed. Several different factors should be investigated including varied EBCTs, influent TOC concentrations, and influent PFAS concentrations. RSSCT is a powerful tool which allows researchers to elucidate long-term performance on a timescale of weeks or months rather than years. While it is an established tool for GAC, RSSCT testing of IX resins is still in its infancy and additional research is needed to understand the physical and analytical challenges associated with scaling. Advancement of IX RSSCT methods would help researchers more easily conduct side-by-side comparisons of GAC vs IX performance for a given water quality and contaminant target.

3.6.3 Rapid Small-Scale Column Testing

This Section provides an overview on the four RSSCT that were performed as part of this project. The experimental testing was done approximately over a two-week period evaluating virgin and reactivated GACs at two different EBCTs. Testing was done on the ozone/BAC effluent to compare removal of TOC and of PFAS by the four experimental conditions according to the Test Plan provided in Appendix B. The following sections will provide a summary of the results and recommendations, while Appendix B provides a more in-depth presentation of the data and findings.

3.6.3.1 Methods Summary

This RSSCT experiment examined breakthrough of TOC and eight PFAS compounds. The conditions examined are two carbon types, virgin and reactivated Calgon Filtrasorb 400 (F400), and two EBCT, 10 and 20 minutes. The source water was spiked with an AccuStandard standard reagent containing 14 PFAS compounds, eight of which were target compounds. The target concentration for each compound was 50 ng/L above ambient concentration. The average concentration of TOC and PFAS compounds in the RSSCT influent is provided in Table 3-56.

Table 3-56. Concentrations of TOC and PFAS Compounds in RSSCT Influent.

Parameter	Units	Concentration
TOC	mg/L	4.57
Perfluorobutanesulfonic Acid (PFBS)	ng/L	55
Perfluorooctanoic Acid (PFOA)	ng/L	67
Perfluorooctanesulfonic Acid (PFOS)	ng/L	40
Perfluorohexanoic Acid (PFHxA)	ng/L	212
Perfluorohexanesulfonic Acid (PFHxS)	ng/L	55
Perfluoropentanoic Acid (PFHpA)	ng/L	62
Perfluorononanoic Acid (PFNA)	ng/L	62
Perfluorodecanoic Acid (PFDA)	ng/L	42
Perfluorotridecanoic Acid (PFDrDA)	ng/L	18
Perfluorotetradecanoic Acid (PFTA)	ng/L	17

Spike recoveries were calculated based on the difference in measured PFAS concentration in RSSCT Feed and Raw Water, divided by the PFAS concentration in the DI water standard (which was spiked an equivalent aliquot of stock standard). A more detailed description of the experimental setup can be found in the Appendix B.

3.6.3.2 TOC Removal Results Summary

Figure 3-25 shows the TOC breakthrough curves for all four test conditions as a function of BVT. The virgin and reactivated carbon perform similarly for each EBCT based on the summary of results for different target removals and statistical analysis presented in Table 3-57. Different GAC and EBCTs are represented by abbreviations, V-10min, R-10min, V-20min, R-20min. V-10min and V-20min represent virgin GAC with 10 and 20 min EBCT, respectively. Initially there is a greater variability in bed volumes between the virgin and reactivated carbons, when targeting higher percent removal of TOC. Lower removal targets can be maintained for longer number of bed volumes and the difference between reactivated and virgin carbon gets smaller to approximately 10% range.

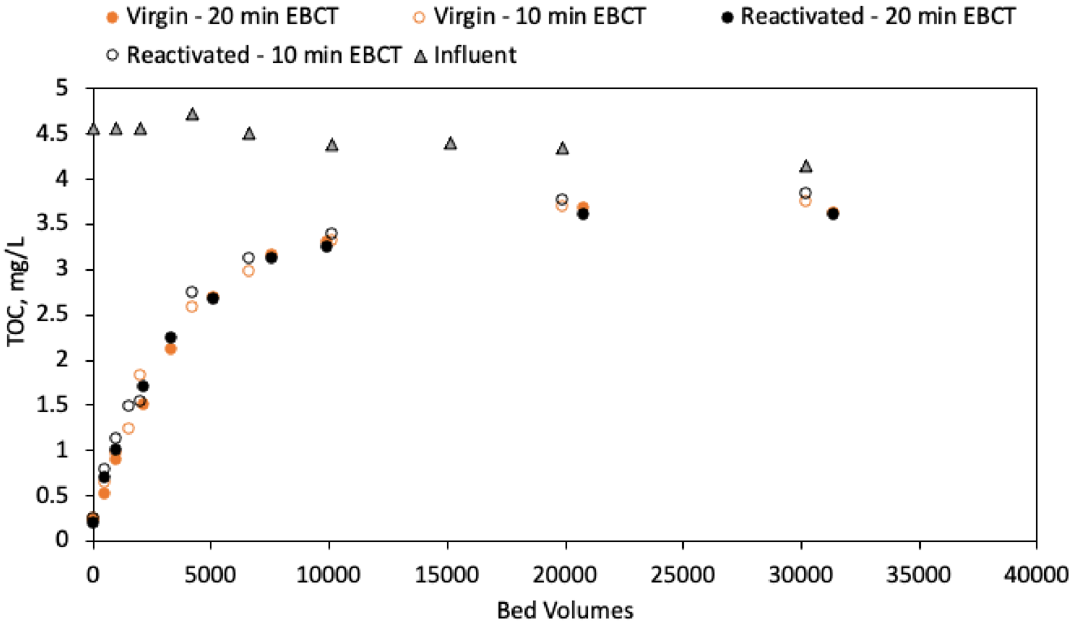


Figure 3-25. TOC Concentration versus Bed Volume for Influent and various Carbon Types and EBCTs.

Table 3-57. Bed Volumes for Different RSSCT Columns Testing and TOC Removals.

Carbon	Removal Target			
	90% (1-log)	68% (0.5-log)	50% (0.3-log)	30% (0.15-log)
V-10min	275	1600	3175	7675
R-10min	200	1550	3025	6225
V-20min	350	1975	3700	6975
R-20min	250	1700	3350	7475
Average	269	1706	3313	7088
St. Dev.	62.5	190	290	646
RSD (%)	23.3	11.1	8.8	9.1

Figure 3-26 shows the TOC breakthrough versus number of equivalent days of operation for single column. The 20-minute EBCT extends TOC breakthrough further than the 10-minute condition. To maintain at least 0.5-log TOC removal (68% or C/C_0 of 0.32), the 10-minute EBCT configuration would need media replaced after just 11 days and the 20-minute EBCT would need media replaced after 25 days.

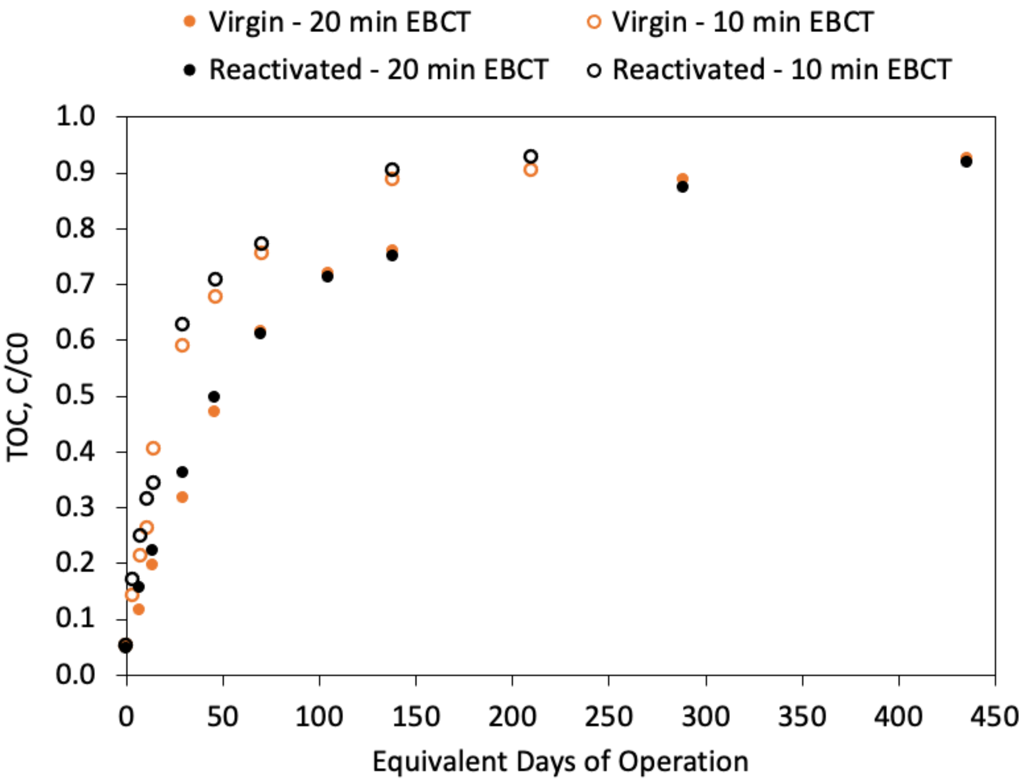


Figure 3-26. TOC Breakthrough Curves in Equivalent Days of Operation of Single Columns.

The results of the RSSCT indicate that there are no significant differences in performance between the virgin and reactivated GAC. TOC removal by adsorption appears to be challenging due to shorter bed volumes to breakthrough. This is highly dependent on influent TOC levels and effluent TOC targets. The dependence on influent TOC increases the need for optimal upstream tertiary treatment. Optimization of GAC configuration, operation, and carbon usage will be necessary to manage TOC breakthrough.

3.6.3.3 PFAS Removal Results Summary

Figure 3-27 shows the breakthrough curves of the 8 tested PFAS compounds. PFHxA, PFBS, and PFHpA have considerably faster breakthrough than longer chain PFAS. Figure 3-28 displays the breakthrough curves for PFOA under all four test conditions. Similar to TOC removal, the longer EBCT condition results in extended operational time to control PFOA. The reactivated carbon performed slightly better than the virgin carbon.

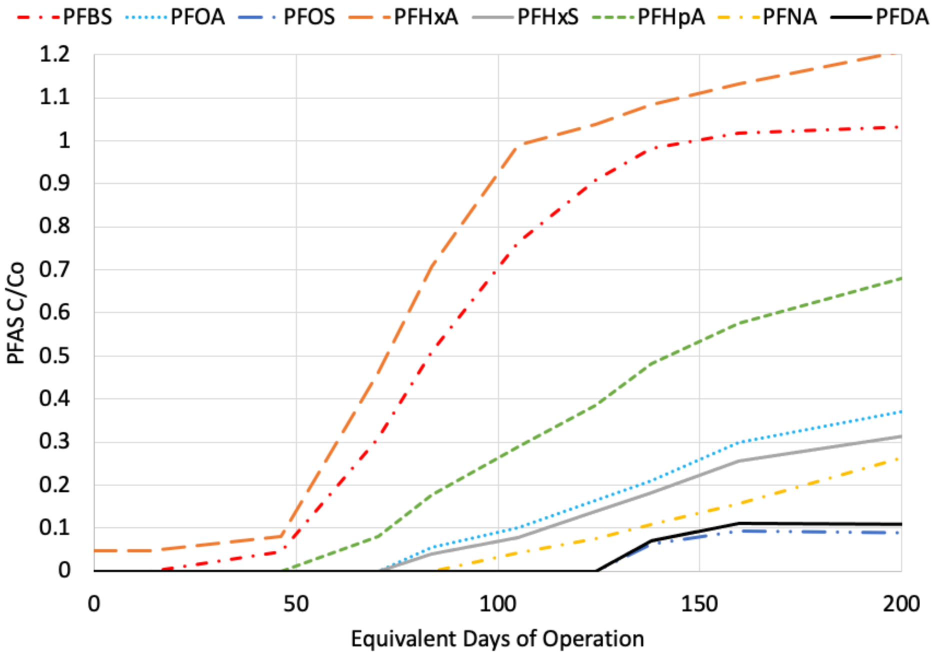


Figure 3-27. PFAS Breakthrough Curves for Virgin Calgon F400 with EBCT of 10 Minutes.

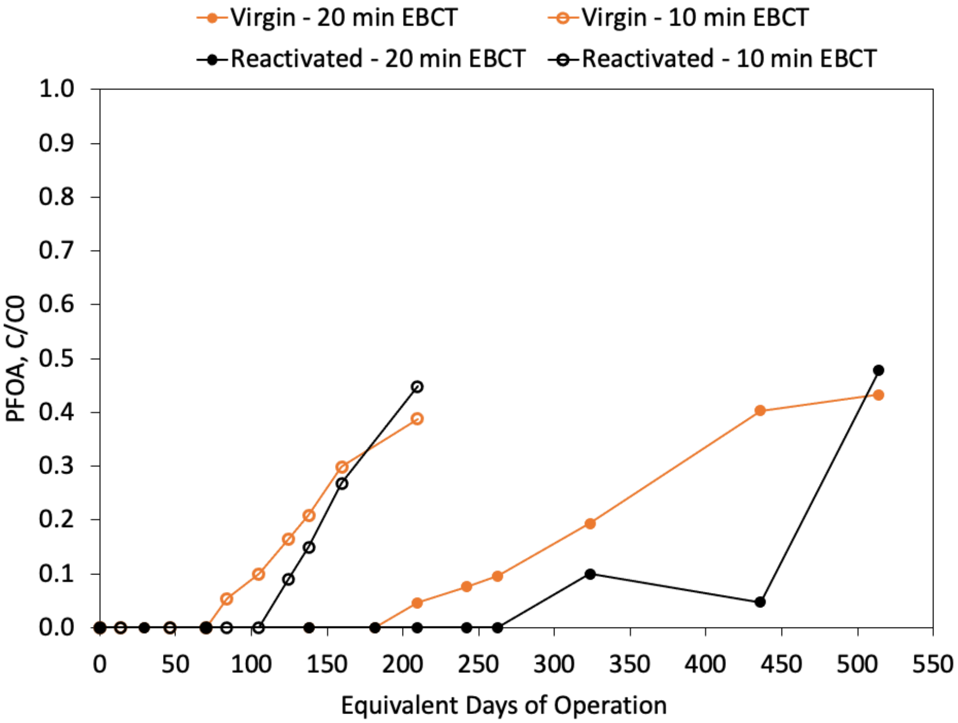


Figure 3-28. PFOA Breakthrough Curves with Various Carbon Types and EBCTs.

3.6.3.4 Recommendations for Design

Facilities looking to control both TOC and PFAS must find a balance between the two since TOC breakthrough occurs more rapidly than PFAS. To manage TOC, larger bed configurations may be necessary to operate at a higher EBCT. This will create a GAC media replacement frequency that is more manageable than the frequency with a shorter EBCT. The RSSCT were modeled to perform simulations with an 8-column GAC system to represent full-scale operation. Table 3-58 provides projected GAC media replacement frequency in days and consumption in lbs/1,000 gallons for removal of TOC, PFBS, and PFOA. Notably the TOC removal of even 0.5-log (68%) is more costly than removal of PFBS or PFOA by 1-log. Therefore, TOC removal goals may be primary for certain potable reuse projects looking to control TOC by GAC as a polishing step with an added protection against PFAS. Table 3-58 shows that media replacement for 0.5-log removal of TOC will be needed after 39 days at a 10-minute EBCT compared to 120 days at a 20-minute EBCT. Higher TOC removal through upstream biological treatment and BAF can achieve other treatment objectives such as lowering DBPFP and the requirements for GAC media usage. Since TOC removal is highly dependent on the effluent target TOC concentration, these objectives must be balanced with PFAS removal, which generally are expected to have higher number of bed volumes before breakthrough.

Table 3-58. Summary of Simulations with 8-column GAC System and Modeled GAC Consumption in lbs/1,000 Gallons of Treated Water.

	PFOA	PFBS	TOC			
	90%	90%	90%	68%	50%	30%
EBCT	1-log	1-log	1-log	0.5-log	0.3-log	0.15-log
GAC Replacement Frequency, days						
10 Min	116	70	4.8	39	72	105
20 Min	360	180	18.0	120	180	233
GAC Consumption lbs/1,000 gal						
10 Min	0.264	0.438	6.383	0.786	0.426	0.292
20 Min	0.170	0.340	3.404	0.511	0.340	0.263

In facilities where TOC does not need to be further treated, GAC systems can be operated longer due to higher number of bed volumes to breakthrough for PFAS. In this case, a 10-minute EBCT may be sufficient to provide PFAS removal with a reasonable media replacement frequency. Based on the data presented in Table 3-58, media replacement for 1.0-log removal of PFOA will be needed after 116 days at a 10-minute EBCT compared to 76 days for PFBS. If preferred, longer EBCTs can be used to prolong replacement frequency (e.g., replacement frequency for PFOA with 20 min EBCT is approximately 360 days). Smaller MW PFAS with shorter carbon chains, such as PFBS tend to have less BVs before breakthrough. For 1.0-log removal of PFBS media replacement will be needed after 76 days for GAC system with 10-minute EBCT and 180 days for 20-min EBCT. Alternatively, the removal of these compounds can be accomplished using other treatment options. Possible options include NF, which will retain a small residuals stream and provide TOC removal, or selective IX resins. Between PFOA and PFOS, which have California NLs of 5.1 and 6.5 ng/L, PFOA appears to require a sooner changeout and therefore should drive the GAC usage. PFBS, is a shorter carbon chain compound than either PFOA and PFOS and breakthroughs sooner, resulting in carbon usage of 0.340lbs/1,000 gallons. This is about double the consumption for removal of PFOA at EBCT of

20 min, however due to its relatively high NL in CA of 500 ng/L it may or may not need to take priority during development of design criteria for GAC system depending on the PFBS concentration in the feed water relative to that of the PFOA, or PFOS.

3.6.3.5 Summary of RSSCT Findings

In general, smaller molecular weight (MW) PFAS have a shorter number of BVs before breakthrough. Notably, PFHxA, PFBS, and PFHpA have faster breakthrough than PFAS with longer carbon chains. In context of California regulations for PFAS NLs in drinking water, PFOA may require sooner changeout for GAC, than for PFOS removal, indicating PFOA may drive GAC usage.

TOC removal by adsorption appears to be challenging due to shorter bed volumes to breakthrough than needed for PFAS. For facilities targeting removal of both TOC and PFAS the GAC system design would need to be balanced to accommodate target removal goals. For 1-log removal of PFOA with a 20 min EBCT GAC system consisting of 8 reactors, carbon consumption is estimated on the order of 0.140 lbs/1,000 gallons. Whereas for 1-log removal of TOC, carbon consumption of 3.4 lbs/1,000 gallons would be needed. On the other hand, if PFAS removal is primary purpose, there is some additional benefit in associated removal of TOC. When comparing these relative costs for 10-min vs. 20-min EBCT columns, generally the 20-min EBCT provides a lower carbon consumption and allow for a longer replacement frequency. The projected cost difference may become sufficient to offset additional capital costs for a bigger number of parallel GAC vessels and would need to be evaluated further during design phases of the project.

In both TOC and PFAS testing, there were no significant differences in performance between virgin and reactivated carbon. Therefore, there may not be a significant advantage to using virgin carbon, which is more costly. A limitation of this RSSCT include not varying influent TOC and PFAS concentrations. Specifically with TOC, the number of bed volumes to breakthrough is dependent on the influent TOC concentration. This RSSCT was tested on ozone/BAF effluent with TOC concentration of 5 mg/L. The carbon consumption may vary for facilities where TOC concentration is not an issue, or where more TOC removal is needed.

CHAPTER 4

Design and Operational Guidelines

4.1 Purpose of Guidance Document

The purpose of this guidance document is to provide design and operational guidelines for implementing the ozone coupled with biologically active filtration (ozone/BAF) process for potable reuse. The guidelines are a summary of the previous chapter findings along with industry experience by the authors. The intention of these guidelines is to provide broad and general information for practitioners of potable reuse. These general guidelines may not reflect project-specific considerations, which must be considered.

4.2 Introduction to Ozone/BAC in Potable Reuse

The most promising form of BAF considered in potable reuse in terms of organics removal performance is based on using exhausted granular activated carbon (GAC). As GAC media is exhausted, more and more biological mass grows eventually leading to biologically activated carbon (BAC) filtration. In such a mode, the removal of dissolved organic carbon (DOC) is achieved biologically and not by sorption. Other substrate medias such as sand, anthracite, and biochar may be considered and are summarized in Chapter 3, but BAC typically provides the best performance. In all further discussions in this chapter, ozone/BAC is presented as the recommended form of ozone/BAF.

The use of ozone/BAC in potable reuse is at least in the design stage or is in progress for implementation at full-scale for at least three facilities in the United States. Two of these projects, OneWater Nevada of Truckee Meadows Water Authority and the Sustainable Water Initiative for Tomorrow program in eastern Virginia, tested treatment trains that met all drinking water standards and other project goals without the need for reverse osmosis (RO) membranes. The other project, located in City of San Diego, uses ozone/BAC as an additional barrier and pre-treatment to full advanced treatment (FAT) and meeting criteria for surface water augmentation. This Section provides on overview of the history of how ozone/BAC became recognized as beneficial and a valuable alternative for potable reuse projects.

4.2.1 Description

The ozone/BAC process is synergistic. Although ozone and BAC are typically designed and operated as two separate unit operations with ozone in series prior to BAC, the ozone process is essential towards supplying bioavailable organic carbon and dissolved oxygen (DO) to propagate and sustain the biomass in the BAC. In addition to ozone providing constituent of emerging concern (CEC) removal and pathogen disinfection, ozone oxidizes the recalcitrant organic carbon in wastewater effluent that has been biologically treated. The oxidation of this recalcitrant organic carbon breaks longer chain bonds and makes some of the organic carbon bioavailable. Furthermore, the process of ozonation supersaturates the wastewater effluent with DO. The combination of bioavailable organic carbon and supersaturated DO along with already existing nutrients (i.e., nitrogen, phosphorous) in the wastewater effluent creates an environment for biomass to grow on a substrate (i.e., GAC) and degrade bioavailable organic carbon including bulk and trace organic compounds such as total organic carbon (TOC) and CECs, respectively. Additionally, the BAC process may function as a granular media filter to reduce turbidity and suspended solids while retaining and/or minimizing the sloughing of the biomass.

4.2.2 Value Proposition

There are several treatment technologies that can be broadly used for the removal of organic compounds. The needs for robust treatment in potable reuse against organics extend beyond typical concerns in drinking water that can be summarized as control of disinfection byproducts (DBPs), taste, and odor compounds, and, where applicable, control of algal toxins and any specific contaminants due to polluted water source. Concerns around the presence of organics in wastewater include many more classes of compounds, including pharmaceuticals, organic solvents, pesticides, herbicides, synthetic compounds, volatile organic compounds, and the list goes on with more and more compounds found each year in the water bodies around the world.

There are several treatment technologies available, including ozone/BAC, GAC, nanofiltration (NF), RO, and advanced oxidation process (AOP). Several past studies have evaluated ozone and ozone/BAC as alternative and more economical treatment options than RO and AOP that are typically used in groundwater injection and surface water augmentation (SWA) projects in California. For example, Water Research Foundation (WRF) 08-05 showed that at relatively high ozone dosing, expressed as ozone to TOC (O_3:TOC) ratio of 1.5, ozone/BAC treatment should be more than 4 times lower in capital costs and more than 6 times lower in operating costs than membrane filtration (MF) – RO – ultraviolet light-based advanced oxidation (UV/AOP) with peroxide (UV/H_2O_2) treatment for a 50 million gallon per day (MGD) facility. Even with additional treatment steps such as MF and UV to provide treatment redundancy against pathogens, the estimated capital and operations and maintenance (O&M) costs for a 10 MGD facility were approximately 37% less than equivalent FAT treatment train (Gerrity et al. 2014; Plumlee et al. 2014). Adding redundancy to organics removal, such as GAC or ion exchange (IX) for addressing perfluoroalkyl substances for example, is not expected to tip the scale back in favor of FAT. Another important benefit to inland applications is that ozone/BAC treatment train would not use an RO or NF to generate a concentrate stream that would require a plan for disposal.

4.2.3 History

Over the past decade, ozone/BAC studies at pilot-, demonstration-, and full-scale facilities have been conducted to evaluate and optimize the implementation of ozone/BAC for both drinking water and potable reuse. Landmark studies such as WRF 08-05 introduced the effectiveness of ozone-based solutions at removing CECs. WRF 11-02 demonstrated that ozone/BAC-based treatment trains without RO can meet both chemical and pathogen criteria for potable reuse. WRF 13-10 showed ozone/BAC-based treatment trains cost 50% less than RO-based treatment trains on a life-cycle cost basis and do not generate significant waste streams. WRF 14-12 demonstrated that ozone/BAC provided an additional barrier to mitigate spikes in trace organics, such as 1,4-dioxane and N-Nitrosodimethylamine (NDMA). The WRF 14-12 project also built off the concept that ozone/BAC alone can meet California's definition of Advanced Oxidation in potable reuse application. Full-scale installations in El Paso (Texas USA), Gwinnett County (Georgia USA), Windhoek (Namibia), and Melbourne (Australia) are examples of ozone/BAC-based treatment trains for reuse that have operated successfully for decades. Additionally, ozone/BAC-based treatment trains have been a key enabling technology globally in drinking water treatment of impaired surface waters for over 40 years to address pathogens, taste and odor compounds, and disinfection by-product precursors.

4.2.4 Drivers

Potable reuse is now considered an integral component of water resource management in many communities around the world. The treatment solutions exist today to reliably produce safe drinking water from reclaimed water. Treatment trains with and without RO are currently being evaluated and implemented for full-scale potable reuse applications. RO-based treatment trains pose significant implementation challenges for some utilities around the world due to their high capital and operating cost along with the difficulty of managing the concentrated waste streams when ocean discharge is not available, as is the case with many inland applications. Alternatives to RO-based treatment trains often include ozone/BAC as one of the enabling technologies in a multiple-barrier approach to meeting treatment objectives. Ozone/BAC-based treatment trains have been proven to produce a high-quality reclaimed water meeting drinking water standards at a significantly lower cost and environmental footprint than full advanced treatment (FAT).

4.2.5 Applications

Ozone/BAC may be used as a process in a treatment train for any potable reuse application including groundwater recharge, surface water augmentation, raw water augmentation, and treated water augmentation. Ozone/BAC may be used to provide pathogen removal, bulk organics removal, and/or trace organics removal of CECs. Ozone/BAC may be implemented as a pre-treatment step, post-treatment step, or as the major unit operation in the treatment train. Many considerations should be given to the use and location of ozone/BAC in a treatment train configuration based on source water quality and purified water goals. If membranes are needed for additional pathogen, bulk organics, trace organics, or total dissolved solids (TDS) removal, then ozone/BAC is often best implemented as a pre-treatment step prior to membrane applications. It is well documented that ozone/BAC reduces and transforms the bulk organics that are often responsible for fouling of membranes; thus, the membranes may be designed and operated for higher flux rates and lower pumping head requirements and more efficient cleaning cycles. If GAC is needed for additional bulk organics and/or trace organics removal, then ozone/BAC is best implemented as a pre-treatment prior to GAC. Ozone/BAC will reduce the bulk organics and trace organics load and extend the adsorptive capacity and life of the GAC to reduce the frequency of carbon change-outs. If UV or UV/AOP is needed for additional pathogen and/or trace organics removal, then ozone/BAC is best implemented as a pre-treatment step prior to UV. Ozone/BAC will significantly increase the UV transmittance (UVT) of water to reduce the power requirements for UV to achieve a target dose. Additionally, ozone/BAC may reduce the hydroxyl radical scavenging demand to reduce the UV and/or oxidant dose requirements for the AOP. In applications where the concentration of bulk organics in the wastewater effluent is low enough to meet the project-specific potable reuse goals, then ozone/BAC could be a post-treatment or final step in the treatment train; however, this appears to be atypical based on the current survey of ozone/BAC applications and potable reuse regulatory requirements.

4.2.6 Knowledge Gaps

Both ozone/BAC-based treatment trains and potable reuse are still relatively new, and there is a legitimate need to identify and address knowledge gaps and additional optimization needs with respect to public health while also synthesizing and compiling the abundance of information from past studies. While potable reuse regulations still do not exist in many countries, we do have expert guidance on pathogen log reduction compliance in places like California (CA) and Australia. However, a clear understanding of the impacts of CECs and TOC on downstream environmental buffers and drinking water treatment plants (DWTPs) is still evolving. Recent research including WRF 13-03, Water Environment and Reuse Foundation (WE&RF) 14-12, WE&RF 15-10, and WE&RF 15-11 demonstrate the importance of critical control points (CCPs), treatment redundancy and reliability, and process optimization in the context of purified water quality. Other studies such as WRF 03-14, WRF 06-06, and WRF 15-10 indicate that TOC, as a bulk organic parameter, is not necessarily significant from a public health perspective; however, the impact of TOC on DBP formation is a critical element of drinking water regulations (i.e., U.S. Environmental Protection Agency [EPA] Stage 2 D/DBP Rule). Ozone alone, behaving like an AOP in wastewater, has been consistently demonstrated as a best available technology for significantly reducing the concentration of most CECs in wastewater. The addition of BAF following ozone has been shown to mitigate ozone oxidation by-products including NDMA along with some CECs that are not well removed during ozonation (Hübner et al. 2014; Hübner, von Gunten, and Jekel 2015). However, there is a need for utilities and regulators to have a health-based context to develop performance criteria for ozone/BAC treatment trains so the focus can be narrowed down to the most relevant and challenging CECs. This includes guidance for using the best available monitoring and analytical techniques to measure and ensure reliable CEC removal (Miklos et al. 2019).

4.3 Health-Based Water Quality Considerations for Ozone/BAC

While the design and operation of ozone/BAC may offer many benefits for the performance of downstream unit operations (i.e., GAC, MF, RO, AOP, etc.) in a potable reuse scheme, health-based water quality considerations will often drive the implementation of ozone/BAC. A holistic evaluation of source water quality, wastewater treatment plant (WWTP) performance, pre-treatment and post-treatment unit operations around ozone/BAC, and purified water quality goals must be considered.

4.3.1 Pathogens

The ozone dose, and thus the design of the ozone system, is often dictated first and foremost by the degree of disinfection needed for the potable reuse treatment train. Pathogens represent an acute health hazard. Log reduction targets for reference pathogens are outlined in various water reuse regulations. A potable reuse scheme consisting of multiple treatment processes can be implemented in series to achieve the overall log reduction targets. Individual treatment processes may be given pathogen log reduction targets based on pathogen crediting frameworks. The application of ozone in the potable reuse scheme at Facility D has utilized the concentration multiplied by contact time (CT) concept used in drinking water applications for achieving 1-log removal of *Cryptosporidium*. However, this approach may not be broadly applicable or desirable in other applications (not targeting removal of *Cryptosporidium*) as the ozone decay in treated wastewater is typically very fast which limits the viability of the CT concept in ozone systems for potable reuse. In addition, there are concerns regarding bromate formation, when targeting any significant removal of *Cryptosporidium* (e.g., > 0.2-log). Thus, it is important to identify disinfection goals for the ozone system.

Like chlorine, ozone is a very powerful disinfectant for viruses. Unlike with chlorine as a disinfectant, removal of protozoa (*Giardia* and *Cryptosporidium*) and coliform bacteria is still feasible with ozone but increases ozone dose requirements considerably. This is especially highlighted if removal of *Cryptosporidium* is needed, which quickly becomes a determining factor in sizing the ozone system. Refer to Figure 4-1 that shows relative difference in Ozone CT versus log removal value considering water temperature of 20°C and EPA's CT Framework. To achieve 1-log removal of *Cryptosporidium,* an Ozone CT of 4 mg-min/L is needed. At this CT, the removal of *Giardia* and virus is far above the 6-log removal maximum that can be claimed for disinfection for any one pathogen in CA (SWRCB 2018a).

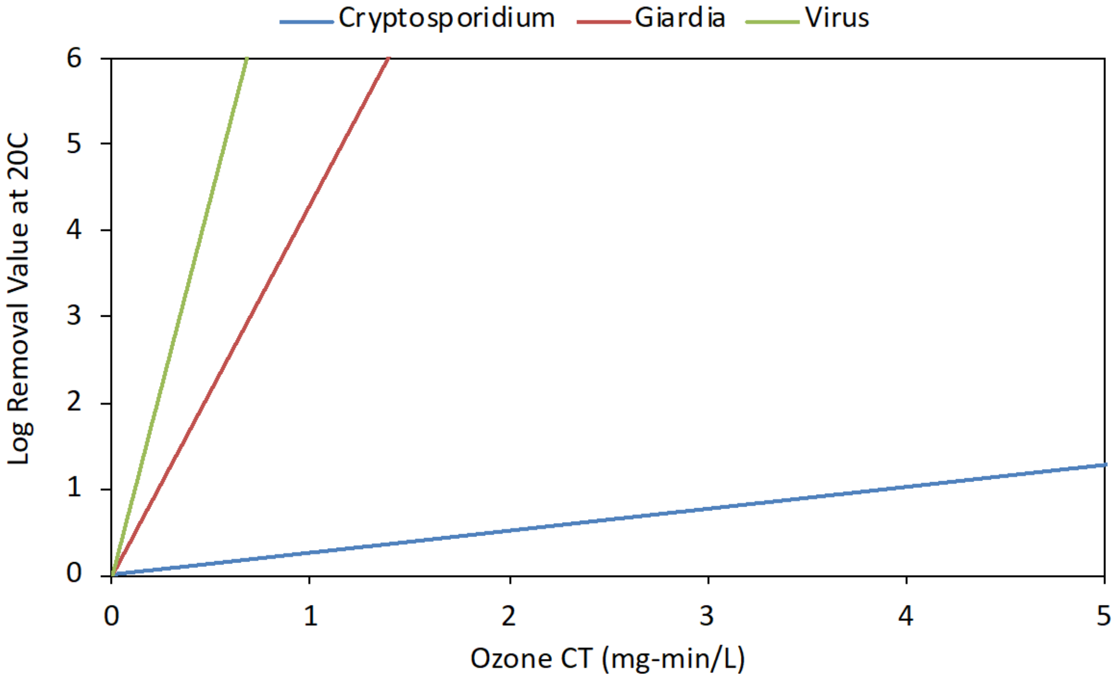


Figure 4-1. Pathogen Log Removal Value versus Required Ozone CT at 20°C.

On the other hand, if ozone disinfection was only needed for virus and *Giardia* a smaller CT with a still significant pathogen log removal can be achieved as illustrated by Figure 4-2. In this example, an Ozone CT to target 3-log removal of *Giardia* (0.7 mg-min/L at 20C), should also provide more than 6-log removal of virus. In this case, the removal of *Cryptosporidium* falls below the 0.5-log minimum and therefore would not be credited (at least for projects in CA).

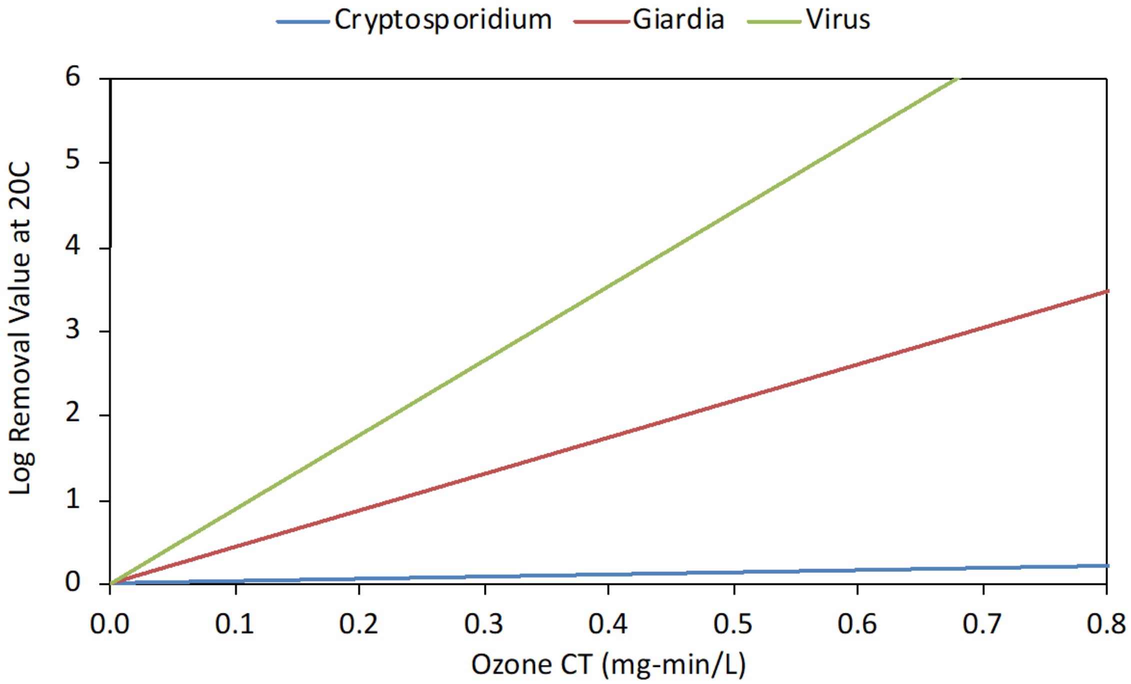


Figure 4-2. *Giardia* and Virus Log Removal Value versus Required Ozone CT at 20°C.

From the findings presented in Chapter 3, a balanced approach can be taken in selecting ozone dosing. A target O_3:TOC ratio of 0.6 was identified to provide significant removal of many CECs and keeping bromate formation to below maximum contaminant level (MCL) of 10 µg/L. This ratio is expected to mesh well with the target log removal of 6-log for virus and 3-log removal of *Giardia*. Figure 4-3 provides a plot of ozone decay and associated CT over the HRT in contactor based on the modeled data from one of the participating facilities, assuming TOC concentration of 7.0 mg/L and pH 7.0. The initial decay up to 1 min of hydraulic retention time (HRT) is not counted as typically this section of contactor is considered as part of dissolution zone and is only credited based on effluent residual leaving that zone. Under these conditions, the sizing of the ozone contactor can be reduced to 3 min. Note that this HRT should really be accounted for a baffling factor and transfer efficiency. These were assumed at 0.90 baffling factor, which can be readily achieved with pipeline contactors. Note that the applied dose of 4.5 mg/L was needed and equates to O_3:TOC ratio of 0.64, which is just above the recommended ratio to provide removal of CECs balanced by the bromate formation.

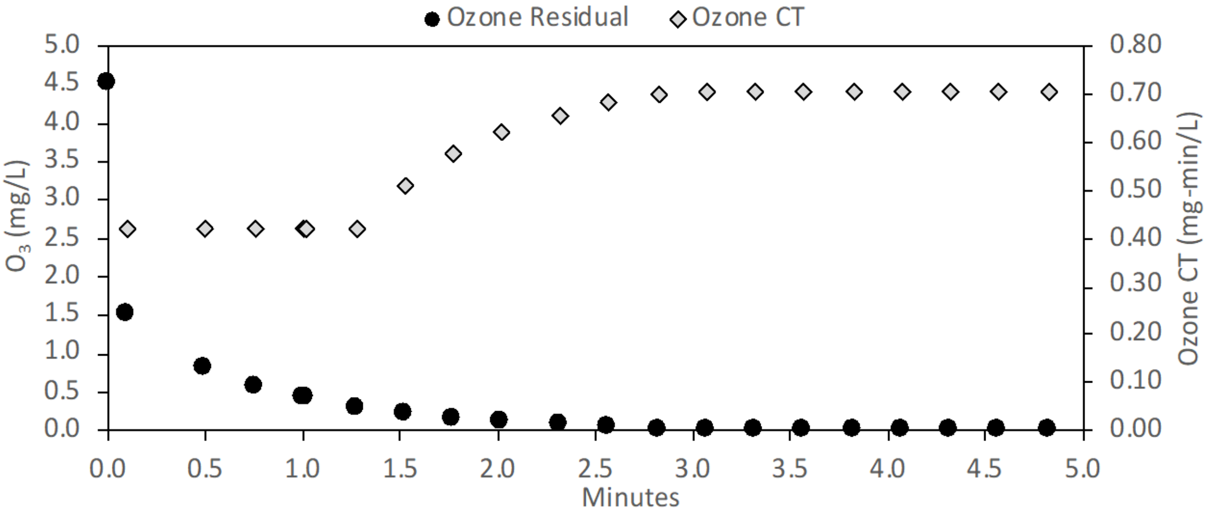


Figure 4-3. Ozone Decay and CT. Applied ozone dose of 4.5 mg/L, O_3:TOC =0.64, TOC = 7.0 mg/L, pH 7.0.

While additional research and bench or pilot-scale studies are needed to identify major drivers for pathogen inactivation during ozonation of treated wastewater including the impacts of turbidity and particle shielding, these efforts should address correlation of pathogens with specific water quality surrogates for practical implementation. As discussed in Chapter 3, the use of monitoring TOC concentration in ozone feed water allows for calculation of O_3:TOC ratio. The calculated O_3:TOC ratio should also be corrected for nitrite concentration and considered as an alternative surrogate parameter which has been shown with removal of CECs to correlate with pathogen removal in a potable reuse applications. Operating at a constant target O_3:TOC ratio can be used not only during the design stages but also as a control strategy for achieving target removals of CECs (that are amenable to oxidation) and pathogen removals. An O_3:TOC ratio of 0.6 goal should provide a synergistic overlap between achieving disinfection goals for virus and *Giardia*, CECs removal, and bromate formation control.

BAC's primary function is biological removal of organics, so it's not typically thought of providing any pathogen removal. However, BAC is also a filtration process, which contains granular media and underdrain, which is similar to conventional filters found in drinking water where filtration credits are granted for microbial removal. For typical conventional filtration at drinking water treatment plants, maximum log reduction values of 2.0, 2.5, and 2 are attainable for viruses, *Giardia* cysts, and *Cryptosporidium* oocysts. As such, additional studies are needed to determine whether pathogen removal is achieved and can be correlated to a removal of a surrogate parameter such as turbidity. Thus, in the future, BAC may potentially be claimed to provide additional pathogen removal protection to alleviate the need for higher O_3:TOC dosing.

4.3.2 Trace Organic Compounds

While ozone treatment alone has been shown to be effective in reducing trace organics and CECs at the Los Angeles Sanitation District's Donald C. Tillman Advanced Water Purification Facility (DCTAWPF) pilot (Trussell Technologies 2018) at an average ozone dose of 0.7 O_3:TOC ratio, the combination of ozone and BAC allows for more efficient biodegradation of bulk and trace organics.

Reungoat et al. (2012) investigated the use of ozone/BAC in three full-scale reclamation plants with O_3:TOC ratios reaching 0.6 to 0.8 mg O_3/mg DOC. They found the combination of chemical oxidation and biological filtration improved treated water effluent quality by removing more than 90% of trace organics. A higher ozone dose and an increased filtration empty bed contact time (EBCT) had a positive effect on the overall removal of DOC, trace organics, and non-specific toxicity, although the relationship was not linear. For example, overall removal increased when EBCT went from 9 to 18 minutes but did not change when it was increased to 45 minutes.

Reungoat et al. (2010) identified ozone dose as a key parameter for the performance of ozonation. An ozone dose 0.5 mg O_3/mg DOC was able to eliminate most of the micropollutants by more than 70%, where a dose of 0.1 mg O_3/mg DOC did not affect the concentration of micropollutants.

As previously mentioned, a calculated O_3:TOC ratio of 0.6 goal would optimize a high removal rate for the majority of CECs while achieving disinfection goals for virus and *Giardia*. Additional pre- or post-treatment measures should complement the ozone/BAC process when any regulated and recalcitrant CECs are present in the ozone influent or effluent and recalcitrant (i.e., 1,4-Dioxane, NDMA, Perfluorooctanoic acid [PFOA], Perfluorooctanesulfonic acid [PFOS]).

4.3.3 Bulk Organics

As summarized in Section 3.2.2.1, past studies demonstrate that the ozone/BAC process provides about 30% removal of bulk organics as measured by TOC. This percent removal appears to be somewhat independent of the concentration of influent TOC but may certainly be dependent upon the nature of the influent TOC. If there is a regulatory limit on TOC in the finished water and/or if the amount of TOC in the finished water combined with the use of chlorine adversely impacts regulated DBP formation (i.e., total trihalomethanes [TTHM] and sum of five common haloacetic acids [HAA5]) in the finished water, then additional treatment (i.e., RO or GAC) is needed to further reduce TOC of the purified water. Section 3.4.1.2 indicates a target goal of 2 mg/L TOC in the finished water should provide regulated DBP compliance. Alternatively, reducing the TOC in the wastewater effluent prior to ozone/BAC through higher sludge retention time (SRTs) and/or more effective biological wastewater treatment may provide numerous benefits to the ozone/BAC process and the overall advanced water treatment (AWT) train.

4.3.4 Disinfection Byproducts

As discussed in Section 4.3.3, TOC targets should be considered because TOC is a precursor to DBP formation for the chlorination of purified water. O_3:TOC ratio may need to be limited to minimize bromate formation; while the exact O_3:TOC ratio should be determined on a site-specific basis. However, bromate mitigation strategies are described in Section 3.4.1.1 that will allow operation at higher O_3:TOC ratios not solely limited by bromate formation. Aside from bromate formation concerns, O_3:TOC ratio may be used to optimize TOC removal by BAC.

4.3.5 Total Dissolved Solids

Ozone/BAC will not significantly impact the concentration of TDS in the secondary wastewater effluent. This is important if the TDS of the source water is high and/or TDS reduction is needed to meet purified water quality targets.

4.3.6 Summary of Health-Based Ozone/BAC Design Considerations.

A target O_3:TOC ratio of 0.6 would guarantee removal of many CECs, while also achieving disinfection goals for virus and *Giardia*. As mentioned in Chapter 3, recalcitrant CECs, such as per- and polyfluoroalkyl substances (PFAS) would need to be addressed by additional treatment processes such as GAC. Employing GAC should also provide additional TOC removal that would also decrease DBP precursor concentration. O_3:TOC ratio may be limited by bromate formation, but bromate formation is very site-specific and bromate mitigation strategies exist. Additional considerations for TDS and inorganics removal may be accomplished by addition of side-stream processes such as IX, NF, electrodialysis reversal (EDR), and RO.

4.4 Process Design of Ozone/BAC-Based Treatment Trains

This Section provides an overview on the typical factors for consideration during process design and building blocks of the ozone/BAC systems.

4.4.1 Feed Water Quality

As with any process design for water treatment, characterizing and quantifying the influent water quality is essential towards sizing an ozone/BAC process to meet performance goals. The type of secondary wastewater treatment will have a significant impact on the viability of the ozone/BAC process. Section 3.4.7.1 indicated that a survey of past projects revealed only one example of ozone/BAC being used on effluents with high ammonia levels (i.e., non-nitrified effluent), and this example demonstrated that the ozone/BAC process was significantly less effective with respect to TOC and NDMA removal. This poor performance could be attributed to the presence of excessive concentrations of ammonia and/or nitrites. Therefore, the use of ozone/BAC on non-nitrified effluents is not recommended. Furthermore, ammonia and/or nitrite bleed through should be evaluated closely and/or optimized for any ozone/BAC process with nitrified wastewater.

Free chlorine in the secondary or tertiary effluent should be quenched prior to ozone as it will react and directly consume ozone. While chloramines react slowly with ozone and provide bromate formation control, they should be quenched prior to BAC as they may kill beneficial microorganisms.

Historic variability in TOC, alkalinity, pH, nitrite, nitrate, ammonia, bromide should be documented and considered during design of an ozone system. At least 1 year, but preferably 5 years, of monitoring data should provide designers with needed information to account for average and maximum conditions on any water quality parameter.

4.4.2 Bench-Scale, Pilot-Scale, or Demonstration-Scale Testing

As with many unit operations and treatment trains, treatability testing (either bench-scale, pilot-scale, or demonstration-scale) of ozone/BAC may be very effective to understand source water quality impacts, demonstrate ability to meet performance goals, optimize the process, and establish basis of design requirements for full-scale implementation. The variability of the water quality of wastewater effluent from project to project and temporally within a project may pose treatment challenges that need to be address and quantified. Furthermore, the impact of pre-treatment steps on ozone/BAC and the impact of ozone/BAC on post-treatment steps will also be site-specific. While bench-scale testing is a very effective tool, care must be taken when extrapolating results to full-scale design that do not account for temporal variability.

Treatability testing or bench-scale testing can be a useful tool to inform pilot testing and full-scale design. Prior to the bench-scale testing, a literature assessment should be conducted to understand CEC removal under specific conditions. Literature review offers the experience of other studies in the same target contaminants of interest and provides a general sense of expected performance, often by binning into contaminant removal quartiles, or with central tendency models (Terry and Summers 2018). CEC removal by ozone can be tested by performing bench-scale ozonation experiments with sample wastewater collected at different times. To ozonate the samples, typically a stock ozone solution is prepared first. This is done by continuously adding ozone and oxygen gas into a chilled reactor until ozone concentration reaches a steady maximum (e.g., between 60 – 90 mg/L). Stock solution can be verified using colorimetric based methods such as Standard Method 4500-O_3 B. An aliquot of the stock solution is then added to a wastewater sample using a pipette. Addition of ozone stock solution causes dilution of the tested sample and needs to be accounted. Samples that receive a lower volume of the stock solution can be supplemented with laboratory reagent water to achieve the same level of dilution as the sample that that receives the highest applied ozone dose. In cases where dilution factor of greater than 1:2 is needed, direct ozonation of sample solution may be used. An example of the apparatus is provided in Figure 4-4.

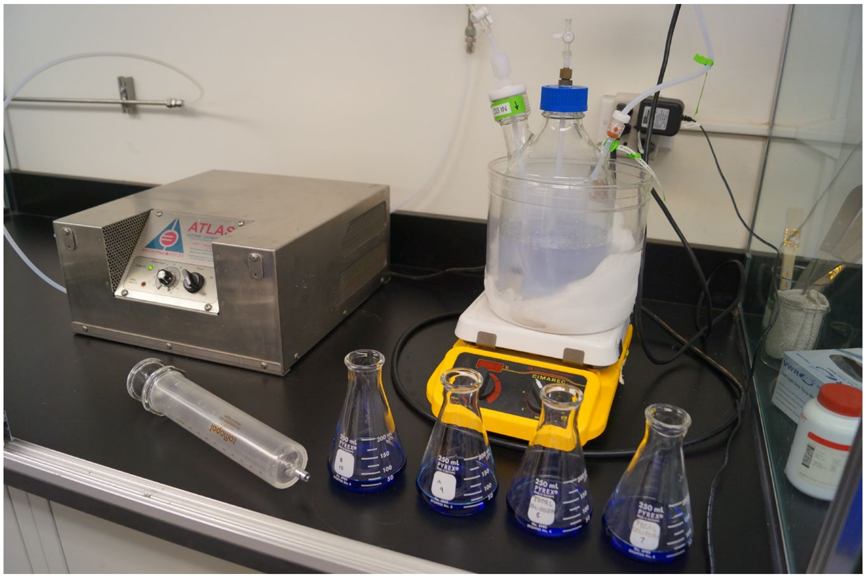


Figure 4-4. Bench-scale Ozone Apparatus.

During this testing, ozone demand and decay rate should be recorded at various O_3:TOC dosing conditions. Periodic ozonated and non-ozonated samples are sent out for measuring select target CECs. This information would serve two purposes: i) evaluate variability in feed water quality, including changes in ozone demand and decay as well as variability in CEC concentrations and ii) assess relative removal of target CECs and provide a measure of potential disinfection credit by calculating ozone CT for specific dosing conditions (see example of ozone decay curve in Figure 4-3).

To evaluate treatment performance under site-specific conditions, pilot-scale testing is almost always required or recommended for potable reuse projects. Figure 4-5 shows an example of a pilot-scale ozone system that includes a serpentine ozone contactor. Figure 4-6 provides an example of a pilot scale BAF system. While pilot- or demonstration-scale testing can be costly, time-consuming, and logistically difficult because all treatment processes must be continuously operated, it is often justified and provides critical information affecting design and demonstration of meeting water quality standards, needed for permitting. BAC filters do require an acclimation period of 2-3 months to reach steady-state performance (Terry and Summers 2018; Zearley and Summers 2012) which should be added into the testing duration.

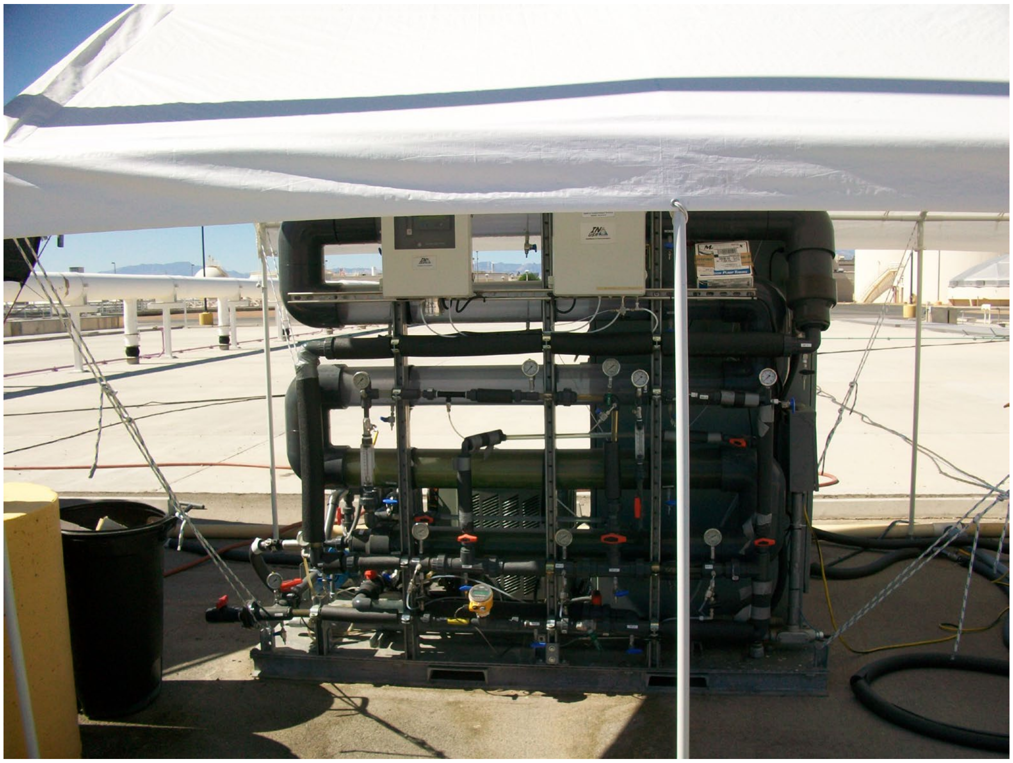


Figure 4-5. An Example Pilot-scale Ozone System with Built-in Serpentine Pipeline Contactor.

There are numerous advantages of operating a pilot-scale ozone/BAF system to evaluate performance over various conditions with the actual wastewater. Such testing would further the understanding of variability of feed water quality that can be more accurately accounted for in the design. For example, Figure 4-7 details a frequency distribution plot for some of the key parameters, such as TOC and pH that affect ozone demand and decay, and temperature throughout the year that impacts disinfection performance periodically collected over a full year.

Figure 4-6. An Example Pilot-scale BAF System.

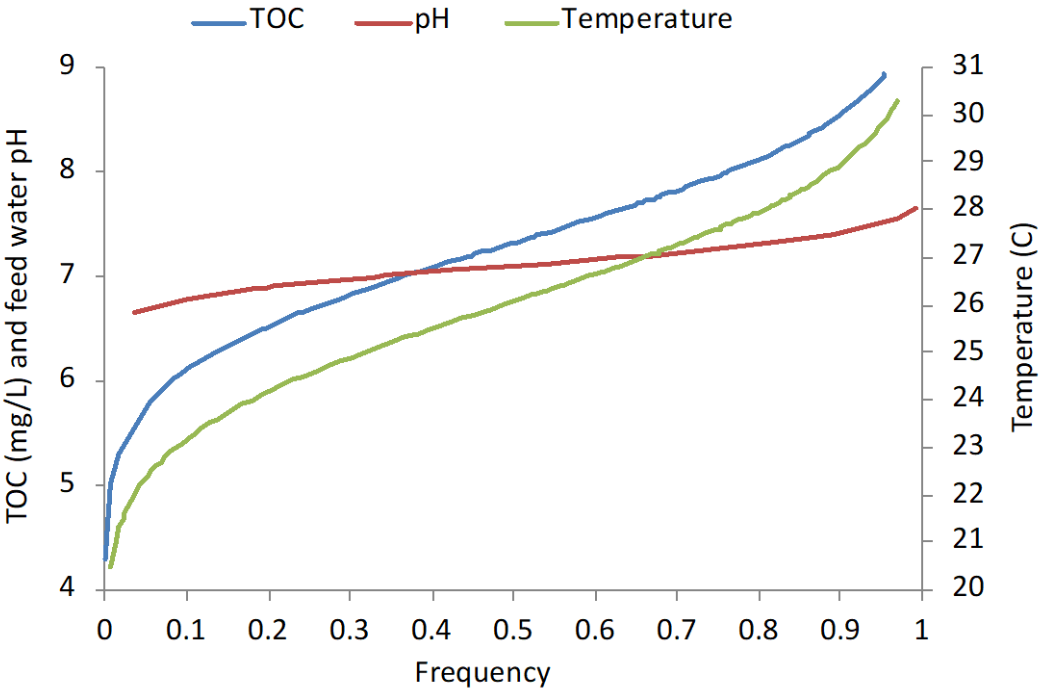


Figure 4-7. An Example Frequency Plot of Feed Water TOC Concentration, pH, and Temperature.

Figure 4-8 shows an example plot of collected ozone demand data over a range of different O_3:TOC ratios collected during specific days of operating a pilot-scale O_3 system. Collecting this type of data allows refinement of the target O_3:TOC dosing needed to achieve project goals in regard to CEC removals and disinfection. Additionally, it provides understanding of expected variability in ozone demand and establishing upper and lower control limits. In Figure 4-8, the upper control limits are determined using 2 standard deviations (95% percentile) to represent an expected normal variability in ozone dosing. Compiling this type of data can lead to substantial cost savings in the design of full-scale systems and ensure that the system has enough capacity to meet treatment objectives, even under challenging feed water quality conditions.

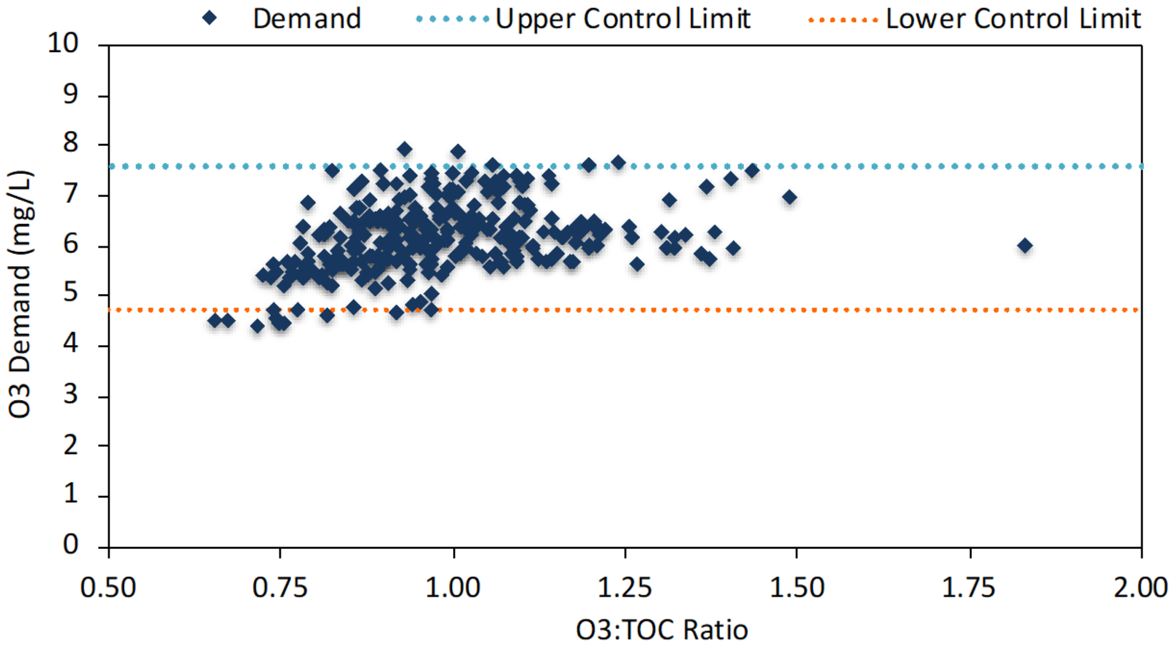


Figure 4-8. An Example Ozone Demand Data over Different O_3:TOC Dose Conditions (n = 360 over 4 years).

Scale-up methods that utilize BAF bench-scale data to predict pilot- and/or full-scale treatment performance and inform full-scale system design have been developed, validated, and used for many processes, such as adsorption by GAC and membrane filtration (Allgeier and Summers 1995; Crittenden et al. 1991), but not for BAF. Two major limitations of bench-scale biofiltration methods are the need for acclimated media and filter bed depth (Terry et al. 2019). A scale-up method was recently developed (Terry et al. 2019) that combines recirculating columns for the acclimation of attached biomass and single-pass flow-through methods that evaluate filter performance at EBCTs equivalent to those at the full-scale. Perhaps most importantly, results of this study showed that DOC removal in either drinking water or treated municipal wastewater was independent of filter hydraulic loading rates (HLRs), confirming that primary substrate utilization is not rate-limited by external mass transfer, but bioreactions at the media surface. This allows for the use of much lower HLRs and therefore shorter filter media depths at the bench scale to yield equivalent EBCTs to those at the full scale. This bench-scale method has been verified by demonstrating an average absolute difference of only 2 percent for DOC removal among 14 paired comparisons between bench- and pilot-scale results (Terry et al. 2019).

4.4.3 Treatment Train Design

Whether the ozone/BAC process is the heart of the treatment train (i.e., carbon-based advanced treatment [CBAT]) or is a pre-treatment step for an RO-based treatment train (i.e., FAT), potable reuse goals may only be achieved through a multiple-barrier approach that addresses all the source water quality challenges to meet the performance requirements for the project. Therefore, the design of the ozone/BAC process along with all other unit operations in the treatment train should be evaluated holistically.

4.4.3.1 Performance Goals

For potable reuse applications, performance goals are primarily driven by regulatory compliance and the need to protect public health and the environment. Meeting disinfection goals through pathogen log reductions is of primary importance due to the acute hazard. One of the first steps in any potable reuse design is to determine the overall pathogen log reduction credits needed to comply with regulatory requirements. This will often dictate not only what various unit operations may be needed, but also how much pathogen removal is needed from the ozone/BAC process; thus, impacting the design criteria and equipment sizing and selection. The next step is to determine the criteria for chemical compliance with respect to meeting the finished water regulatory compliance (i.e., MCLs, notification limits [NLs], environmental limits) which often represent chronic hazards. This will help assess if the unit operations required for meeting the pathogen log removal goals can also meet the chemical compliance targets, or if those systems need to be modified or supplemented with additional treatment steps. Finding that optimal design between meeting both pathogen and chemical criteria can be an iterative design exercise when also factoring in important considerations such as capital equipment cost, operating cost, footprint, operability, and constructability. Additional performance goals may now include non-regulated CEC removal as a proactive measure anticipating future regulations and ensuring public acceptance. Table 3-50 in Section 3.4.9 along with Section 3.4.8 provides an excellent summary of various viable unit processes and treatment trains for potable reuse applications.

4.4.3.2 Pre-Treatment

The most important design consideration for any potable reuse treatment train including CBAT or FAT is the source water quality and the upstream wastewater treatment. A high-quality and reliable secondary effluent water quality can allow the performance goals discussed in Section 4.4.3.1 to be more effectively and efficiently achieved. Nitrifying wastewater plants with higher SRTs not only reduce the concentration of CECs, but also may reduce the ozone dose of the ozone/BAC process, the organic fouling potential of membrane processes, and the scavenging demand for AOP. Tertiary treatment (especially through coagulation and/or filtration) prior to ozone/BAC may also offer water quality improvements to achieve pathogen goals and reduce TOC loading. This pretreatment should also impact the ozone dose requirement and provide some attenuation of feed water quality variability from upstream biological process, in addition to providing other benefits, such as manganese and phosphorus removal.

4.4.3.3 Post-Treatment

Post-treatment steps after ozone/BAC may not only be necessary to meet overall potable reuse performance goals, but they may also benefit significantly from the upstream performance of ozone/BAC. Section 3.4.8 details many of the unit operations that would typically be located downstream of ozone/BAC.

4.4.4 Reliability and Redundancy

Mechanical reliability and redundancy are typical considerations for any full-scale treatment design. These considerations are often driven by the uptime requirements for a project to meet production goals. Lower uptime requirements may allow for some reasonable frequency of equipment failure, downtime, and repair time. Higher uptime requirements may require fully redundant/standby pieces of equipment or process trains to immediately be brought online to maintain production. Additionally, ozone equipment is complex and includes several ancillary components such as feed gas conditioning and off-gas collection and destruct systems that can be more prone to maintenance, repairs, and failures. The ozone process is essential towards sustaining the biomass in the BAC. Therefore, in most cases, it is likely that ozone will require some degree of mechanical redundancy.

4.5 Equipment Selection and Sizing Basics for Ozone/BAC

This Section provides a general list and definition of considerations for equipment selection and sizing for ozone/BAC systems. Since many equipment aspects of an ozone/BAC system are common to drinking water and other water treatment applications and are not unique to potable reuse applications or CEC removal, detailed information regarding the design, engineering, and operation of ozone/BAC systems may be found elsewhere in many available documents, manuals, and books for these treatment processes. This Section does highlight equipment aspects that are important or may differ from commonly understood principles and practice of ozone and BAC systems and that are unique to the implementation of ozone/BAC for potable reuse.

4.5.1 Ozone

Table 4-1 summarizes key items for selection and sizing ozone equipment. In addition to the selection and sizing considerations, unique aspects for potable reuse are highlighted that are different than drinking water or non-potable reuse projects. Additional discussion of specific components on an ozone system are provided in the following sections.

Table 4-1. Summary of Ozone Equipment Selection and Sizing Considerations.

Equipment	Key Selection and Sizing Considerations	Unique Aspect for Potable Reuse
Ozone Generator	• Production capacity based on maximum ozone dose and flow rate • Turndown capability • Power and production efficiency at higher ozone concentrations	Higher ozone doses (relative to drinking water) may require ozone generator with ability to produce high ozone gas concentrations
Oxygen Source	• Liquid oxygen (LOX) vs On-Site Generation (i.e., VSA, PSA) • Capacity	None
Ozone Dissolution System	• Sidestream versus fine bubble diffusers	• See following page

Equipment	Key Selection and Sizing Considerations	Unique Aspect for Potable Reuse
Ozone Dissolution System (Continued)	- Mass transfer efficiency (MTE)	- Higher ozone doses (relative to drinking water) require an efficient ozone dissolution system to achieve reasonable MTE
Contactor	- Contact time - O_3:TOC ratio versus CT as a control method - Pipeline versus baffled over/under	- Ozone demand/decay is high for secondary wastewater effluents - Contact time requirement may be as low as 3 minutes for lower O_3:TOC ratios
Cooling Water	- Process water cooling versus chillers to cool closed loop generator cooling system - Temperature of process water if used for open loop cooling system - Directly related to ozone generator production efficiency	None
Degasification and Off-Gas Treatment	- Air release valve type and location - Foam mitigation and/or liquid trap	- High gas:liquid ratio and robust mixing may create foam in the secondary effluent that needs to be mitigated for a reliable off-gas treatment system
Residual Quenching	- Typically, not needed with high dissolved ozone decay rates in wastewater along with adequate contact time, but must be considered closely - May be required to quench free chlorine prior to ozone or chloramines prior to BAC - Sodium bisulfite (SBS) or calcium thiosulfate	- Free chlorine in secondary effluent will consume ozone - Chloramines in in secondary effluent will assist with bromate control but may inhibit biological activity in BAC - Impacts of over-quenching on BAC are not well understood

4.5.1.1 Ozone Dose, Production Rate, and Contact Time

Ozone dose is the most important design parameter for sizing an ozone system. Ozone dose, along with the flow rate through the ozone system, will determine the size of all the equipment from the oxygen source to the ozone generator to the off-gas ozone destruct system. As described in the previous Section, the optimal ozone dose and ozone dose range (minimum to maximum) is often best determined through site-specific treatability testing with representative water quality to achieve performance objectives. A design safety factor may often be applied to the ozone dose range depending on the confidence level of the dose determination and the uncertainty in the application (refer to Section 4.4.2 for discussion on importance of bench- and pilot-scale testing for design considerations). Ozone dose may be defined as an “applied,” the dose injected into the water, or “transferred,” the dose that is dissolved in the water. It important to use the applied ozone dose that accounts for MTE when sizing equipment such as the oxygen source or the ozone generator.

Ozone production rate is a product of the applied ozone dose and flow rate through the ozone system. Ozone production rate, typically in units of pounds per day, will determine the size of the ozone generator(s).

Contact time, or HRT, is the time available for the ozone to react with the water in an ozone contactor. HRT is defined as the volume of the ozone contactor divided by the flow rate through the contactor. While ozone contactors may have contact times as long as 20 minutes for drinking water applications with water matrices that have low ozone demand and decay, the contact times for ozone in reclaimed wastewater are often lower than 15 minutes and may be a low as 3 minutes.

4.5.1.2 Ozone Generator

Ozone generator capacity is typically based on the maximum applied dose and water flow. Many ozone generators can now efficiently produce higher ozone gas concentrations (i.e., >10%) which may be beneficial to reduce oxygen usage and improve ozone dissolution, but the power and cooling water requirements required to achieve high ozone gas concentrations at the production target should be weighed. From there considerations should be made to the number of generators to allow mechanical redundancy and process turndown in ozone production to minimum ozone dose at the same time running at optimal energy efficiency to reduce operating costs.

4.5.1.3 Oxygen/Feed Gas Source

Modern day ozone generators and ozone applications are more efficient when using oxygen gas, rather than air, as the feed gas source. Oxygen gas can be generated on site from compressed air using an on-site oxygen generator such pressure swing adsorption (PSA) or vacuum swing adsorption (VSA). Oxygen gas can also be supplied from LOX that is delivered and stored on-site. Many factors going into comparing LOX to on-site oxygen generators including footprint, maintenance requirements, fire code/permitting considerations, and, of course, cost. When using LOX, a method for adding nitrogen to the oxygen gas stream is a necessary requirement for most ozone generator technologies to optimize their efficiency.

4.5.1.4 Ozone Dissolution

Since MTE is an important design parameter that has significant economic impacts with respect to oxygen usage and ozone generator sizing, especially at the higher ozone doses in potable reuse applications, careful consideration should be given to designing and selecting the optimal ozone dissolution system for the application. The two common ozone dissolution systems are side stream injection and fine bubble diffusers. Broadly speaking, side stream injection will use more energy, but potentially require less maintenance and downtime than the fine bubble diffuser systems. The optimal fine bubble diffuser depth is between 18 and 22 ft which requires a more traditional baffled over/under or serpentine, tank-style contactor instead of a pipeline contactor.

4.5.1.5 Cooling Water

Current ozone generators are typically cooled using a closed loop cooling water system with controlled water chemistry. Heat is typically eliminated from the closed loop system through a heat exchanger using process water which flows through the other side of the heat exchanger and is returned to the process. The temperature of the generator cooling water has an impact on the ozone generator production efficiency, and, thus, becomes an important consideration when targeting higher ozone gas concentrations for the higher ozone dose potable reuse applications. With process water cooling, the temperature of the generator cooling water is limited to the process water temperature which can be high, especially in the summer, for reclaimed water. In addition, water quality must be sufficient to prevent fouling the heat exchanger, so often process water is sourced from a more highly treated location downstream (i.e., MF, RO, GAC) of the ozone/BAC process. Another option is to use a chiller to control the closed loop generator water temperature. Being able to achieve lower cooling water temperatures may reduce the cost and improve the performance of the ozone generator. While process water cooling is more common due to simplicity, lower cooling costs, and less maintenance, high reclaimed water temperatures for some locations may drive a more careful consideration of chillers when considering the ozone generator cost and performance.

4.5.1.6 Ozone Contactor and Degas

Depending on the treatment goals, contactor size will vary for applications requiring disinfection. Relatively longer contact times of 5-15 min may be needed, because a portion of contactor is used for the dissolution zone, where residual ozone is more difficult to monitor. Contactor configurations for disinfection include pipeline, over-under, serpentine, or a custom combination of over-under/serpentine. The baffling factor is an important parameter in applications requiring disinfection that utilize EPA’s framework for achieving pathogen removal. The baffling factor relates to the amount of short circuiting that occurs in a contactor and is multiplied by the HRT to calculate the disinfection time, T, in the CT method. Baffling factor can be estimated through computational fluid dynamics during design and determined empirically by performing a tracer test after construction is complete. For applications targeting CEC oxidation, the contact time required can be shorter, long enough for ozone residual to decay (e.g., 3-5 minutes) for O_3:TOC ratios below 1.0 and can be accomplished in a smaller contactor tank or pipeline. Pipeline contactors typically have the greatest hydraulic efficiency while reducing headloss which could be advantageous for the overall hydraulic profile and pumping requirements for a facility.

4.5.1.7 Off-Gas Handling and Destruct

Off-gas handling and destruction from the ozone contactor is essential to any ozone process to prevent release of fugitive ozone emissions from unreacted and undissolved ozone. Fugitive ozone emissions are harmful to human health and the environment. Due to the high ozone doses required for wastewater applications resulting in high levels of gas being added to the process, off-gas collection can be very challenging for potable reuse applications. These high levels of gas can create turbulence and foam (from the mixing of gas and secondary effluent) in the ozone contactor, especially pressurized pipeline contactors. A well-designed off-gas collection point (or multiple points) along with robust air release valves are needed to adequately release the gas and minimize adverse impacts from foam. Foam can cause the float assembly or orifice button in an air release valve to stick (thus, allowing water to pass through). For this reason, a liquid trap should be installed between the air release valves and the ozone destruct units to prevent water from reaching the catalyst and rendering it ineffective. A thoughtful off-gas design and maintenance program is essential for the application of ozone in reclaimed water to minimize downtime and equipment failures.

4.5.1.8 Quenching

Quenching of the dissolved ozone residual, if present, at the end of ozone contactor may be necessary to protect downstream equipment with incompatible materials of construction. For this reason, it is good design and operational practice to have a dissolved ozone residual quenching system installed and ready to operate either continuously or as needed. The ozone demand and decay of secondary wastewater effluent is typically high enough that dissolved ozone residual may be below detection limits at the end of the contactor depending on the ozone dose and contactor size. An oxidation-reduction potential (ORP) monitor is a simple and reliable instrument to detect ozone residual before and after quenching.

Chloramines are often present in secondary effluent to minimize biological growth and fouling of equipment and processes throughout an advanced treatment facility. Chloramines may have the added benefit of assisting with bromate control during the ozonation process. However, chloramines are not readily consumed during ozonation and their presence in the ozonate effluent could be harmful to the biology in the BAC. Chloramines should be quenched prior to BAC. Sodium bisulfite and calcium thiosulfate are common and effective quenching chemicals for both dissolved ozone and chloramines. Attention should be given to designing an accurate quenching system as overdosing of quenching chemicals is generally not cost effective. Furthermore, the impacts of overdosing a quenching agent on BAC performance are not well understood. A recent study showed excess sodium bisulfite may negatively impact BAF performance for removal of NDMA (Hogard et al. 2021).

4.5.2 Biologically Active Filter

The Section describes the design of a BAF system including an EBCT, HLR, and filter media. Specific design components discussed include vessel, underdrain, backwash, and instrumentation design considerations.

4.5.2.1 Empty Bed Contact Time and Hydraulic Loading Rate

Empty bed contact time is a critical design parameter. EBCT can be calculated according to Equation 4-1.

$$\mathrm{EBCT}=\frac{V_{bed}}{Q_i}=\frac{D_{bed}}{\mathrm{HLR}} \qquad \text{(Equation 4-1)}$$

where: V_{bed} = media bed volume

Q_i = influent flow rate

D_{bed} = media bed depth

HLR = hydraulic loading rate

A fundamental design parameter for BAF is the HLR or filter loading rate, which is defined as the volumetric flow rate divided by the cross-section area of the filter (Equation 4-2).

$$\text{HLR}=\frac{Q_i}{A_{bed}} \qquad \text{(Equation 4-2)}$$

where: A_{bed} = media bed volume

Q_i = influent flow rate

Based on nine full-scale and fifteen pilot-scale advanced treatment facilities surveyed through the questionnaire and literature review, BAF system HLRs range from 2 gpm/sf to 6 gpm/sf with a median value of 3 gpm/sf.

The correct EBCT should be selected based on the anticipated range of influent water quality and the desired water quality goals. The hydraulics of the facility can impact the media depth selected to fit within an existing profile to reduce pumping and therefore, the number of filters selected is based on achieving the desired EBCT. The BAF systems are then sized to achieve the desired EBCT at the peak design flow rate. In practice, the actual operating BAF EBCTs are often longer than the specified EBCTs due to operating flows being lower than the peak design flows. If EBCT is allowed to increase during lower flows, the HLR of the filter decreases, which can improve the degree of contaminant biodegradation and decrease the headloss through the bed.

Among a total of thirty-seven (37) demonstration-scale, pilot-scale, and full-scale advanced treatment facilities that were reviewed as a part of this study, the BAF EBCTs ranged from 6.5 to 32 minutes, with an average EBCT of 17 minutes and more than 50 percent of the facilities operating at 15 minutes or longer EBCTs (Sari et al. 2020). In comparison, BAF EBCTs in potable reuse applications are greater than those observed in drinking water applications, which range from 2 minutes to greater than 20 minutes and typically between 5 and 15 minutes (Brown et al. 2020).

In general, constituent removal increases with increasing BAF EBCT. However, there is a diminishing return with respect to increasing EBCT. Gifford, Selvy, and Gerrity (2018) developed a linear equation for the optimum EBCT of GAC-based biofilters depending on the O_3:TOC ratio. In general, the optimal EBCT calculated using this equation is lower than most facilities employing biofiltration.

A previous study showed there was no clear correlation between EBCT and DBP precursor removal (Arnold et al. 2018), although longer EBCT seemed to remove bulk organic matter to a greater extent (Arnold et al. 2018; Reungoat et al. 2012; Sundaram et al. 2020). Recalcitrant CECs, such as sucralose, Tris(2-carboxyethyl) phosphine (TCEP), PFOA, and N, N-diethyl-meta-toluamide (DEET), that were previously known as non-biodegradable by BAF treatment, were removed to a higher extent by extending the BAF EBCT to 20 minutes at three facilities employing ozone at dosages ranging from O_3:TOC ratio of 0.7 to 1.3 (Sari et al. 2020). The increase in recalcitrant CEC removal, however, was not solely attributed to the increase in EBCT, but also due to enhanced residual adsorption by the GAC filter media, even though it was already exhausted. This indicates the potential impacts of EBCT on CEC removal via both biodegradation and adsorption pathways in BAF systems.

It is also important to consider media replacement with EBCT selection. If GAC media is utilized and there is a planned replacement frequency to remove a CEC like PFAS, then it may be advantageous to extend the EBCT to provide increased exhaustion period of the GAC media and potentially save on O&M costs for downstream GAC, since it would reduce PFAS loading.

Based on a review of TOC and NDMA removal in this study, the minimum EBCT recommended is 10 minutes. TOC removal starts to plateau around an EBCT of 10 minutes, so increasing the EBCT further provides diminishing returns (Arnold et al. 2018; Bacaro et al. 2019). Bacaro et al. (2019) found there were diminishing returns for NDMA removal beyond an EBCT of 10 minutes; average NDMA removals at EBCTs of 10 and 20 minutes were ~90% and ~98%, corresponding to average effluent NDMA concentrations of ~30 ng/L and <10 ng/L, respectively. Higher EBCTs may be necessary for compounds that are generally more resistant to biodegradation than TOC or natural organic matter (NOM). Selecting an EBCT depends on the water quality goals, influent water characteristics, and desired O_3:TOC dosing to balance both capital and recurring costs of purchasing and replacing filter media.

Pilot or demonstrating testing should be conducted to target the EBCT and HLR necessary to achieve water quality goals for the system's source water and optimize design and operation of the biofilter.

4.5.2.2 Media Selection

Granular media selection is important when designing a BAF. Key components to consider include:

- Granular media profile (mono-media, dual-media, or tri-media)
- Type of media material (GAC, anthracite, or sand)
- Effective size
- Media depth

In potable reuse applications, filter media supports a biologically active layer to establish and colonize the filter media surface. The most common filter media are GAC, anthracite, and silica sand. Assessment of a total of 32 advanced treatment facilities indicated that more than 80% of facilities utilized GAC. Almost half of these facilities used GAC as the sole filter media, and a small number of facilities employed dual-media or tri-media filters consisting of GAC and sand, GAC and anthracite, or a combination of GAC, sand, and anthracite (Sari et al. 2020). Compared to biological drinking water treatment, where most filters are comprised of dual media with GAC or anthracite over sand (Brown et al. 2020), mono-media filters using GAC are more common in BAF systems for potable reuse applications.

Media selection is critical as it controls microbial growth and activity and therefore the biodegradation of CECs. GAC media has the benefit of providing a higher surface area, which promotes more biological activity on the filter media. In addition, GAC also removes dissolved constituents via media adsorption. A recent study showed that GAC had better microbial growth control compared to sand alone by promoting higher bacterial decay rates and hosting less bacterial cells despite of the similar cell concentrations in the GAC and sand filter effluents (Vignola et al. 2018). The microbial communities that developed on the surface of the GAC and sand media were statistically different, most likely due to differences in the intraparticle porosity, specific surface area, surface chemistry, and adsorption capacity between the two media types (Vignola et al. 2018).

Table 4-2 summarizes media size, uniformity coefficient, and other specifications of sand, anthracite, and GAC media. Specifications for granular media generally follow the AWWA Standard for Granular Filter Material, ANSI/AWWA B100-01, which is often used in drinking water biofiltration applications (Brown et al. 2020). Based on the questionnaire, for those advanced treatment facilities that employed GAC in BAF systems for potable reuse, the majority employed GAC that is made of bituminous coal with particle size ranging from 12×40 to 8×20 and more than half of the GAC was exhausted offsite using treated wastewater effluents, whereas a small number of facilities employed virgin GAC followed by an acclimation period ranging from three months up to 292 days (literature review). The filter configuration (gravity vs. pressure) also impacts the effective size of the media selected.

Table 4-2. Typical Granular Media Specifications.

Filter Material	Effective size (mm)	Uniformity Coefficient Maximum (UC)	Specific Gravity
Sand	0.4-0.8	1.3-1.4	2.6-2.7
Anthracite	0.8-2.0	1.3-1.7	1.4-1.8
GAC	0.42-2.4	1.3-2.4	1.2-1.7

Filter media depth is dependent on the EBCT and filter loading rate or existing hydraulic profile limitations. Typically, deep bed filters are used for economic reasons to reduce footprint requirements. Bed depths typically range between 3 and 16 feet. Initial clean-bed headloss and terminal headloss considerations are important when selecting filter media bed depths.

Another important consideration when thinking about filter media is the anticipated replacement timing which impacts the overall life-cycle cost of the treatment system. Advanced treatment facilities vary widely in approach to media replacement. Some surveyed facilities replace their GAC filter media every 2-3 years whereas others had not replaced their filter media following 27 years of operation, but instead topped off the media as it breaks down over time and is lost during backwashes. This highlights the need to not only consider replacing filter media based on adsorptive capacities, but also physical degradation over time.

4.5.2.3 Filter Configuration

Pressure vessels and gravity filters are used in potable reuse applications. The selection of the filter configuration will depend on the target capacity and the hydraulics of the treatment processes for the potable reuse facility. Most advanced treatment facilities using BAF have gravity-based systems (13 out of 14 facilities surveyed as a part of this project). Of the survey respondents, 75% of the gravity-based systems had downward flow.

4.5.2.4 Underdrains

The underdrains of a BAF are specific to the filter configuration (gravity vs. pressure). Given that the majority of advanced treatment facilities employ gravity-based systems, this Section focuses on design considerations for underdrains applicable to gravity-based systems in downflow mode. The three main types of underdrains used most often include nozzle underdrains, block underdrains, and gravel. Uniform flow and backwash distribution, durability, and cost are important factors in selecting an underdrain system. Underdrains can be susceptible to biofouling or scale formation. Pressure transmitters are useful to provide an early indicator of underdrain fouling and they should be installed to measure headloss across individual filters.

4.5.2.5 Backwashing Regime

The specific backwashing regime employed is related to the density of the filter media and the desired bed expansion. Similar to drinking water facilities with biofiltration, the majority of AWT facilities utilize air scour and an unchlorinated backwash. A typical backwash regime consists of air scour, simultaneous air scour/backwash, low-rate backwash, high-rate backwash, then followed by another low-rate backwash and filter-to-waste as needed.

Additional backwashing optimization to avoid elevated headloss can be necessary in reuse applications. Disinfectants can be utilized in the backwash water for biomass control and to reduce high clean-bed headloss conditions. It is recommended to design the backwash system with injection ports for the flexibility to dose chlorine or oxidants to the backwash.

Filter bumping can be helpful to reduce air binding given the high levels of DO following ozonation (Aquino 2017). Gas binding accumulation in the filter media can hinder water flow through the filter, potentially leading to a decrease in filter efficiency. A hydraulic bump cycles every 4 hours was shown to be beneficial in eliminating gas binding in the biofilters following ozonation (Trussell et al. 2016).

The frequency of backwashes ranges in AWT applications. Backwash frequencies range from daily to monthly. Detachment and particle breakthrough in the BAF filtrate does occur with operation of an ozone/BAF system targeting bulk organic removal. Biomass sloughing is attributed to microbial community overgrowth and/or die-off. Optimization of filter backwashing can curb excessive accumulation of solids and/or biological growth (extracellular polymeric substance [EPS]), but also to ensure that there is sufficient biological activity for contaminant degradation. Further study on the effect of different backwashing regimes on BAF performance in relation to CEC removal is still currently warranted.

4.5.2.6 Key Instrumentation

The key instrumentation for BAC is summarized in Table 4-3. Online headloss monitoring across the BAC is most important to inform when a backwash is needed. Alternatively, BAC filters can operate on a timer for a certain number of run hours before a backwash is initiated. Filter effluent turbidimeters and particle counters can recognize bacterial sloughing events and can be needed to demonstrate log removals of pathogens. Online TOC and UV_{254} analyzers can be used as indicators for CEC removal.

Table 4-3. Online Instrumentation.

Monitoring Parameter	Location(s)	Method	Purpose
Headloss	Influent/Effluent	Online	Inform if backwash is needed
Turbidimeter	Effluent	Online	Performance and potential log removal credits
Particle Counts	Effluent	Online	Recognize sloughing events
TOC	Influent/Combined Effluent	Online/Grab	Surrogate for CEC removal and may be needed for regulatory reasons
UV_{254}	Influent/Combined Effluent	Online/Grab	Surrogate for CEC removal
Temperature	Influent or Effluent	Online/Grab	Affects biological growth and activity

4.5.3 Integration of Ozone with BAC

4.5.3.1 Process Design Considerations

Table 4-4 summarizes the key process design criteria for implementation of ozone/BAC in potable reuse for CEC removal.

Table 4-4. Summary of Key Ozone/BAC Process Design Criteria for CEC Removal.

Design Parameter	Target Design Value	Additional Considerations
O_3:TOC Ratio	≥ 0.6	May be lower based on bromate formation or higher based on treatment goals (i.e., disinfection, TOC removal, additional CEC removal)
Transferred Ozone Dose	= O_3:TOC x TOC + Nitrite Demand	Use reasonable TOC and nitrite values (i.e., median, 90th percentile) based on historical data
Applied Ozone Dose	= Transferred Ozone Dose/MTE	Use this value to calculate ozone generator production demand
Contactor HRT	~3 minutes	• Confirm with ozone demand/decay testing on representative sample of water • May be higher based on treatment goals (i.e., CT for disinfection)
EBCT	10-15 minutes	Confirm with treatability testing vs treatment goals, may be optimized against O_3:TOC ratio
Hydraulic Loading Rate	2-6 gpm/sf	Optimize to filter design (i.e., headloss, constructability, footprint)

4.5.3.2 Controls Integration

While an ozone system and a BAC system may be designed, procured, constructed, and even operated as separate processes, the performance of ozone/BAC with respect to bulk and trace organics removal is very synergistic and interdependent. As discussed elsewhere in this chapter, instrumentation and controls integration between the ozone and BAC systems is beneficial towards monitoring and control strategies along with assessing key performance indicators (KPIs). A combined control system document that includes both systems and any shared instrumentation should enable easier implementation by the system integrator and streamline maintenance and spare parts requirements. Therefore, attention should be given during the design phase to ensure that compatible, and even identical, hardware and software are specified for instrumentation and controls.

4.5.3.3 Single Supplier Systems

Some major water treatment equipment suppliers manufacture and sell both ozone and filtration systems. Purchasing an ozone/BAC process from a single supplier may be advantageous when considering contracting, performance guarantees, and equipment warranties along with streamlining design, construction, startup, and long-term service support.

4.6 Operation of Ozone/BAC Systems

As ozone consists of relatively complex equipment and BAC is a sensitive biological process, care and attention must be given to ensure the operations of a robust and reliable ozone/BAC process.

4.6.1 Key Performance Indicators

Key performance indicators for the ozone/BAC process include TOC removal, bromate formation, NDMA removal, and backwash frequency. KPIs may be based on readily available data (i.e., online monitoring) and can be used by operations to assess the long-term performance of the ozone/BAC process and to make decisions on troubleshooting and optimization needs. KPIs are often tracked through a historian to evaluate changes over time.

4.6.1.1 TOC Removal

TOC removal, measured as a percentage, is an excellent KPI for evaluating the synergistic ozone/BAC performance. Consistent TOC removal indicates a well-performing and healthy ozone/BAC system. Inconsistent or decreasing TOC removal may indicate that troubleshooting and optimization are needed. Upsets or declining performance of the biological wastewater treatment process may increase or change the nature of the TOC, impacting performance. Excessive ammonia could impact the health of the biomass towards bulk and trace organics removal. Nitrite, if not accounted for in the ozone dosing control, consumes ozone.

4.6.1.2 Bromate Formation

Bromate formation, measured as an absolute value, is an excellent KPI for evaluating the ozone dose. Increasing bromate formation may indicate an increase in influent bromide levels, a change in influent water quality parameters such as chloramines or other parameters that impact bromate formation reaction kinetics, a decrease in ozone demand, or an issue with ozone dissolution.

4.6.1.3 NDMA Removal

NDMA removal, measured as a percentage, is an excellent KPI for evaluating BAC performance. Consistent NDMA removal across the BAC indicates a well-performing and healthy ozone/BAC system. Inconsistent or decreasing net NDMA removal may indicate issues with changing influent water quality resulting in more NDMA or NDMA precursors in the secondary wastewater effluent, excessive ozone dosing, or an unhealthy biomass and poorly performing BAC. NDMA, unlike TOC, is unique in that it may be formed by ozone (as an oxidation byproduct [OBP]) and then removed by BAC, so it is generally recommended to profile the NDMA formation and removal across the ozone/BAC process.

4.6.1.4 Backwash Frequency

Backwash frequency, measured in days or run hours, as triggered by a headloss target is an excellent KPI for evaluating the performance of the BAC. Consistent and not too frequent backwashing frequency indicates a healthy BAC system. Excessive backwashing frequency may disturb the healthy biomass of the BAC. If backwashing frequency were to increase, numerous issues could be the cause including a change in influent water quality as indicated by total suspended solids (TSS) or turbidity, change in inorganics such as calcium or alkalinity that could form precipitates on the BAC, or a poor underdrain/backwashing system.

4.6.1.5 Clean-Bed Headloss

Clean-bed headloss, which is the headloss following a backwash is another useful KPI to monitor long-term performance of the BAC filters. An ineffective backwashing regimen may result in accumulation of media fines and particulates and increase in the clean-bed headloss. This would lead to a decrease in filter run time and necessitate increase in backwash frequency. The recommended approach to mitigate increase in clean-bed headloss is to periodically check that the backwashing achieves 20-30% media expansion. In addition, it is recommended to check the amount of fines by stratifying media during a modified backwash regimen, where flow is gradually decreased. This test coupled together to measure the depth of media should be performed approximately every 2-3 years to monitor losses of media due to attrition and accumulation of unwanted fines that increase headloss.

4.6.2 Startup, Commissioning, and Validation

4.6.2.1 Initial Startup of Ozone/BAC with Fresh GAC

The startup and commissioning of an ozone/BAC system has many similarities to the startup and commissioning of any ozone and granular media filter or GAC system. One of the key differences is that a BAC system must become biologically acclimated before it can achieve steady-state performance. Typically, a BAC system is loaded with fresh GAC (virgin or reactivated) upon initial startup. Therefore, the primary treatment mechanism upon initial startup of an ozone/BAC system is adsorption. Biological acclimation of the GAC occurs naturally over time with DO, nutrients, bioavailable organic carbon, and microorganisms being supplied from the ozonated wastewater effluent. As the GAC begins to exhaust its adsorptive capacity and as a biofilm forms, the BAC system continues to transition its treatment mechanism from adsorption to biodegradation until nearly all adsorptive capacity is exhausted and the microbial community is fully established. Section 3.2.2.3 describes that the plateauing of TOC removal over time during the startup period indicates a steady-state condition where the dominant bulk organic removal mechanism has shifted from adsorption to biodegradation. Thus, TOC removal may be considered a good performance indicator for BAC acclimation during startup. Section 3.5.3.7 describes that acclimation period of fresh GAC to achieve steady-state TOC removal may be 3 to 6 months.

This transitioning dynamic of acclimation during startup will lead to some variable performance in terms of headloss, backwashing requirements, and effluent water quality until steady-state conditions are achieved. Headloss will continue to increase from an initial lower value with a clean-bed to a higher value accounted for the biofilm on the media. Backwashing may occur less frequently during this transitional period due to this lower headloss. Bulk and trace organic constituents that are more adsorptive will be more readily removed initially until the BAC system adsorptive capacity is exhausted and the biology is fully acclimated. Typically, a higher rate of TOC removal will be seen while the BAC system is acclimating until its adsorptive capacity is exhausted. This temporary period of higher adsorption capacity and bulk organics removal may be beneficial to downstream unit operations and meeting finished water purity goals during startup; however, some CECs that are weakly adsorbed and depend on biodegradation (i.e., NDMA) to be removed may be present at higher concentrations in the Ozone/BAC effluent during startup until acclimation is complete (Sundaram et al 2020). In the case of a CEC like NDMA that often has a regulatory limit (i.e., California NL) and is both an ozone OBP and recalcitrant to adsorption, the ozone dose may need to be limited and/or downstream UV photolysis may need to be sized and operated to treat higher concentrations of NDMA during the acclimation period relative to steady-state. Alternatively, and perhaps less desirable, the Ozone/BAC effluent can be operated at a minimum flow rate while the off-specification water is diverted and returned to the WWTP until regulatory compliance is met.

Online TOC analyzers are readily available and useful in potable reuse schemes, or most utilities and commercial labs can readily measure TOC in grab samples. The use of online TOC analyzers in the influent and effluent of the ozone/BAC process enables both the use of O_3:TOC as a control strategy for ozonation and ΔTOC as a performance surrogate for BAC during startup and long-term operation.

Once the BAC system reaches steady-state performance, validation of the performance of the ozone/BAC system at the end of commissioning may be conducted to prove its performance in a type of challenge test. Validation testing is often conducted by spiking the water with a target compound to measure its removal at various operating conditions. This may demonstrate a regulatory requirement, project contractual requirement, and/or an optimized operating condition. Section 3.3.2.1 describes that aldehydes are both poorly oxidized and often formed as ozone OBPs while also being biodegradable and not readily adsorbed with greater than 50% removal through BAC. Thus, aldehydes may be a good and economical candidate as indicator CECs with similar chemical properties for a challenge test to demonstrate the performance of a steady-state BAC process. The draft direct potable reuse (DPR) regulations in California currently propose that an ozone/BAC system be validated with formaldehyde (SWRCB 2021b).

4.6.2.2 Subsequent Startups of Ozone/BAC After Extended Shutdowns

The BAC is a biological process that is dependent upon the upstream ozonated wastewater effluent for the microbial community to survive and thrive. Once the Ozone/BAC process has been sorptively exhausted and biologically acclimated, it should be operated continuously as much as possible to maximize uptime. Design and operation considerations to maximize uptime may include increasing the reliability and redundancy of the BAC equipment along with upstream unit operations including ozone, secondary biological treatment process, and pumps and ancillary equipment that are critical to operations.

Brief shutdowns (i.e., hours) often occur at treatment facilities due to power outages or common equipment failures and maintenance requirements. If these brief shutdowns cause the BAC to cease operation, then it is not anticipated that the microbial community will be significantly impacted. Furthermore, the BAC process should be able to quickly produce water of a similar quality prior to shutdown after being brought back online. WRF 11-02 and WRF 14-12 demonstrated that the BAC process is very robust and could even quickly return to normal performance (with respect to TOC removal) after shutdowns that were more extended (multiple days). The long-term effects of shutdowns that are weeks or months long are not completely known, but extended periods are suspected to have an adverse impact on the microbial community and BAC performance; therefore, all efforts should be made to avoid extended shutdowns of the BAC and/or contingency plans should be put in place for these scenarios.

4.6.3 Control Strategies

The two most common monitoring and control strategies for performance of ozone/BAC systems are focused on the real-time monitoring and control of the ozonation process. BAC systems are typically monitored in real time or through grab samples while being passively controlled (i.e., ensuring EBCT setpoint by not exceeding a maximum flow rate). The selected monitoring and control strategy may be determined by the drivers for the ozonation process—pathogen removal, bulk organics removal, trace organics removal, or bromate control.

4.6.3.1 Ozone

Controlling to a constant O_3:TOC ratio setpoint using a feedforward control loop is a relatively easy-to-implement control strategy. A TOC analyzer is needed on the influent to the ozonation process. As discussed in previous chapters, O_3:TOC ratio correlates to CEC removal and bromate control while its use for pathogen crediting, even though studies indicate a good correlation between O_3:TOC ratio and MS2 bacteriophage inactivation (a surrogate for virus), has not yet been approved in a regulatory framework. Since the TOC in treated wastewater effluent often changes diurnally and seasonally, O_3:TOC ratio serves to adjust the ozone dose towards the changing TOC levels which may represent a significant portion of the ozone demand of the water. If nitrite is present in the treated wastewater effluent, an online nitrite analyzer should also be used at the influent to the ozonation process to correct the ozone dose calculated from the O_3:TOC ratio to account for the ozone demand of nitrite.

Controlling to a CT is the most common method for obtaining pathogen disinfection credit using the EPA disinfection framework for virus, *Giardia*, and *Cryptosporidium*. The control algorithm for CT is more complex as it relies on temperature-dependent equations and often multiple dissolved ozone readings in the ozone contactors to calculate an integrated CT. Furthermore, the CT approach is a feedback control loop which may create some response lag that needs to be accounted for in the algorithm. An additional challenge with CT approach is the reliability of dissolved ozone analyzers. Operational experience has shown that dissolved ozone analyzers need to be routinely calibrated and cleaned in a wastewater matrix much more so than in a drinking water matrix. If O&M staff do not consistently monitor the performance of the dissolved analyzers, then their use in any control strategy may be challenging for ozone/BAC in potable reuse applications.

Whether O_3:TOC ratio or CT is selected as the ozone control method for the application, measuring changes in UV_{254} across the ozonation process provide an additional layer of monitoring to confirm sufficient ozone dose is being transferred for CEC and pathogen removal.

4.6.3.2 BAC

BAC is both a biological and filtration process. The control strategies of a BAC are very similar to that of a granular media filter with backwashing being the main action triggered by changes in headloss, a timer, or excessive effluent turbidity. Low- and high-rate backwashing schemes along with air scouring for gravity filters appear to have similar effectiveness to BAC as with granular media filters. Since the BAC process is typically downstream of high quality (clarified or filtered) secondary effluent, the BAC should have a reduced solids loading rate as compared to a typical tertiary filter and as a result function primarily to treat influent water biologically and not be used as conventional filter. Under this scenario, the majority of the headloss in the BAC is due to air-binding (especially if BAC is treating influent immediately after ozonation), excessive buildup of biomass and/or carbon media fines. While little evidence is available regarding headloss in BAC filters and excessive biomass, air-binding and build-up of fines have been reported by participants in this project. Section 3.5.3.6 indicates that most facilities backwash the BAC filter once per week, which is much less frequent that a typical tertiary filter for solids removal.

Another unique aspect of the controls of a BAC system downstream of ozonation compared to a typical granular media filter is the presence of excessive amounts of DO on the media. Since the ozonated effluent is supersaturated with DO, gas binding of the media may occur as evidenced by premature increases in headloss across the BAC filter bed. Section 3.5.3.6 reports that multiple projects have successfully implemented a hydraulic bump step to mitigate the effects of gas binding. The hydraulic bump is a short low flow backwash for several seconds or minutes occurring every few hours during the filter run. Another option is to implement a short rest period, where influent flow is diverted to other filters and allows some of the trapped gas to evolute out. Therefore, it is recommended that any BAC control scheme include programming to add such capability to control headloss due to air binding to ensure good flow distribution, to minimize backwash waste, and to help maintain a healthy BAC.

The practical online instrumentation to directly monitor and control the microbial community in a BAC does not exist today. The most pragmatic online surrogates are ensuring the EBCT via a maximum flow rate setpoint and monitoring ΔTOC, as discussed previously.

“Offline” biological monitoring tools do exist that could potentially be used to make operational changes to the BAC. To understand biological activity, the biological monitoring parameters shown in Table 4-5 can be used to assess CEC removal from biodegradation compared to chemical/physical processes. Biofilm formation rate was found to be the most useful biological monitoring tool for routine use in WRF 4620 (Hooper et al. 2019). The biofilm formation rate measures adenosine triphosphate (ATP) from a coupon installed on a pipe loop collecting BAF effluent. Other biological monitoring tools (e.g., EPS, microbial community characterization, and enzyme activity) are not recommended for routine monitoring, but can be useful during startup (e.g., acclimation/reacclimation), optimization, troubleshooting, and/or research studies. Utilities should consider collecting baseline samples so that relative biological abundance can be compared during troubleshooting.

Table 4-5. Recommended Monitoring for Biological Parameters.

Parameter	Sampling Location	Description	Performance Indication
ATP	Filter media	ATP measures the cellular energy present in the biofilm. It includes measurements from both live and dead cells.	Indicates biological activity and is more of a qualitative measurement than quantitative measurement.
Biofilm formation rate	Effluent coupon racks	A coupon is installed in a pipe loop for a set duration of time and ATP is measured from the coupon.	A method to reduce variability of measuring ATP in filter media or aqueous samples (influent/effluent) that is not dependent on when the sample is taken related to filter run time
Microbial community structure	Filter media	16S rRNA sequencing is used to identify specific class, family, or genus-level microorganisms.	Provides information on “who” is present in the system. Requires the use of molecular microbial methods; typically performed at specialty labs and universities.
EPS	Filter media	Proteins and polysaccharides secreted by bacteria in biofilms	Possible indicator of hydraulic performance issues
Enzyme activity	Filter media	A measurement of phosphatase or esterase enzyme activity	Indicates effective activity of the filter biology (Keithley and Kirisits 2019)

Microbial community analysis using 16S rRNA sequencing and metagenomics provides class, family, or genus-level identification to characterize the microbial community diversity and identify organisms with specific functional capabilities. These data can demonstrate how operational changes impact the microbial community present and contaminant degradation.

Microbial community analysis is typically conducted at universities or specialty laboratories. Advancements in metagenomics will likely make microbial community analysis more common in our industry in the future.

4.6.4 Maintenance and Troubleshooting

As with any ozone system, a preventative and routine maintenance program should be implemented to maximize both performance and uptime. While the maintenance requirements for ozone system are generally well documented and understood, Section 3.5.1.1 provides a summary of the failure rate and downtime for ozone system at a potable reuse facility that includes common issues such as electrical/power, gas leaks, and off-gas ozone catalyst changeouts.

The BAC system would have similar maintenance requirements to any granular media filter or GAC system and care should be given to periodically topping off the carbon bed with new GAC to account for annual losses from attrition and backwashing. A unique aspect of a BAC filter relative to a GAC filter is that it is not desirable to replace the media. Section 3.5.3.8 indicates that approximately 3% of the media bed may need to be replaced each year.

For potable reuse applications, routine verification and calibration of online instrumentation is critical to promote both optimal performance and public health protection. Wastewater effluent poses many challenges to online instrumentation due to fouling of sensors, drifting of accuracy, and an ever-changing water quality matrix. Based on the aforementioned KPIs and monitoring and control strategies, maintaining the accuracy of online analyzers such as TOC, nitrite, UVT, and dissolved ozone residual for the ozone/BAC process is essential. Practitioners of ozone/BAC for potable reuse should invest in the personnel and training to proactively maintain all online instrumentation as best as possible.

CHAPTER 5

Public Outreach

5.1 Frequently Asked Questions

Communication and outreach tools are essential for developing and implementing a potable reuse program. FAQs may assist agencies with expediting the implementation of safe and sustainable ozone/BAF treatment trains in potable reuse applications.

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Frequently Asked Questions Related to CEC Removal by Ozone/BAC Treatment in Potable Reuse Applications

1. What is the fate of CECs through ozone and ozone with biological activated carbon based treatment, and how does it correlate to performance goals from real-world data?

Ozone/BAC (which includes biological active carbon instead of typical granular activated carbon) provides an excellent barrier to many types of CECs with removals of greater than 50%. Some CECs are resistant to both oxidation and biodegradation, such as synthetic organic compounds (e.g. flame retardants, contrast agents, etc.) but do not typically pose a significant health risk. Further treatment may be necessary to meet health-based goals for more recalcitrant compounds, such as PFAS and NMOR.

2. What are the advantages and disadvantages of various Ozone/BAC-based treatment train configurations?

Advantages of Ozone/BAC-based treatment train configurations include less residual waste (i.e. no brine disposal) and often enhanced treatment redundancy, and overall lower cost.

Disadvantages of Ozone/BAC-based treatment train configurations include lack of TDS and nutrient removal (if source water quality is poor) and higher TOC in effluent. If high TOC in the effluent is an issue (e.g. DBP formation potential is too high to meet drinking water standards due to poor source water quality and/or low product TOC performance targets), then it may be mitigated through the use of GAC and/or SAT after Ozone/BAC.

3. Is Ozone/BAC suitable for potable reuse (i.e. surface water augmentation, groundwater recharge, raw water augmentation)?

Yes. Ozone/BAC is a suitable advanced treatment process for all potable reuse applications. Whether it is selected and the degree to which additional treatment is implemented is highly dependent upon site-specific considerations including source water quality, regulations, cost, and residual management options.

4. Does Ozone/BAC do a better job against the bulk of CECs than RO?

Both Ozone/BAC and RO are considered best available technologies for addressing a majority of CECs. Reverse osmosis is more effective for removal of recalcitrant organics such as PFAS, whereas Ozone/BAC is not. On the other hand, Ozone/BAC provides a barrier for small molecular weight organics such as acetone, formaldehyde, and NDMA and is more effective at removing these types of compounds than RO. In the California context where regulations are more prescriptive, Ozone/BAC can be used together with RO to improve the performance of the overall treatment train, increase treatment redundancy, and achieve higher pathogen log removal needed for more direct forms of potable reuse. In other cases, such as One Water Nevada or Hampton Roads Sanitation District in Virginia, both of which include a relatively large environmental buffer, it may suffice to rely solely on CBAT to accomplish treatment goals and to meet all drinking water standards.

5. Are there standard process design criteria specific to Ozone/BAC for potable reuse, including unique equipment characteristics?

The equipment used for ozone and BAC is the same as what has been traditionally used in water treatment for decades. Due to higher ozone doses used on wastewater effluent compared to drinking water, ozone injection and dissolution must be given careful consideration to ensure high mass transfer efficiency. On the other hand, the high ozone decay rate in wastewater effluent compared to drinking water often allows for much smaller ozone contactors. A BAC filter is the same as a conventional granular media filter which is commonly used in both drinking water and wastewater reclamation applications.

The ozone system can be sized based on applied O3:TOC ratio between 0.5-1.5 depending on desired removal of CECs and/or target ozone residual for pathogen removal based on CT. BAC filters are typically designed to provide EBCT of 10-20 minutes.

6. What are the maintenance lessons learned from existing Ozone/BAC systems?

Both ozone and BAC systems can provide stable operation for years with an appropriate maintenance program. For example, ozone generators have a long service life of 10+ years, while support systems such as cooling, power supply, and oxygen supply systems will require more frequent maintenance. BAC systems are similar to conventional filtration systems and employ automatic valves that are simple but require periodic maintenance due to wear of components and seals over time. Backwash systems consisting of air supply and water pumps may require some preventive maintenance to support long operational life. Additionally, BAC systems don't require frequent media regeneration and replacement is only needed for periodic replenishment (~3% per year).

7. What are the real-time process monitoring and control approaches (operational and performance) for integrated Ozone/BAC systems?

Applying the proper ozone dose in real-time is essential for responding to fluctuating source water quality while maintaining consistent treatment performance. The effluent from a wastewater treatment plant will vary, often diurnally, leading to significant swings in TOC, ammonia, nitrate, and nitrite. The proper ozone dose is dependent upon the ozone demand in the influent water. Both TOC and nitrite have significant impacts on the ozone demand. And the ozone demand and decay may be very high in wastewater creating challenges for traditional process monitoring and control approaches, such as the CT method where dissolved ozone residual may be difficult to measure and dissolved ozone analyzers may be difficult to maintain. A new and promising process monitoring and control approach targets a constant O3:TOC ratio and varies the ozone dose based on changes in TOC concentration to maintain this constant O3:TOC ratio. If nitrite is present in the water, then the ozone dose must be corrected to account for the ozone demand attributed to nitrite. TOC and nitrite analyzers are now available to implement this control method in real-time, which also has the advantage of being a feed-forward control loop allowing for fast response to changing water quality conditions. In addition, process performance of ozone can be monitored based on changes in the UVT of the feed water, while BAC process performance is primarily monitored for stable removal of TOC.

8. What unique benefits does Ozone/BAC provide when considering treatment train options?

Ozone/BAC is typically one of the first unit operations in an advanced water treatment train. Since Ozone/BAC significantly improves the water quality (i.e. reduces the bulk organic load), all unit operations downstream of Ozone/BAC will be more efficient. This may result in a reduction of capital equipment costs (i.e. higher flux rate through the MF system means less membranes, lower UV dose for the AOP system) and a reduction in O&M costs (less frequent chemical cleanings of both MF and RO systems due to more controlled organic fouling and lower energy use by MF, RO, and UV/AOP due to ability to reduce the use of chloramines for control of biological fouling, which also lowers chemical costs). For CBAT treatment trains, Ozone/BAC provides similar benefits of lowering the organics concentration for subsequent use of GAC for additional removal of TOC and significantly improves UVT for downstream disinfection by UV and UV/AOP system performance.

9. Are there substantial cost differences between the use of Ozone/BAC and other treatment processes?

The cost of an advanced water purification facility is very site-specific and dependent upon many factors including source water quality, product water treatment targets, cost of power and chemicals, and residual management. Additionally, the cost must be viewed holistically with respect to the entire treatment train and not with just one single unit operation. However, generally speaking as a rule of thumb, an Ozone/BAC-based treatment train without RO (i.e. CBAT) is less expensive than an RO-based treatment train. This is even more true when brine management becomes a significant implementation challenge and further increases project costs.

10. What are recommended public outreach methods to promote Ozone/BAC?

To educate and inform the public and interested stakeholders (e.g. schools, elected officials, regulators, local organizations and the medical community) in these processes, it has been important to promote on-site tours of demonstration and pilot-scale facilities so they can see firsthand the treatment process in operation. Several utilities have included graphical representations of treatment trains on their websites. PowerPoint presentations have been conducted at public meetings and in virtual online meetings during the pandemic. In some cases, videos have been made demonstrating the treatment train process using both real images as well as animations to help show how each treatment process works and how it removes different CECs, pathogens, and achieves drinking water and other standards. In addition, the use of demonstration facilities to provide purified water tastings has proven to be an excellent approach toward changing views and public acceptance of new treatment trains for potable reuse projects.

Dedicated project websites have also shown to be vital in making information available to the public and project stakeholders 24/7. This would include testimonials (written or videotaped) from knowledgeable people in the industry or from local and regional colleges/universities that are willing endorse the validity of these new treatment processes.

Glossary of Terms —
Carbon-based Advanced Treatment (CBAT) • Concentration x Time (CT) • Constituents of Emerging Concern (CEC) • Disinfection byproduct (DBP) • Empty Bed Contact Time (EBCT) • Granular Activated Carbon (GAC) • Ion Exchange (IX) • Membrane Filtration (MF) • N-Nitrosomorpholine (NMOR) • Operations & Maintenance (O&M) • Ozone-enhanced Biologically Active Carbon (Ozone/BAC) • Ozone to Total Organic Carbon ratio (O3:TOC) • Per- and polyfluoroalkyl Substances (PFAS) • Reverse Osmosis (RO) • Soil Aquifer Treatment (SAT)• Total Dissolved Solids (TDS) • Total Organic Carbon (TOC) • Ultraviolet (UV) • Ultraviolet Advanced Oxidation Process (UV/AOP) • Ultraviolet Transmittance (UVT)

5.2 Handout

The following handout provides an example of messaging for agencies and may serve as the basis to begin a meaningful public outreach campaign. This handout may shorten the learning curve for a utility toward customizing a robust public outreach effort that includes videos, interactive exhibits, and demonstration facilities specific to the utility and their respective community.

THE
Water
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Evaluation of CEC Removal by Ozone/BAC Treatment in Potable Reuse Applications

THE CHALLENGE

Potable reuse is now considered an integral component of water resource management in many communities around the world. The treatment solutions exist today to reliably produce safe drinking water from reclaimed water. Treatment trains with and without Reverse Osmosis (RO) are currently being evaluated and implemented for full-scale potable reuse applications. RO-based treatment trains pose significant implementation challenges for some utilities due to their relatively high capital and operating costs along with the difficulty of managing the concentrated waste streams when ocean discharge is not available, as is the case with many inland applications. Alternatives to RO-based treatment trains often include Ozone-enhanced Biologically Active Carbon (Ozone/BAC) in a multiple-barrier approach. This is often referred to as Carbon-Based Advanced Treatment (CBAT). While it is important to recognize that there is not a “one size fits all” solution for potable reuse, Ozone/BAC-based treatment trains have been proven to produce a high-quality reclaimed water meeting drinking water standards at a significantly lower cost and environmental footprint than RO-based treatment trains.

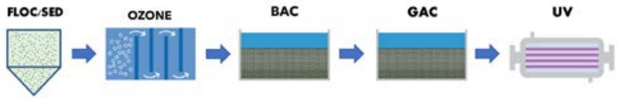
Although Ozone/BAC has been around for over a decade, its application in potable reuse is still emerging, and there is a legitimate need to identify and address knowledge gaps and additional optimization needs with respect to public health, safety, and perception. While potable reuse regulations still do not exist in many countries, we do have expert guidance on pathogen log reduction compliance in locations like California and Australia. On the other hand, our understanding of Constituents of Emerging Concern (CECs) is still evolving. There is a need for utilities and regulators to have a health-based context to develop performance criteria for Ozone/BAC-based treatment trains so the focus can be narrowed down to the most relevant and challenging CECs.

One of the greatest obstacles to the implementation of potable reuse projects continues to be public perception and acceptance. WRF-4832 is focused on developing treatment guidelines to lessen concerns of CECs while enabling broader implementation of Ozone/BAC-based treatment trains.

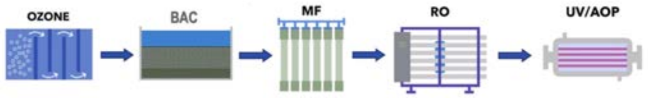
Chart 1:

EXAMPLES OF OZONE/BAC TREATMENT TRAINS FOR POTABLE REUSE

Carbon-Based Advanced Treatment — Example treatment train for groundwater injection in Virginia at Hampton Roads Sanitation District



Ozone-BAC Full Advanced Treatment — Example treatment train for direct potable reuse in California



THE RESEARCH

Factors for Consideration

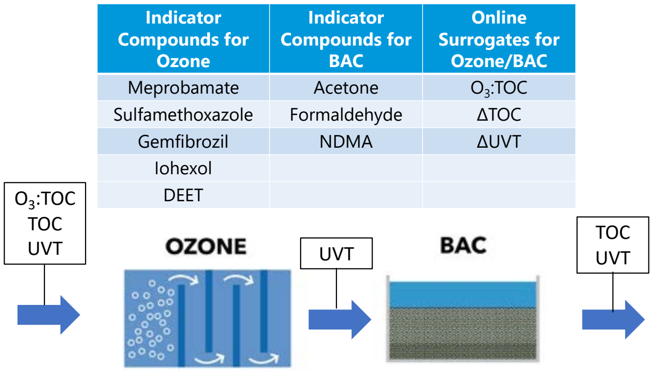
Identifying which CECs are both recalcitrant through an Ozone/BAC-based treatment train and toxicologically relevant is a key consideration for implementation. Many CECs that may be present in treated wastewater are mitigated as they are readily oxidizable and/or biodegradable through the Ozone/BAC process. By understanding the fate and chemical properties of the recalcitrant CECs through the Ozone/BAC process, we can now assess additional treatment barriers (upstream and/or downstream) that may be needed to fully address CECs that are toxicologically relevant (see Chart 2).

Continually measuring the hundreds of CECs that may be present in treated wastewater is not practical from an implementation and operational perspective. An additional challenge is characterizing the water quality and narrowing down the CECs to those that are toxicologically relevant. To design the appropriate multiple-barrier treatment train to protect public health, there are many CECs that may be present in detectable concentrations that may be safe but are representative of a larger family of chemicals with similar structures or reactivity. Therefore, it is more practical to assess the treatment efficiency of a unit process or treatment train for this group of CECs, which are called performance-based indicators.

Surrogate parameters are important for ensuring the performance of an Ozone/BAC process from a CEC removal perspective. Since online sensors do not yet exist to continually identify and measure CECs in real-time, surrogates are online parameters that are readily available for monitoring and control of the Ozone/BAC process in real-time. These surrogate parameters provide an indirect performance assessment of CEC removal (see Chart 3).

Chart 3:

EXAMPLES OF PERFORMANCE-BASED INDICATORS AND SURROGATES



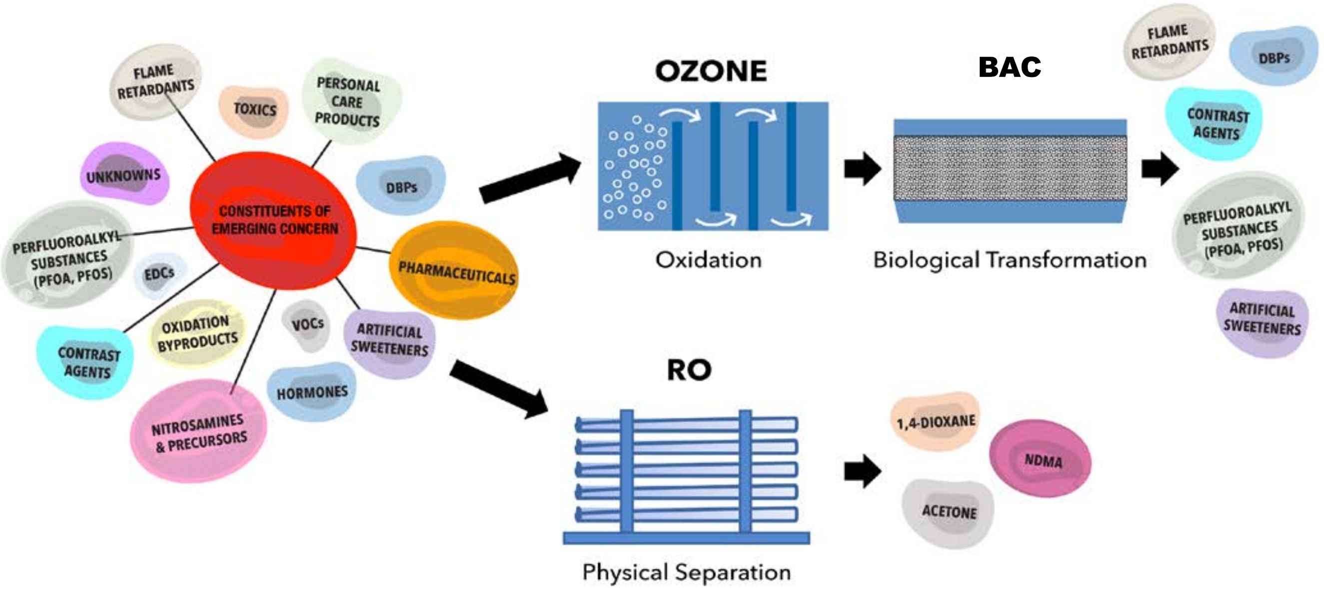
Indicator Compounds for Ozone	Indicator Compounds for BAC	Online Surrogates for Ozone/BAC
Meprobamate	Acetone	O_3:TOC
Sulfamethoxazole	Formaldehyde	ΔTOC
Gemfibrozil	NDMA	ΔUVT
Iohexol		
DEET		

In terms of project implementation, an important consideration is whether you have a treatment facility near the ocean where you have the capability for brine disposal. For facilities located inland, brine disposal may be cost-prohibitive. Non-RO treatment trains, such as CBAT may become a viable and robust option. The type/quality of source water entering the treatment plant is another consideration.

Given these factors, how do you determine which is a superior treatment option for your facility? And in some instances, is combining technologies to your advantage? That depends on a range of factors at each site, source waters, and the capability for brine or residual waste disposal.

Chart 2:

SOURCE WATER INPUT AND REMOVAL OF CECS WITH OZONE/BAC AND RO



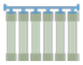
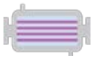
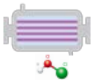
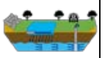
Treatment Train Options

In the California context where regulations are more prescriptive, we can use Ozone/BAC together with RO to enhance treatment redundancy in direct potable reuse. In other cases, such as OneWater Nevada or Hampton Roads, CBAT can accomplish treatment goals (without needing to include RO). Chart 4 (below) provides a toolbox which can be used for selecting the various components of a CBAT treatment train depending on project goals.

Ozone/BAC has been a key enabling technology in drinking water treatment for decades due to its ability to simultaneously remove pathogens and address critical water quality challenges, such as taste and odor compounds, and disinfection byproduct precursors. (Trussell et al., 2016). There are currently numerous studies investigating the use of Ozone/BAC for water reuse. While there is an increasing interest in implementing Ozone/BAC to act as a CEC barrier, the majority of Ozone/BAC pilot- and full-scale facilities do not evaluate the full range of design and operational conditions and configurations needed to achieve potable reuse regulations that include control of pathogenic microorganisms and standards for discharging into a water body.

Chart 4:

TOOLBOX OF UNIT PROCESSES FOR CBAT POTABLE REUSE TREATMENT TRAINS FOR DIFFERENT PROJECT TYPES

Project Type	Biological Treatment and Filtration 	Ozone (CECs) 	Ozone (CT for Disinfect.) 	BAC 	MF 	GAC 	IX 	UV 	UV/AOP 	Pipeline Cl_2 + DWTP 	Aquifer 	Total Pathogen LRV (Reqd.)
Groundwater Injection	✓ X O	X		✓ X	# (0/4/4)	✓ X			X # (6/6/6)		✓✓✓ (6/0/0)	*12/10/10* *(12/10/10)*
Surface Water Augmentation	✓ X O		X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O		X # (6/6/6)			*12/16/11* *(8/7/8)*
Direct Potable Reuse	✓ X O # (1/2.5/2.5)		X # (6/6/1)	✓ X	# (0/4/4)	✓ X	O		X # (6/6/6)	✓ X # (6/3/1 + 4/3/2)		*23/24.5/16.5* *(20/14/15)*
Projects w/o Pathogen-Based Requirements	✓ X O	X		✓ X		✓ X		X				N/A

✓=TOC X=CECs O=Nutrients #=Pathogen Credit: anticipated log removal values (LRV) for Virus/Giardia/Cryptosporidium

[Total pathogen LRV requirements are based on California's current and draft potable reuse regulations]

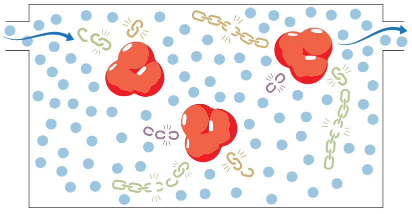
These hypothetical treatment train examples are intended to illustrate the various tools that exist to achieve certain treatment goals. These alternative non-RO treatment trains need to demonstrate treatment equivalency in states such as California to comply with the potable reuse reguilations.

GLOSSARY OF TERMS — Biologically Active Carbon (BAC) · Drinking Water Treatment Plant (DWTP) · Free Chlorine (Cl2) · Granular Activated Carbon (GAC) · Ion Exchange (IX) · Log Reduction Value (LRV) • Microfiltration (MF) · Ultraviolet (UV) · Ultraviolet Advanced Oxidation Process (UV/AOP)

THE PROCESS UP CLOSE — A close-up view of how the water is further purified through each of these key steps in the process. Examples are from OneWater Nevada's treatment process.

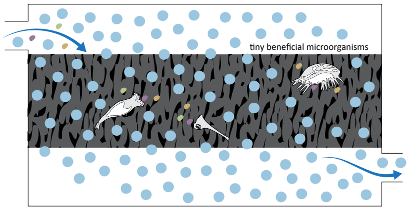
Ozonation

Ozone is a powerful oxidant used to break down organic constituents into smaller, more readily biodegradable molecules.



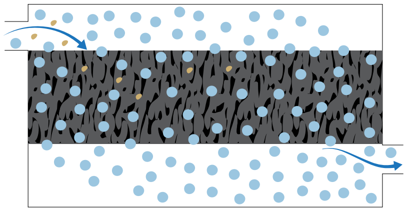
Biologically Active Filtration

Microbiologic organisms and carbon adsorption aid in the biodegradation and removal of dissolved organic constituents.



Granular Activated Carbon

Polishing step for further removal of trace amounts of dissolved organic constituents, such as pharmaceuticals or disinfection byproducts.



Project Findings

This study collected design, operational, and water quality data from several demonstration and/or pilot projects, and full-scale Ozone/BAC studies and projects around the world through a curated questionnaire and interviews, all of which was then compiled into a comprehensive database. Assessment of CEC performance data obtained from multiple facilities in order to identify the most relevant and challenging CECs from which to develop performance criteria for Ozone/BAC treatment trains was also integrated.

Each process has some shortcomings with respect to CEC removal (more compounds get through Ozone/BAC vs RO). These tools can be employed based on the context with which they are needed in implementing the treatment.

Of all the CECs that exist, Ozone/BAC is good at removing some types and RO is good at removing others. Ozone/BAC can be used in conjunction with other unit processes to achieve project goals and improve the overall treatment results. For some potable reuse projects, CBAT alone can achieve these goals. For other potable reuse projects with more stringent regulations, Ozone/BAC can be combined with RO to achieve exceptional water quality. Since there isn't a "one size fits all solution," a variety of powerful tools (i.e. Ozone/BAC, GAC, MF, UV, IX) are available to implement in these different treatment train strategies.

It's important to consider a full range of options when evaluating which treatment train is going to be the most effective for a specific geographic area, and also for the source waters entering the reuse facility.

WHERE DO WE GO FROM HERE?

The research objectives for Reuse-4832 encompassed the need to synthesize over a decade of results — from pilot demonstrations and full-scale projects, to numerous research studies both completed and in-progress — to quantify the removal of CECs through Ozone/BAC treatment of wastewater effluent for potable reuse. By analyzing these findings to identify commonalities, differences, trends, and gaps, this research has strived to provide guidance for utilities considering potable reuse and which treatment train is best suited to your area based on your source waters and geography. Hopefully, these findings help save time and money in evaluating treatment considerations and efforts toward safely enhancing the water supply in your community.

HIGHLIGHTS OF WHAT WE FOUND

Ozone/BAC is one of the best available technologies for removing a wide range of CECs including pharmaceuticals, personal care products, endocrine disrupting compounds, hormones, taste and odor compounds.

A multi-barrier approach for a CBAT treatment is best to address remaining health relevant CECs (e.g. NMOR, PFAS) as well as to provide additional mitigation of other synthetic organics such as flame retardants, contrast agents, etc.

Measurements of removal of indicator compounds by ozone can provide information on process performance to achieve health-based targets for CEC removal:

- Ozone - mebrobamate, sulfatheoxazole, gemfribrozil, iohexal, DEET
- BAC - Formaldehyde, acetone, NDMA

Monitoring of surrogate parameters using on-line meters can provide assurance of process performance for removal of CECs in real-time:

- Ozone - Ozone: TOC ratio, change in UVT
- BAC - TOC removal

Source water quality matters and can impact Ozone/BAC system design and performance (e.g. TOC, nitrite, ammonia).

Final water quality considerations vary depending on project type:

- Bromate mitigation strategies depending on influent water bromide concentration and ozone dose to provide removals of CECs and/or achieve disinfection
- Removal of recalcitrant synthetic organics, such as PFAS
- Additional TOC removal for mitigation of disinfection byproducts formation
- Total dissolved solids and nutrient objectives to meet secondary drinking water standards as well as applicable basin plan or national pollutant discharge elimination system permit requirements
- Pathogen log reduction value (LRV) credits based on type of potable reuse and regulatory context

APPENDIX A

Literature Review

Table A-1. Thirty-seven Ozone/BAF Facilities Reviewed in this Study.

Project ID	Project Scale	Country	Nutrient Reduction Treatment	Type of Ozonation	Ozone Dose/O_3:DOC/O_3:TOC	Filter Media Type	EBCT Range (min)	Type of Surrogate Parameters	Data Source	Supplemented with WQ data? (Y/N)
A	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Ozone + H2O2	0.8–1.3 O_3/TOC	GAC	15	TOC, ΔUVT, COD, Conductivity	Survey	Yes
B	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	0.7 O_3/DOC	GAC	15	TOC, UVT	(Brown and Caldwell and Trussell Technologies 2018)	Yes
C	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Ozone + H2O2	0.9–1.5 O_3/TOC	GAC	10–20	TOC, ΔUVT	Survey	Yes
D	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	0.8–1.2 O_3/TOC	GAC	15	TOC, ΔUVT	Survey	Yes
E	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	1 O_3:TOC, 5.6 mg/L O_3	GAC	13–19	TOC, EfOM	(Trussell et al 2016)	Yes
F	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	0.9–2 O_3/TOC	GAC	10–20	TOC, ΔUVT	Survey	Yes
G	Demo-/Pilot-scale	USA	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.5–1 O_3/DOC	GAC	10	TOC, ΔUVT, EEM	(Schimmoller et al 2016)	Yes
H	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	0–1.1 O_3/TOC	GAC	15–23	TOC, ΔUVT, EEM, COD	Survey	Yes
I	Full-scale	USA	Membrane bioreactor	Conventional ozone	2–8 mg/L O_3	GAC	9	TOC	(Daniel B. Stephens & Associates 2010; Marley et al 2010; Schimmoller et al 2016)	Yes
J	Full-scale	Australia	BNR Nitrogen removal	Conventional ozone	0.65 O_3/DOC	Anthracite	--	--	(Blackbeard et al 2016)	Yes
K	Full-scale	USA	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.35–0.65 O_3/TOC	GAC	18–30	TOC, COD	Survey	Yes
L	Full-scale	USA	BNR Nitrogen removal + PAC + Lime stabilization	Conventional ozone	5 mg/L O_3	GAC	10–16	TOC	Snyder et al 2014)	Yes
M	Full-scale	Switzerland	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.35–0.97 O_3/DOC	Sand, GAC virgin and loaded	14–14.5 (virgin), 18 (loaded)	--	(Bourgin et al 2018)	Yes
N	Full-scale	USA	BNR Nitrogen + Phosphorus removal	Ozone + H2O2	1–5 mg/L O_3	GAC and sand	6.5	TOC, AOC	Survey	Yes
O	Full-scale	Namibia	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.1–0.5 O_3/DOC	GAC	14	ΔUVT, DOC	Survey	Yes
P	Full-scale	Switzerland	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.4 mg/L	Sand	19–28	--	Survey	Yes
Q	Demo-/Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	1 O_3/TOC	GAC supported by sand	5–10	TOC, ΔUVT	(Vaidya et al 2019)	No
R	Full-scale	Germany	BNR Nitrogen removal	Conventional ozone	0.3 O_3/DOC	MBBR	--	--	Miehe n.d.s	No

Project ID	Project Scale	Country	Nutrient Reduction Treatment	Type of Ozonation	Ozone Dose/O_3:DOC/O_3:TOC	Filter Media Type	EBCT Range (min)	Type of Surrogate Parameters	Data Source	Supplemented with WQ data? (Y/N)
S	Full-scale	Germany	Membrane bioreactor	Conventional ozone	0.3–1 O_3/DOC	Sand	38	COD	Survey	No
T	Demo-/Pilot-scale	USA	High purity oxygen activated sludge	Conventional ozone	0.5–1.5 O_3/TOC	GAC supported by sand	0-20	CT10 (ozone exposures), CECs	Li et al 2017)	No
U	Pilot-scale	USA	Membrane bioreactor	Conventional ozone	0.5–1.5 O_3/TOC	GAC and anthracite	5-15	--	(Gifford, Selvy, and Gerrity 2018)	No
V	Pilot-scale	USA	Membrane bioreactor	Conventional ozone	0.1–2.25 O_3/TOC	GAC and anthracite	2-20	--	(Arnold et al 2018)	No
W	Pilot-scale	USA	Membrane bioreactor	Conventional ozone	0–1.3 O_3/TOC	GAC and anthracite	2-20	--	(Bacaro et al 2019)	No
X	Pilot-scale	USA	BNR Nitrogen removal	Conventional ozone	1.3–1.4 O_3/TOC	GAC	15	--	(Tackaert et al 2019)	No
Y	Pilot-scale	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.3–0.9 O_3/DOC	GAC	11–18 (15)	--	Internal communication	No
Z	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.87–0.87 O_3/DOC	GAC	28-35	--	Internal communication	No
AA	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.29 O_3/DOC	GAC	50 (BAC 1), 25 (BAC 2)	--	Internal communication	No
AB	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.2 O_3/DOC	GAC and anthracite	--	--	Internal communication	No
AC	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.67 O_3/DOC	Sand	4-5	--	Internal communication	No
AD	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.7 O_3/DOC	Sand	--	--	Internal communication	No
AE	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.7 O_3/DOC	GAC and PAC	--	--	Internal communication	No
AF	--	Germany	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.5–1.4 O_3/DOC	GAC and sand	15	--	Internal communication	No
AG	--	Austria	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.6–1.1 O_3/DOC	--	--	--	Internal communication	No
AH	--	Austria	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.2–1.2 O_3/DOC	GAC and anthracite	--	--	Internal communication	No
AI	--	Switzerland	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.33–0.5 O_3/DOC	Sand	--	--	Internal communication	No
AJ	--	Switzerland	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.35 O_3/DOC	Sand	--	--	Internal communication	No
AK	--	Switzerland	BNR Nitrogen + Phosphorus removal	Conventional ozone	0.6–2 O_3/DOC	Sand and PAC	--	--	Internal communication	No

Table A-2. Ozone and Hydroxyl Radical Reaction Constant Rates (k_{O3} and k_{OH}, respectively) for Known Compounds.

Compounds	k_{O3} (M^{-1} s^{-1})	k_{OH} (M^{-1} s^{-1})	Source
17b-Estradiol	2.21 x 10^5 – 3.69 x 10^9	–	(Deborde et al 2005)
1-Phenoxy-2-propanol	320	–	(Benner et al 2008)
2,4-D	5.3 (pH 2)	3.2 x 10^9	(Blackbeard et al 2016)
4-Methoxy-1-naphtalene Sulfonic acid	3600	–	(Benner et al 2008)
4-methyl- benzotriazole	7.8 x 10^2	~8.6 x 10^9	(Lee et al 2014)
Acebutolol	1.9 x 10^3	4.6 x 10^9	(Benner et al 2008)
Acesulfame	88	4.55 x 10^9	(Kaiser et al 2013)
Acetaminophen	2.5 x 10^5 (pH 2)	–	(Javier Rivas et al 2011)
Alachlor	3.8	7 x 10^9	(Haag and Yao 1992)
Amisulpride	1.5 x 10^5	–	(Bourgin et al 2018)
Antypirine	6.15 x 10^5 (pH 2)	–	(Javier Rivas et al 2011)
Atenolol	1.7 x 10^3	7.05 x 10^9	(Benner et al 2008; Song et al 2008)
Atrazine	6–7.9	2.4–3.0 x 10^9	(Westerhoff et al 2005)
Benzotriazole	20	6.2 x 10^9 (pH 10.2)	(Vel Leitner and Roshani 2010)
Bezafibrate	590	7.4 x 10^9	(Bourgin et al 2017)
Bisphenol A	7 x 10^5	1 x 10^{10}	(Deborde et al 2005)
Butylparaben	4.4 x 10^5 (pH 6)	9.2 x 10^9	
Caffeine	650	5.9 – 6.9 x 10^9	(Broséus et al 2009)
Candesartan	563	–	(Bourgin et al 2018)
Carbamazepine	3 x 10^5	8.8 x 10^9	(Huber et al 2003)
Carbofuran	620	7 x 10^9	(Haag and Yao 1992)
Chlorothiazide	1.5	5.7 x 10^9	(Bourgin et al 2017)
Clarithromycin	4 x 10^4	7.5 x 10^9	(Huber et al 2003)
Clorofibric acid	20	4.7 x 10^9	(Packer et al 2003; Huber et al 2005)
Cyanazine	7.34–61.8	1.9 x 10^9	(Broséus et al 2009)
DEA	0.2	2 x 10^9	(Beltrán et al 2000)
DEET	10	4.95 x 10^9	(Song et al 2009; Gerrity et al 2012)
DIA	7.5	2.1 x 10^9	(Beltrán et al 2000)
Diazepam	0.75	7.2 x 10^9	(Huber et al 2003)
Diclofenac	1 x 10^6	7.5 x 10^9	(Huber et al 2003)
Diuron	14.8	4.6 x 10^9	(Bourgin et al 2017)
Endrin	0.02	1 x 10^9	(Haag and Yao 1992)
Erytromycin	–	3.00 x 10^9	(Abdelmelek et al 2011)
Estriol	1.01 x 10^5 –3.89 x 10^9	–	(Deborde et al 2005)
Estrone	6.2 x 10^3 –2.1 x 10^7	1.1 x 10^9 –7 x 10^{10}	

Compounds	**k_{O3} (M^{-1} s^{-1})**	**k_{OH} (M^{-1} s^{-1})**	**Source**
Ethinyl Estradiol - 17 alpha	1.83×10^5 –3.65×10^9	1.08×10^{10}	(Rosenfeldt and Linden 2004; Deborde et al 2005)
Ethylparaben	3.4×10^5 (pH 6)	7.7×10^9	
Fluconazole	2	4.4×10^9	Lee et al 2014)
Flumequine	6.4 (pH 2)	–	(Javier Rivas et al 2011)
Furosemide	6.8×10^4	1×10^{10}	(Lee et al 2014)
Gabapentin	2.2×10^4	9.1×10^9	(Lee et al 2014)
Gemfibrozil	5×10^4	1.0×10^{10}	(Lee and von Gunten 2012)
Hydrochlorothiazide	1.64×10^4 (pH 9)	5.7×10^9	(Real et al 2009)
Ibuprofen	9.1	7.4×10^9	(Huber et al 2003)
Iohexol	–	3.21×10^9	(Jeong et al 2010)
Iopromide	0.8	3.3×10^9	(Huber et al 2003)
Irbesartan	23	–	(Bourgin et al 2018)
Ketorolac	4.4×10^5 (pH 2)	–	(Javier Rivas et al 2011)
Lamotrigine	4	2.1×10^9	(Bourgin et al 2017)
Levetiracetam	1	3.8×10^9	(Lee et al 2014)
Levonorgestrel	1427	9	(Broséus et al 2009)
Lidocaine	7.3×10^4	$1 \times 10e^{10}$	(Lee et al 2014)
Medroxyprogesterone	558	–	(Broséus et al 2009)
Mefenamic acid	6.4×10^6	$1 \times 10e^{10}$	(Lee et al 2014)
Meprobamate	1	4×10^9	(Lee and von Gunten 2012)
Methoxychlor	270	2×10^{10}	(Haag and Yao 1992)
Methylbenzotriazole	460	–	(Bourgin et al 2018)
Methylparaben	2.5×10^5 (pH 6)	6.8×10^9	
Metoprolol	2.0×10^3	8.39×10^9	(Song et al 2008)
Musk ketone	1	2×10^8	(Lee and von Gunten 2012)
N(4)-acetyl sulfamethoxazole	2.5×10^2	6.8×10^9	(Lee et al 2014)
N,N-Diethyl-m-toluamide	0.1	5.0×10^9	(Bourgin et al 2017)
Nalidixic acid	–	6.74×10^9	(Abdelmelek et al 2011)
Naproxen	2×10^5	9.6×10^9	(Packer et al 2003; Huber et al 2005)
Norethindrone	2215	–	(Broséus et al 2009)
Oxazepam	1	9.1×10^9	(Lee et al 2014)
Perfluorooctanoic acid	<1	$<1 \times 10^9$	(Blackbeard et al 2016)
Phenazone	5.3×10^4	5.3×10^9	(Bourgin et al 2017)
Phenytoin	10	5×10^9	(Lee and von Gunten 2012)
Primidone	1	7×10^9	(Real et al 2009; Lee and von Gunten 2012)
Progesterone	480	–	(Barron et al 2006)

Compounds	**k_{O3} (M^{-1} s^{-1})**	**k_{OH} (M^{-1} s^{-1})**	**Source**
Propranolol	1 x 10^5	1.0 x 10^{10}	(Benner et al 2008)
Propylparaben	4.1 x 10^5 (pH 6)	8.6 x 10^9	
Ranitidine	4.1 x 10^6	1 x 10^{10}	(Lee et al 2014)
Roxithromycin	7 × 10^4	–	(Huber et al 2003)
Simazine	4.3 (pH 5)	2.9 x 10^9	(Blackbeard et al 2016)
Sotalol	1.4 x 10^4	1 x 10^{10}	(Lee et al 2014)
Sucralose	<0.1	1.6 x 10^9	(Bourgin et al 2017)
Sulfamethoxazole	2.6 x 10^6	5.5 x 10^9	(Huber et al 2003)
Sulfapyridine	2 x 10^5	8.2 x 10^9	(Lee et al 2014)
TCEP	1	6 × 10^8	(Watts and Linden 2009; Lee and von Gunten 2012)
Tramadol	4 x 10^3	6.3 x 10^9	(Zimmermann et al 2012)
Triclosan	4 x 10^7	1 × 10^{10}	(Suarez et al 2007; Lee and von Gunten 2012)
Trimethoprim	3 x 10^5	8.92 x 10^9	(Abdelmelek et al 2011
Tris (chloroethyl) phosphate	<1	<1 x 10^9	(Blackbeard et al 2016)
Tris (chloropropyl) phos. Isomers	<1	<1 x 10^9	(Blackbeard et al 2016)
Tris (dichloro-propyl) phosphate	<1	<1 x 10^9	(Blackbeard et al 2016)
Valsartan	38	6.7 x 10^9	(Lee et al 2014)
Venlafaxine	8.5 x 10^3	1 × 10^{10}	(Lee et al 2014)

Table A-3. Complete List of CECs Identified and Monitored by the Ozone/BAF Facilities Reviewed in this Study.

Compound	Category
1,1-Dichloroethane	Personal care products
1,1-Dichloroethylene	Industrial chemicals
1,1-Dichloropropene	Industrial chemicals
1,1,1-Trichloroethane	Industrial chemicals
1,1,1,2-Tetrachloroethane	Pharmaceuticals
1,1,2-Trichloroethane	Industrial chemicals
1,1,2,2-Tetrachloroethane	Industrial chemicals
1,2-Dichloroethane	Industrial chemicals
1,2-Dichloropropane	Industrial chemicals
1,2,3-Trichlorobenzene	Industrial chemicals
1,2,3-Trichloropropane	Industrial chemicals
1,2,4-Trichlorobenzene	Industrial chemicals
1,2,4-Trimethylbenzene	Industrial chemicals
1,3-Dichloropropane	Other CECs
1,3-Dichloropropene	Pesticides
1,3,5-Trimethylbenzene	Industrial chemicals
1,4-Dioxane	Industrial chemicals
1,7-Dimethylxanthine	Pharmaceuticals
2-Butanone	VOCs
2,2-Dichloropropane	Industrial chemicals
2,3,7,8-Tetrachlorodibenzodioxin (2,3,7,8-TCDD)	Pesticides
2,4-Dichlorophenoxyacetic acid (2,4-D)	Herbicides
2,4-Dichlorophenoxybutyric acid (2,4-DB)	Herbicides
2,4’-Dichlorodiphenyldichloroethane (2,4’-DDD)	Pesticides
2,4’-Dichlorodiphenyldichloroethylene (2,4’-DDE)	Pesticides
2,4’-Dichlorodiphenyltrichloroethane (2,4’-DDT)	Pesticides
2,4-Dinitrotoluene	Industrial chemicals
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	Herbicides
Fenoprop (2,4,5-TP)	Herbicides
2,6-Dinitrotoluene	Industrial chemicals
3-Hydroxycarbofuran	Pesticides
3,4-Dichloroaniline	Pesticides
3,5-Dichlorobenzoic acid	Herbicides
4-androstene-3,17-dione	Hormones
4-Methyl-2-pentanone	Industrial chemicals
4-nonylphenol (semi-quantitative)	Nonylphenols
4-tert-Octylphenol	Nonylphenols
4,4’-Dichlorodiphenyldichloroethane (4,4’-DDD)	Pesticides
4,4’-Dichlorodiphenyldichloroethylene (4,4’-DDE)	Pesticides
4,4’-Dichlorodiphenyltrichloroethane (4,4’-DDT)	Pesticides
4'- and 5-Hydroxydiclofenac	Pharmaceuticals
Acenaphthene	Industrial chemicals
Acenaphthylene	Industrial chemicals
Acesulfame	Artificial sweeteners
Acetaldehyde	Personal care products
Acetaminophen	Pharmaceuticals
Acetochlor	Herbicides
Acetone	Personal care products
Acifluorfen	Herbicides

Compound	Category
Acrylamide	Industrial chemicals
Alachlor	Herbicides
Albuterol	Pharmaceuticals
Aldicarb	Pesticides
Aldicarb sulfone	Transformation products (aldicarb)
Aldicarb sulfoxide	Transformation products (aldicarb)
Aldrin	Pesticides
Aliskiren	Pharmaceuticals
Alpha-BHC	Pesticides
alpha-Chlordane	Pesticides
Amisulpride	Pharmaceuticals
Amisulpride N-oxide	Transformation products (amisulpride)
Amoxicillin	Pharmaceuticals
Amoxicillin (semi-quantitative)	Pharmaceuticals
Andorostenedione	Hormones
Anthracene	Industrial chemicals
Antipyrine	Pharmaceuticals
Atenolol	Pharmaceuticals
Atorvastatin	Pharmaceuticals
Atrazine	Pesticides
Azithromycin	Pharmaceuticals
Baygon	Pesticides
Bendroflumethiazide	Pharmaceuticals
Bentazon	Herbicides
Benz(a)anthracene	Aromatic hydrocarbons
Benzene	Industrial chemicals
Benzo(a)pyrene	Aromatic hydrocarbons
Benzo(b)fluoranthene	Aromatic hydrocarbons
Benzo(g,h,i)perylene	Aromatic hydrocarbons
Benzo(k)fluoranthene	Aromatic hydrocarbons
Benzophenone	Aromatic hydrocarbons
Benzotriazole	Industrial chemicals
Beta-BHC	Pesticides
Bezafibrate	Pharmaceuticals
Bisphenol A	Endocrine disruptors
Bromacil	Herbicides
Bromate	DBP
Bromobenzene	Industrial chemicals
Bromochloroacetic Acid	DBP
Bromochloroacetonitrile	DBP
Bromochloromethane	Industrial chemicals
Bromodichloromethane	Flame retardant
Bromoethane	Industrial chemicals
Bromoform	Industrial chemicals
Bromomethane	Industrial chemicals
Bromoxynil	Pesticides
Butachlor	Herbicides
Butalbital	Pharmaceuticals
Butylbenzylphthalate	Industrial chemicals
Butylparaben	Personal care products

Compound	Category
Caffeine	Pharmaceuticals
Candesartan	Pharmaceuticals
Carbadox	Pharmaceuticals
Carbamazepine	Pharmaceuticals
Carbaryl	Pesticides
Carbendazim	Pesticides
Carbofuran	Pesticides
Carbon disulfide	VOCs
Carbon tetrachloride	Industrial chemicals
Carisoprodol	Pharmaceuticals
Cephalexin	Pharmaceuticals
Cetirizine	Pharmaceuticals
Cetirizine N-oxide	Transformation products (cetirizine)
Chloramphenicol	Pharmaceuticals
Chlordane	Pesticides
Chloridazon	Herbicides
Chlorobenzene	Industrial chemicals
Chlorobenzilate	Pesticides
Chloroethane	Industrial chemicals
Chloroform	DBP
Chloromethane	Industrial chemicals
Chloroneb	Fungicides
Chlorotetracycline	Pharmaceuticals
Chlorothalonil	Fungicides
Chlorothiazide	Pharmaceuticals
Chlorotoluron	Herbicides
Chlorpyrifos	Pesticides
Chrysene	Aromatic hydrocarbons
Cimetidine	Pharmaceuticals
Cimetidine (semi-quantitative)	Pharmaceuticals
Ciprofloxacin	Pharmaceuticals
cis-1,2-Dichloroethylene	Industrial chemicals
cis-1,3-Dichloropropene	Pesticides
Citalopram	Pharmaceuticals
Clarithromycin	Pharmaceuticals
Clarithromycin N-oxide	Transformation products (clarithromycin)
Clofibric Acid	Pharmaceuticals
Codeine	Pharmaceuticals
Combined PFOS PFOA	PFAS
Cotinine	Pharmaceuticals
Cyanazine	Herbicides
DACT	Pesticides
Dalapon	Herbicides
DCPA	Herbicides
DEA	Personal care products
DEET	Pesticides
Dehydronifedipine	Pharmaceuticals
Delta-BHC	Pesticides
Desethyl Atrazine	Transformation products (atrazine)
Desisopropyl Atrazine	Transformation products (atrazine)

Compound	Category
Dexamethasone	Pharmaceuticals
Di-(2-Ethylhexyl)adipate	Personal care products
Di-isopropyl ether	Industrial chemicals
Di-n-Butylphthalate	Industrial chemicals
Di-N-octylphthalate	Industrial chemicals
Di(2-Ethylhexyl)phthalate	Pesticides
DIA (1,8-Diaminooctane)	Fungicides
Diatrizoate sodium	Medical contrast agent
Diazepam	Pharmaceuticals
Diazinon	Pesticides
Dibenz(a,h)anthracene	Aromatic hydrocarbons
Dibromoacetic Acid	DBP
Dibromoacetonitrile	DBP
Dibromochloromethane	DBP
Dibromomethane	Industrial chemicals
Dicamba	Pesticides
Dichloroacetic Acid	DBP
Dichloroacetonitrile	DBP
Dichlorodifluoromethane	Household chemicals
Dichloromethane	VOCs
Dichlorvos	Pesticides
Dichlorprop	Herbicides
Diclofenac	Pharmaceuticals
Dieldrin	Pesticides
Diethylphthalate	Pharmaceuticals
Dilantin	Pharmaceuticals
Diltiazem	Pharmaceuticals
Dimethoate	Pesticides
Dimethylphthalate	Industrial chemicals
Dinoseb	Herbicides
Diphenhydramine	Pharmaceuticals
Diquat	Herbicides
Diuron	Herbicides
Doxycycline	Pharmaceuticals
Doxylamine	Pharmaceuticals
Endosulfan I (Alpha)	Pesticides
Endosulfan II (Beta)	Pesticides
Endosulfan Sulfate	Transformation products (endosulfan)
Endothall	Pesticides
Endrin	Pesticides
Endrin aldehyde	Pesticides
Eprosartan	Pharmaceuticals
EPTC	Herbicides
Equilin	Hormones
Erythromycin	Pharmaceuticals
Estradiol	Hormones
Estriol	Hormones
Estrone	Hormones
Ethinyl Estradiol - 17 alpha	Hormones
Ethyl benzene	Industrial chemicals

Compound	Category
Ethyl Glyoxal	Industrial chemicals
Ethylparaben	Personal care products
Fexofenadine	Pharmaceuticals
Fexofenadine N-oxide	Transformation products (fexofenadine)
Flumeqine	Pharmaceuticals
Fluoranthene	Industrial chemicals
Fluorene	Industrial chemicals
Fluoxetine	Pharmaceuticals
Fluroxypyr	Pesticides
Formaldehyde	Personal care products
Frusemide	Pharmaceuticals
Furosimide	Pharmaceuticals
Gabapentin	Pharmaceuticals
Galaxolide	Personal care products
gamma-Chlordane	Pesticides
Gemfibrozil	Pharmaceuticals
Glyphosate	Herbicides
Heptachlor	Pesticides
Heptachlor epoxide	Transformation products (Heptachlor)
Heptachlor epoxide (isomer B)	Transformation products (Heptachlor)
Hexachlorobenzene	Fungicides
Hexachlorobutadiene	Industrial chemicals
Hexachlorocyclopentadiene	Industrial chemicals
Hexazinone	Pesticides
Hydrochlorothiazide	Pharmaceuticals
Hydrocortisone	Pharmaceuticals
Ibuprofen	Pharmaceuticals
Indeno(1,2,3,c,d)pyrene	Aromatic hydrocarbons
Indomethacin	Pharmaceuticals
Iohexol	Medical contrast agents
Iopamidol	Medical contrast agents
Iopromide	Medical contrast agents
Irbesartan	Pharmaceuticals
Isobutylparaben	Personal care products
Isophorone	Industrial chemicals
Isopropylbenzene	Industrial chemicals
Isoproturon	Herbicides
Ketoprofen	Pharmaceuticals
Ketorolac	Pharmaceuticals
Lamotrigine	Pharmaceuticals
Levetiracetam	Pharmaceuticals
Lidocaine	Pharmaceuticals
Lincomycin	Pharmaceuticals
Lindane	Pesticides
Linuron	Herbicides
Lopressor	Pharmaceuticals
Losartan	Pharmaceuticals
m-Dichlorobenzene (1,3-DCB)	Pesticides
m,p-Xylenes	Industrial chemicals
Malathion	Pesticides

Compound	Category
MCPA	Pesticides
Meclofenamic Acid	Pharmaceuticals
Mecoprop	Pesticides
Meprobamate	Pharmaceuticals
Metalaxyl	Fungicides
Metazachlor	Herbicides
Metformin	Pharmaceuticals
Methiocarb	Pesticides
Methomyl	Pesticides
Methoxychlor	Pesticides
Methyl Glyoxal	Industrial chemicals
Methylparaben	Personal care products
Metolachlor	Pesticides
Metoprolol	Pharmaceuticals
Metribuzin	Herbicides
Molinate	Herbicides
Monobromoacetic Acid	DBP
Monochloroacetic Acid	DBP
MTBE	Industrial chemicals
n-Butylbenzene	Industrial chemicals
N-Nitrosodi-n-propylamine	NItrosamines
N-Nitrosodibutylamine	Nitrosamines
N-Nitrosodiethylamine	NItrosamines
N-Nitrosodimethylamine	Nitrosamines
N-Nitrosodiphenylamine	Nitrosamines
N-Nitrosomethylethylamine	Nitrosamines
N-Nitrosomorpholine	Nitrosamines
N-Nitrosopiperidine	Nitrosamines
N-Nitrosopyrrolidine	Nitrosamines
n-Propylbenzene	Industrial chemicals
Naphthalene	Pharmaceuticals
Naproxen	Pharmaceuticals
Nicotine	Pharmaceuticals
Nifedipine	Pharmaceuticals
Nifedipine (semi-quantitative)	Pharmaceuticals
Norethisterone	Hormones
Norfloxacin	Pharmaceuticals
Norgestrel	Hormones
o-Chlorotoluene	Industrial chemicals
o-Dichlorobenzene (1,2-DCB)	Industrial chemicals
o-Xylene	Industrial chemicals
OUST (Sulfameturon-methyl)	Herbicides
Oxamyl	Pesticides
Oxazepam	Pharmaceuticals
Oxolinic acid	Pharmaceuticals
Oxycodone	Pharmaceuticals
Oxytetracycline	Pharmaceuticals
p-Chlorotoluene	Industrial chemicals
p-Dichlorobenzene (1,4-DCB)	VOCs
p-Isopropyltoluene	Industrial

Compound	Category
Paraquat	Herbicides
Parathion	Pesticides
Paraxanthine	Pharmaceuticals
PCB 1016 Aroclor	Industrial chemicals
PCB 1221 Aroclor	Industrial chemicals
PCB 1232 Aroclor	Industrial chemicals
PCB 1242 Aroclor	Industrial chemicals
PCB 1248 Aroclor	Industrial chemicals
PCB 1254 Aroclor	Industrial chemicals
PCB 1260 Aroclor	Industrial chemicals
Pendimethalin	Herbicides
Penicillin G	Pharmaceuticals
Penicillin V	Pharmaceuticals
Pentachlorophenol	Pesticides
Pentoxifylline	Pharmaceuticals
Perchlorate	Endocrine disruptors
Perfluorobutane sulfonate	PFAS
Perfluorobutanesulfonic acid	PFAS
Perfluorobutanoic acid	PFAS
Perfluorodecane sulfonate	PFAS
Perfluorodecanoic acid	PFAS
Perfluorododecanoic acid	PFAS
Perfluoroheptanoic acid	PFAS
Perfluorohexane sulfonate	PFAS
Perfluorohexanesulfonic acid	PFAS
Perfluorohexanoic acid	PFAS
Perfluorononanoic acid	PFAS
Perfluorooctane sulfonate	PFAS
Perfluorooctanesulfonic acid	PFAS
Perfluorooctanoic acid	PFAS
Perfluoropentanoic acid	PFAS
Perfluorotetradecanoic acid	PFAS
Perfluorotridecanoic acid	PFAS
Perfluoroundecanoic acid	PFAS
Permethrin	Pesticides
Phenanthrene	Industrial chemicals
Phenazone	Pharmaceuticals
Phenytoin	Pharmaceuticals
Picloram	Herbicides
Prednisone	Pharmaceuticals
Primidone	Pharmaceuticals
Progesterone	Hormones
Propachlor	Herbicides
Propazine	Herbicides
Propranolol	Pharmaceuticals
Propylparaben	Personal care products
Pyrene	Aromatic hydrocarbons
Quinoline	Alkaloid
Ranitidine	Pharmaceuticals
Roxithromycin	Pharmaceuticals

Compound	Category
Salicylic Acid	Pharmaceuticals
sec-Butylbenzene	Industrial compound
Sertraline	Pharmaceuticals
Simazine	Pesticides
Styrene	Aromatic hydrocarbons
Sucralose	Artificial sweeteners
Sulfachloropyridazine	Pharmaceuticals
Sulfadiazine	Pharmaceuticals
Sulfadimethoxine	Pharmaceuticals
Sulfamerazine	Pharmaceuticals
Sulfamethazine	Pharmaceuticals
Sulfamethizole	Pharmaceuticals
Sulfamethoxazole	Pharmaceuticals
Sulfamethoxazole + N4-Acetyl-Sulfamethoxazole	Pharmaceuticals
Sulfasalazine	Pharmaceuticals
Sulfathiazole	Pharmaceuticals
t-Butyl Alcohol	Industrial chemicals
TCEP	Flame retardants
TCPP	Flame retardants
TDCPP	Flame retardants
Tebuconazole	Pesticides
Telmisartan	Pharmaceuticals
Temazepam	Pharmaceuticals
Terbacil	Herbicides
Terbuthylazine	Herbicides
Terbutryn	Pesticides
tert-Amyl methyl ether	Fuel additives
tert-Butyl ethyl ether	Fuel additives
tert-Butylbenzene	Aromatic hydrocarbons
Testosterone	Hormones
Tetrachloroethylene	Dry cleaning agents
Tetracycline	Pharmaceuticals
Theobromine	Alkaloids
Theophylline	Pharmaceuticals
Theophylline (semi-quantitative)	Pharmaceuticals
Thiabendazole	Fungicides
Thiobencarb	Pesticides
Toluene	VOCs
Tonalid	Personal care products
Total Haloacetic Acids	DBP
Total PCBs	Industrial chemicals
Total Trihalomethanes	DBP
Total xylenes	VOC
Toxaphene	Pesticides
Tramadol	Pharmaceuticals
Tramadol N-oxide	Transformation products (tramadol)
trans-1,2-dichloroethylene	Industrial Chemicals
trans-1,3-dichloropropene	Pesticides
trans-nonachlor	Transformation products (chlordane)
Trichloroacetic Acid	DBP

Compound	Category
Trichloroethylene	Industrial chemicals
Trichlorofluoromethane	Industrial chemicals
Trichlorotrifluoroethane	Industrial chemicals
Triclocarban	Personal care products
Triclopyr	Pesticides
Triclosan	Personal care products
Triethyl phosphate	Industrial chemicals
Trifluralin	Herbicides
Trimethoprim	Pharmaceuticals
Tris(chloroethyl) phosphate	Flame retardants
Tris(chloropropyl) phosphate isomers	Flame retardants
Valsartan	Pharmaceuticals
Venlafaxine	Pharmaceuticals
Venlafaxine N-oxide	Transformation products (venlafaxine)
Vinyl chloride	Industrial Chemicals
Warfarin	Pharmaceuticals

APPENDIX B

RSSCT Experimental Test Plan

B.1 Introduction and Objectives

One of the key knowledge gaps identified in the Chapter 3 analysis was a need to further understand the long-term effectiveness of granular activated carbon for simultaneous removal of total organic carbon and perfluoroalkyl substances. Effluent TOC is an important consideration for carbon-based advanced treatment facilities for potable reuse, mainly for its role in the formation of disinfection byproducts with effluent chlorination. PFAS, a group of synthetic industrial chemicals used for a variety of products ranging from cookware to cleaning products, are environmentally persistent and pose various chronic health risks to humans. The United Stated Environmental Protection Agency developed a health advisory concentration limit of 70 ng/L for the sum of perfluorooctanesulfonic acid and perfluorooctanoic acid, and several states have developed maximum contaminant levels and notification limits for these compounds.

GAC is effective for the removal of organic contaminants including TOC and trace organics such as PFAS. Rapid small-scale column testing is a laboratory method used to elucidate long-term adsorption performance on an accelerated timeframe. For example, years of full-scale GAC operation can be tested in a matter of weeks by scaling down the bed media and flow rate. Much of the literature on RSSCT for the removal of TOC and/or PFAS with GAC has been conducted on drinking water sources such as contaminated groundwater, but little research exists for the performance of this technology on ozone/biologically active filtration effluents which contain different compositions of TOC and higher concentrations of TOC. An ozone/BAF effluent will be sourced and spiked with consistent levels of PFAS. In addition, two different carbon types and two empty bed contact times for each carbon will be tested, resulting in 4 test conditions. The main objectives of this RSSCT are as follows:

- Further elucidate the breakthrough of TOC as a function of EBCT in ozone/BAF effluent
- Further elucidate the breakthrough of PFAS as a function of influent TOC concentration and EBCT in ozone/BAF effluent
- Use the results of RSSCT to configure a feasible GAC system design for simultaneous removal of TOC and PFAS in ozone/BAF effluent

B.2 Source Water and Spiking Reagents

Ozone/BAF effluent will be sourced from the Facility D. General water quality including pH, alkalinity, TOC, TDS, and turbidity will be measured in the source water in addition to background levels of PFAS. Eight PFAS were selected based on state and/or federal health-based thresholds, including MCLs in select states. These eight compounds and the rationale for testing are summarized in Table B-1. The source water will be spiked with a standard reagent containing a suite of 14 PFAS (associated with EPA method 537), with each compound spiked at a target concentration of 50 ng/L (above ambient concentrations) based on the high-end of observed concentrations in the Chapter 1 survey data.

Table B-1. Summary of Target PFAS Compounds.

PFAS[a]	C-Chain Length	Target Concentration	Rationale for Including
Perfluorobutanesulfonic acid (PFBS)	4	50 ng/L	• MI MCL • Help elucidate shorter-chain behavior • Present in ozone/BAF effluent data from Chapter 1 survey • CA NL since March 2021
Perfluorohexanoic acid (PFHxA)	6	50 ng/L	• MI MCL • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluorohexanesulfonic acid (PFHxS)	6	50 ng/L	• Action level/MCL/guidance value in MA, MI, MN, NH, VT • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluoroheptanoic acid (PFHpA)	7	50 ng/L	• Action level/MCL/guidance value in CT, MA, VT • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluorooctanoic acid (PFOA)	8	50 ng/L	• EPA health advisory • MCL/action level/NL/guidance value in CA, CT, MA, MI, MN, NH, NJ, NY, NC, VT • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluorooctanesulfonic acid (PFOS)	8	50 ng/L	• EPA health advisory • MCL/action level/NL/guidance value in CA, CT, MA, MI, MN, NH, NJ, NY, NC, VT • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluorononanoic acid (PFNA)	9	50 ng/L	• MCL/action level in CT, MA, MI, NH, NJ, VT • Present in ozone/BAF effluent data from Chapter 1 survey
Perfluorodecanoic acid (PFDA)	10	50 ng/L	• MA MCL • Help elucidate longer-chain behavior

[a] Perfluoroundecanoic acid, perfluoroodecanoic acid, perfluorotridecanoic acid, perfluorotetradecanoic acid, N-Methylperfluorooctanesulfonamidoacetic acid, and N-Ethylperfluorooctanesulfonamidoacetic acid will also be spiked as part of the suite of PFAS compounds included in the standard reagent

B.3 RSSCT Conditions and Sampling Plan

The source water sample will be tested at two different EBCTs (10 min and 20 min) by varying the feed flow to the column. Two different carbon types will be tested at both EBCTs: virgin Calgon Filtrasorb 400 (F400) and reactivated Calgon F400, both provided by Calgon Carbon. This results in a total of 4 testing conditions. Each column will be sampled out to 30,000 bed volumes treated. Higher frequency TOC sampling will occur from 0 to 5,000 BVT which is the expected TOC breakthrough based on RSSCT conducted for Los Angeles Sanitation District's Donald C. Tillman Advanced Water Purification Facility pilot (Trussell Technologies 2018). Breakthrough will be defined as 2 mg/L which has been documented to be acceptable for controlling downstream DBP formation (Arnold et al. 2018). Groundwater studies have shown PFAS breakthrough between 20,000 BVT and 100,00 BVT depending on several factors such influent TOC and PFAS concentrations and the selection of breakthrough threshold (Belkouteb et al. 2020; McNamara et al. 2018; C. Zeng et al. 2020). For this study, higher frequency PFAS sampling will occur from 10,000 to 22,500 BVT which is the expected breakthrough for PFAS in these matrices. Breakthrough will be conservatively defined as 5 ng/L, which represents the California NL for PFOA (5.1 ng/L). A sampling matrix of the 4 test conditions is summarized Table B-2.

Table B-2. Sampling Matrix for the 4 RSSCT Conditions.

Facility D Column - Virgin
# of Samples at each Bed Volumes Treated

EBCT	0		500		1000		1500		2000		3000		4000		5000		7000		10000		12500		15000		17500		20000		22500		30000	
	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS
10	1	1	1	0	1	0	1	0	1	1	1	0	1	0	1	1	1	0	1	1	0	1	0	1	0	1	1	1	0	1	1	1
20	1	1	1	0	1	0	1	0	1	1	1	0	1	0	1	1	1	0	1	1	0	1	0	1	0	1	1	1	0	1	1	1

Facility D Column - Reactivated
# of Samples at each Bed Volumes Treated

EBCT	0		500		1000		1500		2000		3000		4000		5000		7000		10000		12500		15000		17500		20000		22500		30000	
	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS	TOC	PFAS
10	1	1	1	0	1	0	1	0	1	1	1	0	1	0	1	1	1	0	1	1	0	1	0	1	0	1	1	1	0	1	1	1
20	1	1	1	0	1	0	1	0	1	1	1	0	1	0	1	1	1	0	1	1	0	1	0	1	0	1	1	1	0	1	1	1

B.4 Data Analysis

The RSSCT data will be used to understand the long-term TOC and PFAS removal performance attained with two types of GAC and with a treated wastewater effluent (with higher TOC than typical groundwater RSSCT studies). Breakthrough curves will be developed, and polynomial models will be developed to characterize the curves. From there, the models will be used to configure representative full-scale GAC systems (with lead-lag reactors) for the treatment of these constituents in ozone/BAF effluent. This will include optimal reactor size (e.g., EBCT) and carbon regeneration frequency (e.g., GAC consumption in pounds per treated flow). This will serve as guidance to utilities who wish to use GAC as a post-treatment polishing step in CBAT trains for potable reuse.

APPENDIX C

RSSCT Results and Conclusions

C.1 Introduction

This Section will review the methods, results, and recommendations from the rapid small scale column testing. The RSSCT evaluated 4 different conditions to evaluate the removal of TOC and PFAS from ozone/biologically active filtration effluents. The objectives of the RSSCT are as follows:

- Determine time to breakthrough of TOC as a function of EBCT in ozone/BAF effluent
- Determine time to breakthrough of PFAS as a function of TOC concentration and EBCT in ozone/BAF effluent
- Use results of RSSCT to configure a feasible GAC system design for simultaneous removal of TOC and PFAS in ozone/BAF effluent

C.2 Methods

This Section will discuss methods and materials used during the actual testing. This includes the carbon preparation, source water, PFAS spike, experimental setup and sampling during RSSCT.

C.2.1 Carbon Preparation

The virgin and reactivated Calgon Filtrasorb 400 (F400) carbons were prepared for use in this RSSCT. To prepare the carbon, it is first crushed using a grinder and sifted through mesh sieves to obtain the desired size of 80x100. Then, the carbon was washed with deionized water. The wash step removes impurities and is repeated to a total of 72 washes until the supernatant water is clear. Next, the carbon is degassed by boiling the carbon and DI water in a beaker to eliminate gases that may be trapped in the carbon pores. Once this is done, the carbon is dried overnight at 105 °C. The carbon is then placed next to the RSSCT setup to reach room moisture content. Moisture content is checked by weighing the carbon before and after drying. Once at ambient temperature, the carbon is reweighed and added to the columns. 3.078 g of Virgin Calgon F400 and 3.305 g of Reactivated Calgon F400 was used in this testing.

C.2.2 Source Water Characteristics

Approximately 300 gallons of ozone/BAF effluent was sourced from Facility D. General water quality and background PFAS concentrations are given in Table C-1 and Table C-2. The 1.6 MGD Ozone system was operated to achieve 1-log *Cryptosporidium* inactivation according to the EPA's Ozone CT framework.

Table C-1. General Water Quality of RSSCT Raw Water.

Parameter	Raw	Units
TOC	4.79	mg/L
pH	7.01	Standard
Temperature	26.6	°C

Parameter	Raw	Units
Alkalinity	232	mg/L as $CaCO_3$
Turbidity	0.064	NTU
Conductivity	4,155	µS

Table C-2. RSSCT Raw Water PFAS Concentrations.

Name	Short Name	Raw Water Concentration (ng/L)	Molecular Weight (g/mol)
Perfluorobutanesulfonic acid	PFBS	8.2	300.1
Perfluorooctanoic acid	PFOA	10	414.1
Perfluorooctanesulfonic acid	PFOS	2.3	500.1
Perfluorohexanoic acid	PFHxA	170	314.1
Perfluorohexanesulfonic acid	PFHxS	2.2	400.1
Perfluoropentanoic acid	PFHpA	5.4	264.1
Perfluorononanoic acid	PFNA	<2	464.1
Perfluorodecanoic acid	PFDA	<2	514.1
Perfluorotridecanoic acid	PFTrDA	<2	664.1
Perfluorotetradecanoic acid	PFTA	<2	714.1

C.2.3 Spike Recovery QA/QC

The source water was spiked with an AccuStandard standard reagent containing 14 PFAS compounds, each at a target concentration of 50 ng/L above ambient concentration. Table C-3 displays the spike recovery and concentration of PFAS in the raw water, RSCCT feed, and standard in DI water. Spike recoveries were calculated based on the difference in measured PFAS concentration in RSSCT Feed and Raw Water, divided by the PFAS concentration in the DI water standard (which was spiked an equivalent aliquot of stock standard). Most PFAS had recoveries in range of 88-102% with a few PFAS that had lower recoveries. Notably PFHxA concentration in diluted PFAS Standard was measured at a higher concentration than the difference in PFHxA concentration in Raw Water and RSSCT Feed. This resulted in a poor spike recovery performance of 21%. Since DI water used was not analyzed, it is unclear whether there was a contamination from the sample bottle or handling for PFHxA. PFDA, PFTrDA, and PFTA had spike lower recoveries of 40-64%, possibly due to adsorption to the sample storage containers and apparatus materials. However, since the concentration in column effluent had a measurable change over the duration of the experiment, the data was still usable to assess breakthrough of PFHxA, PFDA, PFTrDa, and PFTA.

Table C-3. Spike Recovery of PFAS.

PFAS	Unit	Raw Water	RSSCT Feed	PFAS Std in DI	Spike Recovery
PFBS	ng/L	8.2	55	53	88.3%
PFOA	ng/L	10	67	63	90.5%
PFOS	ng/L	2.3	40	41	92.0%
PFHxA	ng/L	170	212	200	21.0%
PFHxS	ng/L	2.2	55	56	94.3%
PFHpA	ng/L	5.4	62.4	56	101.8%
PFNA	ng/L	<2	62.2	62	100.3%
PFDA	ng/L	<2	42.2	66	63.9%
PFTrDA	ng/L	<2	18	45	40.0%
PFTA	ng/L	<2	17	41	41.5%

C.2.4 Experimental Setup

Two different EBCTs (10-minute and 20-minute) were tested by varying the feed flow to the column. For each EBCT, two carbon types were tested: virgin Calgon F400 and reactivated Calgon F400, both of which were provided by Calgon Carbon. All four test conditions were sampled out to approximately 30,000 BVT. The apparatus consists of parallel glass columns filled with media according to the parameters in Table C-4. Feed water was stored in 5-gallon kegs and flows from the last to the first keg using nitrogen gas as the pressure source. Before reaching the columns, feed water flows through a 0.02 mm cartridge filter to remove microorganisms.

The RSSCT modelled full-scale columns with target media diameters of 0.845 mm and EBCTs of 10 and 20 minutes. Table C-4 shows the RSSCT parameters corresponding to the full-scale column. The EBCTs for RSSCT were determined based on prior method described previously as shown in formula below (Crittenden, Berrigan, and Hand 1986; Crittenden at al. 1991; Westerhoff et al. 2005):

$$EBCT_{SC} = EBCT_{FS} \times \left({dp_{SC}}/{dp_{FS}} \right)^2 \qquad \text{(Equation C-1)}$$

where: $EBCT_{SC}$ = empty bed contact time for the small-scale column,

$EBCT_{FS}$ = empty bed contact time for the full-scale column,

dp_{SC} = GAC particle diameter for small-scale column,

dp_{FS} = GAC particle diameter for full-scale column.

Time to specific bed volumes treated by RSSCT measured in hours for RSSCT was converted to days for full-scale columns using a ratio of the empty bed contact times of the small scale and full-scale and elution time using the following formula:

$$t_{FS} = t_{SC} \times \frac{EBCT_{FS}}{EBCT_{SC}} \qquad \text{(Equation C-2)}$$

where: $EBCT_{SC}$ = empty bed contact time for the small-scale column,

$EBCT_{FS}$ = empty bed contact time for the full-scale column,

t_{SC} = runtime for small-scale column,

t_{FS} = runtime for full-scale column.

Breakthrough curves for TOC and PFAS were fitted using the following polynomial equation:

$$\frac{C}{Co} = a + bx + cx^2 + dx^3 \qquad \text{(Equation C-3)}$$

where: C/Co = Ratio of effluent concentration to the influent concentration

a, b, c, d = fitting parameters

x = number of bed volumes treated

Table C-4. RSSCT Physical Parameters Corresponding to Full-scale EBCT.

Parameter	Value	Value	Units
Full-Scale Column			
Target EBCT	10	20	min
Target Media Diameter	0.845	0.845	mm
Carbon Mesh Size	12x40	12x40	
RSSCT			
Target Media Diameter	0.162	0.162	mm
Carbon Mesh Size	80x100	80x100	
EBCT	0.739	0.369	min
Column Diameter	1.1	1.1	cm
Media Bed Depth	8	8	cm
Flow Rate	10.3	20.6	mL/min
Hours of Operation	192	384	hours
BV	31,188	31,188	
Volume	237	237	liters
Total Volume	474	474	liters total
Total Volume	125	125	gallons total

C.2.5 Sampling Schedule

PFAS can be present in many materials which increases the risk of contamination during sampling, transport, and storage. To account for the potential contamination, quality control samples were included through the PFAS sampling events. These included both field blanks and equipment blanks. The field blanks were taken both in the field and after unloading the sample water in the laboratory. Sample influent was taken and stored for analysis when influent water started from a new sample container to supply RSSCT.

In order to capture the breakthrough of TOC and 8 PFAS compounds, higher frequency in sampling occurred around the expected time of breakthrough. For TOC, breakthrough was defined as 2 mg/L in the effluent samples and higher frequency of sampling occurred in the first 5,000 BVT. For PFAS, breakthrough was defined at 5 ng/L in the effluent sample and higher frequency sampling occurred between 10,000 to 22,500 BVT. Table C-5 outlines the sample times in BVT and runtime for the TOC and PFAS analytes. The collected effluent samples were analyzed using EPA 537.1 for PFAS and SM 5310 C for TOC.

Table C-5. Sampling Schedule for TOC and PFAS according to BV and Runtime.

	BV Translated in Runtime		
BV	**10 min EBCT**	**20 min EBCT**	**Analytes**
0	0	0	TOC and PFAS
500	3h 10min	6h 15min	only TOC
1,000	6h 15min	12h 30 min	only TOC
1,500	9h 20 min	18h 30 min	only TOC
2,000	12h 30 min	25 hours (1d 1h)	TOC and PFAS
3,000	18h 30 min	37 h (1d 13h)	only TOC
4,000	25 hours (1d 1h)	49 h (2d 1h)	only TOC
5,000	30h 45m (1d 6h 45 min)	2d 13h 45m	TOC and PFAS
7,000	1d 19h 15m	4d 12h 30m	only TOC
10,000	2d 13h 45m	5d	TOC and PFAS
12,500	3d 4h 45m	6d 9h 30m	only PFAS
15,000	3d 20h	7d 17h	only PFAS
17,500	4d 12h	9d	only PFAS
20,000	5d	10d 6h 15m	TOC and PFAS
22,500	5d 18h 45m	11d 13h 30m	only PFAS
30,000	7d 17h	15d 9h 30m	TOC and PFAS

C.3 Results

This Section will summarize the results of this RSSCT, including the breakthrough curves for the four test conditions.

C.3.1 Virgin Calgon F400—EBCT 10 Minutes

The TOC and PFAS breakthrough curves for a 10-minute EBCT using Virgin Calgon F400 in equivalent days of operation are shown in Figure C-1 and Figure C-2. For TOC, 1-log removal (90%) is not sustained beyond 275 BVs. To achieve 0.5-log TOC removal (68%), GAC media needs to be replaced at 1,600 BVs or 11 equivalent days of operation at full-scale. PFHxA, PFBS, and PFHpA have considerably faster breakthrough than longer chain PFAS.

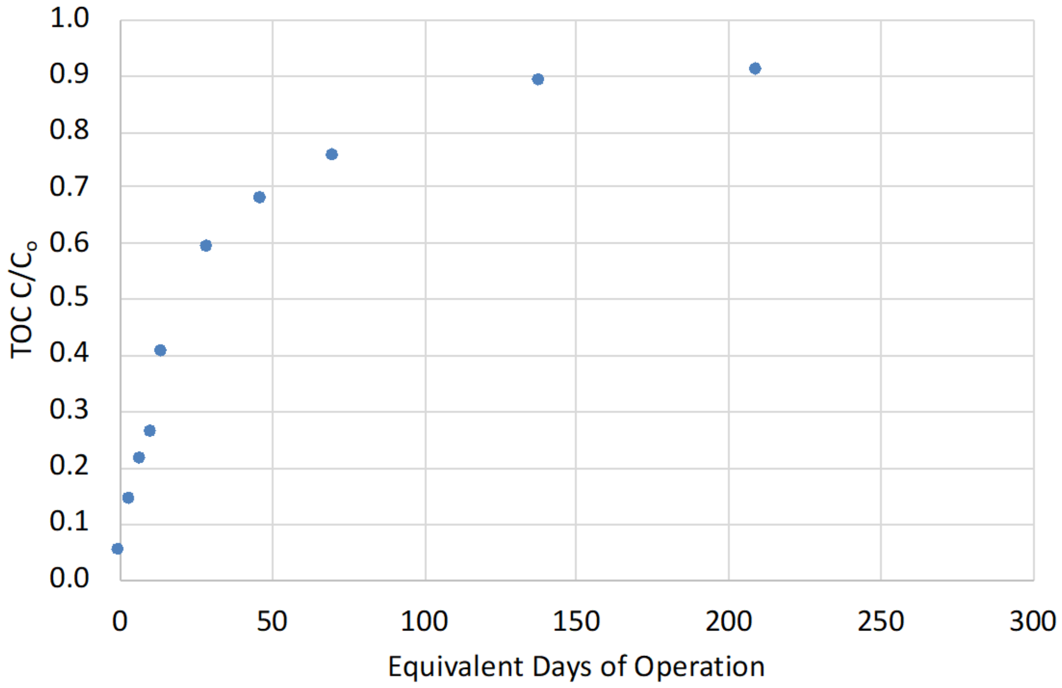


Figure C-1. TOC Breakthrough Curve for Virgin Calgon F400 with 10-minute EBCT.

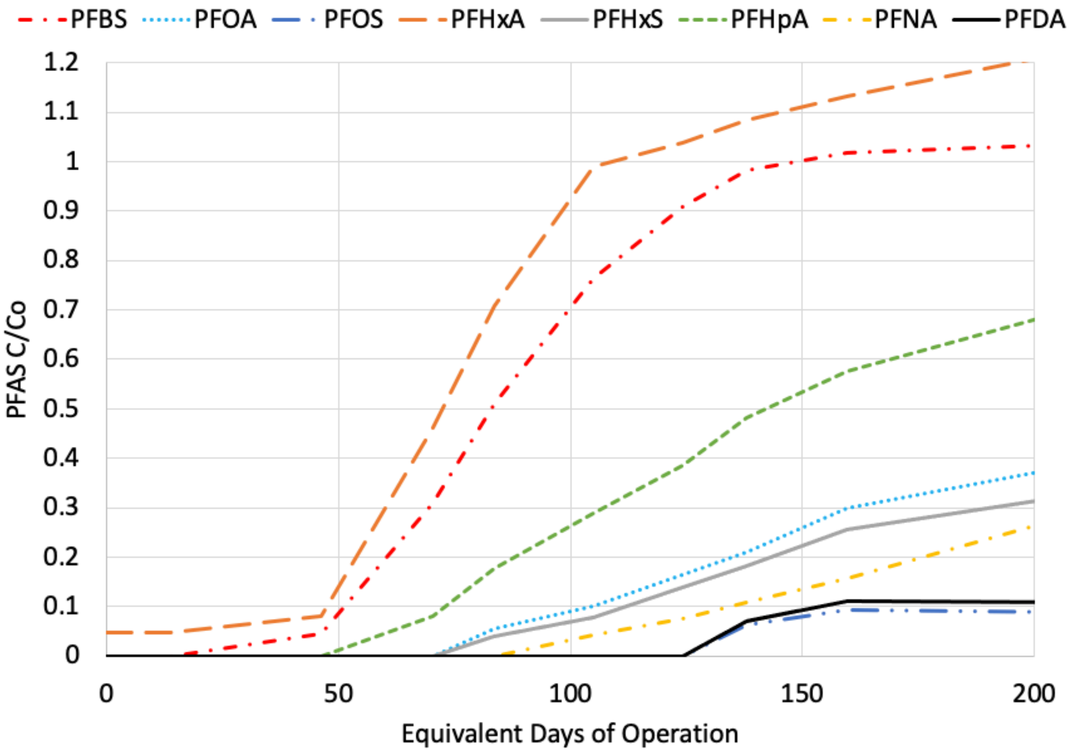


Figure C-2. PFAS Breakthrough Curves for Virgin Calgon F400 with 10-minute EBCT.

C.3.2 Virgin Calgon F400—EBCT 20 Minutes

The TOC and PFAS breakthrough curves for a 20-minute EBCT using Virgin Calgon F400 in equivalent days of operation are shown in Figure C-3 and Figure C-4. For TOC, 1-log removal (90%) was also not sustained beyond 350 BVs. For 0.5-log TOC removal (68%), GAC media would need to be replaced at 1975 BVs or 27 equivalent days of operation at full-scale. Similar to the RSSCT run for 10-minute EBCT, PFHxA, PFBS, and PFHpA have considerably faster breakthrough than longer chain PFAS as shown in Figure C-4.

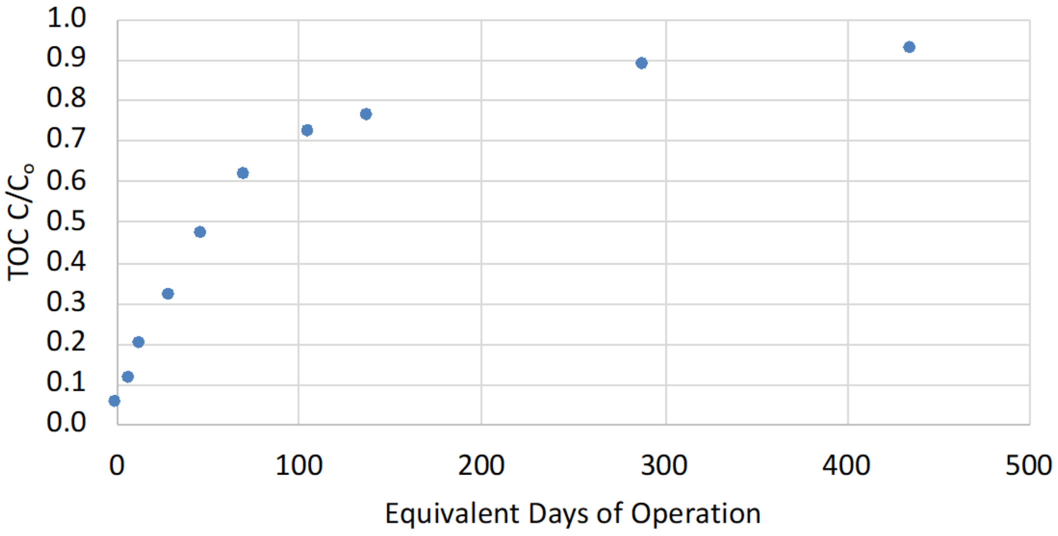


Figure C-3. TOC Breakthrough Curve for Virgin Calgon F400 with 20-minute EBCT.

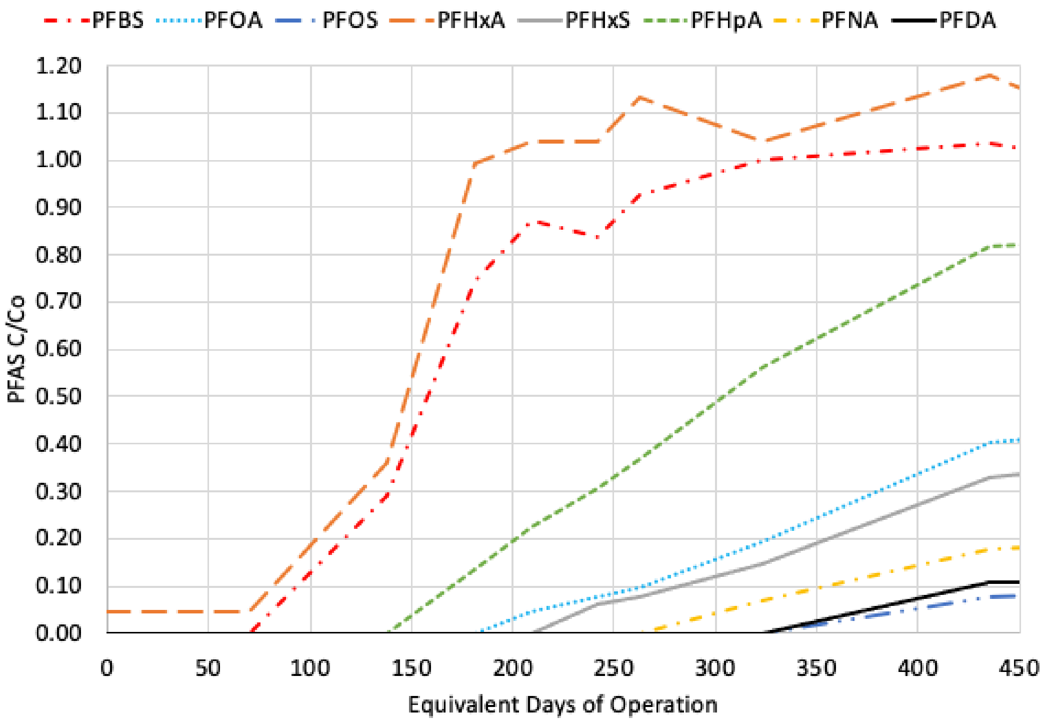


Figure C-4. PFAS Breakthrough Curves for Virgin Calgon F400 with 20-minute EBCT.

C.3.3 Reactivated Calgon F400—EBCT 10 Minutes

The TOC and PFAS breakthrough curves for a 10-minute EBCT using Reactivated Calgon F400 in equivalent days of operation are shown in Figure C-5 and Figure C-6. For TOC, 1-log removal (90%) is not sustained beyond 500 BVs. To achieve 0.5-log TOC removal (68%), GAC media needs to be replaced at 6700 BVs or 46 equivalent days of operation. Similar to the other conditions, PFHxA, PFBS, and PFHpA have considerably faster breakthrough than longer chain PFAS.

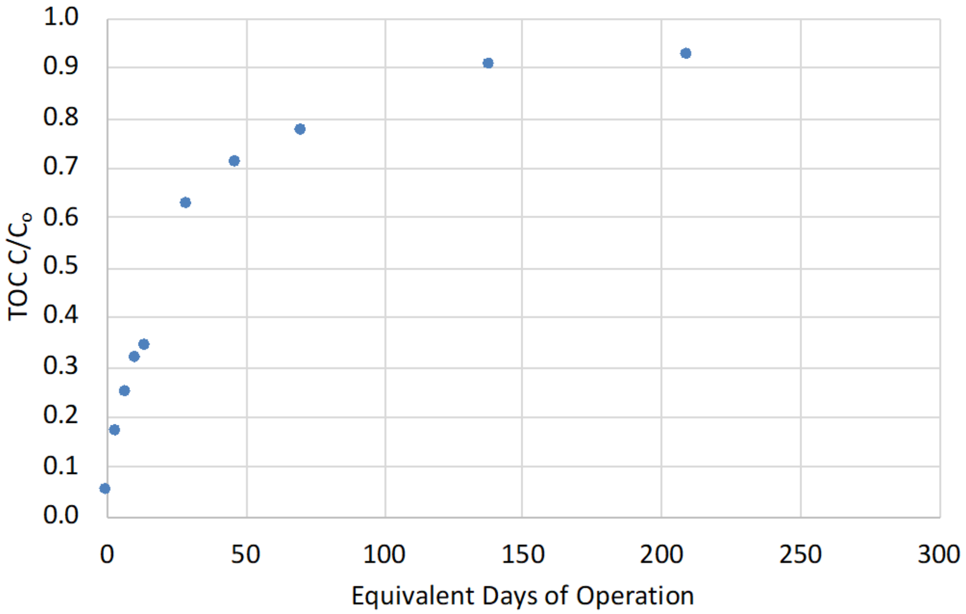


Figure C-5. TOC Breakthrough Curve for Reactivated Calgon F400 with 10-minute EBCT.

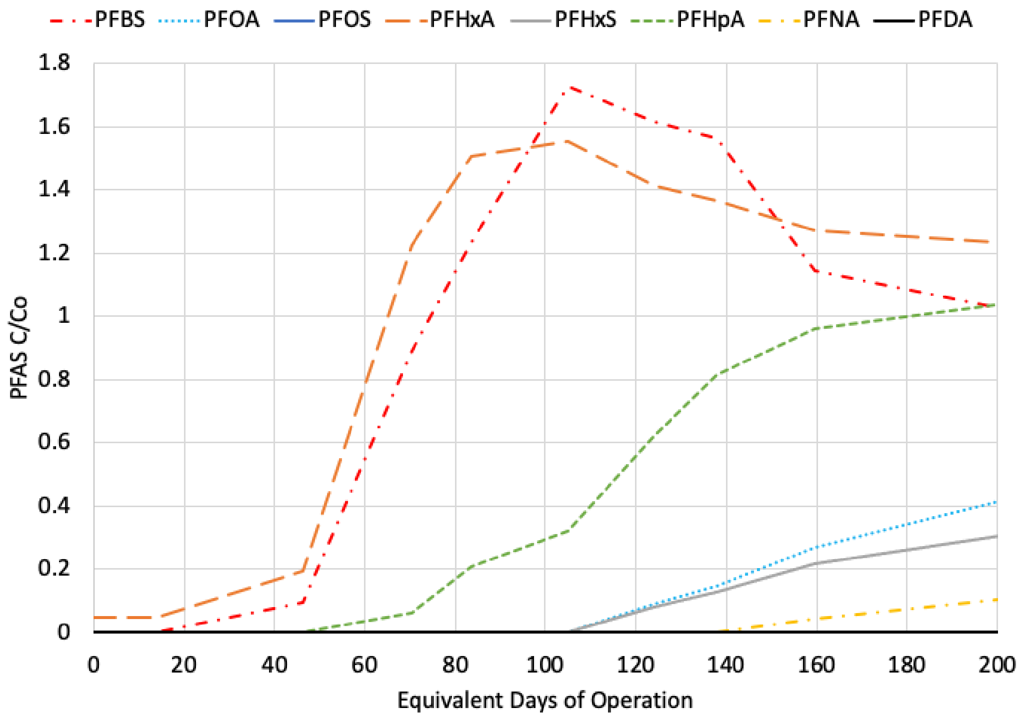


Figure C-6. PFAS Breakthrough Curves for Reactivated Calgon F400 with 10-minute EBCT.

C.3.4 Reactivated Calgon F400—EBCT 20 Minutes

The TOC and PFAS breakthrough curves for a 20-minute EBCT using Reactivated Calgon F400 in equivalent days of operation are shown in Figure C-7 and Figure C-8. For TOC, 1-log removal (90%) is not sustained beyond 500 BVs. To achieve 0.5-log TOC removal (68%), GAC media needs to be replaced at 7500 BVs or 105 equivalent days of operation. PFHxA, PFBS, and PFHpA have considerably faster breakthrough than longer chain PFAS.

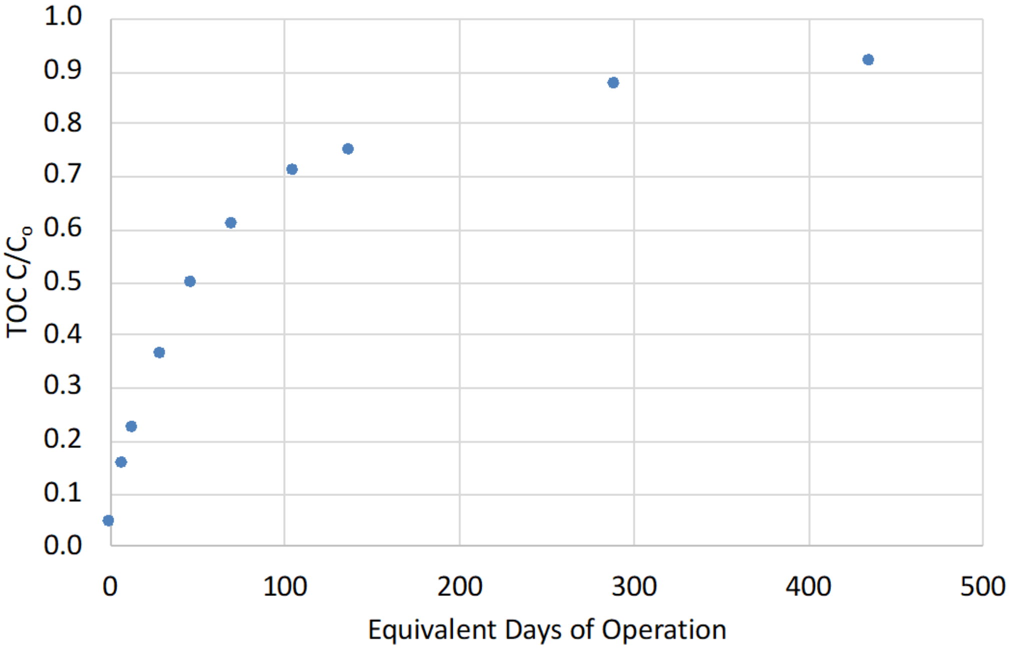


Figure C-7. TOC Breakthrough Curve for Reactivated Calgon F400 with 20-minute EBCT.

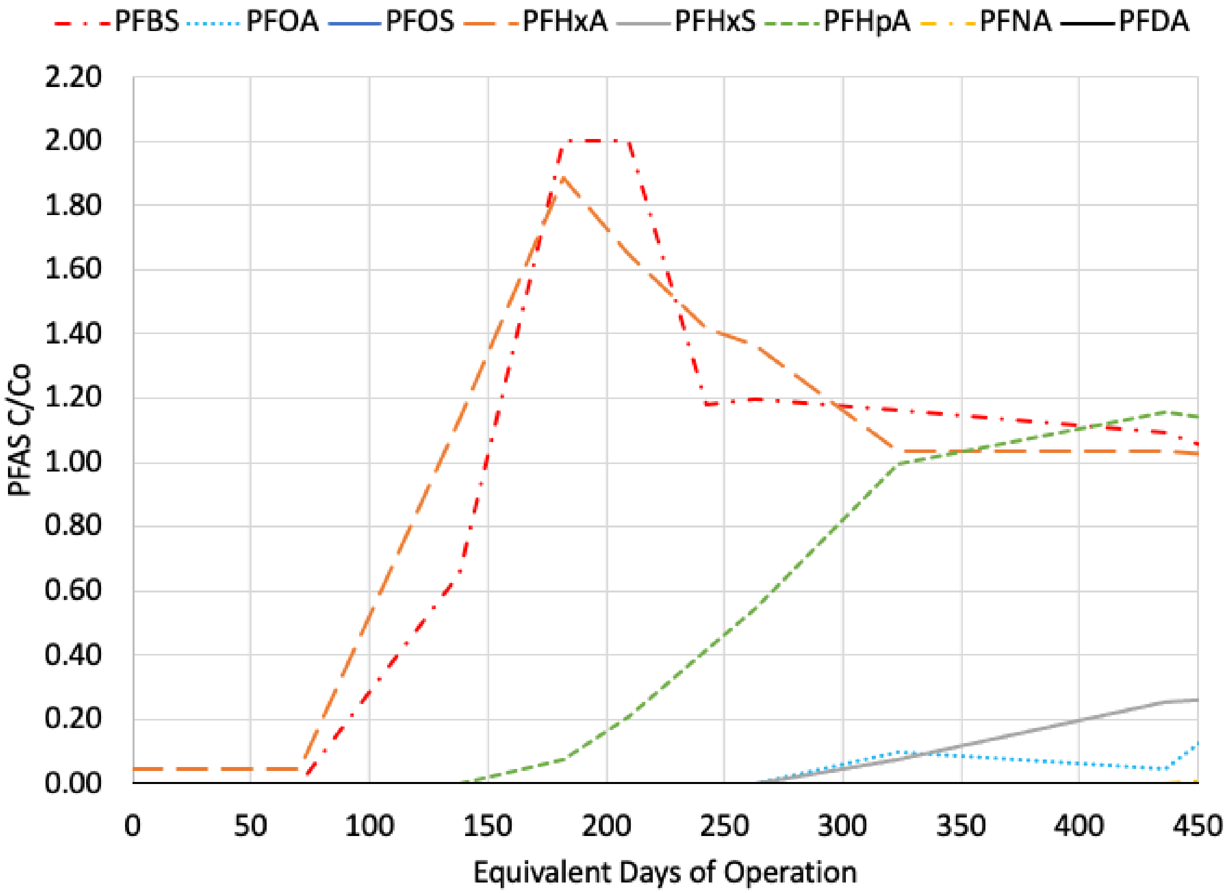


Figure C-8. PFAS Breakthrough Curves for Reactivated Calgon F400 with 20-minute EBCT.

C.4 Comparison of RSSCT Runs for TOC Removal Performance

Figure C-9 shows the TOC concentration for the influent water and four test conditions. Throughout the course of the study, influent TOC remains consistent. Virgin and reactivated carbon perform similarly, with 1-log removal (90%) not sustained beyond 500 BVs. RSSCT effluents' TOC concentration was almost the same between virgin and reactivated carbons and for columns with 10 min and 20 min EBCT. This would indicate that even 10 min was sufficient for various organics to adsorb on the carbons. A small difference was observed in the average number of bed volumes to sustain 0.5-log removal of TOC (68%). The 10 min columns (average of reactivated and virgin) needed 1,575 BVs, while 20 min columns took 1,838 BVs, indicating that longer EBCT provided a slight increase in performance of the GAC. However, since these were single runs, the difference may not be statistically significant and due to other external variables, such as variability in carbon preparation. Table C-6 provides further evaluation of the differences in performance of virgin and reactivated carbons. Different GAC and EBCTs are represented in Table C-6 by abbreviations, V-10min, R-10min, V-20min, R-20min. V10-10 and V-20min represent virgin GAC with 10 and 20 min EBCT, respectively. Initially there is a greater variability in bed volumes between the virgin and reactivated carbons, when targeting higher percent removal of TOC. Lower removal targets can be maintained for longer number of bed volumes and the difference between reactivated and virgin carbon gets smaller to approximately 10% range.

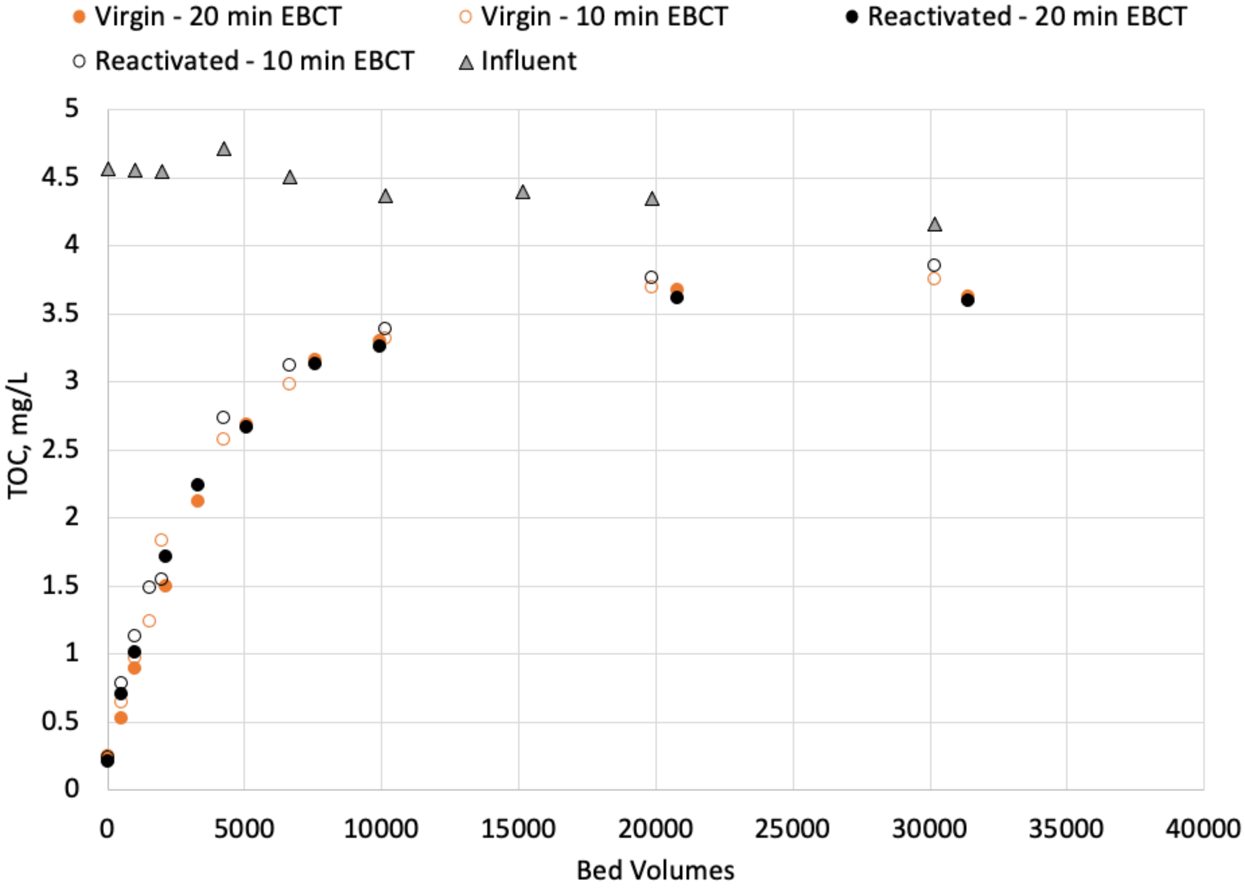


Figure C-9. TOC Concentration versus Bed Volume for Influent and various Carbon Types and EBCTs.

Table C-6. Bed Volumes for Different RSSCT Columns Testing and TOC Removals.

Carbon	Removal Target			
	90% (1-log)	68% (0.5-log)	50% (0.3-log)	30% (0.15-log)
V-10min	275	1600	3175	7675
R-10min	200	1550	3025	6225
V-20min	350	1975	3700	6975
R-20min	250	1700	3350	7475
Average	269	1706	3313	7088
Std. Dev.	62.5	190	290	646
RSD (%)	23.3	11.1	8.8	9.1

Figure C-10 displays the TOC breakthrough curves for all four conditions in equivalent days of operation. For each set of EBCT conditions, the virgin and reactivated carbon perform alike. To operate above 0.3-log (50%) removal of TOC, the GAC media would need to be replaced after 46 days of operation for the 10-minute EBCT. For the 20-minute EBCT, media would need to be replaced after 105 days of operation.

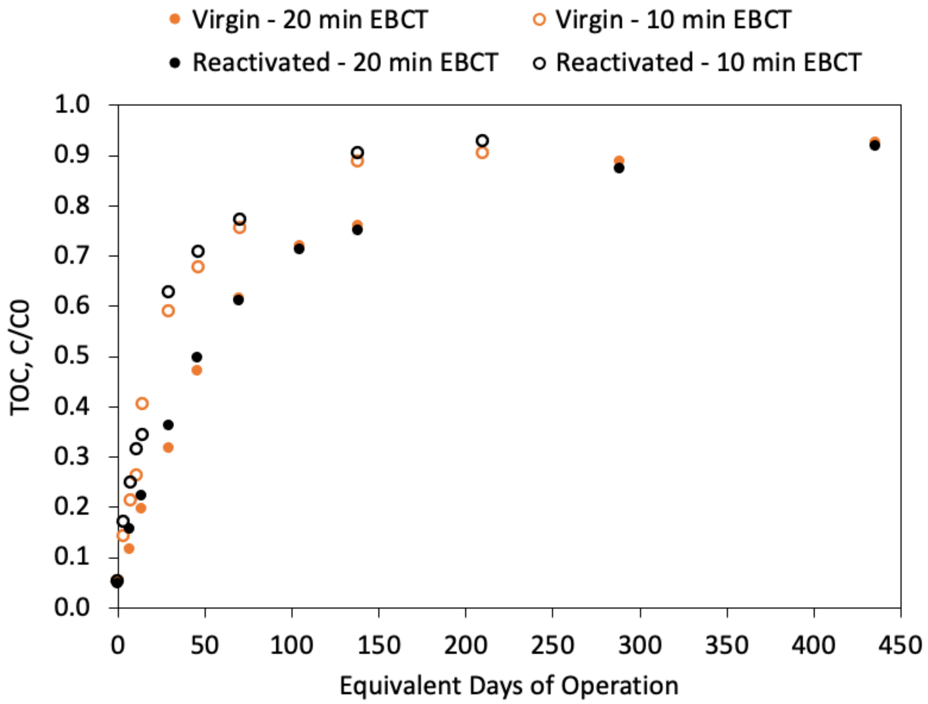


Figure C-10. TOC Breakthrough Curves for various Carbon Types and EBCTs.

C.5 Comparison of RSSCT Runs for PFAS Removal

PFHxA, PFBS, and PFHpA consistently had considerably faster breakthrough than longer chain PFAS, such as PFOA and/or PFOS for both 10 min and 20 min test runs. For example, greater than 1-log removal of PFBS was observed for up to 7,025 BVs or 24 days of operation at full-scale, whereas PFOA took as long 14,600 BVs or 51 days with virgin carbon. Similar to TOC removal, longer EBCT results in extended operational time to control PFOA. Figure C-11 displays all four testing condition breakthrough curves for PFOA. The reactivated carbon conditions performed slightly better than virgin carbon, indicating there may not be a significant advantage in using virgin carbon. Based on ambient PFOA concentration, a shorter EBCT may be sufficient to provide greater than 3 months of operation.

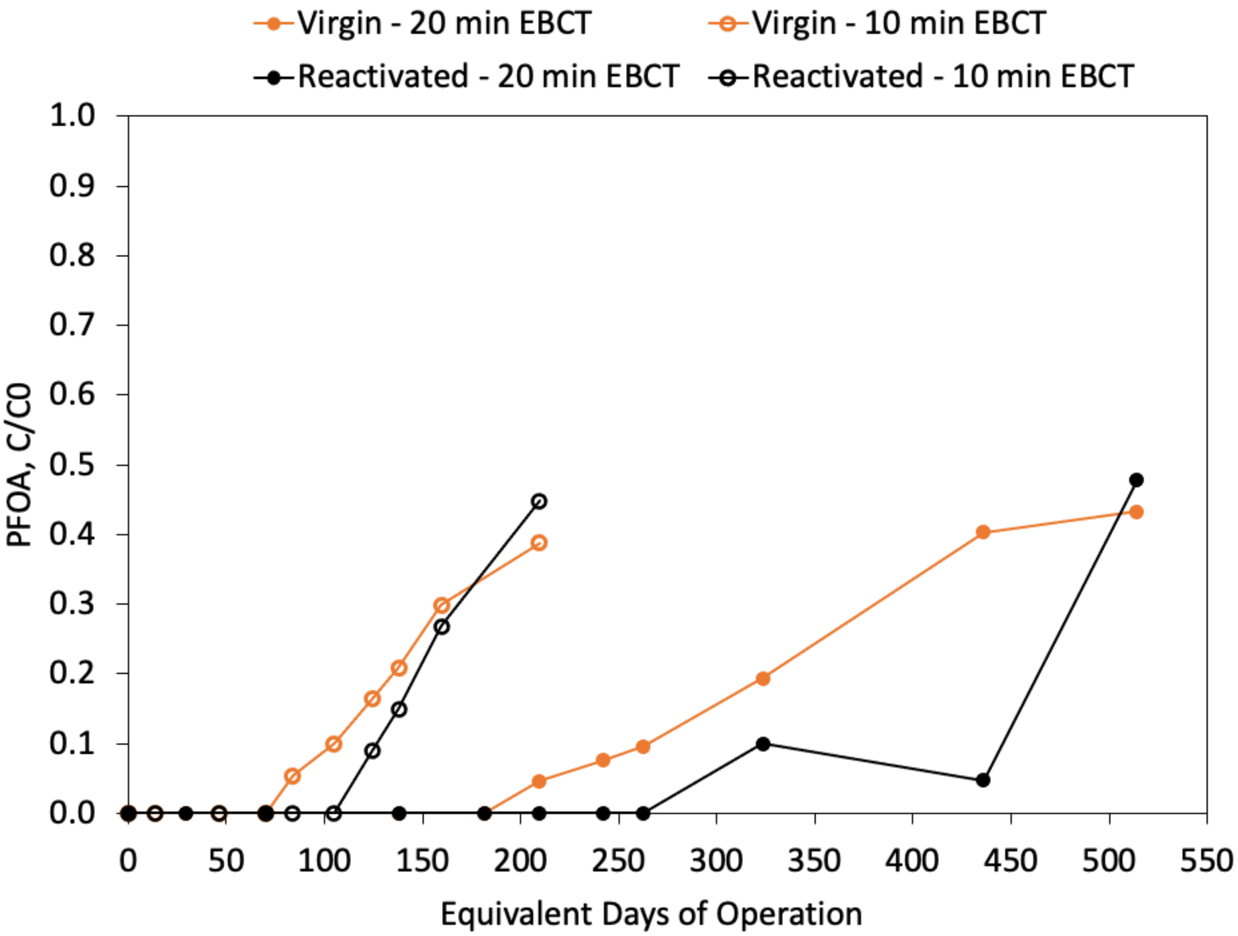


Figure C-11. PFOA Breakthrough Curves for various Carbon Types and EBCTs.

Figure C-12 displays the PFHxS breakthrough curves for all four test conditions. Removal trends of PFHxS was similar to PFOA, with reactivated carbon performing slightly better than virgin carbon. PFHxS removal parallels PFOA removal, consistent with having a similar molecular weight.

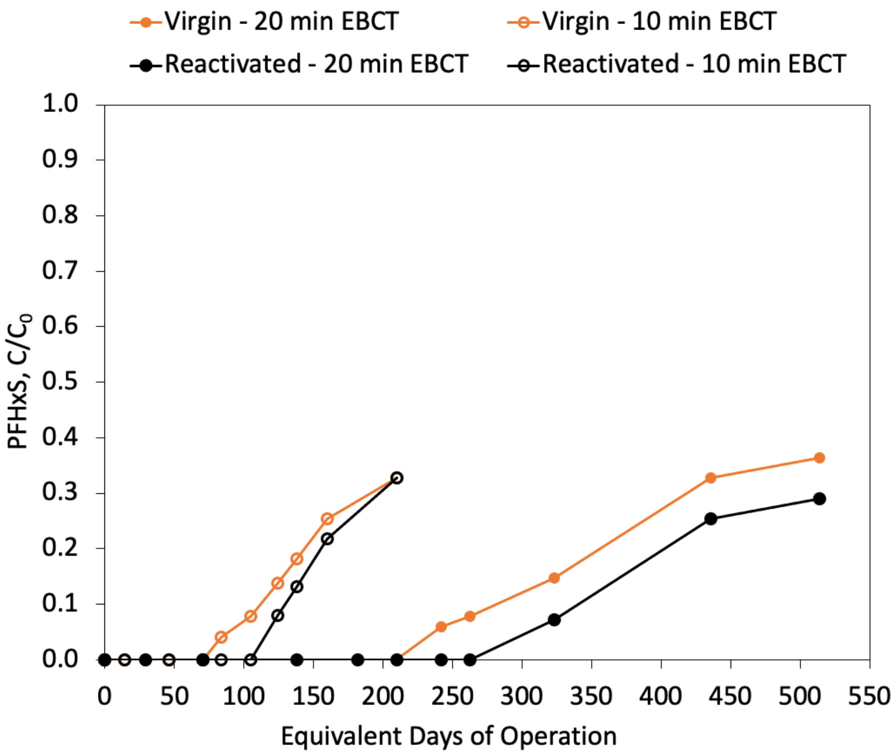


Figure C-12. PFHxS Breakthrough Curves for various Carbon Types and EBCTs.

C.6 Modeling RSSCT Test Results for Full-Scale Design and Cost Comparison

In previous sections the RSSCT results from single columns were compared individually and extrapolated to equivalent days of operation of full-scale size columns. In this Section the breakthrough plots were modeled based on the approach briefly described in Section C.2.4 (see Equation C-3).

Only the breakthrough plots were modeled for TOC, PFBS, and PFOA. These three parameters were identified as potential limiting or design parameters, based on the performance and dataset from this RSSCT testing. Fitting parameters for various carbons and EBCTs for TOC are provided in Table C-7. Table C-8 shows fitting parameters for the PFBS, and Table C-9 for PFOA. Different GAC and EBCTs are represented by abbreviations, V-10min, R-10min, V-20min, R-20min. V10-10 and V-20min represent virgin GAC with 10 and 20 min EBCT, respectively. Similarly, R-10min and R-20min represent regenerated GAC with 10 with 10 and 20 min EBCT, respectively.

Table C-7. Modeling Parameters for TOC Breakthrough.

Term	V-10min	R-10min	V-20min	R-20min
a	0.0412	6.12E-02	4.50E-02	5.49E-02
b	2.04E-04	1.92E-04	1.55E-04	1.82E-04
c	-2.18E-08	-1.77E-08	-9.17E-09	-1.70E-08
d	8.46E-13	5.58E-13	7.44E-14	5.74E-13
R2	0.9927	0.9946	0.999	0.9994

Table C-8. Modeling Parameters for PFBS Breakthrough.

Term	V-10min	R-10min	V-20min	R-20min
a	2.68E-02	2.31E-14	-4.01E-01	7.99E-15
b	-6.17E-05	2.41E-05	6.18E-05	1.84E-05
c	1.27E-08	-1.66E-08	3.39E-09	-1.24E-08
d	-3.60E-13	2.26E-12	-1.50E-13	1.73E-12
R2	0.996	1.000	0.957	1.000

Table C-9. Modeling Parameters for PFOA Breakthrough.

Term	V-10min	R-10min	V-20min	R-20min
a	1.27E-02	1.56E-02	2.21E-02	3.68E-03
b	-1.67E-05	-1.41E-05	-1.71E-05	-1.27E-06
c	2.07E-09	1.21E-09	1.56E-09	-1.46E-10
d	-3.66E-14	-8.31E-15	-2.11E-14	1.43E-14
R2	0.992	0.973	0.985	0.993

An eight column GAC system was considered as a simulation of a full-scale operation. This simulation assumed individual columns are staggered and treat feed flow evenly. As time goes on, additional columns are brought online to keep the concentration of target parameter below objective in the blended product. For brevity, 8-column reactor simulations were performed with virgin carbon media for 10-min and 20-min EBCT. For PFAS and PFBS a target removal of 1-log (90%) was simulated. TOC removal was simulated with target removal goals of 1-log (90%), 0.5-log (68%), 0.3-log (50%), and 0.15-log (30%). This was done since TOC had shortest breakthrough and allowed to compare different target removals goals with that of 1-log PFAS removal. Tables C-10, C-11, and C-12 provide select examples of simulations that detail projected number of days for replacement of media in the staggered columns and concentration of target parameter in the product blend.

Table C-10. Modeling TOC Removal Target of 0.3-log (50%) with 8-column GAC System.

Modelling the TOC of each column and combining to get the TOC of the blend											
Days	BV	Days	1	2	3	4	5	6	7	8	Blend
0	0	0	0.00								0.00
7	1,008	7	1.35	0.00							0.68
18	2,592	18	2.63	1.35	0.00						1.33
27	3,888	27	3.33	2.63	1.35	0.00					1.83
36	5,184	36	3.78	3.33	2.63	1.35	0.00				2.22
45	6,480	45	4.07	3.78	3.33	2.63	1.35	0.00			2.53
54	7,776	54	4.24	4.07	3.78	3.33	2.63	1.35	0.00		2.77
63	9,072	63	4.38	4.24	4.07	3.78	3.33	2.63	1.35	0.00	2.97
0	0	72	0.00	4.38	4.24	4.07	3.78	3.33	2.63	1.35	2.97
9	1,296	81	1.62	0.00	4.38	4.24	4.07	3.78	3.33	2.63	3.01
18	2,592	90	2.63	1.62	0.00	4.38	4.24	4.07	3.78	3.33	3.01
27	3,888	99	3.33	2.63	1.62	0.00	4.38	4.24	4.07	3.78	3.01
36	5,184	108	3.78	3.33	2.63	1.62	0.00	4.38	4.24	4.07	3.01
45	6,480	117	4.07	3.78	3.33	2.63	1.62	0.00	4.38	4.24	3.01
54	7,776	126	4.24	4.07	3.78	3.33	2.63	1.62	0.00	4.38	3.01
63	9,072	135	4.38	4.24	4.07	3.78	3.33	2.63	1.62	0.00	3.01
0	0	144	0.00	4.38	4.24	4.07	3.78	3.33	2.63	1.62	3.01
9	1,296	153	1.62	0.00	4.38	4.24	4.07	3.78	3.33	2.63	3.01
18	2,592	162	2.63	1.62	0.00	4.38	4.24	4.07	3.78	3.33	3.01
27	3,888	171	3.33	2.63	1.62	0.00	4.38	4.24	4.07	3.78	3.01
36	5,184	180	3.78	3.33	2.63	1.62	0.00	4.38	4.24	4.07	3.01

Table C-11. Modeling PFBS Removal Target of 1-log (90%) with 8-column GAC System.

Modelling the PFBS of each column and combining to get the PFBS of the blend											
Days	BV	Days	1	2	3	4	5	6	7	8	Blend
0	0	0	0.00								0.00
37	5,328	37	0.02	0.00							0.01
40	5,760	40	0.14	0.02	0.00						0.06
45	6,480	45	0.37	0.14	0.02	0.00					0.14
50	7,200	50	0.64	0.37	0.14	0.02	0.00				0.24
55	7,920	55	0.94	0.64	0.37	0.14	0.02	0.00			0.35
60	8,640	60	1.26	0.94	0.64	0.37	0.14	0.02	0.00		0.48
65	9,360	65	1.60	1.26	0.94	0.64	0.37	0.14	0.02	0.00	0.62
0	0	70	0.00	1.60	1.26	0.94	0.64	0.37	0.14	0.02	0.62
37	5,328	107	0.02	0.00	1.60	1.26	0.94	0.64	0.37	0.14	0.62
40	5,760	110	0.14	0.02	0.00	1.60	1.26	0.94	0.64	0.37	0.62
45	6,480	115	0.37	0.14	0.02	0.00	1.60	1.26	0.94	0.64	0.62
50	7,200	120	0.64	0.37	0.14	0.02	0.00	1.60	1.26	0.94	0.62
55	7,920	125	0.94	0.64	0.37	0.14	0.02	0.00	1.60	1.26	0.62
60	8,640	130	1.26	0.94	0.64	0.37	0.14	0.02	0.00	1.60	0.62
65	9,360	135	1.60	1.26	0.94	0.64	0.37	0.14	0.02	0.00	0.62
0	0	140	0.00	1.60	1.26	0.94	0.64	0.37	0.14	0.02	0.62
37	5,328	177	0.02	0.00	1.60	1.26	0.94	0.64	0.37	0.14	0.62
40	5,760	180	0.14	0.02	0.00	1.60	1.26	0.94	0.64	0.37	0.62
45	6,480	185	0.37	0.14	0.02	0.00	1.60	1.26	0.94	0.64	0.62
50	7,200	240	0.64	0.37	0.14	0.02	0.00	1.60	1.26	0.94	0.62

Table C-12. Modeling PFOA Removal Target of 1-log (90%) with 8-column GAC System.

Modelling the PFOA of each column and combining to get the PFOA of the blend											
Days	BV	Days	1	2	3	4	5	6	7	8	Blend
0.0	0	0	0.00								0.00
60.0	8,640	60	0.01	0.00							0.00
70.0	10,080	70	0.10	0.01	0.00						0.04
80.0	11,520	80	0.23	0.10	0.01	0.00					0.09
90.0	12,960	90	0.39	0.23	0.10	0.01	0.00				0.15
120.0	17,280	120	0.92	0.39	0.23	0.10	0.01	0.00			0.27
140.0	20,160	140	1.30	0.92	0.39	0.23	0.10	0.01	0.00		0.42
160.0	23,040	160	1.67	1.30	0.92	0.39	0.23	0.10	0.01	0.00	0.58
0.0	0	180	0.00	1.67	1.30	0.92	0.39	0.23	0.10	0.01	0.58
60.0	8,640	240	0.01	0.00	1.67	1.30	0.92	0.39	0.23	0.10	0.58
70.0	10,080	250	0.10	0.01	0.00	1.67	1.30	0.92	0.39	0.23	0.58
80.0	11,520	260	0.23	0.10	0.01	0.00	1.67	1.30	0.92	0.39	0.58
90.0	12,960	270	0.39	0.23	0.10	0.01	0.00	1.67	1.30	0.92	0.58
120.0	17,280	300	0.92	0.39	0.23	0.10	0.01	0.00	1.67	1.30	0.58
140.0	20,160	320	1.30	0.92	0.39	0.23	0.10	0.01	0.00	1.67	0.58
160.0	23,040	340	1.67	1.30	0.92	0.39	0.23	0.10	0.01	0.00	0.58
0.0	0	360	0.00	1.67	1.30	0.92	0.39	0.23	0.10	0.01	0.58
60.0	8,640	420	0.01	0.00	1.67	1.30	0.92	0.39	0.23	0.10	0.58
70.0	10,080	430	0.10	0.01	0.00	1.67	1.30	0.92	0.39	0.23	0.58
80.0	11,520	440	0.23	0.10	0.01	0.00	1.67	1.30	0.92	0.39	0.58
90.0	12,960	450	0.39	0.23	0.10	0.01	0.00	1.67	1.30	0.92	0.58

The results of the modeling full-scale operation with the 8-column GAC system were compiled and presented in Table C-13. The first top half of Table C-13 shows replacement frequency in days for various target removals goals for TOC, PFBS and PFOA. As can be see the 10-min EBCT based system can provide reasonable replacement frequency for removal of PFOA and PFBS, at 116 and 70 days, respectively. TOC removal of 1-log as discussed earlier would be challenging, whereas 0.3-log (50%) removal target perhaps is more realistic and more in line with the projected removals for PFBS.

Table C-13. Summary of Simulations with 8-column GAC System and Modeled GAC Consumption in lbs/1,000 Gallons of Treated Water.

	PFOA	PFBS	TOC			
	90%	90%	90%	68%	50%	30%
EBCT	1-log	1-log	1-log	0.5-log	0.3-log	0.15-log
GAC Replacement Frequency, days						
10 Min	116	70	4.8	39	72	105
20 Min	360	180	18.0	120	180	233
GAC Consumption lbs/1,000 gal						
10 Min	0.264	0.438	6.383	0.786	0.426	0.292
20 Min	0.170	0.340	3.404	0.511	0.340	0.263

Table C-13 also provides projected GAC media consumption in lbs/1,000 gallons. Notably the TOC removal of even 0.5-log (68%) is more costly than removal of PFBS or PFOA by 1-log. Therefore, TOC removal goals may be primary for certain potable reuse projects looking to control TOC by GAC as a polishing step with an added protection against PFAS. On the other hand, if PFAS removal is primary purpose, there is some additional benefit in associated removal of TOC. When comparing these relative costs for 10-min vs. 20-min EBCT columns, generally the 20-min EBCT provides a lower carbon consumption and allow for a longer replacement frequency. The projected cost difference may become sufficient to offset additional capital costs for bigger GAC vessels and would need to be evaluated further during design phases of the project.

C.7 Conclusions and Recommendations

The RSSCT results indicate no significant differences in performance between the virgin and reactivated GAC. Virgin GAC appears to have no appreciable advantage over the less expensive reactivated GAC. TOC removal through BAF appears challenging due to relatively short bed volumes to breakthrough. For example, breakthrough of 10% of influent TOC concentration can happen after as little as 500 bed volumes. This increases the need for optimal upstream treatment, GAC configuration, operation, and carbon usage to manage TOC breakthrough. Run time to breakthrough is highly dependent on influent TOC levels and effluent TOC targets. For example, if targeting 0.5-log removal (68%) of TOC time to breakthrough increases to approximately 6,700-7,500 bed volumes.

Generally, smaller molecular weight PFAS have a shorter number of bed volumes before breakthrough than larger PFAS. Notably, PFHxA, PFBS, and PFHpA have the fastest breakthrough (BV) than PFAS with longer carbon chains such as PFOA and PFOS. Since exhaustion of TOC occurs before PFAS, balancing the two removals is needed for facilities that require control of both.

Facilities looking to control both TOC and PFAS must find a balance between the two since TOC breakthrough occurs more rapidly than PFAS. To manage TOC, larger bed configurations may be necessary to operate at a higher EBCT. This will create a GAC media replacement frequency that is more manageable than the frequency with a shorter EBCT. Based on modeling the RSSCT results and performing simulations with an 8-column GAC system to represent full-scale operation, media replacement for 0.5-log removal of TOC will be needed after 39 days at a 10-minute EBCT compared to 120 days at a 20-minute EBCT. Higher TOC removal through upstream biological treatment and BAF can achieve other treatment objectives such as lowering DBP formation potential and the requirements for GAC media usage. Since TOC removal is highly dependent on the effluent target, these objectives must be balanced with PFAS removal, which generally are expected to have higher number of bed volumes before breakthrough.

In facilities where TOC does not need to be further treated, GAC systems can be operated longer due to higher number of bed volumes to breakthrough for PFAS. In this case, a 10-minute EBCT may be sufficient to provide PFAS removal with a reasonable media replacement frequency. Based on modeling the RSSCT results and performing simulations with an 8-column GAC system to represent full-scale operation, media replacement for 1.0-log removal of PFOA will be needed after 116 days at a 10-minute EBCT compared to 76 days for PFBS. If preferred, longer EBCTs can be used to prolong replacement frequency (e.g., replacement frequency for PFOA with 20 min EBCT is approximately 360 days). Smaller molecular weight PFAS with shorter carbon chains, such as PFBS tend to have less BVs before breakthrough. For 1.0-log removal of PFBS media replacement will be needed after 76 days for GAC system with 10-minute EBCT and 180 days for 20-min EBCT. Alternatively, the removal of these compounds can be accomplished using more selective treatment options. Possible options include nanofiltration, which will retain a small residuals stream and provide TOC removal, or selective ion exchange resins. Between PFOA and PFOS, which have California notification levels of 5.1 and 6.5 ng/L, PFOA appears to require a sooner changeout and therefore should drive the GAC usage. PFBS, is a shorter carbon chain compound than either PFOA or PFOS which breakthroughs sooner, resulting in carbon usage of 0.340lbs/1,000 gallons. This is about double the consumption for removal of PFOA at EBCT of 20 min, however due to its relatively high notification limit in CA of 500 ng/L it may or may not need to take priority during development of design criteria for GAC system depending on the PFBS concentration in the feed water relative to that of the PFOA, or PFOS.

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