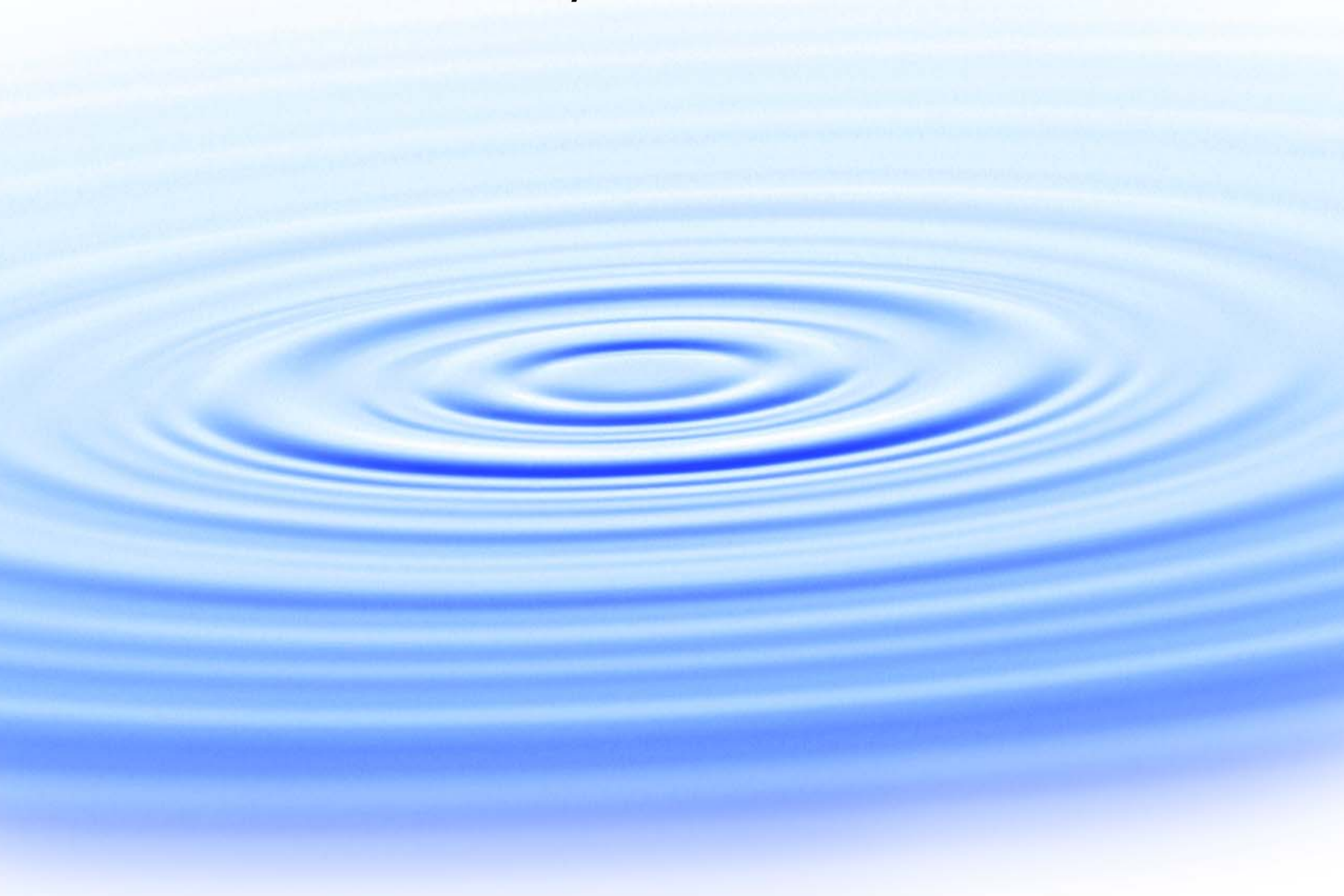




Use of Ozone in Water Reclamation for Contaminant Oxidation

Executive Summary



WaterReuse Research Foundation

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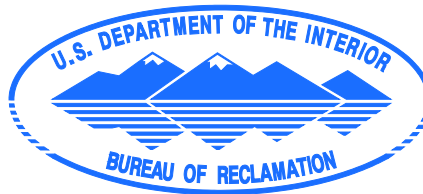
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List of Acronyms

AACE	Association for the Advancement of Cost Engineering
ADI	Acceptable daily intake
AOC	Assimilable organic carbon
AOP	Advanced oxidation process
ARR	Aquifer recharge and recovery
ARWWTP	Al-Ruwais Wastewater Treatment Plant
ATP	Adenosine triphosphate
AWPF	Advanced Water Purification Facility
BAC	Biological activated carbon
BAF	Biologically active filtration
BDF	Buffered demand-free
BDOC	Biodegradable organic carbon
BHA	Butylated hydroxyanisole
BOD	Biochemical oxygen demand
BQ	Benchmark quotient
CCL3	Contaminant Candidate List 3
CCWRD	Clark County Water Reclamation District
CDOC	Chromatographable dissolved organic carbon
CDPH	California Department of Public Health
CFU	Colony-forming unit
COD	Chemical oxygen demand
CT	Concentration x Time (as used for disinfection)
DALY	Disability adjusted life year
DBP	Disinfection byproduct
DEET	<i>N,N</i> -diethyl- <i>meta</i> -toluamide
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWEL	Drinking water equivalent level
DWG	Drinking water goal
Eawag	Swiss Federal Institute for Aquatic Science and Technology
EBCT	Empty bed contact time
EDC	Endocrine-disrupting compound
EEM	Excitation-emission matrix
EEq	Estradiol equivalents
EfOM	Effluent organic matter
EPA	Environmental Protection Agency
EQS	Environmental quality standard
ERM	Electron-rich moiety
EU	European Union
FAT	Full advanced treatment
FCM	Flow cytometry
FDA	Food and Drug Administration
FELST	Fish early life stage toxicity
FI	Fluorescence index
FP	Formation potential

FRI	Fluorescence regional integration
GCGA	Gwinnett County, Georgia
GC-MS/MS	Gas chromatography tandem mass spectrometry
GPM	Gallons per minute
GRR	Groundwater replenishment and reuse
GWRS	(Orange County) Groundwater Replenishment System
HOC	Hydrophobic organic carbon
HPLC-UV	High performance liquid chromatography with UV detection
HRT	Hydraulic residence time
IOD	Instantaneous ozone demand
IPR	Indirect potable reuse
KAUST	King Abdullah University of Science and Technology
KOWWTP	Kloten-Opfikon Wastewater Treatment Plant
LaWWTP	Lausanne Wastewater Treatment Plant
LC-MS/MS	Liquid chromatography tandem mass spectrometry
LoWWTP	Lowood Wastewater Treatment Plant
LOX	Liquid oxygen
LVWPCF	Las Vegas Water Pollution Control Facility
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MF	Microfiltration
MFF	Microfiltration feed
MGD	Million gallons per day
MPN	Most probable number
MRL	Method reporting limit
MTBE	Methyl <i>tert</i> -butyl ether
MWRDGC	Metropolitan Water Reclamation District of Greater Chicago
m/z	Mass-per-charge ratio (as it relates to mass spectrometry)
ND	Non-detect
NDBA	<i>N</i> -nitrosodi- <i>n</i> -butylamine (NDBA)
NDEA	<i>N</i> -nitrosodiethylamine
NDEP	Nevada Department of Environmental Protection
NDMA	<i>N</i> -nitrosodimethylamine
NDPA	<i>N</i> -nitrosodi- <i>n</i> -propylamine
NIST	National Institute of Standards and Technology
NL	Notification level
NMEA	<i>N</i> -nitrosomethylethylamine
NO(A)EL	No observed (adverse) effect level
NPIP	<i>N</i> -nitrosopiperidine
NPYR	<i>N</i> -nitrosopyrrolidine
OCD	Organic carbon detection
OCSD	Orange County Sanitation District
OCWD	Orange County Water District
OECD	Organisation for Economic Co-operation and Development
·OH	Hydroxyl radical
OH&P	Overhead and Profit
OND	Organic nitrogen detection
PAC	Powder activated carbon
pCBA	para-chlorobenzoic acid
PCU	Pinellas County Utilities
PEG	Polyethylene glycol

PFU	Plaque-forming unit
POC	Particulate organic carbon
PPCPs	Pharmaceuticals and personal care products
PSA	Pressure swing adsorption
QA/QC	Quality assurance/quality control
QSAR	Quantitative structure-activity relationship
Q-TOF	Quadrupole time-of-flight
RO	Reverse osmosis
ROC	Reverse osmosis concentrate
ROF	Reverse osmosis feed
ROP	Reverse osmosis product
RSWRF	Reno-Stead Water Reclamation Facility
RWC	Recycled water contribution
RWWTP	Regensdorf Wastewater Treatment Plant
SAT	Soil aquifer treatment
SDWA	Safe Drinking Water Act
SEC	Size exclusion chromatography
SNWA	Southern Nevada Water Authority
SPE	Solid phase extraction
SRT	Solids retention time
SUVA	Specific UV absorbance
t-BuOH	<i>tert</i> -butanol
TCEP	Tris-(2-chloroethyl)-phosphate
TCPP	Tris-(2-chloroisopropyl)-phosphate
THM	Trihalomethane
TI	Treatment index
TKN	Total Kjeldahl Nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TON	Total organic nitrogen
TOrC	Trace organic contaminant
TOX	Total organic halides
TP	Total phosphorus
TSA	Tryptic soy agar
TSB	Tryptic soy broth
TSS	Total suspended solids
TTHMs	Total trihalomethanes
UF	Ultrafiltration
USBR	United States Bureau of Reclamation
UV	Ultraviolet
UVP	UV product
VPSA	Vacuum pressure swing adsorption
WBMWD	West Basin Municipal Water District
WHO	World Health Organization
YES	Yeast estrogen screen

Project Objective:

The primary objective of this project was to characterize the use of ozone in wastewater treatment applications with respect to bulk organic matter transformation, contaminant oxidation, microbial inactivation, and the formation of disinfection byproducts and other transformation products. A secondary objective was to evaluate the synergism between ozone and biological filtration, including biological activated carbon (BAC) and soil aquifer treatment (SAT), in the context of potable reuse applications. Finally, the project intended to compare the treatment efficacy of ozone- and UV-based oxidation and ultimately develop cost estimates for these individual unit processes and corresponding advanced water treatment trains.

Project Background:

Increased public awareness, potential human health effects, and demonstrated impacts on aquatic ecosystems have stimulated recent interest in pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs) in water and wastewater. These trace organic contaminants (TOrcs) are largely unregulated, but their ubiquity has necessitated studies on the efficacy of various treatment processes for their removal and/or transformation. Since municipal wastewater is considered the primary source of PPCPs and EDCs in the environment, expansion and optimization of wastewater treatment processes may be the most efficient strategy to mitigate the potential effects of these contaminants. Ozone is a unique option because its efficacy is similar to that of high-pressure membranes and advanced oxidation processes (AOPs), such as UV/H₂O₂, but ozone has the potential for significantly reduced energy and chemical requirements. Ozone alone has the ability to generate hydroxyl radicals (•OH) when applied to wastewater, but the process can also be augmented with hydrogen peroxide (H₂O₂) to increase the rate of reaction, target recalcitrant contaminants, reduce disinfection byproduct (DBP) formation, or reduce the structural footprint of ozone installations. Ozone is also an effective disinfectant against bacteria, viruses, and protozoan parasites commonly found in wastewater.

Project Approach:

This project characterized the use of ozone in wastewater treatment by evaluating bench-scale dose-response relationships for 19 TOrcs and 3 surrogate microorganisms (*E. coli*, MS2 bacteriophage, and *Bacillus* spores) in 10 secondary wastewater effluents (Table 1). All chemical and microbial contaminants were spiked to supplement the ambient concentrations and allow for a wide range of treatment levels. The target TOrcs were also grouped based on their relative reactivity with ozone and •OH, with Group 1 compounds being highly susceptible to both ozone and •OH and Group 5 compounds being highly resistant to both ozone and •OH.

Table 1. Summary of secondary effluents and target contaminants

Secondary Effluents	Target Microbes	Compound Group	Target Compound
1. Clark County Water Reclamation District, Nevada, USA 2. Metropolitan Water Reclamation District of Greater Chicago, Illinois, USA 3. West Basin Municipal Water District, California, USA 4. Pinellas County Utilities, Florida, USA 5. Gwinnett County, Georgia, USA 6. Lausanne, Switzerland 7. Regensdorf, Switzerland 8. Kloten-Opfikon, Switzerland 9. Lowood, Australia 10. Anonymous, Australia	<i>Escherichia coli</i>	1 (very susceptible to ozone and •OH)	Bisphenol A Carbamazepine Diclofenac Naproxen Sulfamethoxazole Triclosan Trimethoprim
	<i>Bacillus subtilis</i> spores	2 (moderately susceptible to ozone / highly susceptible to •OH)	Atenolol Gemfibrozil
		3 (very resistant to ozone / highly susceptible to •OH)	DEET Ibuprofen pCBA ¹ Phenytoin Primidone
		4 (very resistant to ozone / moderately susceptible to •OH)	1,4-dioxane Atrazine Meprobamate
		5 (very resistant to ozone and •OH)	Musk Ketone TCEP ²

¹ pCBA = para-chlorobenzoic acid

² TCEP = tris-(2-chloroethyl)-phosphate

Four of the 10 secondary effluents were tested with and without laboratory filtration, while the remaining six secondary effluents were tested only after laboratory filtration. Ozone dosing was based on mass-based ozone to total organic carbon (O₃:TOC) or dissolved organic carbon (O₃:DOC) ratios (i.e., mg O₃/mg TOC) of 0.25, 0.5, 1.0, and 1.5. The effects of H₂O₂ addition were evaluated with molar H₂O₂:O₃ ratios of 0, 0.5, and 1.0. Ozone treatment efficacy was also compared with UV photolysis and UV/H₂O₂ using a bench-scale collimated beam apparatus. The UV and UV/H₂O₂ experiments involved UV doses of 50, 250, and 500 mJ/cm² and H₂O₂ doses of 0, 5, and 10 mg/L.

In addition to contaminant and microbial treatment objectives, a number of additional ozone-related parameters were evaluated during the study. These included bulk organic matter transformation, including UV₂₅₄ absorbance, total fluorescence, and assimilable organic carbon (AOC); DBP formation and formation potential, including N-nitrosodimethylamine (NDMA) and bromate; and bioassays capable of measuring the aggregate impact of contaminant mixtures before and after treatment. These bioassays quantified total

estrogenicity, cytotoxicity, and genotoxicity. The formation of transformation products was also monitored during bench-scale ozonation.

Pilot- and full-scale experiments were also performed to verify the efficacy of ozonation in large-scale systems and as part of advanced treatment trains. The pilot-scale experiments consisted of a combined ozone/H₂O₂/UV reactor at a water reclamation facility in Tucson, AZ; an ultrafiltration-ozone/H₂O₂-BAC treatment train in Reno, NV; and a membrane bioreactor-ozone/H₂O₂-reverse osmosis treatment train in Las Vegas, NV. The Las Vegas pilot was also equipped with an online UV absorbance analyzer. Full-scale data sets from the following facilities were also evaluated during the study: the ultrafiltration-ozone-BAC-ozone treatment train in Gwinnett County, GA; the ozone facility in Springfield, MO; the ozone-BAC facility in El Paso, TX; and microfiltration-reverse osmosis-UV/H₂O₂ facilities in Orange County and El Segundo, CA.

The project concluded with an Association for the Advancement of Cost Engineering (AACE) Class 4 cost estimate for a variety of advanced treatment processes and hypothetical treatment trains. These “conceptual level” cost estimates provide reasonable accuracy to within -30% and +50% of actual costs and are appropriate when ≤1% of design is completed. For this study, unit cost curves were developed to assist readers in estimating costs for a range of design conditions, including unit process selection, flow rate, and applied doses. The cost estimates were based on vendor-reported data for recent full-scale installations adjusted to 2011 dollars.

Project Findings:

1.0. Ozone Versus Ozone/H₂O₂

Ozone can be implemented as a standalone oxidation process or it can be supplemented with hydrogen peroxide. The addition of H₂O₂ is generally intended to drive the formation of •OH in order to reduce structural footprints, reduce disinfection byproduct formation, or target more recalcitrant compounds. However, ozone alone is fully capable of generating •OH in wastewater applications due to side reactions with effluent organic matter. Therefore, the following question can be posed: Why should H₂O₂ be added to an ozone process? The following bullets highlight several key issues related to this question.

- 1) ***Efficacy of ozone versus •OH.*** Second-order ozone and •OH rate constants vary significantly depending on the contaminant of interest. This is the basis for dividing the target compounds in this study into five different groups. Some compounds are susceptible to both ozone and •OH (e.g., Group 1: naproxen and carbamazepine; Group 2: gemfibrozil and atenolol), some are only susceptible to •OH (e.g., Group 3: ibuprofen and phenytoin; Group 4: atrazine and meprobamate), and some are resistant to both oxidants (e.g., Group 5: TCEP and musk ketone). Although dissolved ozone is extremely effective in oxidizing a wide variety of compounds, the more resistant chemical compounds require •OH exposure to achieve any level of destruction or transformation. Conversely, some microbes are resistant to •OH-dominated treatment processes and are only inactivated after extended exposure to dissolved ozone.
- 2) ***Decomposition of ozone into •OH.*** Expediting the decomposition of ozone into •OH via H₂O₂ addition may be appropriate in low TOC water matrices. However, ozone rapidly decomposes into •OH through reactions with effluent organic matter in wastewater applications. In fact, ozone and ozone/H₂O₂ generally provide similar

overall •OH exposure in wastewater when sufficient reaction time is provided. Therefore, H₂O₂ addition is often unnecessary for ozone to qualify as an advanced oxidation process, but other issues may impact the design of the process and warrant H₂O₂ addition.

- 3) **Bromate control.** In previous studies, and to some extent in this study, H₂O₂ addition has been shown to reduce bromate formation during ozonation. Some studies call for more relaxed bromate guidelines for environmental discharge (e.g., 3 mg/L), but the U.S. EPA maximum contaminant level of 10 µg/L is often used as the benchmark for ozonation processes, particularly for indirect potable reuse applications. Therefore, the combination of high ozone doses and high bromide levels may necessitate H₂O₂ addition to meet the 10 µg/L bromate benchmark. Other forms of bromate mitigation (e.g., the chlorine-ammonia process) are available and are described in greater detail in the Final Report.
- 4) **Process footprint.** The addition of H₂O₂ allows for rapid conversion of dissolved ozone to •OH, which reduces the reaction time to a matter of seconds. High applied ozone doses without H₂O₂ (e.g., O₃:TOC ratios greater than 1.5) may require large contactors with more than 20 minutes of residence time. This translates into larger process footprints in full-scale applications. In order to achieve a combination of ozone residual and small process footprint, H₂O₂ can be added after a target contact time, or CT, has been reached to quench the remaining ozone residual while still capturing its oxidation benefits.
- 5) **Trace organic contaminants.** As mentioned above, some target compounds are highly resistant to ozone oxidation but are moderately susceptible to •OH oxidation. Despite the fact that ozone naturally decomposes into •OH in wastewater applications, the addition of H₂O₂ may provide a slight benefit in the oxidation of ozone resistant compounds (i.e., Groups 3, 4, and 5) when using higher applied ozone doses (i.e., O₃:TOC > 0.5). However, the benefit generally amounts to less than a 10% increase in oxidation. In drinking water applications or groundwater remediation, the addition of H₂O₂ will likely have a much more significant impact than in wastewater treatment.
- 6) **Microbes.** Dissolved ozone is effective against nearly all microbes, including bacteria, viruses, and protozoan parasites (e.g., *Cryptosporidium* and *Giardia*), so it has become increasingly popular in disinfection applications. Oxidative disinfection is generally governed by the CT framework. This is a reasonable strategy for chlorine and chloramine since they can provide extended exposure times to relatively high oxidant concentrations, but ozone and •OH pose unique challenges. Targeting a residual is possible with ozone, but the residual is considerably less stable, particularly in low-dose (i.e., O₃:TOC < 0.25) wastewater applications. In some cases, this is not necessarily a problem since the natural decomposition of ozone into •OH or the forced conversion with H₂O₂ addition achieves significant inactivation of many microbes, including vegetative bacteria (e.g., *E. coli*) and viruses. However, H₂O₂ addition generally reduces the level of inactivation achieved by ozone alone at the same O₃:TOC ratio, and the level of inactivation is also less consistent. The reduced or lack of CT (i.e., ~0 mg-min/L) also makes it nearly impossible to comply with regulatory guidelines. Furthermore, the inactivation of spore-forming microbes (e.g., *Bacillus* spores, *Cryptosporidium* oocysts, *Giardia* cysts) with •OH is extremely inefficient so H₂O₂ addition is not recommended in applications targeting these microbes. In order to exploit the disinfection benefits of dissolved ozone and the smaller footprints associated with ozone/H₂O₂, it is possible to target a certain CT with dissolved ozone before adding H₂O₂ to expedite the remaining reactions.

- 7) **Organic matter.** Although there are few guidelines and regulations targeting bulk organic matter (other than TOC limits), aesthetic concerns sometimes necessitate reductions in UV absorbance or color, for example. Both dissolved ozone and ozone/H₂O₂ are particularly effective in improving aesthetic parameters, but the addition of H₂O₂ will slightly reduce treatment efficacy.
- 8) **Cost.** The additional costs and complexities associated with chemical storage, handling, and injection may also limit the attractiveness of ozone/H₂O₂. Based on the assumptions below, which allow for simple process scaling, the chemical cost alone would amount to \$658 per year for each mgd of flow rate and mg/L of applied ozone. For a 100-mgd wastewater treatment plant targeting an applied ozone dose of 7 mg/L, the H₂O₂ addition for the ozone/H₂O₂ process would cost approximately \$460,324 per year.
 - a. 50% H₂O₂ = \$0.68/kg
 - b. Process flow rate = 1 mgd
 - c. Ozone dose = 1 mg/L
 - d. H₂O₂:O₃ ratio = 0.5 → H₂O₂ dose = 0.35 mg/L
- 9) **UV vs. UV/H₂O₂.** In contrast to ozone-based treatment processes, the addition of H₂O₂ is generally required for UV-based oxidation. Low-pressure and medium-pressure UV irradiation are extremely effective for microbial inactivation and photolysis of NDMA, but UV light is generally insufficient to destroy trace organic contaminants. With the exception of certain compounds, including diclofenac and triclosan, significant oxidation often requires a combination of high UV doses (e.g., >250 mJ/cm²) and H₂O₂ (e.g., >3 mg/L). This is the basis for the “gold standard” in indirect potable reuse: (1) UV photolysis for NDMA mitigation and (2) UV/H₂O₂ for the oxidation of recalcitrant compounds such as 1,4-dioxane.
- 10) **H₂O₂ Quenching.** Residual H₂O₂ is not a significant concern at this point, but there are benefits to optimizing H₂O₂ dose to prevent chemical waste and alleviate any concerns related to residual discharge. In ozone/H₂O₂ applications, it may be possible to target appropriate H₂O₂:O₃ ratios so as to achieve complete consumption of H₂O₂. Based on stoichiometry, a molar H₂O₂:O₃ ratio of 0.5 should lead to complete consumption, but the complex interactions with other scavengers in the target water matrix often complicate the calculation, as illustrated in the Final Report (see LaWWTP, RWWTP, and KOWWTP bench-scale experiments). Therefore, a trial-and-error approach may be required in real-world applications. On the other hand, UV/H₂O₂ processes will almost always have an H₂O₂ residual due to the disconnect between the amount of chemical required to achieve a reasonable •OH exposure and the limited amount of chemical that is actually consumed in the process. If necessary, H₂O₂ can be quenched with the addition of chemicals, such as calcium thiosulfate, or through catalytic decomposition in activated carbon beds, which are becoming popular in wastewater treatment trains with ozone-based oxidation.

2.0. Oxidant Dosing and Process Control

Ozone is gaining popularity in wastewater treatment applications due to an increased emphasis on trace organic contaminant mitigation and other emerging treatment issues. As a result, process control strategies are evolving to address these new objectives. Simply targeting an ozone dose would appear to be the simplest approach, but ozone dose is a matrix-specific parameter that cannot be used to predict process efficacy without additional water quality information. Furthermore, one must consider *applied* versus *transferred* dose in actual treatment applications due to potential problems with transfer efficiency.

With respect to disinfection, the CT framework has been the industry standard for years, but CT is not necessarily valid in all ozone applications, particularly when ozone doses are lower than the instantaneous ozone demand or when ozone is supplemented with H₂O₂. These conditions lead to an apparent CT of 0 mg-min/L, which does not provide any information on treatment efficacy. Also, CT has limited applicability for predicting contaminant oxidation, reductions in membrane fouling, or bulk organic matter transformation.

Robust parameters such as O₃:TOC, O₃:DOC, changes in UV₂₅₄ absorbance (Δ UV₂₅₄), or changes in total fluorescence (Δ TF) provide useful alternatives to the CT standard. One of the primary benefits of these alternative parameters is that they are broadly applicable to nearly all secondary or tertiary effluents. For example, the same O₃:TOC ratio in two different wastewaters will have the same *relative* impact on UV₂₅₄ absorbance, fluorescence, color, contaminant oxidation, the inactivation of some microbes, and a variety of other metrics. Many of these alternative parameters also exhibit strong correlations with each other, the transformation of chemical contaminants, and the inactivation of microbial indicators and pathogens. Therefore, existing models based on simple water quality analyses can be used to predict whether treatment objectives are being achieved for contaminants with complex analytical methods. Based on information available in the Final Reports for WRRF-08-05 and WRRF-09-10, the following predictions can be made based on a hypothetical dosing scenario:

- Initial matrix = secondary effluent
- TOC = 8.0 mg-C/L
- Target O₃:TOC ratio = 1.0 (no H₂O₂ addition)
- Applied ozone dose = 8.0 mg/L (assuming 100% transfer efficiency)
- Predicted Δ UV₂₅₄ = 51%
- Predicted Δ TF = 85%
- Predicted *E. coli* inactivation = 5.4 logs
- Predicted 1,4-dioxane destruction = 62%

During full-scale operation, observed Δ UV₂₅₄ or Δ TF values could also be used in the reverse direction—to verify the actual O₃:TOC ratio or transferred ozone dose to ensure process integrity. Furthermore, these parameters could be integrated into logic controls to manage ozone dosing in actual treatment systems.

The major limitation with these alternative dosing parameters is that they are not yet recognized by regulatory agencies, which means that CT is still a critical parameter for treatment. However, the draft Groundwater Replenishment Reuse regulations recently published by the California Department of Public Health (2011) emphasized the need for an alternative framework. The regulations mandate the use of unspecified parameters that can be monitored in real-time and can be used to predict treatment efficacy. Δ UV₂₅₄ and Δ TF are ideal candidates for secondary and tertiary effluents, but they have limited applicability in reverse osmosis permeate, which is the actual objective of the new “full advanced treatment” (FAT) regulations.

3.0. Contaminant Oxidation

As mentioned above, 19 target compounds were spiked and evaluated during the study. Due to its high volatility (i.e., not present after spiking), musk ketone was omitted from the data set. Two other compounds (pCBA and 1,4-dioxane) were reported in separate sections of the Final Report so they are not listed below. Destruction of the remaining 16 target compounds

is summarized in Table 2 (ozone) and Table 3 (UV) below. These summaries differentiate the various ozone, UV, and H₂O₂ doses that were used during the bench-scale experiments.

Due to the countless number of trace organic contaminants in the environment, it is impractical to develop oxidation profiles for every known chemical and dosing condition. Grouping contaminants based on their relative resistance/susceptibility to oxidation is a much more reasonable strategy. This strategy is also robust in that compounds with unknown oxidation profiles can often be modeled based on their structural properties—a concept known as quantitative structural activity relationships (QSARs). The groupings used in this study can be described as follows:

- Group 1: Very susceptible to both ozone and •OH
- Group 2: Moderately susceptible to ozone / highly susceptible to •OH
- Group 3: Very resistant to ozone / highly susceptible to •OH
- Group 4: Very resistant to ozone / moderately susceptible to •OH
- Group 5: Very resistant to both ozone and •OH

Table 2 and Table 3 also include a generic indicator in each group to provide an estimate of the expected level of oxidation for an “unknown” compound with similar structural characteristics and rate constants. The indicator was calculated as the average of the target compounds in each group. For ozone-based oxidation, the grouping and indicator framework proved to be quite useful in that each stepwise increase in O₃:TOC ratio led to an additional group of contaminants experiencing greater than 80% oxidation. However, TCEP (Group 5) barely exceeded the 30% threshold even at the highest O₃:TOC ratio, but this was expected since it is a flame retardant specifically designed to resist oxidation. If regulations are ever imposed, it is likely that compounds similar to TCEP will control the design of ozone systems targeting trace organic contaminant mitigation.

With respect to the various pretreatment and ozone dosing conditions, O₃:TOC ratio clearly had the most significant impact on oxidation efficacy. H₂O₂ addition yielded slightly higher destruction of the ozone-resistant compounds (Groups 3, 4, and 5), while H₂O₂ addition was slightly detrimental to the ozone-susceptible compounds. However, the differences were minimal and insignificant based on the standard deviations across the bench-scale experiments. Finally, laboratory filtration had no impact on ozone efficacy.

With respect to UV photolysis and UV/H₂O₂ (Table 3), the same groupings are presented to describe the resistance of the compounds to •OH since this is generally the primary treatment mechanism in UV/H₂O₂. However, UV photolysis is actually effective in destroying several compounds, including diclofenac, triclosan, and even some compounds that are resistant to •OH oxidation (phenytoin and atrazine). These UV-susceptible compounds are typically characterized by aromatic ring structures that more effectively absorb UV light. In general, target compound destruction requires high UV and H₂O₂ doses, and ozone oxidation typically achieves higher levels of contaminant mitigation at relevant dosing levels. As will be discussed below, the principal exception is NDMA for which UV is far superior to ozone.

Table 2. Summary of TOxC oxidation with ozone and ozone/H₂O₂.

Group	Contaminant	O ₃ :TOC / H ₂ O ₂ :O ₃											
		0.25/0	0.25/0.5	0.25/1.0	0.50/0	0.50/0.5	0.50/1.0	1.0/0	1.0/0.5	1.0/1.0	1.5/0	1.5/0.5	1.5/1.0
1	Sulfamethoxazole	84±13	82±13	83±8	98±0	97±1	96±2	99±1	99±1	99±1	99±1	99±1	99±1
	Diclofenac	91±13	90±14	92±8	98±1	98±1	98±1	98±1	98±1	98±1	98±1	98±1	98±1
	Bisphenol A	91±14	91±12	93±6	98±1	98±1	98±1	98±1	98±1	98±1	98±1	98±1	98±1
	Carbamazepine	92±15	89±15	87±12	99±0	99±0	99±0	99±0	99±0	99±0	99±0	99±0	99±0
	Trimethoprim	92±15	90±14	89±11	99±0	99±0	99±0	99±0	99±0	99±0	99±0	99±0	99±0
	Naproxen	90±16	89±15	87±10	98±0	98±0	98±1	98±0	98±0	98±1	98±0	98±0	98±1
	Triclosan	93±9	93±8	96±2	97±1	97±1	97±1	97±1	97±1	97±1	97±1	92±10	97±1
	Indicator	90±14	89±13	90±8	98±0	98±0	98±0	98±0	98±0	98±0	98±0	97±2	98±0
2	Gemfibrozil	81±18	73±17	67±10	99±0	99±0	99±1	99±0	99±0	99±0	99±0	99±0	99±1
	Atenolol	47±8	44±7	47±5	97±1	90±7	85±7	98±1	98±1	98±1	98±1	98±1	97±3
	Indicator	64±13	59±12	57±7	98±1	95±4	92±4	99±1	99±1	99±1	99±1	99±1	98±2
3	Ibuprofen	38±10	38±6	42±8	69±7	72±6	73±6	94±4	96±3	95±3	98±1	98±1	96±3
	Phenytoin	34±15	36±11	36±10	67±13	72±7	73±8	94±4	97±3	95±4	98±1	99±0	97±2
	DEET	26±9	28±7	30±8	57±9	62±8	63±8	88±6	93±5	92±5	97±3	99±1	95±4
	Primidone	30±9	29±5	34±5	60±8	64±5	64±4	91±5	94±5	92±4	97±2	98±2	95±4
	Indicator	32±10	33±6	36±6	63±9	68±6	68±7	92±5	95±4	93±4	98±2	99±1	96±3
4	Atrazine	15±5	14±3	18±5	33±6	36±5	37±6	64±8	70±11	69±9	81±8	87±8	82±9
	Meprobamate	18±5	20±5	23±6	40±8	45±6	45±5	71±9	80±10	79±8	86±8	93±5	88±6
	Indicator	17±5	17±4	20±5	37±6	41±5	41±5	68±8	75±11	74±9	84±8	90±7	85±8
5	TCEP	-1±13	5±5	8±5	9±5	12±5	9±4	15±3	20±6	20±3	23±3	30±4	31±4

* Shading represents >80% oxidation

Table 3. Summary of TOxC oxidation with UV and UV/H₂O₂.

Group	Contaminant	UV Dose (mJ/cm ²) / H ₂ O ₂ Dose (mg/L)							
		50/0	50/10	250/0	250/5	250/10	500/0	500/5	500/10
1	Sulfamethoxazole	6±6	2±14	44±5	39±8	42±13	65±2	67±3	73±5
	Diclofenac	40±2	19±23	91±2	86±5	90±6	98±1	97±1	97±1
	Bisphenol A	5±10	3±11	7±10	11±10	25±21	10±10	22±9	49±18
	Carbamazepine	-2±9	3±4	-3±11	12±7	22±15	-3±8	24±18	42±15
	Trimethoprim	-1±8	2±6	0±5	11±6	18±11	1±4	16±10	37±15
	Naproxen	4±6	3±8	11±4	19±11	29±16	18±8	35±8	53±16
	Triclosan	21±12	13±18	81±8	72±10	79±9	94±3	93±2	95±3
2	Gemfibrozil	3±10	5±7	4±6	11±6	23±14	7±3	15±8	39±16
	Atenolol	5±6	5±6	1±7	15±6	23±8	2±8	15±12	35±14
3	Ibuprofen	4±6	2±4	6±3	12±9	21±14	8±3	24±5	40±16
	Phenytoin	6±12	13±20	28±15	31±12	45±15	44±8	53±4	64±12
	DEET	8±7	3±4	8±6	8±9	17±11	6±2	12±4	31±14
	Primidone	1±8	3±7	3±3	12±9	15±13	7±2	10±17	29±22
4	Atrazine	4±8	-1±2	21±7	16±6	21±9	33±4	32±4	43±9
	Meprobamate	8±12	4±2	11±12	7±5	11±7	12±14	8±6	23±10
5	TCEP	7±7	6±13	9±6	3±11	8±14	8±5	0±5	5±14

* Shading represents >80% oxidation

** Groupings based on ozone and •OH rate constants

4.0. Disinfection

As described above, CT has been the industry standard for evaluating disinfection processes, but this is not always an appropriate parameter for ozone treatment. The high reactivity between ozone and dissolved organic matter in wastewater results in rapid depletion of dissolved ozone at low O₃:TOC ratios. In fact, O₃:TOC ratios greater than 0.3 may be necessary to achieve measurable CT values in secondary and tertiary effluents, although significant inactivation may be achieved for many microbes below this threshold. For O₃:TOC ratios between 0.5 and 1.3, ozone CT exhibits a relatively linear relationship, as described by Eq. 1.

$$\text{Ozone CT (mg-min/L)} = 10 \times (\text{O}_3\text{:TOC}) - 3.3 \quad R^2 = 0.86 \quad (\text{Eq. 1})$$

However, the linear correlation deteriorates for O₃:TOC ratios greater than 1.3. At these higher ozone doses, the varying composition of the dissolved organic matter in different wastewaters has a significant effect on ozone decay, which results in a wide range of CT values. Therefore, O₃:TOC ratio only provides accurate estimates of CT at O₃:TOC ratios less than 1.5. When H₂O₂ is added at molar H₂O₂:O₃ ratios of 0.5 or 1.0, the CT is essentially 0 mg-min/L at all ozone doses despite significant inactivation of vegetative bacteria (e.g., *E. coli*) and viruses. Therefore, alternative dosing frameworks may be warranted in some—or all—ozone applications.

In addition to ozone CT, this study developed microbial inactivation relationships with O₃:TOC ratio, ΔUV₂₅₄, and ΔTF. The relationships are summarized in Figures 1-3 for *E. coli*, MS2, and *Bacillus* spores, respectively. The results indicate that the conventional CT framework is valuable when predicting *E. coli* and MS2 inactivation, but CT is less reliable when predicting *Bacillus* spore inactivation. O₃:TOC ratio, which is an accurate predictor of TOC oxidation, exhibited similar trends as CT, but it was also useful in predicting inactivation for dosing conditions with an apparent CT of 0 mg-min/L. ΔUV₂₅₄ and ΔTF may hold the most promise since they were capable of predicting the inactivation of all three microbes, they were not limited by dosing conditions with an apparent CT value of 0 mg-min/L, and they are capable of being implemented in real-time applications.

For the ozone experiments, the addition of H₂O₂ had an adverse impact on the inactivation of all three microbes, although the impact was much more significant for *Bacillus* spores. With H₂O₂ addition, the inactivation of *E. coli* and MS2 was slightly lower and more variable, but no inactivation was observed for *Bacillus* spores under any of the H₂O₂ dosing conditions. Extended exposure to dissolved ozone (i.e., O₃:TOC > 1.0) is required to achieve *Bacillus* spore inactivation.

Table 4 provides the average levels of inactivation of all three microbes with UV and UV/H₂O₂. UV and UV/H₂O₂ are extremely effective for the inactivation of both vegetative (e.g., *E. coli*) and spore-forming microbes (e.g., *B. subtilis* spores, *Cryptosporidium* oocysts, and *Giardia* cysts), which clearly provides an advantage over ozone-based oxidation. In fact, a common disinfection dose of 50 mJ/cm², achieved the limit of inactivation for *E. coli* and *B. subtilis* spores. MS2 was more resistant to UV than the bacterial surrogates, but 6.5-log viral inactivation was easily achieved with moderate advanced oxidation dosing conditions (i.e., UV dose >250 mJ/cm²). Viral resistance to germicidal UV light (λ = 254 nm) is also reported in the literature and is the basis for the high dose requirements established by the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) for drinking water applications.

Figure 1. Ozone disinfection summary for *E. coli* based on (A) O_3 :TOC ratio, (B) CT, (C) ΔUV_{254} , and (D) ΔTF . Each marker represents the average of four secondary effluents (1-4 from Table 1) for each ozone dosing condition. Vertical error bars represent ± 1 standard deviation based on the range of inactivation observed in the secondary effluents. Horizontal error bars represent ± 1 standard deviation based on the range of CT, ΔUV_{254} , or ΔTF in the secondary effluents.

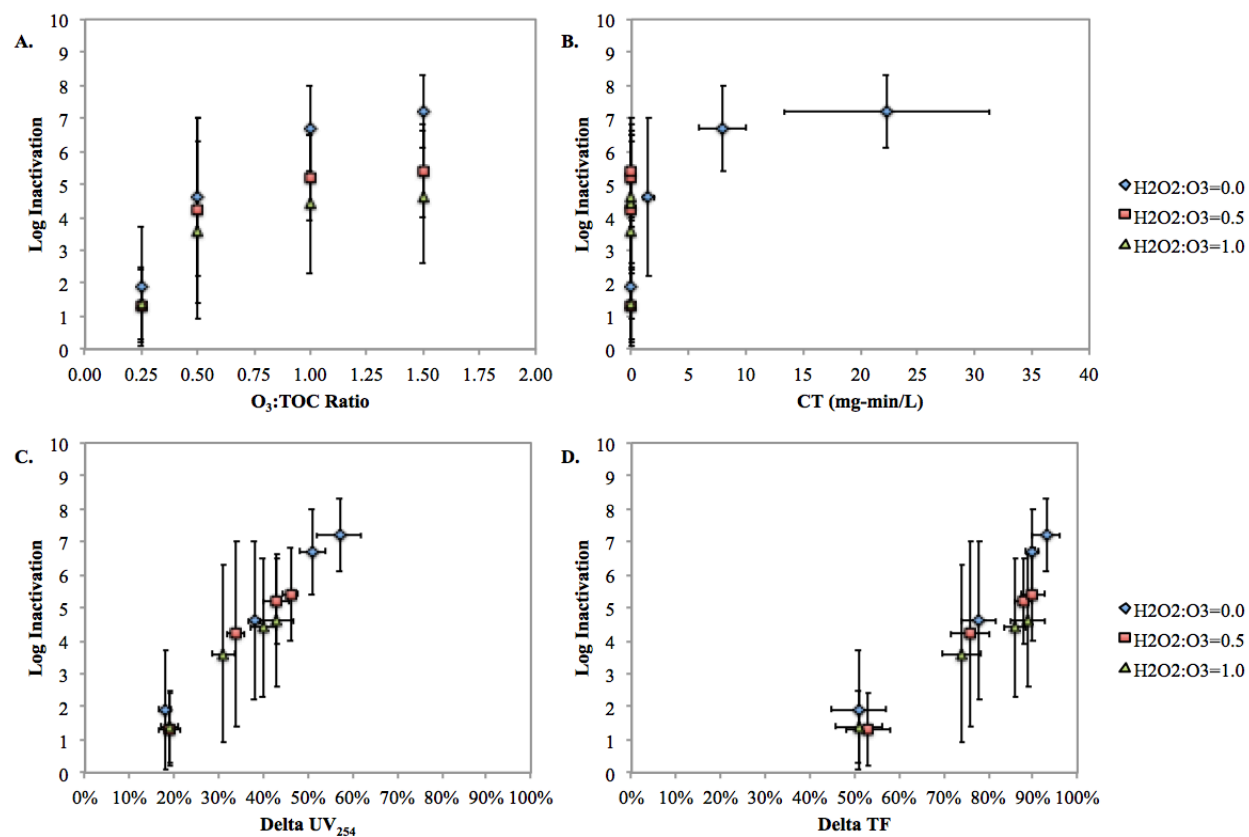


Figure 2. Ozone disinfection summary for MS2 based on (A) O_3 :TOC ratio, (B) CT, (C) ΔUV_{254} , and (D) ΔTF . Each marker represents the average of four secondary effluents (1-4 from Table 1) for each ozone dosing condition. Vertical error bars represent ± 1 standard deviation based on the range of inactivation observed in the secondary effluents. Horizontal error bars represent ± 1 standard deviation based on the range of CT, ΔUV_{254} , or ΔTF in the secondary effluents.

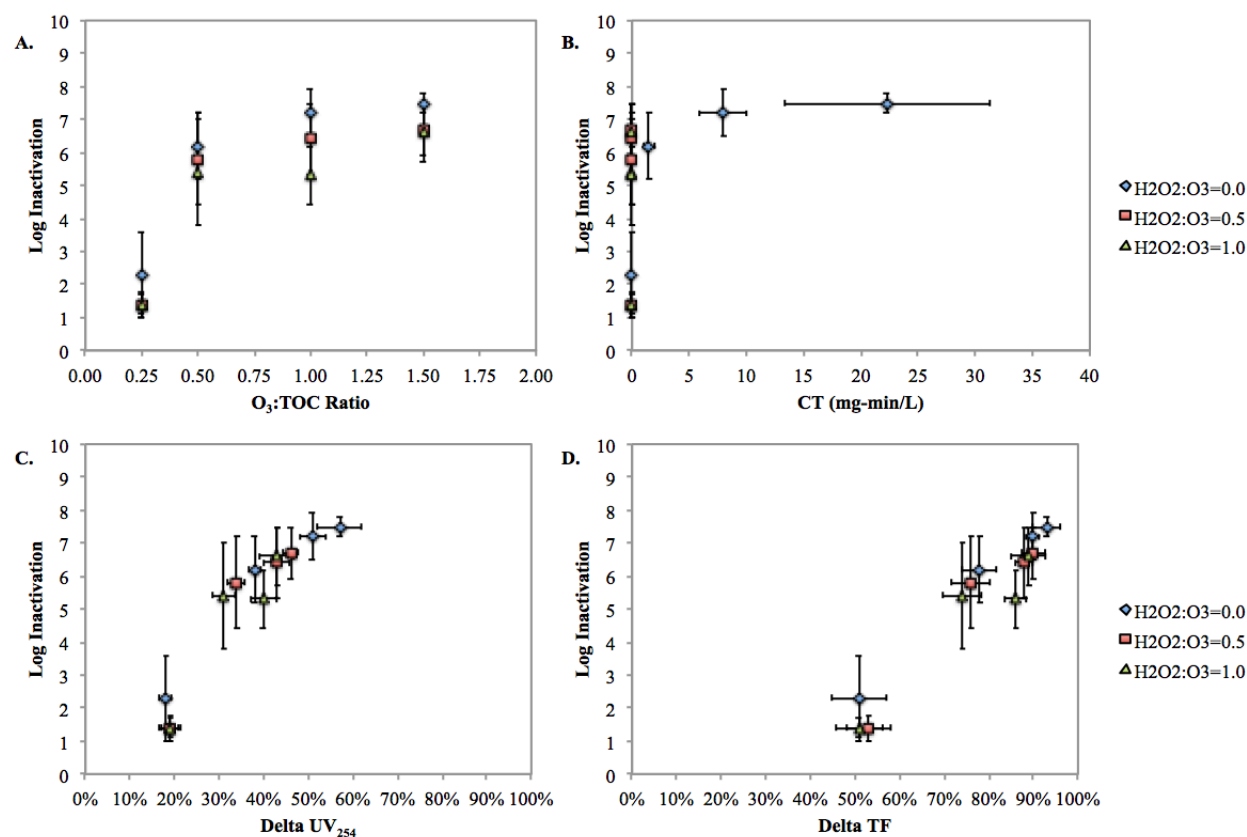


Figure 3. Ozone disinfection summary for *Bacillus* spores based on (A) O₃:TOC ratio, (B) CT, (C) Δ UV₂₅₄, and (D) Δ TF. Each marker represents the average of four secondary effluents (1-4 from Table 1) for each ozone dosing condition. Vertical error bars represent ± 1 standard deviation based on the range of inactivation observed in the secondary effluents. Horizontal error bars represent ± 1 standard deviation based on the range of CT, Δ UV₂₅₄, or Δ TF in the secondary effluents.

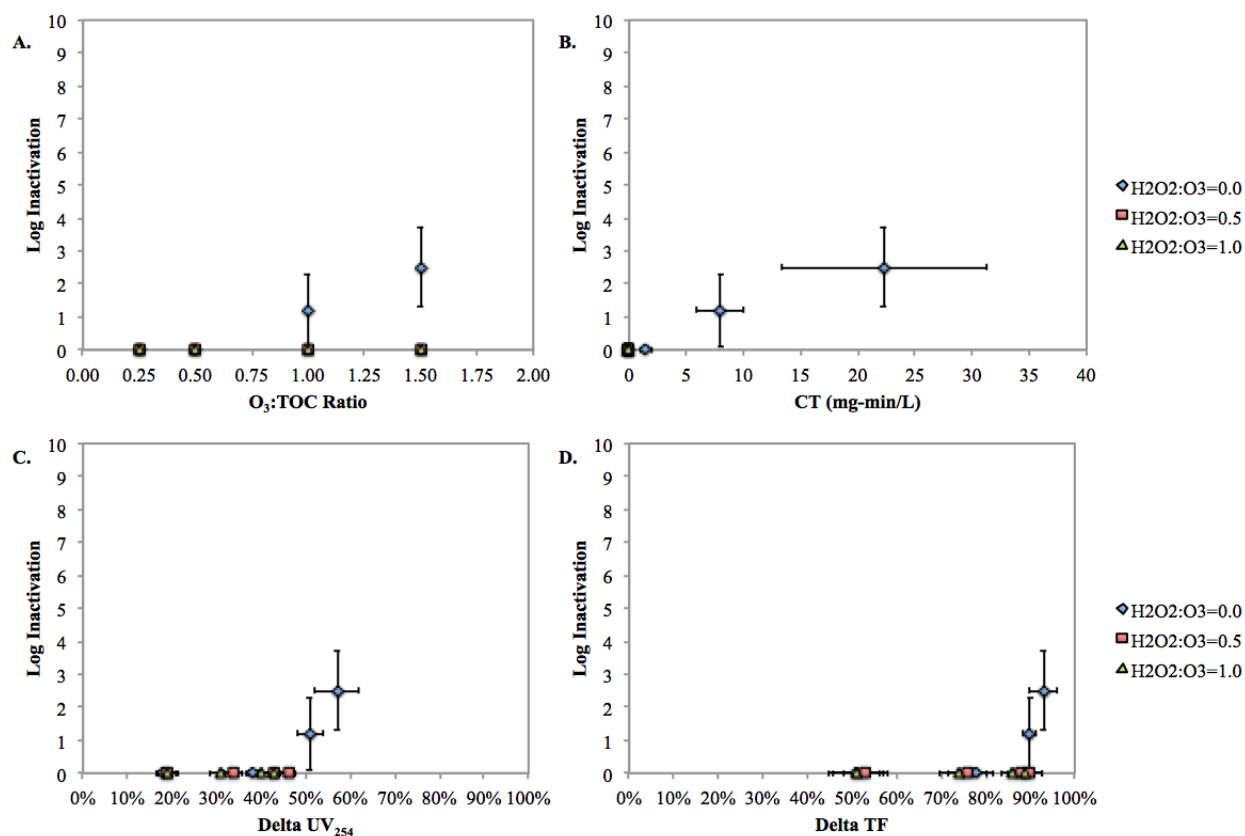


Table 4. Average inactivation with UV and UV/H₂O₂

UV Dose (mJ/cm ²)	<i>E. coli</i>		MS2		<i>Bacillus</i> spores	
	UV	UV/H ₂ O ₂	UV	UV/H ₂ O ₂	UV	UV/H ₂ O ₂
25	5.5 ± 1.8*	6.4 ± 0.4*	1.7 ± 0.1	2.2 ± 0.4	2.5 ± 0.6	2.5 ± 0.5
50	7.1 ± 0.2*	7.1 ± 0.2*	3.0 ± 0.1	3.5 ± 0.4	3.3 ± 0.2*	3.3 ± 0.1*
250	7.1 ± 0.2*	7.1 ± 0.2*	7.1 ± 0.3*	7.3 ± 0.4*	3.4 ± 0.1*	3.4 ± 0.1*
500	7.1 ± 0.2*	7.1 ± 0.2*	7.2 ± 0.2*	7.1 ± 0.1*	3.4 ± 0.1*	3.4 ± 0.1*

* Limited by spiking level in some samples (i.e., reached method detection limit)

5.0. Advanced Treatment Trains

In addition to the bench-scale data presented above, this study evaluated a number of pilot- and full-scale ozone systems. Some of the systems included standalone ozone processes targeting final disinfection (e.g., Springfield, Missouri), while the other systems integrated ozone into larger advanced treatment trains to target a variety of treatment objectives. The bench- and pilot-scale data were generally consistent with each other and are presented in the Final Report. The discussion below focuses on how ozone is currently integrated into full-scale systems and the prospects for future installations.

Particularly in potable reuse applications, conventional wastewater treatment trains are supplemented with a variety of advanced processes to produce a high-quality finished product. This product water is generally discharged to a surface water or groundwater via direct injection or spreading. Treatment trains comprised of microfiltration, reverse osmosis, and UV/H₂O₂ are often considered the standard for potable reuse, particularly in the U.S., but alternative systems are becoming more popular—some have even been operating successfully for decades. Many of these alternative treatment trains incorporate ozone and biological filtration. Many studies have shown that biological filtration is an important component of ozone-based treatment trains since bacteria are effective in mineralizing many of the transformation products generated during ozonation.

The 12-mgd Fred Hervey Water Reclamation Facility is operated by the El Paso Water Utilities in El Paso, Texas. The facility employs a treatment train comprised of a powdered activated carbon biological process, lime stabilization, media filtration, ozone disinfection (~5 mg/L), and biological activated carbon (BAC) with a 10-minute empty bed contact time prior to aquifer recharge. Recharge is accomplished through a combination of injection wells and spreading basins. With respect to the BAC process, the carbon has only been replaced twice in 27 years of operation, although two to four tons of carbon are added each year to replenish the amount that is lost in the underdrains and during backwashes. The minimum, average, and maximum effluent TOC concentrations in 2011 were 1.8 mg/L, 3.2 mg/L, and 5.2 mg/L, respectively. These values indicate that ozone-BAC facilities are capable of achieving relatively low levels of dissolved organic matter.

The F. Wayne Hill Water Resources Center in Gwinnett County, Georgia is one of the largest ultrafiltration wastewater treatment plants in the world. The facility treats approximately 60 mgd with multiple liquid treatment trains, all of which include the following processes: preliminary screening and grit removal; primary clarification; conventional activated sludge with full nitrification, denitrification, and biological phosphorus removal; secondary clarification; and high-pH lime clarification. One treatment train continues with recarbonation and tri-media filtration (sand, anthracite, and garnet), while another treatment train continues with strainers and ultrafiltration. Both trains recombine for preozonation at a dose of 1.0-1.5

mg/L, BAC with a 15-minute empty bed contact time, and final ozone disinfection at a dose of 1.0-1.5 mg/L. The media in the BAC process has not been replaced or regenerated so its adsorption capacity is likely exhausted, thereby isolating the biodegradation mechanism. The effluent is discharged through a 20-mile pipeline to the Chattahoochee River. After years of litigation, Gwinnett County also has a permit to discharge the highly treated effluent directly into Lake Lanier, which is the Atlanta metropolitan area's primary drinking water source.

Another ozone-BAC-ozone treatment train—similar to Gwinnett County—is located at the South Caboolture Water Reclamation Facility in Queensland, Australia. This facility actually includes a third ozonation step upstream of its sand filters. A second facility in Queensland, Australia (Landsborough) includes ozone-BAC, but its final disinfection step is UV rather than ozone. Although both of these facilities were recently decommissioned due to decreased demand for recycled water in the region, other facilities are adopting similar treatment strategies. For example, the Eastern Treatment Plant in Melbourne, Australia was recently upgraded with ozone and biological filtration to increase effluent quality for recycled water applications and environmental discharge.

Membrane filtration is also a popular component of ozone-based treatment trains. The Reno-Stead Water Reclamation Facility in Reno, Nevada piloted an ultrafiltration-ozone-BAC treatment train during the WRRF-08-05 study (described in the Final Report), and the Central Plant of the Clark County Water Reclamation District in Las Vegas, Nevada will soon be upgraded with ultrafiltration and ozone for improved phosphorus removal, oxidation of estrogenic compounds and other TORCs, and microbial inactivation. In New South Wales, Australia, the Gerringong facility is equipped with both microfiltration and UV disinfection downstream of the ozone-BAC processes.

Based on existing literature, the data from WRRF-08-05, and historical performance of the aforementioned facilities, ozone-based treatment trains are viable alternatives to cost- and energy-intensive treatment trains based on reverse osmosis. Although limitations exist, including an inability to reduce salinity and practical limits on TOC removal, ozone-based treatment trains are likely to become more popular in the future.

6.0 Emerging Issues Related to Transformation Products and Disinfection Byproducts

In WRRF-08-05, bulk organic matter transformation was explored with a variety of methods, including absorbance and fluorescence spectra, assimilable organic carbon (AOC), biodegradable organic carbon (BDOC), and organic matter fractionation. These methods indicated that there was significant transformation of organic matter during ozonation—and to a lesser extent UV/H₂O₂—which eliminated the wastewater “identity” at higher doses and converted complex, high molecular weight, hydrophobic organic fractions into simpler, low molecular weight, hydrophilic organic matter. This is particularly important for biological filtration applications, including BAC, since this increases the amount of cosubstrate available to biological communities and improves cometabolism of target compounds.

Since typical ozone and UV/H₂O₂ dosing conditions are generally insufficient to achieve mineralization of organic matter, these treatment processes will often convert target compounds into a variety of “unknown” transformation products. The published literature indicates that these transformation products sometimes increase the toxicity of the treated effluent in relation to the original matrix, which was also supported by several bioassays from WRRF-08-05. This study also developed a framework for identifying “unknown” transformation products with high-resolution analytical methods and provided examples for

several target compounds. Future studies must build upon this framework to determine whether these unique transformation products pose any threat to environmental or human health.

With respect to disinfection byproducts, significant bromate formation was observed in all of the secondary effluents, although the concentrations varied depending on the initial bromide level. An empirical bromide incorporation model was developed to estimate bromate formation based on bromide concentration and ozone dose. The addition of H₂O₂ achieved some degree of bromate mitigation, but more problematic matrices required an optimized chlorine-ammonia strategy, which is described in greater detail in the Final Report.

The most striking DBP observation was the significant amount of NDMA that formed during ozonation of some of the secondary effluents (Table 5). In fact, direct NDMA formation reached 150 ng/L in one of the secondary effluents. For context, some risk calculations set the public health threshold for NDMA at 0.7 ng/L, while the California Department of Public Health established a 10-ng/L notification level. Table 5 highlights several other interesting observations:

- NDMA formation was independent of ozone dose at O₃:TOC ratios greater than 0.5. (Note: A recent WaterReuse Research Foundation project (WaterReuse-11-08) suggests that there is a strong correlation with ozone dose at O₃:TOC ratios below 0.3, but NDMA concentrations plateau beyond that level.)
- NDMA formation was independent of H₂O₂ dose.
- NDMA formation varied significantly between the various matrices.
- Initial NDMA concentrations were not reliable predictors of NDMA formation.

It is unclear why there was so much variability among the secondary effluents, but another WaterReuse Research Foundation project (WRRF-11-08) is exploring this issue. In addition to the direct formation issue, it would not be practical to use ozone or •OH to destroy ambient levels of NDMA due to low reactivity between these species. However, ozone is relatively effective in reducing NDMA formation potential associated with chloramination since the precursors generally differ between these oxidants. This is a matrix-specific application though since the formation potential benefits would have to outweigh the direct formation from ozonation. More viable NDMA mitigation alternatives include high UV doses (~600-700 mJ/cm² for 1.2-log destruction) or downstream biological filtration. The efficacy of aquifer recharge and recovery for NDMA mitigation is described in greater detail in the next section.

Table 5. Summary of direct NDMA formation (ng/L) during ozonation

O ₃ :TOC	0	0.5	0.5	1.0	1.0	1.5
H ₂ O ₂ :O ₃	0	0	0.5	0	0.5	0
WW 1 ¹	<2.5	48	45	42	36	--
WW 2	<2.5	9.8	11	9.2	10	--
WW 3	20	170	170	160	140	--
WW 4	7.1	11	11	11	11	--
WW 5 ²	17	25	23	26	27	--
WW 7	<5	<5	<5	<5	<5	<5
WW 8	66	118	--	96	--	141
WW 10	<5	<5	<5	<5	<5	<5

¹ Numbers refer to list of facilities in Table 1

² Different dosing ratios due to high nitrite concentration relative to TOC

7.0. Simulation of Aquifer Recharge and Recovery

The concept of soil aquifer treatment (SAT) or aquifer recharge and recovery (ARR), which can be described as the recharge of groundwater basins with recycled water, has been used successfully for decades. Numerous research studies have also been performed in the laboratory and the field to validate the use of the environment as a treatment barrier. This barrier is comprised of several treatment mechanisms: filtration, adsorption, biodegradation, natural pathogen die-off, and time. In recent years, time has become an increasingly important treatment component, particularly in potable reuse applications since it offers water agencies a buffer or safety factor against process failures or unforeseen public health threats. During this extended storage or travel time, the true treatment mechanisms lead to significant reductions in contaminant concentrations and pathogen viability.

With respect to WRRF-08-05, ARR was simulated in the laboratory to characterize its efficacy in removing bulk organic matter and TOrCs and also to evaluate the synergistic benefits of pre- or post-ozonation. Individually, ozone and ARR are effective against a wide range of trace organic contaminants (Figure 4), but as mentioned earlier, organic matter transformation during ozonation or post-ARR oxidation leads to increased treatment efficiency (Figure 5). The ARR experiments indicated that O₃-ARR and ARR-O₃ were both effective in targeting bulk organic matter and individual TOrCs. O₃-ARR proved to be more effective for overall reductions in TOC and DOC, while ARR-O₃ proved to be more effective for TOrC mitigation and reductions in absorbance and fluorescence.

Figure 4. Summary of TOrC mitigation with ARR (12 days of retention time) versus ozone (O₃:TOC = 1.0).

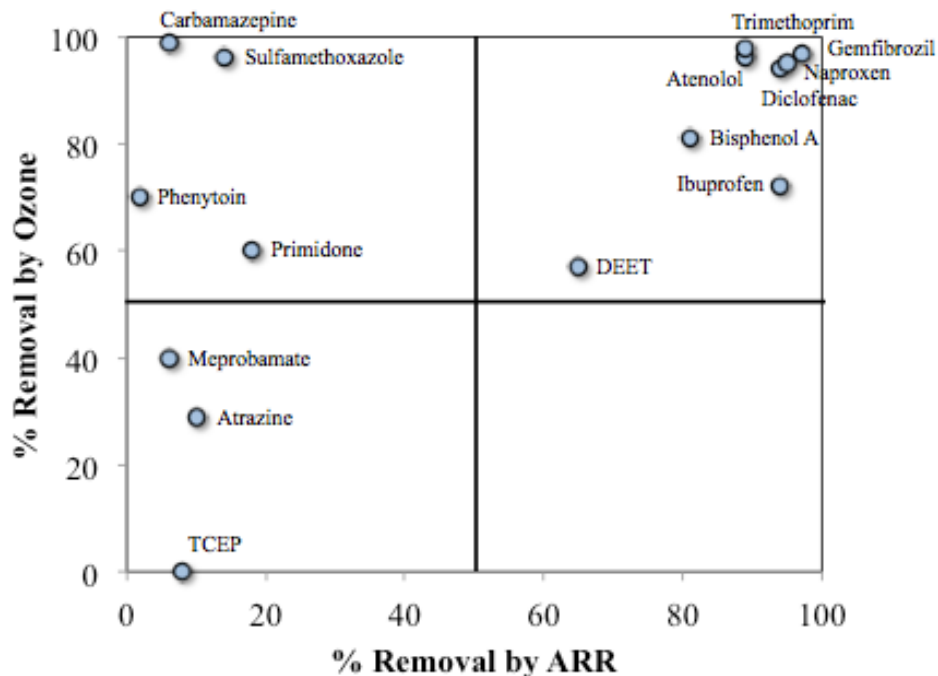
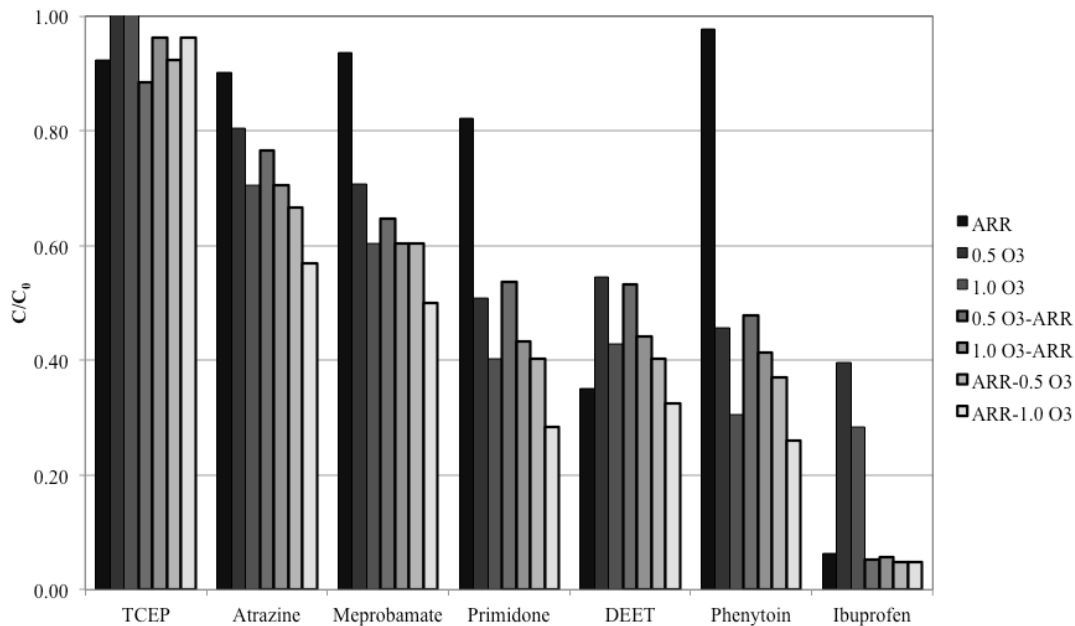


Figure 5. Treatment synergism between Ozone and ARR (12 days of retention time). The treatment conditions specified in the legend differentiate the two ozone doses (i.e., O₃:TOC of 0.5 or 1.0), individual or combined treatment (i.e., O₃, ARR alone, or a combination of O₃ and ARR), and the sequence of combined treatment (O₃-ARR vs. ARR-O₃).



As described in the previous section, biological filtration is an effective barrier against NDMA. In the laboratory-scale simulation of ARR, secondary effluent was spiked with NDMA concentrations as high as 500 ng/L, but NDMA was never detected in the soil column effluent (12 days of retention time). Furthermore, NDMA was never detected in the ARR-O₃ effluent despite the fact that direct NDMA formation was observed when the secondary effluent feed water was ozonated prior to ARR. Therefore, biological filtration is also effective in removing NDMA precursors associated with ozonation.

7.0 Cost Estimates

The project concluded with an Association for the Advancement of Cost Engineering (AACE) Class 4 cost estimate for a variety of advanced treatment processes and hypothetical treatment trains. These “conceptual level” cost estimates provide reasonable accuracy to within -30% and +50% of actual costs and are appropriate when ≤1% of design is completed. For this study, unit cost curves were developed to assist readers in estimating costs for a range of design conditions, including unit process selection, flow rate, and applied doses. The cost estimates were based on vendor-reported data for recent full-scale installations adjusted to 2011 dollars, including contractor overhead and profit (OH&P) and contingency.

A full description of the assumptions and cost models for individual unit processes are provided in the Final Report. A summary of this information is provided in Tables 6-8 below. Table 6 and Table 7 summarize the total capital and annual O&M costs, respectively, for five different advanced treatment trains, while Table 8 illustrates the effects of varying ozone dose on the costs and oxidation efficacy of a 50-mgd ozone-BAC treatment train.

Table 6. Total capital costs (2011 dollars) for hypothetical advanced treatment trains.

Capacity (MGD)	Process Trains and Capital Costs (\$M)				
	O ₃ -BAC	MF-O ₃ -BAC	MF-RO	MF-RO- UV/H ₂ O ₂	MF-O ₃ -RO (O ₃ -MF-RO)
1	\$5.2	\$9.0	\$11	\$11	\$13
5	\$11	\$24	\$38	\$40	\$42
10	\$16	\$38	\$65	\$69	\$71
25	\$31	\$75	\$132	\$142	\$142
50	\$50	\$126	\$226	\$245	\$240
80	\$71	\$180	\$327	\$356	\$344

Table 7. Total annual O&M costs (2011 dollars) for hypothetical advanced treatment trains.

Capacity (MGD)	Process Trains and Capital Costs (\$M)				
	O ₃ -BAC	MF-O ₃ -BAC	MF-RO	MF-RO- UV/H ₂ O ₂	MF-O ₃ -RO (O ₃ -MF-RO)
1	\$0.1	\$0.4	\$0.5	\$0.6	\$0.5
5	\$0.3	\$1.4	\$2.6	\$2.7	\$2.6
10	\$0.6	\$2.4	\$4.8	\$5.1	\$4.8
25	\$1.4	\$5.1	\$11	\$11	\$11
50	\$2.8	\$9.1	\$19	\$21	\$19
80	\$4.3	\$13	\$29	\$31	\$29

Table 8. Cost (2011 dollars) and oxidation efficacy of a 50-mgd ozone-BAC treatment train.

O ₃ Dose	1.5 mg/L	3 mg/L	6 mg/L	9 mg/L
O ₃ :TOC Ratio	0.25	0.5	1.0	1.5
<i>Conceptual-Level Cost Estimate</i>				
Capital Costs	\$49M	\$50M	\$52M	\$53M
Annual O&M	\$2.7M	\$2.8M	\$3.0M	\$3.3M
<i>Average Percent Destruction of Target Compounds</i>				
Group 1	>90%	>90%	>90%	>90%
Group 2	>60%	>90%	>90%	>90%
Group 3	>30%	>60%	>90%	>90%
Group 4	>15%	>30%	>60%	>80%
Group 5	<5%	>5%	>15%	>20%

* TOC assumed to be 6 mg/L

** 10-minute empty bed contact time for the BAC process

Future Recommendations:

This study addressed a wide range of issues related to the use of ozone in water reclamation, but a number of issues still exist and warrant further attention. Direct NDMA formation during ozonation proved to be a significant problem for some of the matrices tested during

this study. Although this may not be a critical issue for some facilities, there are some instances, specifically potable reuse applications, where this could pose a significant design challenge. Additional research is needed to identify why some secondary effluents are particularly vulnerable to ozone-induced NDMA formation and what measures can be taken to mitigate the problem.

NDMA is only one of the potentially harmful byproducts associated with ozonation. WRRF-08-05 and other studies available in the literature highlight the transformation of bulk organic matter and individual contaminants during ozonation, or any oxidation process for that matter. Just as it is impractical to target the entire universe of chemical and microbial contaminants during treatment studies, it is even more impractical to identify the countless transformation products resulting from oxidation. WRRF-08-05 presented a framework for identifying individual transformation products during oxidation, but additional studies are needed to develop strategies to fully characterize the potential environmental and public health risks associated with transformation products. This will involve the use of analytical methods to identify individual transformation products or groups of transformation products, but, more importantly, this will require robust bioassays that are capable to capturing the overall impacts of these mixtures of contaminants. Many agencies are currently targeting this research topic, but the issue will likely require further attention for years to come.

Finally, WRRF-08-05 evaluated the use of ozone in secondary and tertiary treatment applications based on a limited number of treatment objectives and regulatory guidelines. As the industry evolves, additional ozone applications and regulations will become relevant. Therefore, ozone will have to be evaluated in the context of these new frameworks. For example, recent changes to recycled water regulations in California have expanded the opportunities for ozone implementation. Specifically, changes to the NDMA regulations now make it feasible to implement ozone in post-RO applications, which will require further validation due to this unique water matrix and treatment objectives. These recycled water regulations also emphasize the use of TOC removal as an indicator of treatment efficacy. This poses no problems for RO-based treatment trains, but this may hinder the implementation of ozone-based treatment trains in some locations. Therefore, additional studies are needed to optimize ozone-based treatment trains for TOC removal.

Practical Solutions for Water Scarcity



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