Spring 1-1-2018

Evaluating Treatment Approaches for Sustainable Reuse of Greywater, Wastewater, and Stormwater

Kyle Andrew Thompson
University of Colorado at Boulder, kathom198@gmail.com

Recommended Citation

Thompson, Kyle Andrew, "Evaluating Treatment Approaches for Sustainable Reuse of Greywater, Wastewater, and Stormwater" (2018). *Civil Engineering Graduate Theses & Dissertations*. 366.
https://scholar.colorado.edu/cven_gradetds/366

EVALUATING TREATMENT APPROACHES FOR SUSTAINABLE REUSE OF GREYWATER, WASTEWATER, AND STORMWATER

by

KYLE A. THOMPSON

B.Sc., Missouri University of Science & Technology, 2013

M.Sc., University of Colorado Boulder, 2016

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy
Department of Civil, Environmental, and Architectural Engineering
2018

This thesis entitled:
Evaluating treatment approaches for sustainable reuse of greywater, wastewater, and stormwater
written by Kyle A. Thompson
has been approved for the Department of Civil, Environmental, and Architectural Engineering

Dr. Sherri Cook

Dr. R. Scott Summers

Dr. JoAnn Silverstein

Dr. Paul Lander

Dr. Sybil Sharvelle

Date______________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

ABSTRACT

Thompson, Kyle A. (Ph.D., Environmental Engineering, Department of Civil, Environmental, and Architectural Engineering)

Evaluating treatment approaches for sustainable reuse of greywater, wastewater, and stormwater

Thesis directed by Assistant Professor Sherri M. Cook and Professor R. Scott Summers

Water is becoming increasingly scarce; approximately 2 billion people currently live in annual water scarcity, and 3 to 4 billion people are expected to live in water scarcity by 2050 due to population growth alone. Therefore, there is need to determine suitable alternative drinking water sources. Alternative sources present different advantages in terms of supply, initial contamination, and variability. Different technologies may be most effective or sustainable for treating these alternative source waters depending on scale and application (e.g., toilet flushing, irrigation, or potable reuse). Previous reuse research has focused on biological treatment of greywater, passive treatment of stormwater, and reverse osmosis or advanced oxidation for wastewater effluent. The objectives of this dissertation were to (i) study the effectiveness of conventional drinking water treatment (CDWT) for potable reuse of alternative source waters and blends, (ii) compare the environmental sustainability of novel sorbents for micropollutant removal from wastewater effluent, (iii) develop an improved synthetic bathroom greywater that closes matches the characteristics and treatability of real bathroom greywater, and (iv) compare activated carbon and biochar for dissolved organic carbon (DOC) removal from raw and pretreated greywater.

Bench-scale experiments simulating CDWT achieved high turbidity removal in alternative source waters. Average maximum TOC removal with CDWT was 19%, 27% and 37% for greywater, wastewater effluent, and stormwater, respectively. However, no wastewater effluents and only one stormwater met drinking water regulations for disinfection byproduct formation control. Environmental sustainability was assessed using life cycle methodology. For micropollutant removal from wastewater effluent, wood-based biochar was more sustainable than activated carbon in most environmental impact categories. Higher adsorption capacity was associated with greater environmental benefits. A new synthetic bathroom greywater (SynGrey) was developed that closely matches the median characteristics of forty-nine real bathroom greywaters, and matched the treatability of real bathroom greywater in chlorination, biodegradation, and sorption. Five biochars were screened for greywater treatment, and activated carbon removed more DOC than the best biochar from raw, coagulated, aerated, and rainwater-blended greywater. This research will contribute to the selection and design of effective, sustainable treatment systems for potable and nonpotable reuse of alternative source waters.

DEDICATION

This thesis is dedicated to my loving partner Amreen Nasim Thompson.

ACKNOWLEDGEMENTS

I would like to acknowledge funding sources including the Sustainable by Design Residential Academic Program, the Mortenson Center in Engineering for Developing Communities, a Graduate Research Fellowship from the National Science Foundation, a scholarship from Arcadis U.S., Inc., and the U.S. Forest Service Wood Innovations Program.

I would like to acknowledge Dr. Joshua Kearns of North Carolina State University and Jonah Levine of Biochar Solutions and Confluence Energy for biochar samples. Thank you to Heidi Rogé of Housing and Dining Services and Edgar Piñon of Facilities Management for assistance sampling greywater. Thank you to Nicole Brinkman of the USEPA for additional greywater samples. Thank you to Cole Sigmon of the City of Boulder for return activated sludge samples. Thank you to multiple wastewater and drinking water utilities for wastewater effluent and stormwater samples.

I thank my advisors Dr. Sherri Cook and Dr. R. Scott Summers for their guidance and mentorship. I thank the Dr. Cook and Dr. Summers lab groups as well as the other water quality and wastewater research groups for their feedback, assistance, and support. I also thank my committee including Dr. Sybil Sharvelle, Dr. Paul Lander, and Dr. JoAnn Silverstein.

I would like to thank my family, friends, and especially my wife Amreen Nasim Thompson for their love and support, without which I could not have completed this dissertation.

CONTENTS

CHAPTERS

TABLES

FIGURES

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Water scarcity is a severe global challenge. 'Local severe water scarcity' is net water withdrawals over twice the available flow within a 0.5° latitude × 0.5° longitude grid after accounting for environmental requirements.[1] From 1996 to 2005, approximately 4 billion people lived under local severe water scarcity for at least one month each year.[1] Furthermore, 0.5 billion people experienced local severe water scarcity every month of the year.[1] Several major rivers now run dry for part of the year, including the Colorado River, the Yellow River, the Ganges, and the Nile.[2] Once-large terminal lakes have shrunk by 90% or more over recent decades, including the Aral Sea[3] and Lake Chad.[4] The disappearance of these rivers and lakes causes large-scale loss of wildlife habitat and biodiversity.[5,6] Other consequences of water scarcity include reduced harvests,[7] loss of income,[7] freshwater salinization,[8,9] and increased de facto wastewater reuse.[10] De facto wastewater reuse increases the presence of cryptosporidium, disinfection byproduct (DBP) precursors, and endocrine disruptors.[11,12]

The severity and scope of water scarcity are rising. The main driver for increasing water scarcity is population growth.[13] At the watershed scale, population growth alone is expected to increase the number of people living in water scarcity from 2.4 billion in 2000 to 4.3 billion in 2050.[14] Furthermore, climate change is expected to increase the severity of water scarcity for between 0.8 and 3.9 billion people by 2050.[14] In addition to population growth and climate change, causes of increasing water scarcity include changing consumption patterns,[15] expansion of irrigation,[3] economic development,[16] and urbanization.[16]

1.2 Framing

In response to water scarcity, municipalities are considering alternative water sources such as greywater, wastewater effluent, and stormwater. Each of these alternative source waters has distinct advantages and disadvantages and may require different treatment technologies to meet the range of water quality goals for different reuse endpoints. relative to the others. Additional research on the treatment of these alternative source waters is need so that utilities can make economic decisions on approaches for reuse.

In the United States, wastewater effluent that is currently discharged to oceans and estuaries could provide 27% of the U.S. drinking water supply.[17] While wastewater effluent quantity can vary, it is relatively predictable because it is proportional to drinking water use; similarly, wastewater effluent quality is relatively consistent because the wastewater is already treated to permit specifications. Quantitative microbial risk assessments indicate that engineered reuse has lower risk from pathogens than de facto reuse.[18,19] Nevertheless, wastewater reuse faces challenges with social acceptance and poses risks from contaminants of emerging concern. During a period of drought in Australia in the mid-2000's, a wastewater potable reuse project in Toowoomba was canceled after 62% of the residents voted against it.[20] Wastewater effluent contains detectable levels of many compounds which pose uncertain risks to human health. For example, antibiotics such as sulfamethoxazole contribute towards the occurrence of antibiotic resistance genes.[21] Wastewater effluent also contains organic matter that serves as precursors for nitrogenous DBPs,[22] which may be more toxic than regulated DBPs.[23] Research on potable reuse of wastewater effluent has focused on advanced treatment technologies such as sorption,[24] advanced oxidation,[25] or reverse osmosis[22] for removal of trace organic compounds[24,26] and DBP precursors.[27] While these advanced treatment processes may be necessary, cost-effective and expedient wastewater reuse plans would likely take advantage of existing infrastructure, and add advanced treatment after the existing treatment processes to the extent needed. Little research has been conducted on the effectiveness of conventional drinking water treatment (CDWT) (i.e., coagulation, flocculation, sedimentation, filtration, and disinfection) for wastewater effluent. In addition to CDWT, advanced treatment may be required, especially for organic micropollutants. However, a better understanding of the effectiveness of CDWT would enable the determination of the degree of advanced treatment required. Life cycle assessments (LCAs) of advanced treatment processes have found that sorption with activated carbon is more sustainable than advanced oxidation or reverse osmosis for removing organic micropollutants for wastewater effluent.[28] Biochar, an emerging alternative to activated carbon for wastewater treatment, may have additional sustainability benefits such as energy production and carbon sequestration. Nevertheless, research on CDWT in the context of wastewater reuse is limited, and the sustainability of biochar has not been assessed in this context.

Stormwater reuse has received greater public acceptance than wastewater reuse, but is less reliable in terms of both quantity and quality. During the same period of drought in Australia, online surveys about a stormwater reuse project in the city of Orange found that the predominant concern was not water quality but expedience.[29,30] The total supply of stormwater is more difficult to quantify than wastewater effluent since it is weather dependent and will change over time for a given watershed depending on factors such as land use and climate change.[31] Due to this variability, stormwater would require a higher storage volume than wastewater effluent. Furthermore, stormwater quality at a given location can vary by orders of magnitude due to precipitation conditions such as antecedent dry days.[32]

Research on potable reuse of stormwater is limited relative to wastewater effluent. Most previous research on stormwater treatment has had the objective of protecting water bodies.[31] Hence, research on stormwater treatment has focused on passive, structural technologies such as stormwater ponds, constructed wetlands, and bioretention cells.[31] Activated carbon and biochar sorption have also been studied for stormwater.[33] Turbidity, color, fecal indicators, and certain metals such as iron have been identified as priorities when treating stormwater for potable reuse, while nutrients and pesticides are usually below drinking water guidelines.[29,34,35] Some studies have explored stormwater for non-potable reuse such as irrigation,[35] but potable reuse of stormwater may be more cost effective because it could take advantage of existing pipe networks for distribution.[29] Coagulation has been suggested as an appropriate treatment for stormwater due to its low alkalinity.[35] However, there have been only a few studies on stormwater coagulation, and these have focused on treating highly contaminated highway runoff for environmental discharge.[36,37]

Greywater is domestic wastewater that excludes flows from toilets, urinals, and kitchen sinks. Bathroom greywater is wastewater exclusively from baths, showers, and bathroom sinks (i.e., exluding laundry). Bathroom greywater is the least contaminated and most abundant category of greywater.[38] Centralized greywater reuse is not practical because of the high cost of installing new pipe networks. However, decentralized reuse of bathroom greywater could fully meet the water demand for toilet flushing, reducing residential water demand by 30-40% and urban water demand by 10-25%.[39] Furthermore, LCAs have found that decentralized greywater reuse could be more sustainable than centralized wastewater reuse or desalination due to lower energy requirements.[40] However, decentralized greywater reuse presents technical, operational, and financial challenges due to economies of scale. Therefore, greywater reuse treatment technologies must be low-cost and simple to operate.

Previous research on greywater treatment has focused on membrane bioreactors (MBRs), direct membrane filtration, and constructed wetlands.[38] Economic evaluation indicates that greywater treatment with MBRs or direct membrane filtration would cost over 5 $\$/m^3$, well above the typical cost of tap water in Europe or the United States.[41,42] Constructed wetlands are more economically feasible but require significant physical footprint, which could be prohibitive in many cases.[43,44] One study has tested a single biochar as a sorbent for greywater pretreated with a constructed wetland.[45] There have been no previous studies testing a variety of biochars for sorption of microfiltered, coagulated, aerated, or rainwater-blended bathroom greywater. Furthermore, a synthetic greywater recipe is needed to ensure the reproducibility of research due to the temporal and geographical variability of greywater.[46]

To address the above research gaps, firstly, a bench-scale experimental study was conducted on CDWT of alternative source waters (Chapter 2). While CDWT effectively removed turbidity and TOC from the alternative source waters, significant advanced treatment or blending would be required for DBP formation control. Furthermore, CDWT is not effective for the removal of many organic micropollutants in wastewater effluent.[47] Therefore, an LCA was conducted comparing activated carbon and biochar for organic micropollutant removal from wastewater effluent (Chapter 3). Based on the promising results of this LCA, an experimental study was planned to compared biochar and activated carbon for greywater treatment (Chapter 5). However, a literature review revealed that existing synthetic greywater recipes did not sufficiently match the characteristics of real bathroom greywater. For this reason, a new synthetic bathroom greywater (SynGrey) was developed, and its characteristics and treatability were compared to real bathroom greywater (Chapter 4).

1.3 Hypotheses

The following hypotheses have been formulated to address the above research gaps relating to the sustainable treatment of three common alternative source waters (Table 1.1):

1) CDWT of Alternative Source Waters (Chapter 2)

Motivation: To explore the potential for cost-effective reuse by taking advantage of existing drinking water infrastructure in reuse systems.

Hypothesis: CDWT can significantly remove turbidity, organic matter, and DBP precursors from stormwater, wastewater effluent, and blends of these with surface water.

Main Conclusion: While CDWT effectively removed turbidity and organic matter, significant blending or advanced treatment would be required for DBP formation control.

2) Sustainable Organic Micropollutant Removal via Sorption (Chapter 3)

Motivation: To determine the most environmentally sustainable approach to remove organic micropollutants for wastewater effluent.

Hypothesis: When used for micropollutant removal from wastewater effluent, biochar can be more environmentally sustainable than powdered activated carbon.

Main Conclusion: Wood-based biochar with sufficient adsorption capacity is more sustainable than activated carbon for wastewater effluent treatment in most environmental impact categories.

3) Nonpotable Greywater Reuse (Chapters 4 & 5)

Motviation: To determine which treatment technologies would be most environmentally and economically sustainable for bathroom greywater reuse at the decentralized scale.

Part I: Creation of a Synthetic Representative Greywater Recicpe (Chapter 4)

Motivation: To improve the reproducibility of greywater treatment research by developing a synthetic bathroom greywater that more closely matches the composition and treatability of real bathroom greywater.

Hypothesis: A synthetic bathroom greywater (SynGrey) can be developed that has the same composition and treatability by chlorination, biodegradation, adsorption, and coagulation as real bathroom greywater.

Main Conclusion: SynGrey a had the some composition as real bathroom greywater and similar treatability by chlorination, biodegradation, and adsorption.

Part II: Greywater Treatment via Sorption (Chapter 5)

Motivation: Determine whether biochar could be a feasible, sustainable alternative to activated carbon in greywater treatment.

Hypothesis: Biochar has adsorption capacity similar to that of activated carbon for the removal of organic contaminants from bathroom greywater.

Main Conclusion: Biochar would require at least eight times as much mass as activated carbon to reach current treatment objectives in raw or pretreated greywater.

Table 1.1 Summary of gaps in the literature, research questions, methods, and main findings.

Ch. #	Gap in Literature	Question	Methods	Main Finding
2	Conventional drinking water treatment (CDWT) of stormwater or wastewater effluent (WWeff)	Can CDWT remove significant turbidity, TOC, DBP precursors, and calculated cytotoxicity from stormwater or WWeff?	Bench-Scale Tests	CDWT removed high turbidity, moderate TOC, moderate DBP precursors, but negligible calculated cytotoxicity from most stormwaters and WWeffs.
3	Relative environmental sustainability of biochar and activated carbon for WWeff treatment	Is biochar more environmentally sustainable than activated carbon for SMX removal from tertiary wastewater?	Life Cycle Assessment	Wood-based, moderate capacity biochar is more sustainable than activated carbon for SMX removal from WWeff.
4	Synthetic greywater that is representative of real bathroom greywater	Can a synthetic greywater be developed that is representative of real bathroom greywater quality and treatability?	Literature Review, Bench-Scale Tests	A new synthetic greywater was developed that closely matches the water quality and treatability of real bathroom greywater.
5	Sorption with biochar for grewyater treatment	Can biochar achieve comparable removable of DOC from greywater compared to activated carbon?	Bench-Scale Tests	Biochar did not perform as well as activated carbon for DOC removal from greywater.

CHAPTER 2

TOWARDS POTABLE WATER REUSE WITH CONVENTIONAL DRINKING WATER TREATMENT OF STORMWATER, WASTEWATER EFFLUENT, AND BLENDS OF THESE WITH SURFACE WATER

Abstract

Water scarcity is a critical and escalating global challenge. Reuse of alternative source waters (i.e., wastewater effluent or stormwater) can augment water supplies. Incorporating existing infrastructure is a cost-effective reuse strategy. Alternative source waters can be blended with surface water in existing reservoirs, and advanced treatment can be added after existing drinking water treatment facilities to the extent required. However, data on the effectiveness of conventional drinking water treatment (coagulation, flocculation, sedimentation, and filtration) is lacking for these waters. This study used bench-scale methods to assess conventional drinking water treatment on eight stormwaters, five wastewater effluents, and three blends with surface water.

Initial quality and treatability varied based on drainage basin characteristics and precipitation conditions for the stormwaters and treatment for the wastewater effluents. Maximum turbidity removal ranged from 1 to 2 logs among the stormwaters; all wastewater effluents had low initial turbidity. Maximum TOC removal ranged from 16% to 66% among the stormwaters and 23% to 36% among the wastewater effluents. Using a drinking water based coagulation model, DOC removal was accurately predicted (R^2 around 0.80) for two wastewater effluents. DOC remaining in blends was accurately predicted (R^2 0.70 to 0.94) by taking the weighted average of the unblended waters. Coagulating wastewater effluent prior to blending did not meaningfully improve results compared to adding the equivalent amount of alum after blending.While precursors of regulated disinfection byproducts (DBPs) were removed by coagulation, the calculated cytotoxicity of measured DBPs was

negligibly reduced in most samples due to poor removal of haloacetonitrile precursors.[*]

---

[*] Using bench-scale methods, conventional drinking water treatment (coagulation, flocculation, sedimentation, filtration, and disinfection) was tested on the alternative source waters—stormwater, wastewater effluent, and greywater—and blends of these waters with surface water. The effectiveness of this treatment was evaluated for these waters to help determine the degree of blending or advanced treatment required to meet potable water regulations while reusing these waters and taking advantage of existing drinking water infrastructure. However, greywater is more suited for decentralized reuse than conveyance to existing drinking water infrastructure due to the high cost of city-scale pipe networks. Furthermore, coagulation achieved over 90% removal of turbidity from greywater, but TOC and disinfection byproduct formation were an order of magnitude above potable water standards even after treatment. Therefore, data for coagulation of greywater was not included in this chapter. However, data for coagulation of greywater in non-potable reuse contexts can be found in Sections 4.3.3.4, 5.3.3.1, and C.2.4.

2.1 Introduction

In 2016, 1.6 billion people were living in water scarcity (i.e., less than 1000 m^3/person/year), and population growth alone is expected to increase this number to 3.1 billion people by 2050.[14] Furthermore, under a likely climate change scenario, water scarcity would worsen for between 0.5 to 3.1 billion people.[14,48] De facto wastewater reuse is a widespread issue increasing alongside water scarcity. Sixty-three percent of large drinking water utilities in the United States contain some percentage of wastewater effluent and, of these utilities, sixteen have greater than 20% de facto wastewater reuse during average flow.[10] Climate change could increase average de facto reuse from 7.1% to 8% in the western United States.[10] De facto reuse increases the presence of cryptosporidium, disinfection by-product (DBP) precursors, and endocrine disruptors.[11,12] Due to current and projected water scarcity, many drinking water utilities are assessing alternative water sources to augment water supplies.

Alternative drinking water sources include municipal wastewater effluent and stormwater, and each presents unique risks and advantages for reuse. Wastewater effluent quantities are large and not sensitive to drought or precipitation fluctuations. In the United States, 12 billion gallons per year of wastewater effluent is discharged to oceans and estuaries, and recycling this effluent could provide 27% of drinking water supply.[17] Stormwater supply will change depending on land use and climate change,[31] and would require greater storage volume due to higher variability. Wastewater effluent quality is relatively consistent because it is already treated to permit specifications, while stormwater quality at a given location can vary by orders of magnitude due to precipitation conditions.[32] Quantitative microbial risk assessments indicate that engineered reuse has lower risk from pathogens than de facto reuse.[18,19] Nevertheless, stormwater has easier public acceptance. For example, during the Millenium Drought in Australia, a wastewater reuse project was cancelled because the public voted against, but a stormwater reuse project found widespread support.[20,29,30]

Research on potable reuse of wastewater effluent has focused on advanced treatment technologies such as adsorption,[24] advanced oxidation,[49] and reverse osmosis[22] for removal of trace organic compounds,[24,26] DBPs,[22] and DBP precursors.[27] Nitrogenous DBPs, such as haloacetonitriles (HANs) are challenging for reuse due to the poor removal of these compounds by reverse osmosis and the elevated levels of nitrogen in wastewater effluent relative to surfacewaters.[17,22] These advanced treatment processes may be necessary, especially considering social acceptance and uncertainty. However, cost effective reuse plans would likely take advantage of existing infrastructure (i.e, reservoirs, drinking water treatment facilities, distribution networks) and add advanced treatment after the existing treatment processes to the extent needed. Reducing turbidity and organic matter via conventional drinking water treatment (CDWT), i.e., coagulation/flocculation/sedimentation/filtration/disinfection, would increase the effectiveness of downstream advanced treatment (e.g., by decreasing competition for activated carbon adsorption).[50] Coagulation has already been included in full-scale wastewater reuse treatment trains in Windhoek, Namibia[51] and Gwinnett, Georgia.[52] Nevertheless, research on wastewater coagulation in the context of reuse is limited, with most research on municipal wastewater coagulation focused on phosphorus removal[53] or enhancing membrane filtration performance.[54]

Research on potable reuse of stormwater is limited relative to wastewater. Most research on stormwater treatment has the objective of protecting water bodies,[31] and focuses on passive, structural technologies such as stormwater ponds, constructed wetlands, and bioretention cells.[31] Turbidity, color, fecal indicators, and certain metals such as iron have been identified as priorities when treating stormwater for potable reuse, while nutrients and pesticides are usually below drinking water guidelines.[29,34,35] Coagulation has been suggested as an appropriate treatment for stormwater due to its low alkalinity.[35] However, there have been only a few studies on stormwater coagulation, and these have focused on treating highly contaminated highway runoff for environmental discharge.[36,37]

A greater understanding of the effectiveness of CDWT on wastewater effluent, stormwater, and blends of these alternative source waters with surface water is needed. This better understanding would enable determination of (1) the most appropriate water supply augmentation option for a municipality, (2) the degree of contaminant removal to expect from CDWT of blended or unblended alternative source waters, and (3) the degree of blending or advanced treatment necessary before or after the existing drinking water facility

To further this understanding, this study systematically evaluated CDWT of stormwater, wastewater effluent, and blends at the bench-scale. To assess which types of stormwater and wastewater effluent or most treatable with CDWT and most appropriate for reuse, a wide range of samples was collected (i.e., stormwaters from various drainage land uses and precipitation conditions, and wastewater effluents with various degrees of nutrient removal). Two approaches were investigated for predicting DOC removal from blends. The objectives of this study were to (1) determine the effectiveness of CDWT for removal of turbidity, TOC, and DBP precursors from wastewater effluent, stormwater, and blends; (2) compare models for DOC removal from blends; (3) test the impact of pretreatment with CDWT prior to blending; and (4) determine the degree of blending needed for regulatory compliance. The results of this study will provide decision-makers with information to select the most appropriate alternative source water(s) and to determine the necessary degree of blending or advanced treatment to evaluate at the pilot-or demonstration plant scale.

2.2 Methods

2.2.1 Alternative Source Waters and Sampling

One surface water source was selected to represent a typical source water for CDWT. This source water was not significantly wastewater-impacted. Two samples were collected from the Boulder Reservoir, CO, in January (*Surface Water-1*) and March (*Surface Water-2*); both samples had similar water quality with all measured parameters within ±23% except turbidity, which was about five times higher in the March sample due to high wind conditions.

Eight stormwater (StmW) samples were selected based on precipitation (rain or snow; amount; and antecedent dry days) and drainage basin land use (paved, unpaved, or mixed use), as both impact stormwater quality.[55,56] Seven were collected in Colorado. The *Industrial StmW* and *Highway StmW* samples were collected from an industrial area and an interstate highway, respectively, during the same rain event. Two *Parking Lot StmW* samples were collected from the same impervious parking lot at the beginning of two different snow events; the first (*Parking Lot StmW-1*) was collected after 38 antecedent dry days, and the second (*Parking Lot StmW-2*) after 2 antecedent dry days. The *Field StmW* sample was collected from an outfall that drains a university football field with natural grass. The *Campus Manhole StmW* sample was collected during a snowmelt from the last manhole prior to a retention pond that supports a mixed-use drainage basin (i.e., fields, roofs, and roads); from that retention pond, the *Campus Pond StmW* sample was collected during dry weather. The *Suburban Pond Outlet StmW* sample was collected during a rain event from the overflow of a retention pond in a suburban (i.e., mixed use) area in New York. All samples were 10 to 40 L grab samples, except the *Suburban Pond Outlet StmW*, which was a 6-hour composite sample.

The municipal wastewater effluent (WWeff) sources were selected based on the treatment processes used at the wastewater treatment facility, specifically the type and extent of removal for biochemical oxygen demand (BOD), nitrogen (N), and phosphorus (P). One facility achieved only BOD removal without nitrification; two facilities achieved both BOD and nitrogen removal; and two facilities achieved BOD, nitrogen, and phosphorus removal. The *BOD-Removal WWeff* sample was collected from a 4,900 m^3/day facility in California that doses ferric chloride in the collection network for odor control and uses trickling filters and bioflocculation basins for BOD removal (no nitrification). The *N-Removal Filter WWeff* sample was collected from a 6,100 m^3/day facility in Colorado that uses trickling filters for BOD removal and nitrification and uses submerged filters for denitrification. The *N-Removal Bardenpho WWeff* sample was collected from a 4,000 m^3/day facility in Colorado that uses a 4-Stage Bardenpho process for BOD and N removal. The *P-Removal Johannesburg WWeff* sample was collected from a 26,000 m^3/day facility in Nevada that uses ferric chloride and anionic polymer to enhance primary settling and uses a modified Johannesburg process for BOD, N, and P removal. The *P-Removal A2O WWeff* sample was collected from a 390 m^3/day facility in Colorado that uses sequential anaerobic, anoxic, and aerobic processes (A2O) for BOD, N and P removal, followed by alum coagulation and dual-media filtration for additional P removal. All samples were 10 to 40 L grab samples collected before disinfection, except the *N-Removal Bardenpho WWeff* sample was collected after ultraviolet disinfection. An overview of the initial water quality of all fifteen samples is in Table 2.1.

Table 2.1 Initial Water Quality Overview.

Water	pH	Alk. (mg/L as $CaCO_3$)	Turb. (NTU)	UVA_{254} (1/cm)	TOC (mg/L)	DOC (mg/L)	SUVA (L/m/mg)	24-hr Cl Demand (mg/L)
Surface Water								
Surface Water-1	7.8	56	11	0.063	3	3	1.9	2.1
Surface Water-2	8.0	70	51	0.058	3	3	1.7	-
Stormwaters								
Industrial StmW	6.9	85	255	2.063	120	117	1.7	-
Highway StmW	6.7	40	268	1.894	86	87	2.2	-
Field StmW	7.8	76	146	0.203	11	12	1.8	21.3
Campus Manhole StmW	7.3	30	28	0.213	10	7	3.2	13.9
Suburban Pond Outlet StmW	7.8	46	62	0.245	7	6	3.9	15.6
Campus Pond StmW	7.5	197	15	0.216	7	-	3.1	-
Parking Lot StmW-1	8.9	71	148	0.618	22	19	2.8	20.3
Parking Lot StmW-2	8.4	29	54	0.136	4	4	3.3	8.3
Wastewater Effluents								
BOD-Removal WWeff	8.1	353	4.7	0.230	15	13	1.7	>91
N-Removal Filter WWeff	7.8	62	1.6	0.185	10	10	1.8	26.7
N-Removal Bardenpho WWeff	7.8	99	1.7	0.155	8	8	1.9	14.7
P-Removal Johannesburg WWeff	7.9	122	5.2	0.128	8	8	1.6	15
P-Removal A2O WWeff	7.6	95	0.4	0.106	6	6	1.8	9.2

2.2.2 Analytical Methods

Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined using a Shimadzu TOC-V_{SCH} analyzer (Kyoto, Japan). Turbidity was measured with a Hach 2100N Turbidimeter (Loveland, CO, USA). Alkalinity was determined by the bromocresol green-methyl red method with a Hach digital titrator. Ultraviolet absorbance at 254 nm (UVA_{254}) was measured with a Hach DR 6000 spectrophotometer with a 10-mm sample cell. pH was measured with a Thermo Scientific Orion Star A211 pH meter. DOC and UVA_{254} samples were prepared by filtration with 0.45-µm nitrocellulose membranes. Metals (Ag, Al, As, Ba, Cd, Cr, Cu, Mn, Pb, Sb, Se, Th, and Zn) were analyzed using Indium as an internal standard with a Perkin Elmer SCIEX inductively coupled plasma mass spectrometer (model Elan DRC-e) (Waltham, MA, USA).

2.2.3 Jar Test Procedure

Bench-scale jar tests were used to evaluate the treatment capacity of coagulation, flocculation, and sedimentation. Each experiment used six 2-L jars, each with 1 L of sample plus alum ($Al_2(SO_4)_3 \cdot 16H_2O$) doses of 0, 10, 20, 40, 80, and 160 mg/L. The jar testing procedure (i.e., mixing speed and duration) for coagulation, flocculation, and sedimentation has been described previously.[46] There was 10% replication of these experiments. Two raw water samples, *Parking Lot StmW-1* and *N-Removal Bardenpho WWeff*, were also tested with ferric chloride as the coagulant.

2.2.4 DBP Formation and Toxicity

Free chlorine demand under Uniform Formation Conditions (UFC)[57] was determined before and after coagulation: the holding temperature was 20±1 °C, the contact time was 24±1 hours, the pH was adjusted to 8.0±0.2 with a borate buffer, and the free chlorine residual after 24 hours was 1.0±0.4 mg/L as Cl_2. Free chlorine residual was measured with the N,N diethyl-1,4 phenylenediamine sulfate (DPD) method with a Hach pocket colorimeter. Eighteen DBPs were measured using EPA

Methods 551.1 and 552.2[57–59]: total trihalomethanes (TTHM), including chloroform, bromodichloromethane, dibromochloromethane, and bromoform; chloropicrin; four haloacetonitriles (HAN4), including trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile; four unregulated haloacetic acids (HAAs), including bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid, and the five regulated HAAs (HAA5), including chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid. DBP formation analysis was conducted on initial samples and samples coagulated with 40 mg/L alum. This dose was chosen to represent a typical alum dose and because it usually caused maximum or near-maximum removal of turbidity and TOC; the only exception was the *Parking Lot StmW-1*, which required 80 mg/L alum for significant turbidity removal. Three samples (*BOD-Removal WWeff*, *Industrial StmW*, and *Highway StmW*) were not included in the DBP analysis because high TOC or ammonia concentrations which caused impractically high free chlorine demands.

DBP toxicity was estimated by cytotoxicity, which is the tendency of a chemical agent to damage cells, and genotoxicity, which is the tendency of a chemical agent to damage genetic information. Cytotoxicity was calculated by multiplying the molar concentration of each DBP by its corresponding cytotoxicity index (CTI), which is based on the inverse for the lethal concentration for 50% (LC_{50}) of Chinese hamster ovary cells relative to the control.[60] For each water, the calculated cytotoxicity of the measured DBPs was summed for each DBP class (HAN4, chloropicrin, TTHM, HAA5, and other HAAs) and for all measured DBPs to represent the total calculated cytotoxicity. Genotoxicity was calculated the same way but instead using each DBP's corresponding genotoxicity index (GTI), which is based on an inverted 50% tail DNA value, a quantitative measure of DNA damage in Chinese hamster ovary cells.[60]

These approaches provide an indication of relative toxicity but they do not account for synergistic effects or unidentified DBPs.

2.2.5 Blends

Three alternative water sources were blended with surface water using equal volumes: *Parking Lot StmW-1* with *Surface Water-1*, *Field StmW* with *Surface Water-2*, and *N-Removal Bardenpho WWeff* with *Surface Water-1*. Jar test experiments were conducted on each 50:50 blend. The different surface water samples were used due to different timings of the alternative source water sample collection and were not expected to impact results as both were very similar to each other. Also, two alternative source waters (*Field StmW* and *N-Removal Bardenpho WWeff*) were pretreated with coagulation using a 40 mg/L alum dose, and then blended with surface water using equal volumes; the resulting solution was then coagulated again at all six alum doses.

2.2.6 Modeling Treatment Performance

DOC removal was modeled using a Langmuir-based adsorption model (‘Coagulation Model’), calibrated with alum and ferric chloride coagulation data from drinking water facilities treating surface water.[61] This model is accurate for surface water (standard error ±9.5% or 0.4 mg/L DOC)[61] and has been validated at full-scale facilities.[62] The model predicts the nonsorbable fraction of DOC based on the water’s or blend’s initial specific UV absorbance (SUVA), and predicts the removal of the sorbable fraction based on the alum dose and pH after coagulation. For blends, a “Weighted Average of Unblended Waters” approach was also used. First, the weighted averages for turbidity, UVA_{254}, TOC, and DOC at each alum dose were calculated using each water’s experimental data when tested individually (i.e., not blended). Next, these values at each dose were divided by the weighted average of the initial parameters of the individual waters to calculate expected percent removals.

Finally, the blend's measured initial parameters were multiplied by the corresponding expected percent removal.

2.3 Results and Discussion

2.3.1 Stormwater

The stormwaters' initial water quality varied widely for turbidity (between 15 and 268 NTU), for TOC (between 4 and 120 mg/L), for alkalinity (between 29 and 197 mg/L as $CaCO_3$), and for SUVA (between 1.7 and 3.9 L/m/mg) (Table 2.1). Also, the initial turbidity to initial TOC ratio varied from 13:1 to 2:1. Not surprisingly, the treatability of the stormwaters also varied widely, as described below.

2.3.1.1 Turbidity. Maximum turbidity removal was consistently high among the stormwaters, from 1 to 2 logs (Figure 2.1a and Table 2.2). However, due in part to the wider range in initial turbidity, the minimum turbidity values ranged widely from 0.8 to 24 NTU. USEPA guidelines recommend a turbidity of less than 2 NTU for surface water reservoir augmentation.[63] In addition, a settled water turbidity of less than 2 NTU is considered a good target when treating waters with initial turbidity over 10 NTU for filtration.[64] Four of the eight stormwaters (*Field StmW*, *Parking Lot StmW-2*, *Suburban Pond Outlet StmW*, and *Campus Pond StmW*) met this guideline with alum doses ranging from 20 to 40 mg/L. This dose range is comparable to the 75th percentile of alum doses, 30 mg/L, used in CDWT of surface water.[65] A fifth stormwater, *Campus Manhole StmW*, had a minimum turbidity of 3 NTU, and so would have required a low degree of blending or additional treatment to meet the turbidity guideline. Since 40 mg/L alum achieved minimum or near minimum turbidity in most stormwaters (Table 2.2), this dose was used for the DBP analyses (Section 3.1.3). Regarding other coagulants, alum yielded greater turbidity removal than ferric chloride in *Parking Lot StmW-1* (Figure A.2). Overall, these results

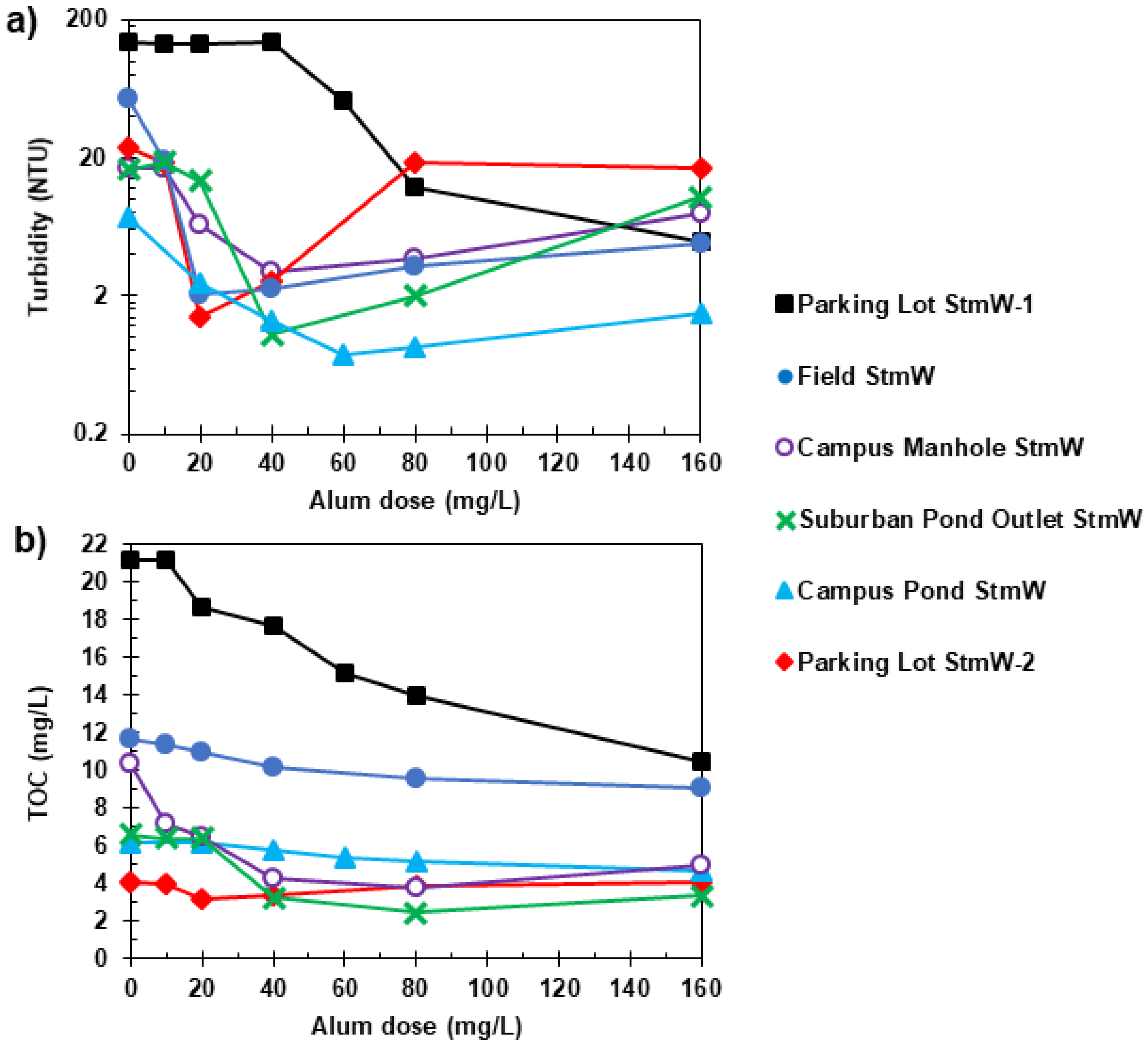


Figure 2.1 The (a) turbidity removal and (b) TOC removal as a function of alum dose for six of the eight stormwaters; *Industrial StmW* and *Highway StmW* had over three times higher TOC than the next highest stormwater and are shown in Figure A.1. The TOC and turbidity values at the 0 mg/L alum dose are for the control (no coagulant but stirred and settled according to the coagulation, flocculation, and sedimentation procedure); the *Campus Manhole StmW*'s TOC at 0 mg/L alum was not available so data from a stirred control, which did not include settling time, was used and expected to be within 10% of the TOC at 0 mg/L alum based on trends in the other seven stormwaters.

Table 2.2. TOC and turbidity removal summary for stormwaters and wastewater effluents. 'Init.' refers to the initial concentration of TOC or turbidity. 'After 40 mg/L Alum' refers to the concentration of TOC or turbidity remaining after treatment with 40 mg/L alum. 'Min.' refers to the minimum turbidity remaining over the range 0 to 160 mg/L alum. 'Alum dose for Target (mg/L)' refers to the alum dose to reach that minimum remaining turbidity. 'Max % Removal' refers to the maximum percent removal of turbidity or TOC over the range 0 to 160 mg/L alum. '% Removal with 40 mg/L Alum' refers to percent removal of TOC with 40 mg/L alum. 'Alum dose for Max Removal (mg/L)' refers to the dose of alum required to reach that maximum percent removal of TOC. Maximum percent removal of TOC was achieved with 160 mg/L alum for all waters except *High StmW* (120 mg/L alum), *Parking Lot StmW-2* (20 mg/L alum), *Campus Manhole StmW* (80 mg/L alum), and *Suburban Pond Outlet StmW* (80 mg/L alum).

[a] The alum dose for minimum turbidity is shown because the target turbidity was not achieved for this sample.

Water	Turbidity					TOC			
	Init. (NTU)	After 40 mg/L Alum (NTU)	Min. (NTU)	Alum dose for Target (mg/L)	Max. % Removal	Init. (mg/L)	After 40 mg/L Alum (mg/L)	% Removal with 40 mg/L Alum	Max % Removal
Industrial StmW	255	192	23	160[a]	91%	120	124	-3%	16%
Highway StmW	268	202	24	120[a]	91%	86	82	4%	20%
Parking Lot StmW-1	148	140	5.0	160[a]	97%	22	18	19%	52%
Parking Lot StmW-2	54	2.5	1.4	20	97%	4.2	3.3	20%	25%
Field StmW	146	2.3	2.0	20	99%	11	10	11%	20%
Campus Manhole StmW	28	3.0	3.0	40[a]	89%	10	4.2	59%	64%
Suburban Pond Outlet StmW	62	1.0	1.0	40	98%	7.3	3.5	53%	66%
Campus Pond StmW	15	1.3	0.8	40	95%	7.0	5.8	17%	33%
BOD-Removal WWeff	4.7	2.2	1.8	20	62%	15	13	10%	23%
N-Removal Filter WWeff	1.6	1.7	0.7	0	58%	9.6	8.3	14%	36%
N-Removal Bardenpho WWeff	1.7	0.6	0.4	0	76%	7.8	6.9	11%	32%
P-Removal Johannesburg WWeff	5.2	0.9	0.9	0	82%	8.3	7.0	15%	25%
P-Removal A2O WWeff	0.4	0.9	0.4	0	0%	6.0	5.6	6%	18%

demonstrate that there are many contexts in which CDWT would be effective and economical for reducing stormwater turbidity in reuse.

Three stormwaters (*Parking Lot StmW-1*, *Highway StmW*, and *Industrial StmW*) had minimum turbidity over 5 NTU after CDWT with up to 160 mg/L alum (**Error! Reference source not found.**a and Figure A.1). All three of these stormwaters were from impervious drainage basins during unfavorable precipitation conditions. Impervious surfaces increase the velocity of overland flow and thus increase sediment transport and turbidity.[66] *Highway StmW* and *Industrial StmW* were collected during a precipitation event with low total rainfall (Table A.1) which increases pollutant concentrations because it results in a lower degree of dilution for a given washoff mass.[67] *Parking Lot StmW-1* was collected after 38 antecedent dry days, during which a layer of dust accumulated on the pavement. In contrast, *Parking Lot StmW-2* was collected from the same location after just 2 antecedent dry days and had approximately three times lower initial and minimum turbidity. These results suggest that stormwater reuse would require careful selection and management of the drainage basin, as well as the ability to divert stormwater from unfavorable precipitation conditions.

2.3.1.2 TOC. TOC removal ranged widely in the stormwaters (Figure 2.1b and Figure A.1). TOC removal with 40 mg/L alum ranged from negligible to 59%, and maximum turbidity removal ranged from 16% to 66% (Table 2.2). These maximum percent removals correspond to minimum TOCs ranging from 2.5 to 101 mg/L. Initial TOC correlated with initial turbidity ($R^2 = 0.73$), and the same three stormwaters with highest initial turbidity (*Industrial StmW*, *Highway StmW*, and *Parking Lot StmW-1*) also had the highest initial TOC. Therefore, like turbidity, initial TOC appears to depend on drainage basin characteristics and precipitation conditions. However, the reasons for the range in TOC percent removal were less clear. Maximum TOC removal and maximum turbidity removal did not correlate, and a wide range of TOC removal was observed in both paved and grassy drainage basins. The maximum percent removal of TOC did, however, correlate loosely with SUVA ($R^2 = 0.59$). Overall, coagulation could achieve significant removal of TOC; the average maximum TOC removal across the eight stormwaters was 37%. Three stormwaters (*Parking Lot StmW*-2, *Campus Manhole StmW*, and *Suburban Pond Outlet StmW*) had TOC less than 5 mg/L after coagulation with just 40 mg/L alum, and one stormwater (*Campus Pond StmW*) had TOC less than 5 mg/L after coagulation with a higher dose of 160 mg/L alum. However, whether the TOC removal would be sufficient for reuse would depend on DBP formation, which will be explored in the following section.

2.3.1.3 Stormwater DBPs, Toxicity, and Metals. For CDWT, the required TOC removal is driven by DBP formation control. An alum dose of 40 mg/L was selected for DBP analyses since this dose achieved maximum or near-maximum removal of TOC and turbidity from the majority of stormwaters. Two stormwaters, *High StmW* and *Industrial StmW*, were not included in the DBP analysis because both had high TOC that caused impractically high free chlorine demands. The measured DBPs were TTHM, HAA5, four other HAAs, HAN4, and chloropicrin. The European Union has a guidance value of 100 μg/L for TTHM,[68] and the U.S. EPA's maximum contaminant levels (MCLs) are 80 μg/L for TTHM and 60 μg/L for HAA5.[69] Overall, DBPs were found to be a critical challenge for stormwater reuse because the high final TOC values of most stormwaters led to DBP formation above the MCLs (Figure 2.2 and Figure 2.3).

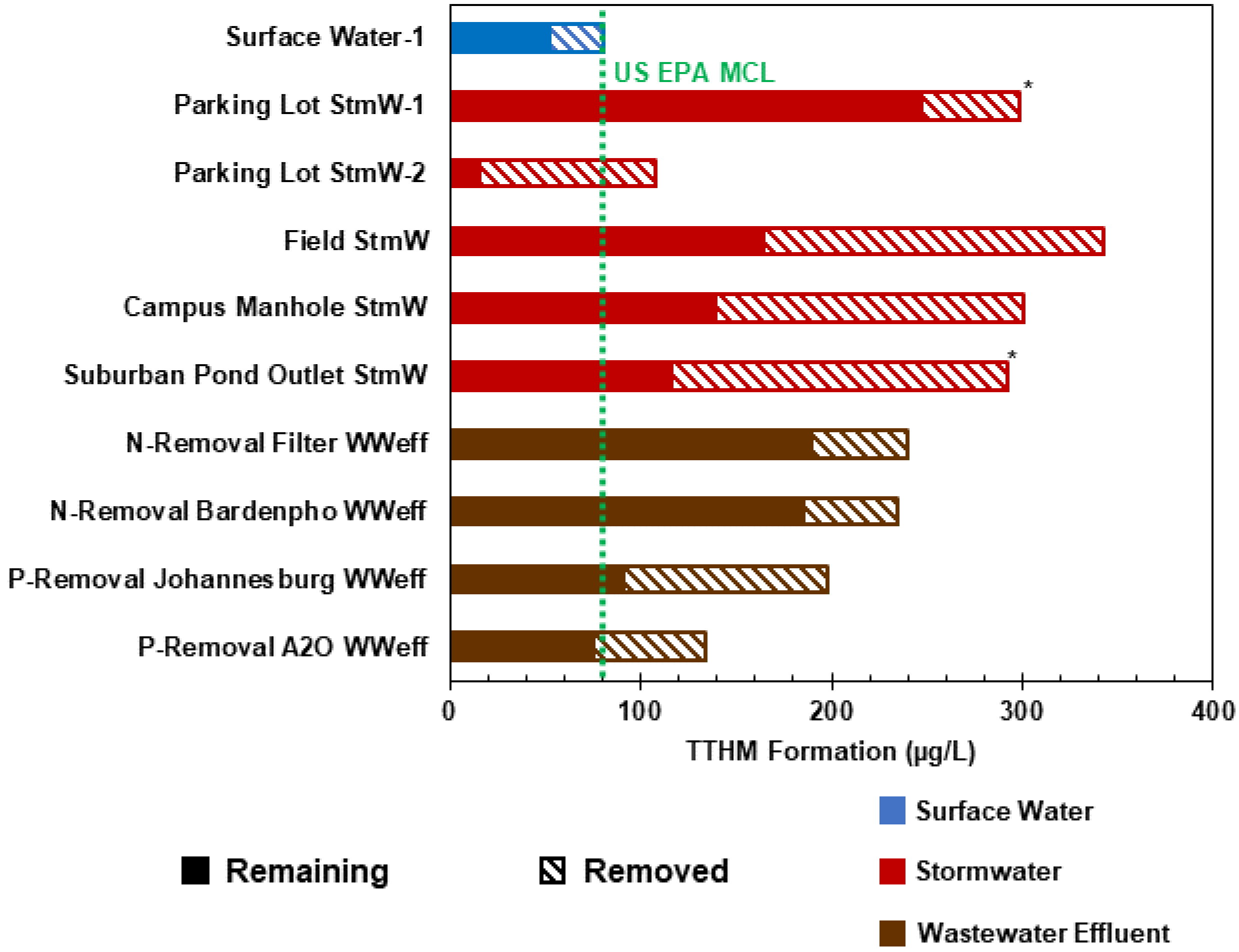


Figure 2.2. TTHM formation under UFC conditions for one surface water, five stormwaters, and four wastewater effluents. The total bar length (solid plus hashed) represents initial TTHM formation; the hashed portion of each bar represents the amount of the TTHM formation in the raw water that was reduced by coagulation and the solid portion of each bar represents TTHM formation in the treated water. All samples were coagulated with 40 mg/L alum, which resulted in near maximum TOC and turbidity removal from most samples included in the DBP analyses; the one except was *Parking Lot StmW-1*, which was coagulated with 80 mg/L alum because it required a higher dose for significant turbidity removal. *Raw *Parking Lot StmW-1* and raw *Suburban Pond Outlet StmW* had chloroform concentrations above the calibrated range of the method (>250 µg/L chloroform), so a conservative concentration of 250 µg/L chloroform were used when estimating the TTHM formation (TTHM formation estimated by using extrapolated chloroform concentrations are presented in Figure A.4).

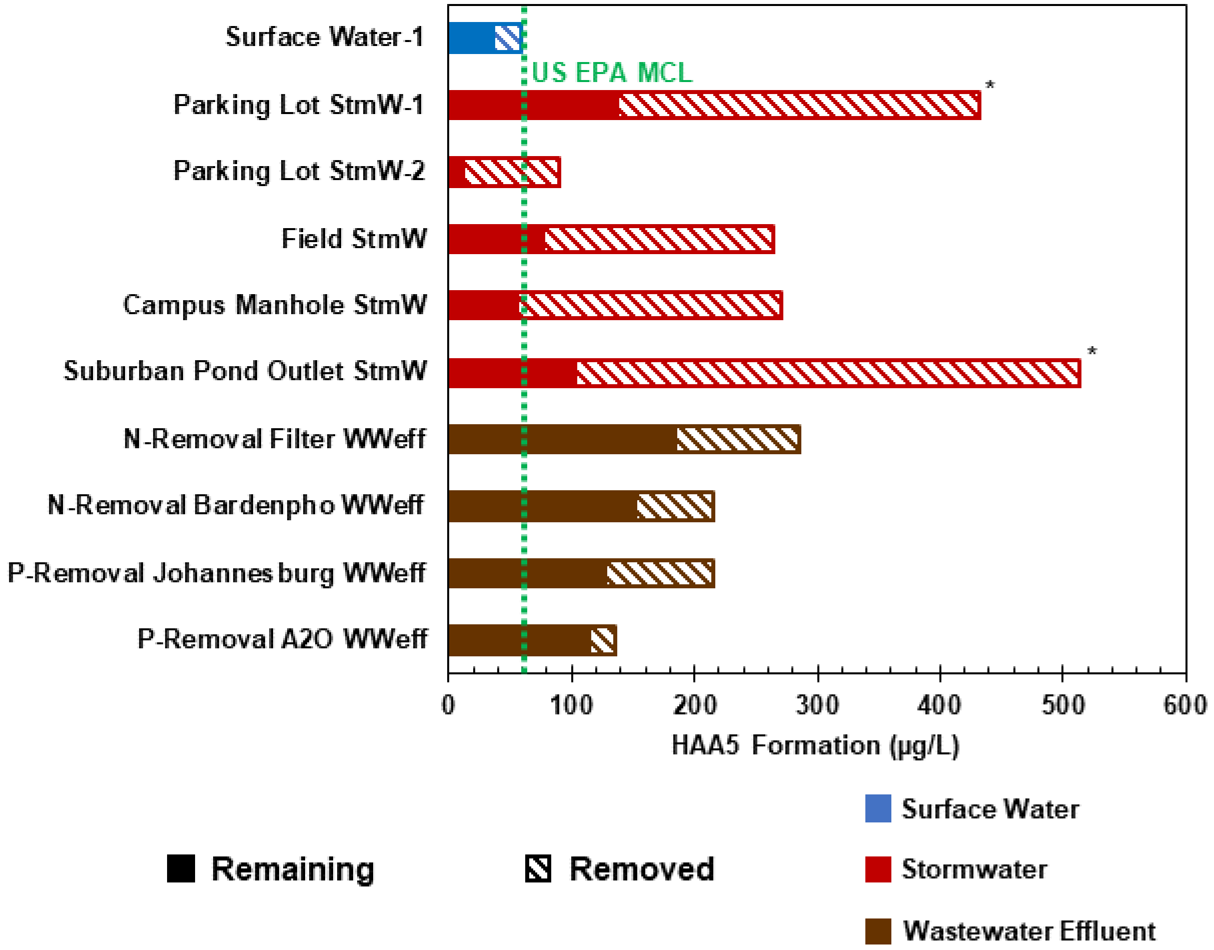


Figure 2.3. HAA5 formation under UFC conditions for one surface water, five stormwaters, and four wastewater effluents. The total bar length (solid plus hashed) represents initial HAA5 formation; the hashed portion of each bar represents the amount of the HAA5 formation in the raw water that was reduced by coagulation and the solid portion of each bar represents HAA5 formation in the treated water. All samples were coagulated with 40 mg/L alum, which resulted in near maximum TOC and turbidity removal from most samples included in the DBP analyses; the one except was*Parking Lot StmW-1*, which was coagulated with 80 mg/L alum because it required a higher dose for significant turbidity removal. *Raw *Parking Lot StmW-1* had a trichloroacetic acid concentration above the calibrated range of the method (>250 µg/L), and Raw *Suburban Pond Outlet StmW* had trichloroacetic acid and dichloroacetic acid concentrations above the calibrated range of the method, so conservative concentrations of 250 µg/L were used for the HAA5 concentrations in this figure. (Extrapolated values are presented in Figure A.5.)

Coagulation reduced the formation of regulated DBPs in all tested stormwater samples; HAA5 formation was reduced by at least 68% and TTHM formation was reduced by at least 50% (including an extrapolated initial TTHM value for *Parking Lot StmW-1*) (Table A.5). However, the high initial TOC and resulting high coagulated TOC of most stormwater samples led to DBP formation above the MCLs after coagulation for all of the stormwaters except *Parking Lot StmW-2* (Figure 2.2 and Figure 2.3). Out of all of the stormwaters and wastewater effluents, *Parking Lot StmW-2* had the lowest initial TOC, the lowest final TOC, the lowest initial DBP formation (108 μg/L TTHM and 90 μg/L HAA5), the lowest final DBP formation (16 μg/L TTHM and 10 μg/L HAA5), and the greatest percent removal of TTHM and HAA5 precursors. In contrast, *Parking Lot StmW-1* had the highest DBP formation after coagulation (247 μg/L TTHM and 138 μg/L HAA5) among the stormwaters, despite being treated with a higher alum dose of 80 mg/L, instead of 40 mg/L alum like the other samples. This difference in DBP formation between two stormwaters collected from the same location but with different numbers of antecedent dry days further emphasizes the importance of being able to divert stormwater when precipitation conditions are unfavorable.

In addition to meeting established DBP regulations, the potential human health impact of DBPs can be evaluated by calculated cytotoxicity. While the regulated and unregulated DBPs' formation decreased, the calculated cytotoxicity did not always decrease. Specifically, the calculated cytotoxicity for three stormwaters (*Parking Lot StmW-1*, *Field StmW*, and *Campus Manhole StmW*) did not significantly change after coagulation (i.e., less than a 13% change), (Figure A.6). For two stormwaters (*Parking Lot StmW-2* and *Suburban Pond Outlet StmW*), the calculated cytotoxicity was reduced by around 50%, though regulated DBPs were reduced by over 75% in these samples (Table A.5). This low reduction of cytotoxicity was mostly due to the poor removal of highly cytotoxic HAN4. Each HAN4 species has a CTI that is about an order of magnitude larger than the CTI of the corresponding HAA species; for example, the HAN4 species dibromoacetonitrile has a CTI of 3.51×10^8, while the corresponding HAA species, dibromoacetic acid, is less toxic and so has a lower CTI of 1.69×10^6.[60] Therefore, even though HAN4 compounds' total molar concentrations made up 12% or less of the measured DBPs, HAN4 accounted for at least 39% of the calculated cytotoxicity in all initial stormwaters and at least 59% of calculated cytotoxicity in all treated stormwaters (Figure 2.4). *Parking Lot StmW-2* and *Football Field StmW*, the two stormwaters with significant reduction in calculated cytotoxicity (Figure A.6), were also the only two waters with substantial (greater than 13%) reduction in HAN4 formation (Table A.5).

In addition to poor HAN4 removal, the calculated cytoxicity also did not decrease in multiple stormwaters because some cytotoxic DBP species were formed at higher concentrations after coagulation than. Specifically, coagulation removes organic carbon but not bromide,[70] which results in increased bromine incorporation in DBPs which can offset the overall reduction in DBP formation. Brominated DBPs tend to be more cytotoxic than their more chlorinated analogs.[60] The Bromine Incorporation Factor (BIF), an index of the relative bromine incorporation of DBPs,[71] increased after coagulation for all stormwaters' TTHMs and HAAs and for most stormwaters' HAN4 (Table A.6). *Campus Manhole StmW* had the highest BIF before and after coagulation for all DBP categories, which could be due to high bromide concentrations attributable to road salt.[72]

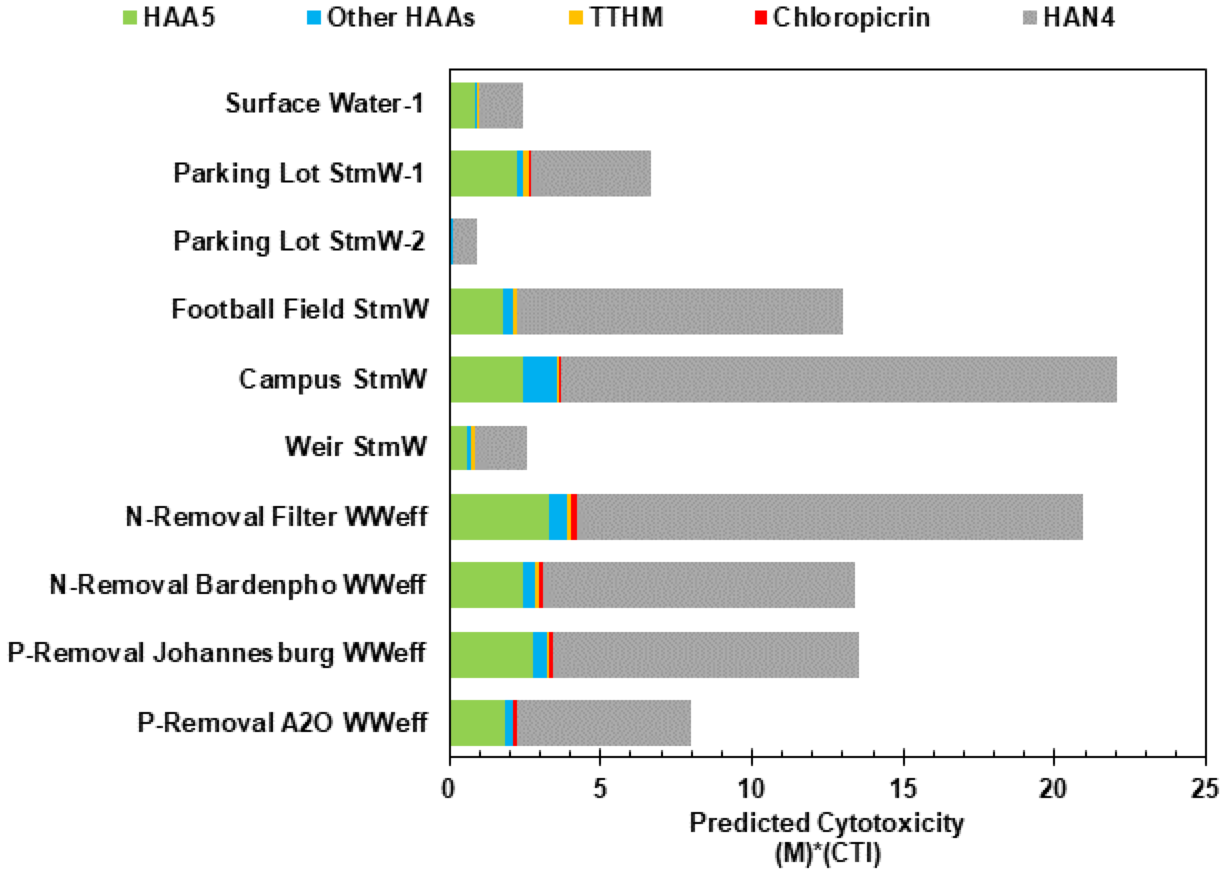


Figure 2.4. Calculated cytotoxicity of measured DBPs formed under UFC conditions in surface water, stormwater, and wastewater effluent samples after coagulation with 40 mg/L alum, except for *Parking Lot StmW-1*, which was coagulated with 80 mg/L alum.

Based on the carbon normalized DBP yields (i.e., the ratio of the DBP concentration to the TOC concentration) of the treated stormwaters, not even impractically large alum doses would be sufficient to achieve DBP regulatory compliance in most stormwaters without blending. TTHM yields of the treated stormwaters ranged from 8 to 35 μg/mg$_C$ (Table A.4); compared to TTHM yields in surface waters (28±1 μg/mg$_C$), this range is wider but overlapping.[57] Since DBP data was only experimentally determine for stormwaters treated with a single alum dose, DBP yields were used to estimate the final TOC needed to achieve DBP regulatory compliance.[73] The final TOC needed to achieve regulatory compliance for both TTHM and HAA5 ranged from 2.0 to 5.6 mg/L (Table A.4). None of the stormwaters would have met this target, even at an alum dose of 160 mg/L, except for *Parking Lot StmW-2*, which had the lowest initial TOC. Since alum coagulation alone would not be sufficient to meet DBP regulations for most stormwaters, advanced treatment or blending with relatively clean surface water would be required.

Public health implications can also be evaluated by looking at calculated genotoxicity and metals concentrations. Among the stormwaters, the calculated genotoxicity was reduced by an average of 44% (Figure A.7), which is a greater average reduction than calculated cytotoxicity (20%) (Figure A.6), but a lower average reduction than TTHM (65%) or HAA5 (78%) (Table A.5). Both toxicity estimates were reduced less than regulated DBPs. Compared to calculated cytotoxicity, calculated genotoxicity was less dominated by HANs and more driven by bromoacetic acid and chloropicrin. Nevertheless, increased bromine incorporation also contributed to the poor removal of predicted genotoxicity. For example, the predicted genotoxicity of *Campus Manhole StmW* was reduced by only 8%, because increasing bromine incorporation of HAN4 and HAA5 nearly offset a 75% reduction in chloropicrin formation. In terms of metals, multiple stormwaters had aluminum or manganese concentrations over twice as high as U.S. EPA and WHO aesthetic guidelines (Table A.2).[74,75] However, none of the stormwaters exceeded a health-based standard for metals,[69,74] indicating that control of DBP precursors is a more critical challenge than metals removal for stormwater reuse.

2.3.2 Wastewater Effluent

The range in initial water quality was much narrow for wastewater effluents than for stormwaters (Table 2.1). pH ranged only 7.6 to 8.1, and SUVA ranged only 1.6 to 1.9 L/mg/m. The initial TOC of the wastewater effluents ranged from 6 to 15 mg/L, by less than a factor of 3, compared to the factor of 30 difference between the lowest and highest stormwaters. The two denitrified wastewater effluents (*N-Removal Filter WWeff* and *N-Removal Bardenpho WWeff*) had especially similar water quality, with TOC, SUVA, pH, and turbidity within 25% of each other, even though the first was denitrified with attached growth biological processes and the latter was denitrified with suspended growth biological processes. Therefore, engineers could plan for a lower degree of uncertainty regarding influent quality when designing pilot-scale or demonstration-scale projects for wastewater reuse than stormwater reuse.

2.3.2.1 Turbidity. Little or no coagulant was required to meet the turbidity target, 2 NTU, in wastewater effluent (Figure 2.5). Three wastewater effluents (*N-Removal Filter WWeff*, *N-Removal Bardenpho WWeff*, and *P-Removal A2O WWeff*) had initial turbidity less than 2 NTU. *P-Removal Johannesburg WWeff* had initial turbidity of 5.2 NTU, but this turbidity was reduced to 0.9 NTU with sedimentation alone. For *BOD-Removal WWeff*, a small dose of 20 mg/L alum was required to reduce the turbidity from 4.7 NTU to 1.8 NTU. The initial turbidities of these wastewater effluents were within the ranges reported previously for each treatment category.[17] Initial turbidity of wastewater effluents were lower than any of the stormwaters, and on the low end of the range compared to surface waters, for which the 10th and 90th percentiles are 0.12 and 24 NTU, respectively.[76]

2.3.2.2 TOC. Lower initial TOC was associated with higher degrees of nutrient removal at the wastewater facility. *BOD-Removal WWeff* had the highest initial TOC (15 mg/L), followed by *N-Removal Filter WWeff* (10 mg/L), *N-Removal Bardenpho WWeff* (8 mg/L), *P-Removal Johannesburg WWeff* (8 mg/L), and *P-Removal A2O WWeff* (6 mg/L). This data indicates that wastewater effluents with greater nutrient removal may be more suitable for potable reuse. Furthermore, the average initial TOC of the wastewater effluents was 9 mg/L, much lower than the average initial TOC of the stormwaters, which was 33 mg/L. However, the wastewater effluent TOC

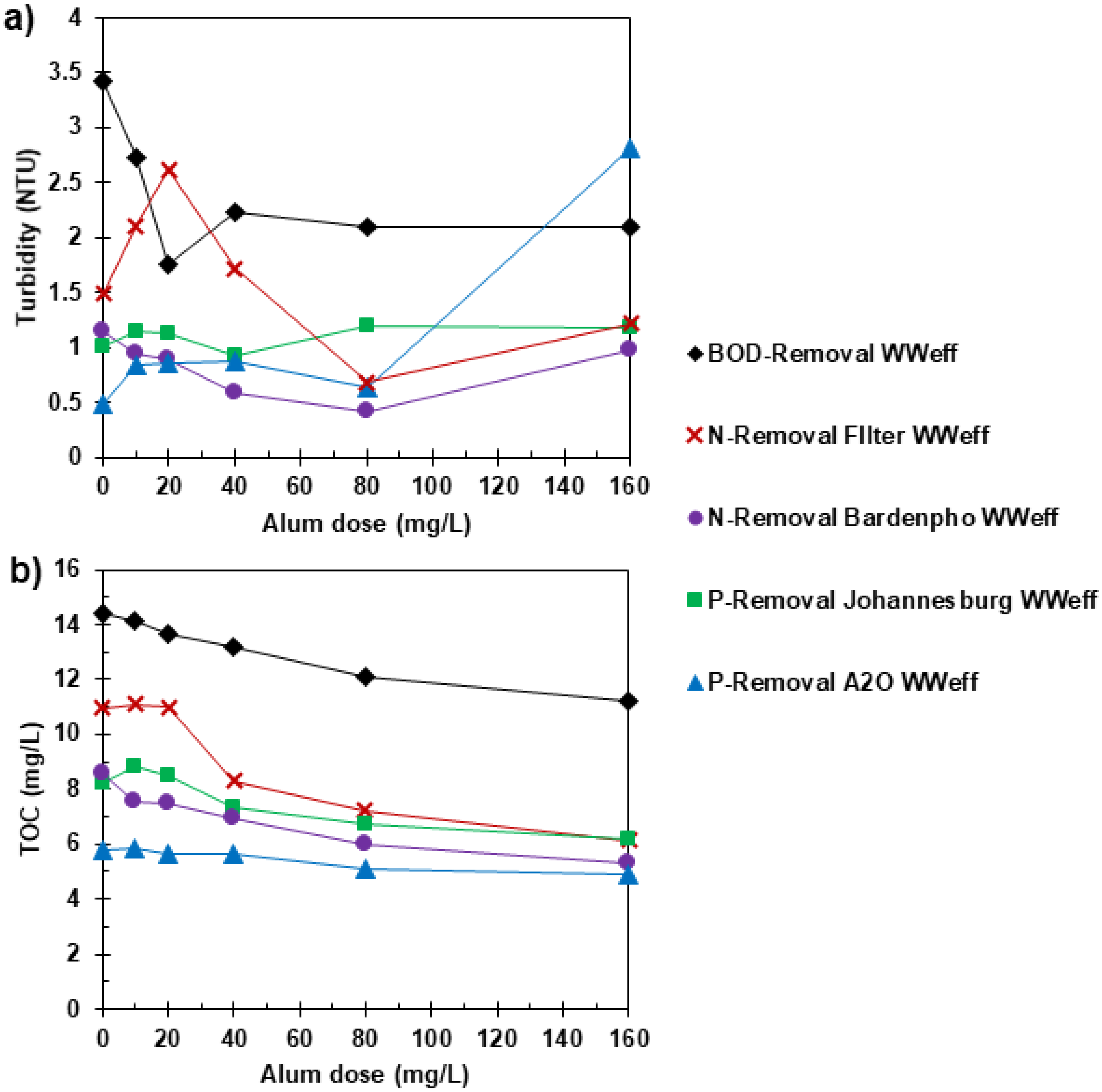


Figure 2.5. (a) Turbidity and (b) TOC removal from five wastewater effluents (WWeff) over alum doses from 0 to 160 mg/L. The TOC and turbidity values at 0 mg/L are for samples that have undergone the rapid mix, flocculation, and sedimentation processes but without the addition of coagulant.

is high compared to the surface waters used as drinking water influent in the United States, for which the 10th and 90th percentiles are 0.35 mg/L and 5.3 mg/L, respectively.[76]

TOC removal from the wastewater effluents varied based on previous treatment. *BOD-Removal WWeff, P-Removal Johannesburg WWeff*, and *P-Removal*

A2O WWeff had low maximum TOC removal ranging from 18% to 25%. Each of these three wastewater effluents had some degree of exposure to coagulants in upstream processes (Section 2.2.1). This upstream chemical treatment may have already removed some portion of the sorbable fraction of organic carbon, diminishing the effectiveness of additional coagulation. In contrast, the two wastewater effluents with no prior exposure to coagulants (*N-Removal Filter WWeff* and *N-Removal Bardenpho WWeff*) had higher maximum TOC removal of 32% to 36%.

The effectiveness of coagulation in *N-Removal Filter WWeff* and *N-Removal Bardenpho WWeff* was comparable to the effectiveness of coagulation in low-SUVA surface waters. Studies on coagulation often focus on DOC removal since the particulate organic carbon (POC) (i.e., TOC minus DOC) is generally small and readily removed by coagulation.[61] In the case of these two wastewater effluents, initial POC was negligible, so TOC and DOC removal are virtually equivalent. *N-Removal Filter WWeff* and *N-Removal Bardenpho WWeff* had initial SUVA values of 1.8 to 1.9 L/mg/m and DOC removal of 17% to 20% after coagulation with 40 mg/L alum. These SUVAs and DOC removals are on the low end of the range compared surface waters (SUVA 1.4 to 6.1 L/mg/m[61] and DOC removal of 5% to 66% with 40 mg/L alum).[77] In surface waters, lower SUVA is loosely correlated with a lower proportion of removable DOC.[61] Hence, surface waters that have SUVA less than 2 L/mg/m have DOC removal that is more similar to the wastewater effluents (10% to 31% with 40 mg/L alum).[77] Also, surface waters with low SUVA tend to be more microbially influenced,[78] which may further explain their similar treatment results with biologically treated wastewater.

2.3.2.2 Wastewater Effluent DBPs, Toxicity, and Metals. Similar to stormwater, DBPs are a critical challenge for wastewater reuse. The carbon normalized DBP yields of the wastewater effluents were comparable to surface waters (Table A.4), but the high TOC in the wastewater effluents led to the formation of regulated DBPs above the U.S. EPA MCLs for all the wastewater effluents, even after coagulation with 40 mg/L alum (Figure 2.2 and Figure 2.3). *BOD-Removal WWeff* was not included in the DBP analysis because its ammonia concentration, over 40 mg/L as N, which would have caused an impractical high free chlorine demand. Among the samples analyzed, the wastewater effluents varied less widely in DBP formation than the stormwaters; for example, the lowest to highest initial HAA5 formation varied by a factor of 2 among the wastewater effluents, while it varied by a factor of over 5 among the stormwaters.

DBP formation appears related to the degree of nutrient removal. For example, *N-Removal Filter WWeff* and *N-Removal Bardenpho WWeff*, had similar initial TTHM formation at 240 and 235 μg/L, respectively, and these samples were also similar to two other denitrified wastewater effluent as reported in the literature (233 to 255 μg/L).[79] These denitrified wastewater effluents also had similar DBP formation after coagulation (185 to 190 μg/L TTHM formation and 151 to 184 μg/L HAA5 formation). In the wastewater effluents with phosphorus removal (*P-Removal Johannesburg WWeff* and *P-Removal A2O WWeff*), DBP formation was similar to each other and lower than the denitrified wastewater effluents. After coagulation, TTHM formation was 75 to 91 μg/L and HAA5 formation was 114 to 127 μg/L. These DBP results further emphasizes that initial quality and treatment results are more consistent for wastewater effluents than stormwaters, especially at a given level of upstream nutrient removal.

While coagulation reduced regulated DBP formation, when considering the health impact of DBPs, it was found that the calculated cytotoxicity of the measured DBPs was unchanged after coagulation (±4%). As was the case for stormwaters, this negligible reduction in calculated cytotoxicity was due to the poor removal of HAN4 (i.e., less than 7% reduction) and increased BIF (Table A.6). Similar trends in bromine incorporation and DBP cytotoxicity have been observed after treating blended and unblended wastewater effluent with activated carbon, which also removes DOC but not bromide.[71] Unlike for HAA5 and TTHM, the carbon normalized yields for HAN4 increased after coagulation in all wastewater effluents (Table A.4), possibly due to increased organic nitrogen to carbon ratios. Predicted genotoxicity (Figure A.7) was reduced more than predicted cytotoxicity (Figure A.6), but less than regulated DBPs (Table A.5).

Based on the DBP yields of the treated wastewater effluents, the highest alum doses tested would not be sufficient to achieve DBP regulatory compliance without blending. The maximum final TOC needed to achieve U.S. EPA regulatory compliance for both TTHM and HAA5 ranged from 2.7 to 3.5 mg/L for the coagulated wastewater effluents (Table A.4), and none of the wastewater effluents would have met this target, even at an alum dose of 160 mg/L. Since alum coagulation alone would not be sufficient to meet DBP regulations for wastewater effluents, advanced treatment or blending with relatively clean surface water would be required. For example, *P-Removal A2O WWeff* had the lowest DBP formation after coagulation, yet it would require a blending ratio of about 30:70 with coagulated *Surface Water-1* to meet the MCLs for both TTHM and HAA5. None of the wastewater effluents with nutrient removal had metals concentration above U.S. EPA standards or WHO guidelines,[69,74,75] so the required blending ratio would be driven by DBPs, not metals.

2.3.3 Alternative Source Waters Blended with Surface Water

2.3.3.1 Blending without Pretreatment. Blends of alternative source waters with surface waters were done to simulate both de facto and planned blended reuse. In terms of turbidity and TOC, *Parking Lot StmW-1* and *Field StmW* were the third and fourth most contaminated stormwaters out of eight, respectively (i.e., close to the average). The *N-Removal Bardenpho WWeff* sample was the median wastewater effluent in terms of TOC and turbidity. For all three cases, the majority of the TOC in the blend (around 70% to 90%) came from the alternative source water, and for both stormwater blends, the majority of the turbidity came from the stormwaters.

The treatability of the blended alternative source waters generally mirrored the treatment of the corresponding unblended alternative source waters. For example, the 50:50 blend of *Field StmW* with surface water (Figure 2.6) and the unblended *Field StmW* sample (Figure 2.1) both had very effective turbidity removal, around 98% removal with 40 mg/L alum, but poor TOC removal, around 10% removal with 40 mg/L alum. The turbidity in the blend of *Parking Lot StmW-1* with surface water showed a different trend. Rather than the percent removals being similar at each dose between the blended and unblended stormwater, blending at a 50:50 ratio reduced the alum dose for effective turbidity removal (i.e., around 90% removal) by half, from 80 mg/L to 40 mg/L (Figure A.8).

2.3.3.2 Blending after Pretreatment (Two-stage Coagulation). The pretreatment of *N-Removal Bardenpho WWeff* with CDWT before blending it with surface water only slightly improved turbidity removal and did not have an impact on TOC removal relative to adding the same total amount of alum at once to the blend (Figure 2.7). The total amount of alum used was represented by an 'effective alum dose'; since the alternative source water was pretreated with 40 mg/L alum and then diluted by a factor of two with the surface water to make the blend, the effective alum dose was calculated as 20 mg/L from pretreatment plus the secondary alum dose used to coagulate the blend. For turbidity removal, two-stage coagulation resulted in around 0.5 NTU lower turbidity. This slight increase in turbidity removal was likely because many of the particulates from the alternative source water were removed from the system during the pretreatment and were therefore incapable of charge reversal or resuspension in the blend. However, turbidity below 1 NTU was already achieved without pretreatment at alum doses of only 20 mg/L, so the primary goal of pretreatment would be TOC removal. For the other water quality parameters, very

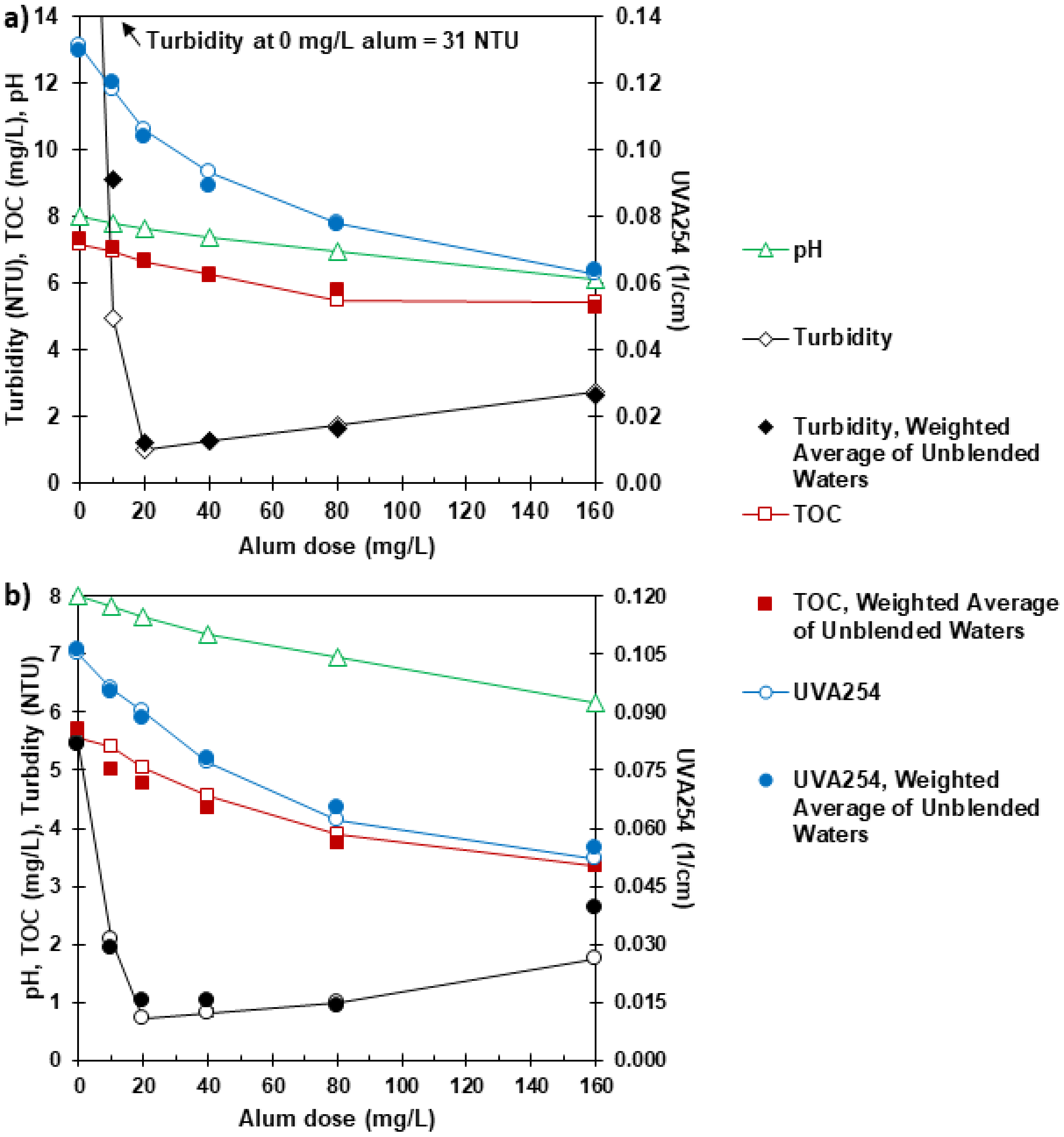


Figure 2.6. Turbidity, TOC, and UVA254 removal by alum coagulation from (a) the 50:50 blend of *Field StmW* with *Surface Water-2* and (b) the 50:50 blend of *N-Removal WWeff-B* with *Surface Water-1*. The "Weighted Average of Unblended Waters" values refer to the average of the unblended alternative source water and surface water at each alum dose. Experimental replicates at 40 mg/L alum were within ±8% or ±0.2 NTU for both blends. Figure A.8 shows the results of the 50:50 blend of *Parking Lot StmW-1* with *Surface Water-1*.

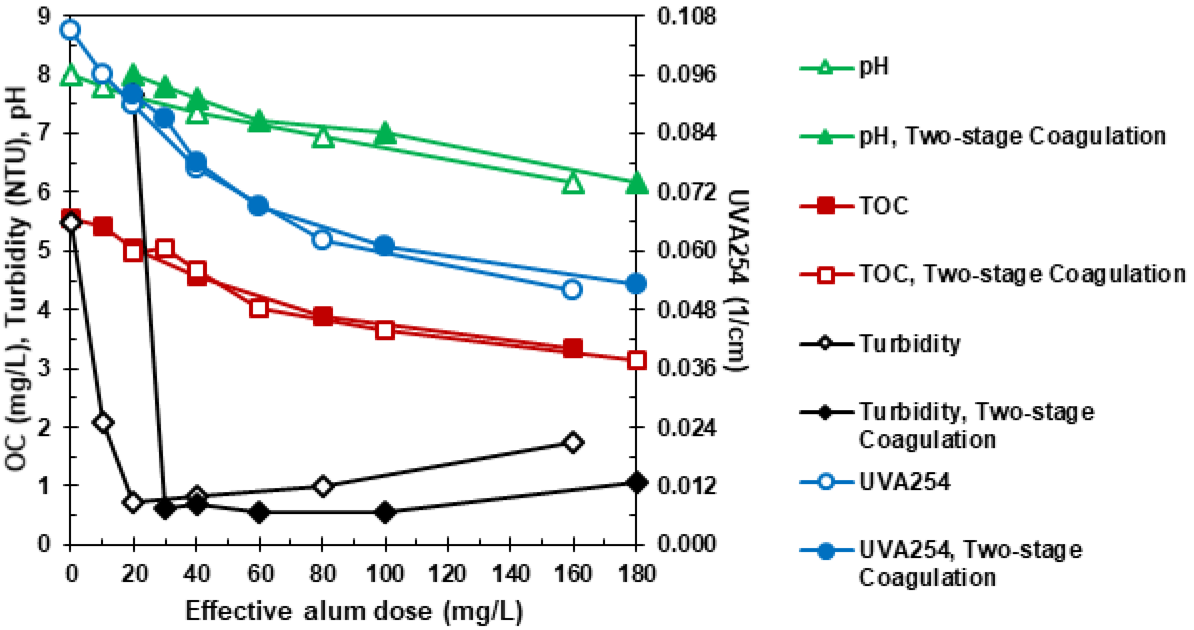


Figure 2.7. The treated turbidity, DOC, pH, and UVA$_{254}$ of a 50:50 blend of *N-Removal Bardenpho WWeff* with *Surface Water-1* after coagulation with alum. "Two-stage Coagulation" refers to the 50:50 blend of *N-Removal Bardenpho WWeff* that had previously been coagulated with 40 mg/L alum with raw *Surface Water-1*. "Effective alum dose" refers to the total overall alum dose, taking into account the 40 mg/L pre-treatment dose in the wastewater effluent and the dose applied to the 50:50 blend with surface water.

similar results were achieved regardless of whether the pretreatment was used (i.e., ±0.4 pH, ±6% DOC, TOC, and UVA$_{254}$). Therefore, the important factor was the total quantity of alum added, not whether the alum is added before or after blending.

2.3.4 Predicting DOC Removal

2.3.4.1 Unblended Alternative Source Waters. The accuracy of the Coagulation Model[61] varied among the wastewater effluents and stormwaters. The Coagulation Model was only accurate for wastewater effluents not previously exposed to chemical treatment. For *N-Removal Bardenpho WWeff* and *N-Removal Filter WWeff*, the Coagulation Model was accurate, with standard error of 7.0% to 7.4% and R^2 of 0.79 to 0.83. However, the Coagulation Model overpredicted DOC removal from the other three wastewater effluents, likely because their sorbable fraction had been reduced by previous chemical treatment. For stormwaters, the accuracy of the Coagulation Model varied from accurate for *Parking Lot StmW-1* (R^2 of 0.92 and standard error of 8%) to inaccurate for *Highway StmW* (standard error of 29%).

Errors in the Coagulation Model tended to be overpredictions of removal, and the errors tended to increase with increasing alum dose. For example, seven of the eight stormwaters had higher R^2 if the dose range was constricted to 10 to 80 mg/L alum (Table A.7). These trends indicate that error was due to the Coagulation Model predicting a nonsorbable fraction of DOC that was too low. This issue can be addressed by calibrating the Coagulation Model with a site-specific nonsorbable fraction.[61] However, this solution is only practical if the nonsorbable fraction of the source water is consistent over time. For example, a jar test was conducted on an earlier sample of wastewater effluent from the same facility as *N-Removal Bardenpho WWeff* (Table A.8).[80] Calibrating a site-specific nonsorbable fraction based on the earlier wastewater effluent sample increased the accuracy of the Coagulation Model for *N-Removal Bardenpho WWeff* from good to excellent, improving the R^2 to 0.92 and the standard error to 4% (Figure A.9). In contrast, the Coagulation Model was not accurate for *Parking Lot StmW-2* (standard error over 18%), regardless of whether a site-specific nonsorbable fraction was optimized using data from the *Parking Lot StmW-1*. The feasibility and accuracy of a site-specific Coagulation Model for wastewater effluent but not stormwater further emphasizes that wastewater effluent is more consistent and predictable than stormwater in the context of reuse.

2.3.4.2 Alternative Source Waters Blended with Surface Water. Calculating DOC removal by using a Weighted Average of Unblended Waters was more accurate than using the Coagulation Model for all three blended alternative source waters (Figure 2.8 and Figure A.10). Specifically, the Weighted Average of Unblended Waters was accurate for DOC removal from all three blended alternative

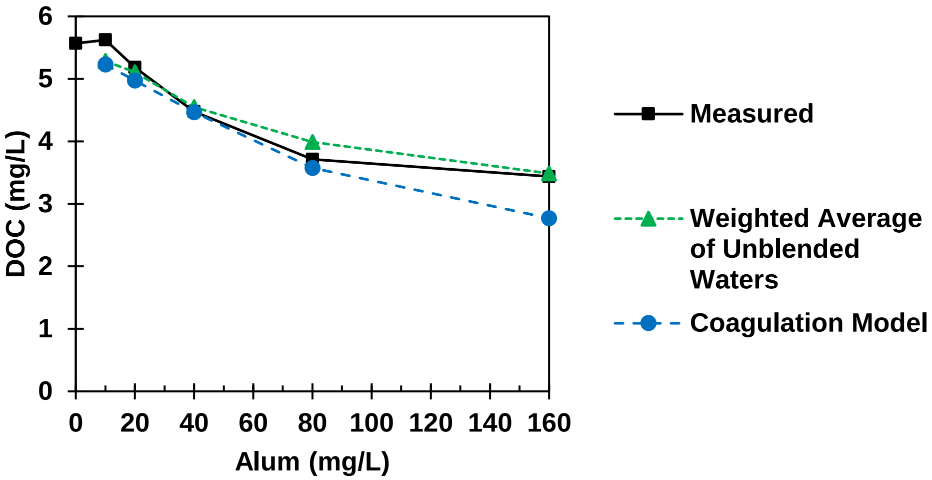


Figure 2.8. Two methods (the Coagulation Model and the Weighted Average of Unblended Waters) for predicting DOC removal from 50% *N-Removal WWeff-B* + 50% *Surface Water-1*.

source waters, with R^2 values of 0.70 or greater and standard errors of 6% or less (Table 2.3). When applied to the other water quality parameters, the Weighted Average of Unblended Waters had similar accuracy for TOC or UVA_{254} as for DOC, but was not reliably accurate for turbidity (Table A.10).

The Coagulation Model was not accurate for the blend of *Football Field StmW* with surface water (standard error of 18%), but it was sufficiently accurate for the blends of *Parking Lot StmW-1* with surface water and *N-Removal Bardenpho WWeff* with surface water (R^2 of 0.81 or greater and standard error of 10% or less). These results reflect the accuracy of the Coagulation Model for the respective unblended alternative source waters (Section 2.3.4.1). Considering the ease of modeling in terms of the time and data required, the Coagulation Model has the advantage of requiring fewer measurements than the Weighted Average of Unblended Waters (i.e., only the initial DOC, initial UVA_{254}, and post-coagulation pH of the blended solution). Thus, despite the poor performance for one of the blends, there are still situations where the Coagulation Model might be preferred to the Weighted Average of Unblended Waters. Both approaches were more accurate for the wastewater effluent blend than either stormwater blend, providing yet another example of the relative predictability of the wastewater effluents compared to the stormwaters.

Table 2.3. Estimating DOC removal from blends.

	Weighted Average of Unblended Waters		CoagulationModel	
	R^2	Std. Error (%)	R^2	Std. Error (%)
Parking Lot StmW-1 + Surface Water-1	0.94	6%	0.92	8%
Field StmW + Surface Water-2	0.70	5%	-1.90	18%
N-Removal Bardenpho WWeff + Surface Water-1	0.94	4%	0.81	10%
Required Inputs	Jar tests on unblended waters, initial DOC of blend		DOC, UVA254, and post-coagulation pH of blend	

2.4 Conclusion

This study used bench-scale methods to test the effectiveness of CDWT on stormwater, wastewater effluent, and blends with surface water. Removal of organic matter, turbidity, and DBP precursors were compared among different types of stormwater and wastewater effluent. Two models were investigated for predicting DOC removal by coagulation from blends of alternative source waters with surface water. CDWT was also tested as pretreatment prior to blending. DBP formation was identified as a key challenge for both stormwater and wastewater reuse.

- CDWT effectively removed turbidity from stormwaters, though highly turbid stormwaters from paved surfaces required alum does of at least 60 mg/L for significant removal. All wastewater effluents included in this study could reach turbidity less than 2 NTU with 20 mg/L alum or less.

- TOC removal by coagulation of wastewater effluents was comparable to low-SUVA natural surface waters. TOC removal from stormwaters varied widely, from negligible to 59% with 40 mg/L alum.
- The Coagulation Model accurately predicted DOC removal from wastewater effluents that had not been previously exposed to chemical treatment (R^2 of 0.79 to 0.83). The Coagulation Model was overall less accurate for stormwaters than wastewater effluents.
- The Weighted Average of Unblended Waters accurately predicted DOC removal from all three blended alternative source waters (R^2 of 0.70 or higher and standard error of 6% or less). The accuracy of the Coagulation Model for blends of alternative source waters varied depending on whether the Coagulation Model had been accurate for the corresponding unblended alternative source water.
- In terms variation from most to least contaminated samples, variation at a single sampling location, and the accuracy of models, wastewater effluent was overall more consistent than stormwater. Increased storage or equalization could further enhance the relative consistency of wastewater effluent.
- Pretreating wastewater effluent with coagulation prior to blending provided negligible benefit compared to adding an equivalent total mass of alum after blending.
- Only one wastewater effluent and none of the stormwaters exceeded a USEPA primary standard for metals.
- DBPs present a critical challenge for reuse of both wastewater effluent and stormwater. All but the least contaminated stormwater sample would require advanced treatment or a high degree of blending to comply with standards for DBPs.

- Coagulation had little impact on the calculated cytotoxicity of measured DBPs in all wastewater effluents and most stormwaters. The poor removal of predicted cytotoxicity was due to poor removal of HAN4 and increased bromine incorporation.

CHAPTER 3

ENVIRONMENTAL COMPARISON OF BIOCHAR AND ACTIVATED CARBON FOR TERTIARY WASTEWATER TREATMENT

Reprinted with permission from (K. A. Thompson, K. K. Shimabuku, J. P. Kearns, D. R. U. Knappe, R. S. Summers and S. M. Cook, *Environ. Sci. Technol.*, 2016, **50**, 11253–11262). Copyright (2016) American Chemical Society.

Abstract

Micropollutants in wastewater present environmental and human health challenges. Powdered activated carbon (PAC) can effectively remove organic micropollutants, but PAC production is energy intensive and expensive. Biochar adsorbents can cost less and sequester carbon; however, net benefits depend on biochar production conditions and treatment capabilities. Here, life cycle assessment was used to compare 10 environmental impacts from the production and use of wood biochar, biosolids biochar, and coal-derived PAC to remove sulfamethoxazole from wastewater. Moderate capacity wood biochar had environmental benefits in four categories (smog, global warming, respiratory effects, non-carcinogenics) linked to energy recovery and carbon sequestration, and environmental impacts worse than PAC in two categories (eutrophication, carcinogenics). Low capacity wood biochar had even larger benefits for global warming, respiratory effects, and non-carcinogenics, but exhibited worse impacts than PAC in five categories due to larger biochar dose requirements to reach the treatment objective. Biosolids biochar had the worst relative environmental performance due to energy use for biosolids drying and the need for supplemental adsorbent. Overall, moderate capacity wood biochar is an

environmentally superior alternative to coal-based PAC for micropollutant removal from wastewater, and its use can offset a wastewater facility's carbon footprint.[†]

[†] In Chapter 2, conventional drinking water treatment was found to achieve significant and easily-predicted DOC removal in wastewater effluent. However, due to poor removal of nitrogenous DBP precursors (Chapter 2) and organic micropollutants,[47] advanced treatment such as sorption would be required. The removal of organic micropollutants such as sulfamethoxazole from wastewater effluent using activated carbon and biochar has been experimentally evaluated.[33] However, the relative sustainability of these materials for this application remained unclear. Therefore, the following life cycle assessment (LCA) was conducted. This chapter is an environmental LCA, as such social and economic impacts were not included in the scope. The same relative environmental sustainability of biochar and activated carbon would hold true regardless of whether micropollutant removal is conducted with the goal of potable reuse, non-potable reuse, or aquatic discharge.

3.1 Introduction

Wastewater treatment facilities (WWTFs) seek to reduce the negative impacts of organic micropollutants (e.g., antibiotics and endocrine disrupting compounds) on aquatic life and downstream drinking water quality by removing these compounds during treatment.[21,81,82] Adsorption with powdered activated carbon (PAC) is an effective treatment option[83] for tertiary wastewater treatment that has shown lower environmental impacts than other options (e.g., reverse osmosis, ozone/ultraviolet-light oxidation).[28] However, PAC also has negative environmental impacts, especially because it is commonly generated from non-renewable coal and requires energy-intensive thermal activation to develop adsorption properties.[84] A potentially lower cost and environmentally friendlier alternative is biochar, which is carbonized biomass not subjected to further physical or chemical activation.

Biochar adsorbents have demonstrated sorption capacity for agrichemicals,[85,86] pharmaceuticals and personal care products,[87,88] and endocrine disrupting compounds.[89] Biochar ($350-$1,200 per tonne[90]) costs less than PAC ($1,100-$1,700 per tonne[91]), on a mass basis, and can have environmental benefits including energy co-production,[92–94] carbon sequestration,[92–98] and bio-waste valorization (e.g., by using yard,[93,95] food,[94,99] and agricultural wastes[100] and biosolids[33,94] as feedstocks). The adsorption capacity of biochars for organic micropollutants, though, ranges from negligible to similar to that of PAC depending on solution characteristics, precursor material, and biochar production conditions.[33,101–103] Since adsorption capacity determines the mass of adsorbent needed for treatment, it also influences cost and environmental impacts. To date, the relationships between biochar adsorption capacity, cost, and environmental impacts, as well as the comparison with prevalent adsorbents such as PAC have not been quantified.

Previous life cycle assessments (LCAs) have identified important biochar properties that affect environmental performance. The feedstock moisture content, energy content, and alternative uses and production conditions have been found to influence overall environmental performance.[94] Many studies quantified only global warming impact or net energy production,[93–96,98,104] so analysis using a broader set of environmental impacts will help to further identify influential properties and environmental trade-offs. In addition, most biochar LCAs have focused on the application of biochar as an agricultural soil amendment and energy generation co-product,[92–98,104–106] but no studies to-date have assessed comparative life cycle impacts of using biochar in engineered wastewater treatment applications.

Future requirements for micropollutant removal from wastewater effluents are expected in coming years,[82,107] and the implementation of new treatment capabilities must be balanced against overall environmental protection (e.g., minimizing energy requirements and associated air pollution of new treatment technologies). The objective of this study was to quantify relative environmental impacts of using biochar adsorbents for tertiary wastewater treatment made from wood and biosolids compared to coal-derived PAC. LCA methodology was used to assess impacts associated with adsorbent generation, use, and disposal for removal of sulfamethoxazole (SMX), a prevalent human and livestock antibiotic, from wastewater effluent. Uncertainty and sensitivity analyses were conducted to determine the results' sensitivity to modeling assumptions. This study aims to elucidate the most effective ways to reduce environmental impacts of and to identify environmental tradeoffs between adsorbents used for micropollutant control in tertiary wastewater treatment. In addition, this study aims to assist in the selection of environmentally preferred adsorbents from the perspective of feedstock selection and production conditions.

3.2 Materials and Methods

The production and use of PAC, wood biochar, and biosolids biochar for tertiary wastewater treatment was evaluated using a comparative LCA methodology following the ISO 14040 framework.[108] The main processes in each scenario and the LCA system boundary are summarized in Figure 3.1. The functional unit was 75% removal of sulfamethoxazole (SMX) from 47,300 m^3/day (12.5 MGD) of secondary wastewater effluent over 40 years. The 75% SMX removal target was chosen as a representative goal because: (i) SMX has a common occurrence in wastewater and in surface water at concentrations shown to endanger aquatic ecosystems.[109–111] (ii) For the sorbent doses used in this study, 75% SMX removal is expected for any SMX

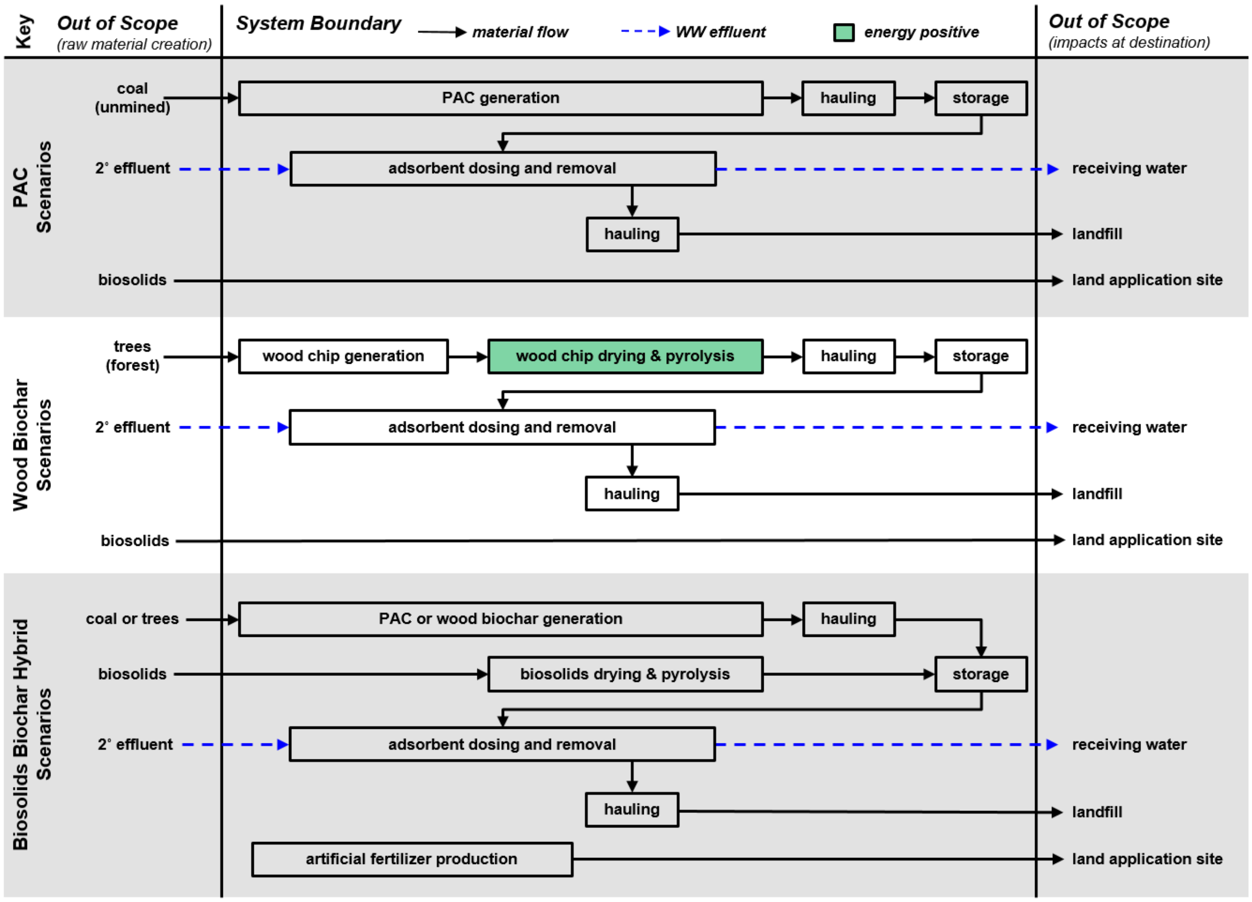


Figure 3.1. Process flow diagram of the main processes in each of the PAC, wood biochar, and biosolids biochar scenarios for tertiary wastewater treatment.

concentration typically found in wastewater effluent.[33] (iii) Emerging regulations on micropollutants are considering 80% as a general target,[82] and SMX has a relatively low tendency for adsorption compared to other organic micropollutants present in wastewater effluent;[112,113] therefore, 75% SMX removal is expected to result in greater than 75% removal of other micropollutants, which is representative of proposed removal targets. The Boulder, Colorado WWTF provided data on biosolids quantity, composition, and fate,[37] and its location was used for hauling distances.

The adsorbent dose necessary to achieve 75% SMX uptake (dose_{75}) from wastewater effluent over a 60-minute contact time was experimentally determined in previous bench-scale work.[33] In that previous study, SMX adsorption was quantified at initial concentrations ranging from 50 ng/L to 1 mg/L, and SMX proportional removal was independent of concentration at or below 10 ug/L.[33] Typical SMX concentrations in wastewater effluent are ≤0.178 μg/L in China,[114] ≤2.00 μg/L in Germany,[115] and ≤3.25 μg/L in the USA.[116] The dose_{75} for the commercial bituminous coal-based PAC was 70 mg/L.[33] Using wood and biosolids as feedstocks, biochars were generated using different pyrolysis conditions and classified based on their experimentally determined adsorption capacities (i.e., dose_{75}) relative to PAC: low capacity (600 mg/L),[33] and moderate capacity (150 mg/L).[33] While these biochars had adsorption capacities lower than PAC, they have high adsorption capacities compared to many other biochars.[33] The low capacity wood biochar was generated in a full-scale pyrolysis facility where pine wood chips were exposed to a temperature gradient from 400 to 1200˚C.[117] The moderate capacity wood biochar was produced from pine wood pellets in a 1-gallon top-lit updraft gasifier under high draft (850˚C) conditions.[33] The properties of the moderate capacity biosolids biochar were estimated using data from biosolids and wood biochars. Pyrolysis mass yield and elemental composition of each biochar were based on measurements from a previous study[33] (see Table B.2). Bench-scale batch reactors were used to experimentally determine the aluminum sulfate (alum) dose required to remove an adsorbent from solution and achieve a final turbidity less than 1 NTU (ASTM D2035).[118] A 10 mg/L alum dose was sufficient for all adsorbents. The apparent density of each adsorbent was determined using a tapped apparent density standard method.[119] Table B.2 describes each adsorbents' properties.

3.2.1 Adsorbent Scenarios

Six main scenarios are described below: low-impact PAC, high-impact PAC, moderate capacity wood biochar, low capacity wood biochar, moderate capacity biosolids biochar supplemented with low-impact PAC, and moderate capacity biosolids biochar supplemented with moderate capacity wood biochar. Early in the analysis it was found that the mass of biochar generated from biosolids would be insufficient to meet the 75% SMX removal objective and therefore biosolids biochar would need to be supplemented with other adsorbents. The comparative LCA system boundary (Figure 3.1) does not include activities and processes common to all scenarios (e.g., the production of secondary wastewater effluent and dewatered biosolids). Life cycle stages included raw material acquisition, production, use, and hauling, but not end-of-life impacts (e.g., emissions from a landfill). For each scenario, the amounts and types of materials and energy required to achieve the functional unit were quantified and used to estimate life cycle emissions with data from the US-EI v.2.2[120] and Agri-footprint[121] life cycle inventory (LCI) databases. All emissions were translated into ten environmental impact categories using the EPA's Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI).[122] The 10 TRACI midpoint impact categories are: ozone depletion (kg CFC-11 equivalent), global warming (kg CO2 equivalent), smog (kg O3 equivalent), acidification (kg SO2 equivalent), eutrophication (kg N equivalent), carcinogenics (comparative toxic units, CTU), non carcinogenics (CTU), respiratory effects (kg PM2.5 equivalent), ecotoxicity (CTU), and fossil fuel depletion (MJ surplus).

3.2.2 PAC Scenarios

Life cycle impacts of PAC were estimated for the generation, hauling, and storage of PAC before dosing and the removal and landfilling of spent PAC. Emissions due to coal-derived PAC generation were estimated using Agri-footprint,[121] which accounted for coal extraction and hauling, water and energy production, and direct emissions of carbon dioxide and water vapor.[121] PAC production at four locations (California, Kentucky, Pennsylvania, and Texas)[123] was considered. For each, state-specific electricity production mixes and semi-trailer truck hauling distances to the Boulder WWTF were used. Of the four locations, Kentucky resulted in the highest impacts overall, so this location was used for the "high-impact" PAC scenario. California had the lowest impacts and was used for the "low-impact" PAC scenario.

The number of silos needed for adsorbent storage and associated mass of galvanized sheet steel were based on typical PAC silo dimensions.[124,125] Each silo had a continuously operating air fluidizer system to keep the PAC dry and friable.[124] Electricity requirements for air fluidizers were estimated from commercially available systems.[126] After PAC was dosed and SMX uptake was achieved, the spent PAC was removed from the effluent using alum coagulation and settling. The infrastructure and energy requirements of dosing, coagulation, and settling of all adsorbents were assumed to be the same (e.g., all required the same alum dose). The settled adsorbent was dewatered using a stainless steel belt filter press, and commercially available units[127] were used to estimate energy and infrastructure requirements. Truck emissions from hauling spent adsorbent to a landfill were based on mass and a distance (19.6 km between Boulder WWTF and nearest landfill).

3.2.3 Wood Biochar Scenarios.

Life cycle impacts of wood biochar were estimated for the generation, hauling, and storage of wood biochar before dosing and the removal and landfilling of spent wood biochar. Biochar generation (wood chip generation, drying, and pyrolysis) had the same system boundary as PAC generation. Wood chip generation LCI data accounted for forest harvesting, hauling, and chipping.[120] The electrical energy requirements for wood chip pyrolysis, based on a full-scale facility in Kremmling, CO (Biochar Solutions, Inc.) that co-produces biochar for land application and dried wood pellets for heating, was 0.54 MJ electricity per kilogram of non-ground biochar.[117] Net thermal energy requirements, which are specific to the low capacity wood biochar produced at the full-scale facility (because energy production is dependent on pyrolysis conditions) was -24 MJ thermal energy per kilogram non-ground biochar due heat recovery from pyrolysis gas combustion beyond drying energy requirements.[117] Energy production from the moderate capacity biochar was estimated as the difference between the feedstock (wood)[128] and biochar (calculated from elemental composition)[129] thermal energies, multiplied by the efficiency factor estimated from full-scale data. Energy recovered from pyrolysis gas offsets energy generated from wood chip combustion at the full-scale facility,[117] and the model used this same energy offset. Direct air emissions of treated pyrolysis gas were estimated using modeling[92] and measured data for wood biochar pyrolysis.[106,130,131] The modeling data was most representative of the Colorado full-scale facility since it was for a large-scale wood biochar facility that had air emission regulations and treatment by thermal oxidation and cyclones. The measured data were from various small-scale, low-cost technologies that only captured and combusted a proportion of the pyrolysis gas and did not treat the exhaust with cyclones, so these data were used in the uncertainty assessment to evaluate worst-case air emissions scenarios (see Table B.4 and Table B.5). The energy requirements of grinding wood biochar to a size fraction comparable to PAC (45 µm) were based on commercially available activated carbon grinders.[132] The ground wood biochar was hauled 185 km from the full-scale facility to the Boulder WWTF by truck. The same assumptions and methods as the

PAC scenarios were used to calculate adsorbent storage, dosing, coagulation, dewatering, and disposal hauling.

3.2.4 Biosolids Biochar Scenarios.

Life cycle impacts of biosolids biochar were estimated for the generation, hauling, and storage of biosolids biochar and any supplemental adsorbent; the removal and landfilling of spent adsorbent; and fertilizer production due to biosolids diversion from land application. Biosolids biochar generation was assumed to be at the WWTF and included biosolids drying (from 77.4% to 8% moisture content), pyrolysis, and grinding. Electricity requirements of pyrolysis were based on data from the full-scale wood facility (0.54 MJ/kg non-ground biochar).[41] Thermal energy requirements were based on data for biosolids drying in the Biosolids Emissions Assessment Model[133] and were met using energy recovered from pyrolysis gas and then by natural gas (if needed). Energy recovery was estimated using the same methods as moderate capacity wood biochar with values for typical biosolids[134] and biosolids biochar (calculated from elemental composition)[129] thermal energies. Additional energy required was assumed to be supplied by natural gas. Direct pyrolysis emissions were based on a full-scale biosolids pyrolysis facility's emissions of treated and combusted pyrolysis gas.[134] Biosolids biochar grinding, storage, dosing, coagulation, dewatering, and disposal hauling were calculated using the same assumptions and methods as the wood biochar scenarios.

The diversion of biosolids from land application (fertilizer) to biochar in these scenarios required the production of substitute fertilizers. Fertilizer quantities were based on biosolids content of plant available nitrogen and phosphorus.[135,136] The mass of supplemental adsorbent was based on the biosolids biochar mass and each adsorbents' dose. The impacts of supplemental adsorbents were based on this mass and the calculations described for each type (i.e., PAC or wood biochar scenarios). For storage, biosolids and wood biochars were stored together, whereas biosolids biochar and PAC were stored separately because of their different adsorption capacities.

3.2.5 Uncertainty and Sensitivity Analysis

The aggregate impact of uncertainty in assumed values on the ten TRACI categories was estimated using a Monte Carlo analysis with the software Crystal Ball™. There were 24 uncertainty parameters (Table B.3 and Table B.5) that represent main assumptions about storage systems, and biochar properties, and pyrolysis conditions, and pyrolysis gas air emissions. Each uncertainty parameter was assigned plausible maximum and minimum values based on literature values or typical WWTF operations and was characterized with a uniform probability distribution due to the lack of data to justify assigning any other distribution. The impact categories' uncertainty ranges represent the 25th and 75th percentiles of 100,000 Monte Carlo simulations. If a correlation coefficient's magnitude was greater than 0.8 ($|\rho|>0.8$)), then that impact category was defined as sensitive to that uncertainty parameter.

3.3 Results and Discussion

3.3.1 Wood Biochar to PAC Comparison

Environmental impacts of PAC and wood biochar are compared in Figure 3.2 for the 10 TRACI impact categories. Each category represents the magnitude and type of environmental or human health impacts that are based on the types and quantities of chemicals released into the environment as a result of the processes, materials, and energy used throughout each adsorbent's life cycle. The results show that the production and use of moderate capacity wood biochar for SMX removal results in environmental impacts that are higher than low-impact PAC but lower than high-impact PAC in two categories (eutrophication, carcinogenics);

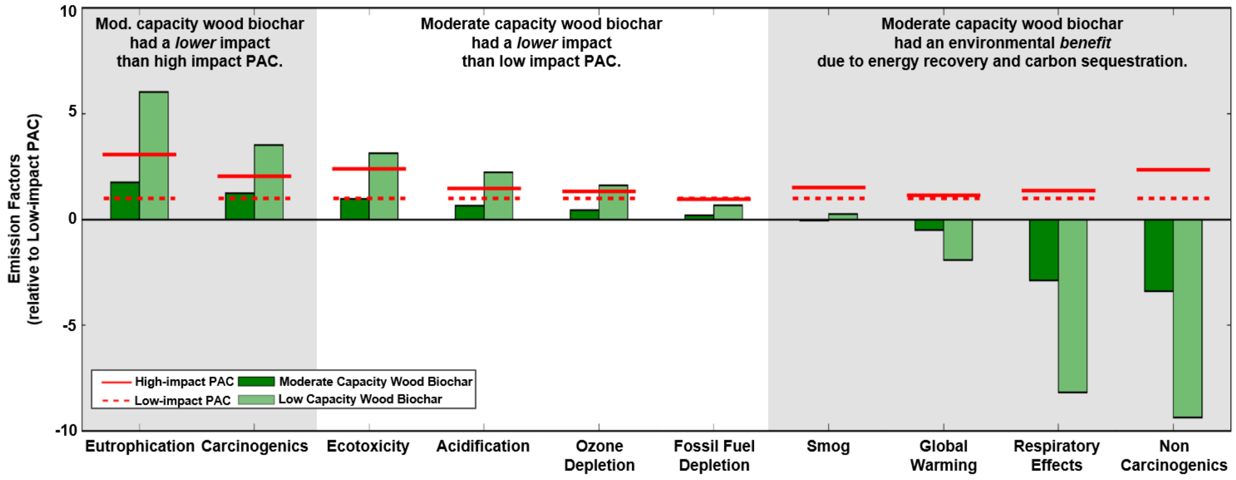


Figure 3.2. Relative environmental impacts for four scenarios: low-impact PAC, high-impact PAC, moderate capacity wood biochar, and low capacity wood biochar. All emission factors (i.e., impacts) are normalized to low-impact PAC. Negative emission factors represent an environmental benefit; positive emission factors represent a negative environmental impact.

environmental impacts that are lower than low-impact PAC in four categories (ecotoxicity, acidification, ozone depletion, fossil fuel depletion); and environmental net benefits in four categories (smog, global warming, respiratory effects, and non carcinogenics) that were not realized with low-impact PAC. Low capacity wood biochar had larger environmental impacts than both PAC scenarios in five categories (eutrophication, carcinogenics, ecotoxicity, acidification, ozone depletion) and lower impacts in the other half of the categories (fossil fuel depletion, smog, global warming, respiratory effects, and non carcinogenics). For low capacity wood biochar, three categories exhibited environmental benefits (global warming, respiratory effects, and non carcinogenics). The wood biochars had similar trends in each impact category, and the magnitude of environmental impacts or benefits scaled with adsorbent quantity (i.e., adsorption capacity) (Figure 3.2). Moderate capacity wood biochar had the lowest overall environmental impacts. It exhibited lower environmental impacts than high-impact PAC in all ten categories, and eight out of ten categories compared with low-impact PAC.

3.3.2 Wood Biochar

The wood biochars had environmental benefits and lower environmental impacts than PAC primarily due to carbon sequestration and energy production during pyrolysis (Figure 3.3). The estimated net amount of carbon sequestration for moderate capacity wood biochar was 0.57 kg CO_2 equivalent (eq.) per kg dry feedstock and for low capacity wood biochar was 0.67 kg CO_2 eq./kg dry feedstock. Both values are comparable to values reported by other studies on the production and use of biochar for land application, which reported a range of 0.07 to 1.25 kg CO_2 eq./kg dry feedstock.[92,94,95,97,98,137] Low capacity wood biochar resulted in greater carbon sequestration than moderate capacity wood biochar primarily because a larger mass of feedstock was converted to biochar to satisfy the larger dose$_{75}$ requirement.

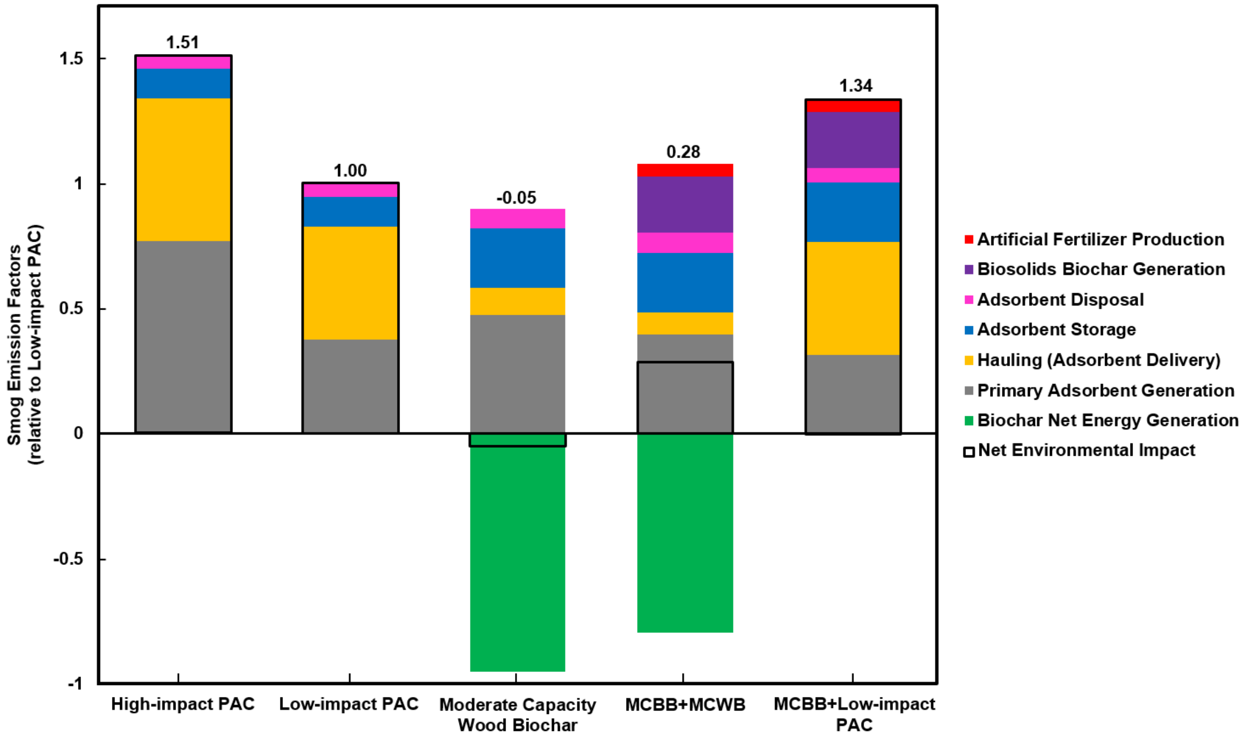


Figure 3.3. Contribution of life cycle processes to the smog impact category for 5 scenarios: high-impact PAC, low-impact PAC, moderate capacity wood biochar, moderate capacity biosolids and wood biochars (MCBB+MCWB), and moderate capacity biosolids biochar supplemented with low-impact PAC (MCBB+low-impact PAC). Adsorbent disposal includes dewatering and landfill hauling. All values are normalized to low-impact PAC.

The estimated energy recovered during the production of moderate capacity wood biochar was 8.6 MJ heat/kg dry feedstock and 7.5 MJ heat/kg dry feedstock for low capacity wood biochar. The energy produced as a percent of feedstock heat content was 44% and 38% for moderate and low capacity wood biochars, respectively, which is similar to another study's value of 37%.[95] In this LCA, the environmental benefit of the energy produced during pyrolysis is due to the offset of energy produced from wood chip combustion, which was the protocol used at the full-scale wood biochar and wood pellet co-production facility before the installation of pyrolysis energy recovery infrastructure. This energy replacement resulted in a net environmental benefit for moderate capacity wood biochar in three impact categories (smog, respiratory effects, and non-carcinogenics) and contributed to net environmental benefits in the global warming category. When considering replacing heat from natural gas instead of wood chips, moderate capacity wood biochar still had lower environmental impacts compared to PAC (see Figure B.12).

In addition to energy production and carbon sequestration, there were several activities in the wood biochar scenarios that resulted in harmful environmental impacts. Figure 3.3 shows the contribution of different life cycle processes' impacts to the overall smog impact. The smog category was selected for display since it had trends similar to and was representative of the other nine impact categories (see Figure B.2 to Figure B.11). For moderate capacity wood biochar, the largest contributor to negative smog impacts was wood biochar generation, mostly due to direct air emissions from pyrolysis gas combustion, wood chip generation, and electricity use. The second largest contributor to smog was silo storage of wood biochar at the WWTP, due mostly to electricity consumption for air fluidization. The impact from this electricity consumption was greatest in the eutrophication and carcinogenics categories (Figure B.2 and Figure B.3). Since moderate capacity wood biochar required over twice as much adsorbent mass as PAC, wood biochar had larger storage and disposal impacts than PAC for all impact categories. Also, the larger doses for lower adsorption capacity biochars can increase costs and make materials handling more burdensome. The third largest contributor to the smog impact was hauling adsorbent from the generation site to the WWTF. The impact of hauling to the WWTF is four times smaller for moderate capacity wood biochar than for PAC because the shorter hauling distance (185 km from the biochar production facility compared to 1664 km from the PAC manufacturer). Overall, for the smog impact category, moderate capacity wood biochar exhibits a net environmental benefit due to energy recovery.

3.3.3 PAC

Results for the two PAC scenarios are summarized in Figure 3.3. PAC generation and hauling to the WWTF were the two largest contributors to negative impacts. Low-impact PAC had a lower smog impact because of the lower emissions from electricity consumption during PAC generation (i.e., electricity production was cleaner in California than in Kentucky) and the shorter hauling distance to Colorado from California (1664 km) than from Kentucky (2118 km). The third and fourth largest contributors to smog were adsorbent storage and disposal. Both PAC scenarios required the same dose of PAC, so each has the same environmental impacts from storage and disposal. Overall, the PAC scenarios exhibited negative environmental impacts in all categories. The most effective ways found to reduce environmental impacts from these results were to decrease net energy use during PAC generation and to reduce hauling. In addition, future research could focus on a diversity of PACs (e.g., in terms of feedstock and activation method) to identify additional approaches for improving environmental performance. For example, while coal-based PACs are the most common,[138] biomass-based activated carbons (e.g., wood-based or coconut-based PACs) might exhibit some similar benefits to wood-biochar (e.g., carbon sequestration). However, the systematic comparison of these sorbents requires further research to determine adsorption capacity and production factors. In this study, coal-based PAC exhibited worse overall environmental performance compared to moderate capacity wood biochar. However, PAC alone was found to be a better environmental option than a scenario employing biosolids biochar supplemented with PAC, as described below (Figure 3.3 and Figure B.1).

3.3.4 Biosolids Biochar

Hybrid scenarios (i.e., supplementing biosolids biochar with PAC or wood biochar) were evaluated because of biosolids feedstock limitations. The quantity of biosolids produced at the Boulder WWTF would generate enough biochar to treat up to one-sixth of effluent for 75% SMX removal. Overall, hybrid scenarios involving moderate capacity biosolids biochar resulted in larger environmental impacts than the low-impact PAC or moderate capacity wood biochar scenarios (see Figure 3.3 and Figure B.1). This trend was mostly due to biosolids biochar generation (especially the energy required for drying) and the artificial fertilizer production needed to replace land applied biosolids (Figure 3.3).

Biosolids drying required 14.9 MJ heat/kg dry biosolids to get from 77% to 8% moisture content by mass. Comparatively, wood chip drying required 0.39 MJ heat/kg dry wood chips to get to 8% moisture content, based on full-scale data. Large energy requirements due to the high moisture content of biosolids feedstock has also been noted by other researchers.[94] There is no environmental benefit for net energy recovery in the biosolids biochar and PAC hybrid scenario because all of the energy produced during pyrolysis (12.2 MJ heat/kg dry biosolids) was needed for biosolids drying. For biosolids biochar, the energy produced as a percent of feedstock heat content was 65%, which is similar to another study's range of 60% to 80%.[139] There is an energy recovery benefit for the wood and biosolids biochar hybrid scenario because pyrolysis heat energy in excess of needs for wood chip drying offset wood chip combustion. This extra energy could not be used for biosolids drying since wood-based and biosolids-based biochars would be generated at different locations.

Artificial fertilizer production resulted in negative environmental impacts. Although not included in this model's scope, it is important to note that biosolids and artificial fertilizers could have different impacts after application. For example, nutrient runoff might be higher from artificial fertilizer,[140] and biosolids land application can imply the risk of contaminating soil and adjacent waterways with heavy metals and persistent organic micropollutants.[141–145]

3.3.5 Uncertainty

To evaluate the impact of major model assumptions on results, a Monte Carlo analysis was used to quantify the uncertainty ranges for each result based on input parameter uncertainty (Table B.3 and Table B.5). Uncertainty ranges (25th to 75th percentiles of the Monte Carlo analysis) for low-impact PAC and moderate capacity wood biochar are shown in Figure 3.4 (a). Since this assessment showed that the smog and respiratory effects conclusions were sensitive to the air emissions data for wood biochar pyrolysis gas, the Monte Carlo uncertainty parameter data was disaggregated back into the separated modeling and measured data as scenarios and evaluated (Figure 3.4, b and c). In addition, new adsorbent scenarios were created to evaluate the impacts of the WWTF location and treatment goal (Sections B.9 and B.10).

Uncertainty ranges for low-impact PAC were generally smaller because it had only three associated uncertainty parameters, while the moderate capacity wood biochar scenario had eighteen. Wood biochar results in the non-carcinogenics category had a strong correlation ($\rho>0.8$) with pyrolysis mass yield since decreasing yield increased energy production because more feedstock was pyrolyzed. This yield is impacted by pyrolysis temperature. Increasing pyrolysis temperature decreases pyrolysis yield,[101] which has three main effects: (i) increasing pyrolysis gas (energy)

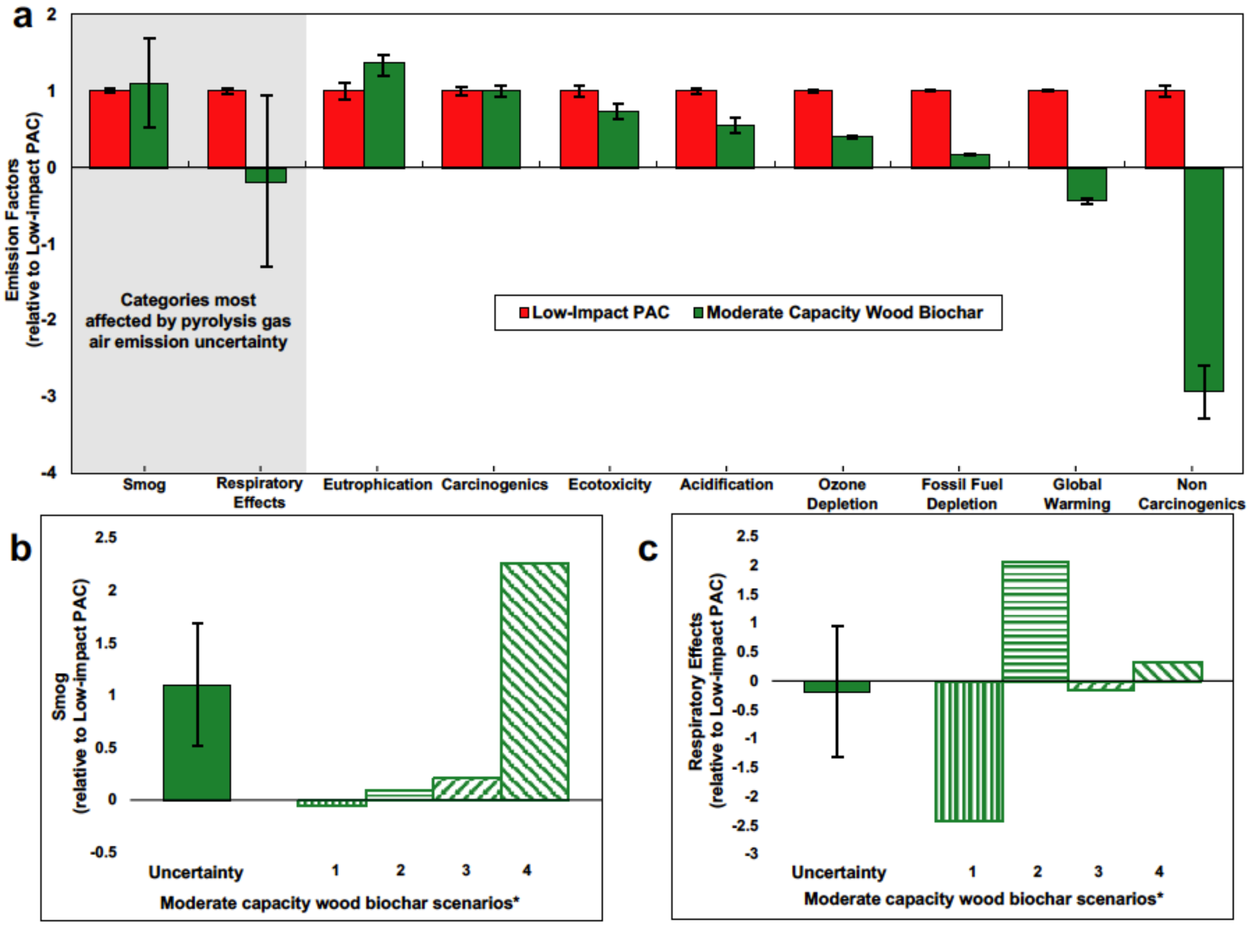


Figure 3.4. Effect of uncertainty in input parameters on environmental impact categories for the low-impact PAC and moderate capacity wood biochar scenarios: Plot (a) shows the results from the Monte Carlo simulations, which included 24 uncertainty parameters (Table B.3 and Table B.5); columns represent the uncertainty results' mean values with error bars representing the 25th and 75th percentiles. Plots (b) and (c) show the comparison of the Monte Carlo results to results from 4 wood biochar pyrolysis gas air emissions scenarios, for the impact categories most impacted by air emissions uncertainty: smog (b) and respiratory effects (c). *Moderate capacity wood biochar scenario descriptions: uncertainty (Monte Carlo results, from a), 1) representative modeling data (large-scale facility with air emissions treatment),[92] 2) flame curtain kiln,[130] 3) Adam retort kiln,[131] and 4) TLUD.[106]

production, (ii) decreasing carbon sequestration, and (iii) increasing adsorption capacity,[33,146] which decreases impacts from hauling and storage. Therefore, for an adsorption application, higher pyrolysis temperatures should be used to have the operational (i.e., less infrastructure and materials handling) and environmental benefits (due to energy recovery) of higher adsorption capacity biochars.

Also, wood biochar results in the smog, respiratory effects, acidification, and global warming, categories were sensitive to the pyrolysis gas air emissions uncertainty. In particular, the smog results are overlapping due to the large wood biochar uncertainty range, and the respiratory effect uncertainty range for wood biochar shows that there could be an environmental benefit or burden (Figure 3.4a). Figure 3.4b shows that wood biochar is expected to have lower smog impacts than PAC, but there is one scenario that results in a significantly larger impact (Scenario 4, see Table B.5). To have a lower smog impact, wood biochar processes need to capture and combust pyrolysis gas to minimize volatile organic carbon emissions. Figure 3.4c shows that the environmental benefit of wood biochar energy recovery can be lost if particulate matter is not removed from the pyrolysis gas (moderate capacity wood biochar Scenario 2). Therefore, air emission control measures, such as thermal oxidation and cyclones, are important to decrease the negative environmental impacts and highlight the benefits of wood biochar.

The impact of the WWTF location relative to the PAC production site was evaluated by setting all electricity consumption mixes to US average and delivery distance for moderate capacity wood biochar and PAC were set to 20, 200, and 2000 kilometers. In these scenarios, wood biochar had lower impacts than PAC in all categories for the distances of 20 and 200 km and lower impacts in eight out of ten categories for the 2000 km distance (see Figure B.14, Figure B.15, and Figure B.16). However, another scenario was considered in which the WWTF was located in California near the PAC production site (California WWTF scenario). For this scenario, PAC was produced with California electricity and delivered to a nearby WWTF (185 km), and moderate capacity wood biochar was produced with Colorado electricity, which uses more coal and fewer renewable energy sources, and delivered to California (1664 km). In this scenario, moderate capacity wood biochar had higher impacts in six out of ten categories than PAC (see Figure B.17), although moderate capacity biochar would still be environmentally beneficial in three categories. Overall, for similar electricity production mixes and delivery distances, wood biochar is more environmentally favorable. This analysis shows that differences in electricity production mixes and delivery distances could make PAC environmentally competitive. However, there are substantial environmental benefits to generating and using an adsorbent from renewable materials near the point-of-use as compared to using coal-based PAC delivered from far away.

The impact of adsorbent dose was evaluated by relaxing the treatment objective to the point at which biosolids biochar alone could treat the entire WWTF effluent flow (i.e., a biochar dose of 25 mg/L and PAC dose of 12 mg/L); and this dose would target other more strongly adsorbing micropollutants. Also, the fate of biosolids at the WWTF was changed to landfilling (instead of land application) so that no scenario required artificial fertilizer production. Under these scenario conditions, moderate capacity wood biochar was still the preferred adsorbent (Figure B.18). The environmental performance of biosolids biochar did improve given these conditions, to the point of similarity with high-impact PAC. In this study, using PAC or wood biochar was found to be environmentally preferable to biosolids biochar. This was particularly the case when biosolids were diverted from land application, necessitating the production of artificial fertilizers. Previous studies have found tradeoffs between biosolids fates in land application, energy generation, and incineration,[141] so future research that compares multiple biosolids fates that include multiple biochar applications could also inform WWTF operation.

With future requirements to remove micropollutants at WWTFs expected,[107] sustainable tertiary treatment options are needed. PAC adsorption was previously found to be an environmentally preferred tertiary wastewater treatment option.[28]

This study suggests that environmental performance can be further improved through the use of wood biochar adsorbent. In particular, wood biochar has significant environmental benefits for climate change mitigation. The moderate capacity wood biochar scenario sequestered enough carbon (about 6.5 gigagrams CO2 eq./yr) to offset all of a WWTF's carbon emissions from energy and chemical use (about 5.0 gigagrams CO2 eq./yr. for a 12.5 MGD facility, assuming 0.29 kg CO2 eq./m3 for a WWTF that has organics and nutrient removal,[147] Section B.8.4) and to result in additional carbon sequestration; in other words, 130% of the carbon emissions could be offset. The results of this study present adsorption with wood biochar as a novel, environmentally sustainable way for WWTFs to remove trace organic micropollutants. Further innovation should be undertaken to develop low cost carbonaceous adsorbents that have high micropollutant adsorption capacities and are made from renewable resources located in close proximity to treatment facilities and disposal sites.

CHAPTER 4

DEVELOPMENT AND EXPERIMENTAL VALIDATION OF THE COMPOSITION AND TREATABILITY OF A NEW SYNTHETIC BATHROOM GREYWATER (SYNGREY)

Adapted from K. A. Thompson, R. S. Summers and S. M. Cook, *Environ. Sci. Water Res. Technol.*, 2017, **3**, 1120–1131 with permission from The Royal Chemical Society.

Abstract

Bathroom greywater, including bathing and handwashing wastewater, can be reused for toilet flushing to reduce 35% of residential water demand. Despite these potential savings, greywater reuse is underutilized and the development of innovative treatment technologies is impeded by a lack of validated synthetic recipes to support laboratory-scale experimentation. The objective of this work was to develop and validate a new, representative synthetic bathroom greywater to enable reproducible and translatable treatment studies. A literature review compiled data from 49 real bathroom greywaters, which was used to set 20 water quality criteria for a synthetic recipe. A new synthetic greywater – SynGrey – was developed to match real bathroom greywater composition across all criteria and was found to be more representative of real greywater than existing recipes. SynGrey's validity was evaluated by comparing its treatability against a real bathroom greywater including via chlorination, aerobic biodegradation, adsorption, and coagulation. Total chlorine residuals were statistically similar between SynGrey and the real bathroom greywater, but doses were an order of magnitude higher than for drinking water. The readily biodegradable fraction of total chemical oxygen demand was about 40% for both greywaters. The dissolved organic carbon percent removal by activated carbon was similar between SynGrey and the real greywater (±14%). Alum coagulation

achieved comparable effluent turbidity, but SynGrey had a much more narrow dose curve, and coagulation achieved substantially greater total organic carbon removal from the real greywater. SynGrey represents a superior synthetic recipe for laboratory-scale experimentation to facilitate the evaluation, selection, and optimization of greywater reuse technologies.[‡]

[‡] Due to the promising results comparing biochar to activated carbon for wastewater effluent treatment (Chapter 3), an experimental study was planned to compare biochar and activated carbon for greywater treatment (Chapter 5). Due to the temporal and geographical variability of greywater, a synthetic greywater was sought to enhance the reproducibility of the research. However, a literature review revealed that none of the existing synthetic greywater recipes sufficiently matched the characteristics of real bathroom greywater. Therefore, a novel synthetic bathroom greywater (SynGrey) was developed before proceeding with the study of biochar for greywater treatment.

4.1 Introduction

Nearly three billion people experience water scarcity in their watershed for at least one month a year.[148] Further, water scarcity and drought frequencies are increasing, especially with population growth and global climate change.[16,149,150] Greywater, defined as wastewater from laundry machines, showers, baths, or handwashing basins, but not from toilets or urinals, is an underutilized water source. Greywater can meet significant water demands; for example, bathroom greywater, which is greywater from showers, baths, and handwashing basins, can be reused for toilet flushing to reduce about 35% of residential and 15% of urban water demands.[39] In addition, there are many additional benefits of source separation—the separation of urine, feces, food waste, and greywater—such as energy and nutrient recovery, water saving, and energy reduction.[151–153] Since bathroom greywater has the highest volume and the lowest pollutant concentration, it is the most viable source for decentralized reuse[38,154] and its treatment could use significantly fewer resources. Specifically, it has the potential to lower pumping energy demands and require less energy and materials for treatment; hence decentralized greywater reuse has the potential to be more environmentally sustainable than centralized wastewater reuse.[40]

Despite these benefits, greywater research and implementation are still limited. Technological improvements are needed to scale up greywater reuse technologies and to reduce the risk of failures that could reduce public acceptance of greywater reuse.[155] A major limiting factor is the lack of access to greywater, especially due to source separation implementation and regulatory barriers,[156] and the lack of long-term storage since greywater degrades and changes composition.[157] Several greywater synthetic media exist (e.g.,[158,159]), but most represent greywater from laundry or kitchen activities and not greywater from bathing and handwashing. Therefore, synthetic laundry or kitchen greywater media are not representative and are ill-suited for bathroom greywater studies. Additionally, all seven existing bathroom-specific greywater recipes[159–164] are also not representative of real bathroom greywater's composition (Figure 4.1 and Figure C.1), and most used non-controlled commercial products, which limits their reproducibility. Therefore, there is a need for a representative, stable, and reproducible synthetic bathroom greywater.

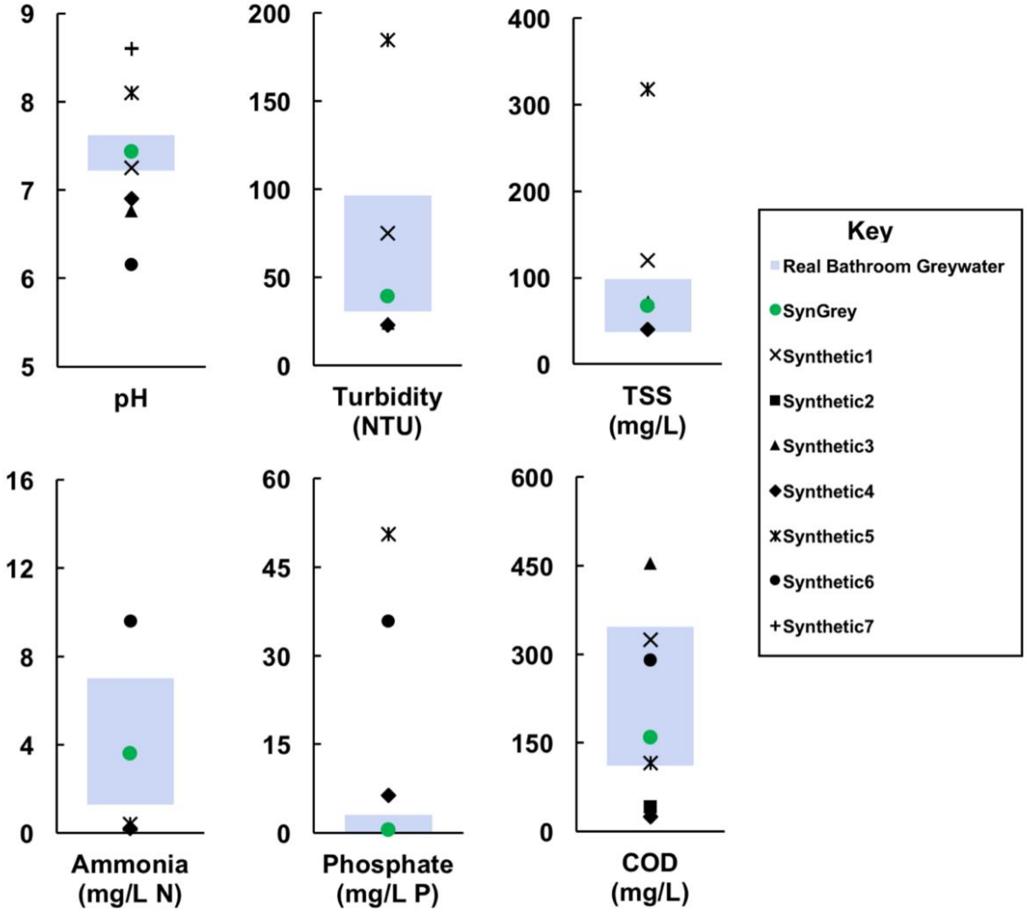


Figure 4.1. Comparison of synthetic greywater recipes with the 25th to 75th percentile range of real bathroom greywaters for pH (n=35), turbidity (n=31), TSS (n=34), ammonia (n=17), phosphate (n=14), and COD (n=41). For the other 14 water quality parameters, see Table C.3 and Figure C.1. Citations for the mean values for the synthetic recipes were 1 = ref. 159, 2 = ref. 163, 3 = ref. 161, 4 = ref. 162 'low concentration', 5 = ref. 162 'high concentration', 6 = ref. 160, 7 = ref. 164. For synthetic recipes 4 and 5, values for all ions, except nitrate and phosphate, were calculated based on ingredients since they were not measured experimentally. For synthetic recipe 1, commercial ingredients (shampoo, conditioner, etc.) are used and expected ranges of TSS, COD, etc. were given. This analysis used midpoints from those ranges.

Furthermore, a synthetic greywater can only progress greywater treatment system design and understanding if it matches not only the composition but also the treatability of real greywater. If a synthetic media does not match in terms of treatability, then the treatment system could be ineffective, inefficient, or even fail when used to treat real greywater. Under-design can lead to failure to meet reuse regulations or risks to human health, while overdesign can lead to prohibitive costs.[155,165] In addition, the environmental benefits of greywater reuse depend on the treatment technology and its effectiveness, energy efficiency, and chemical efficiency.[40,166] Despite this need for similar treatability, synthetic greywaters, in general, have not closely matched the treatment behaviour or effects of real bathroom greywater. For example, one study found that a synthetic recipe yielded an order of magnitude lower free chlorine demand than real bathroom greywater.[167] Irrigation studies using synthetic greywaters have found the synthetic greywaters to harm plants[168,169] while irrigation studies using real greywaters have found real greywater to have statistically similar or better effects on plant growth than tap water or freshwater.[170,171] Therefore, there is still a need for a synthetic greywater that is representative of real bathroom greywater in terms of both composition and treatability to aid in technology selection and design for greywater reuse systems that can maximize economic and environmental benefits.

The overall goal of this research was the development and experimental validation of a new synthetic medium for bathroom greywater. Specifically, the objectives were to (i) determine criteria for a synthetic medium to be considered representative of real bathroom greywater, (ii) create a new bathroom greywater synthetic that matched the composition of real bathroom greywater, and (iii) experimentally validate the new synthetic medium. The first objective of determining criteria for a synthetic greywater included identifying and comparing the composition of real and synthetic bathroom greywaters by compiling and analyzing data from the literature, of which many recent studies and data on real greywaters has not yet been compiled in a comprehensive review. This data is needed, especially since more water parameters are being reported, for greywater system design and implementation, including for setting criteria for synthetics. Review of recent papers yielded 20 criteria, which represented the 25th and 75th percentiles values of 49 real bathroom greywaters for 20 water quality and composition parameter. When evaluating existing synthetic greywaters, the results showed that none of the existing recipes closely matched real bathroom greywater. So, the second objective was pursued and a new synthetic greywater – SynGrey – was developed. SynGrey was designed by using a comprehensive optimization process that adjusted ingredients and concentrations of SynGrey so that its final composition matched the 20 criteria. For the third objective, SynGrey's treatment behavior for multiple processes was experimentally evaluated and compared to real bathroom greywater. Since several treatment approaches are used for greywater treatment, including biological treatment (e.g., membrane bioreactors),[172] coagulation (e.g., alum or ferric chloride),[173] sorption (e.g., granular activated carbon),[174] and disinfection (e.g., ultraviolet[175] and chlorine[164]), the treatability of SynGrey and a real bathroom greywater were evaluated for chlorination, aerobic biodegradation, adsorption, and alum coagulation. The development and experimental validation of a representative synthetic media can enhance the reproducibility of greywater treatment experiments and allow for translatable treatability studies that provide useful data for technology development and for the design and implementation of greywater recycling systems.

4.2 Methods

4.2.1 Development of New Synthetic Bathroom Greywater (SynGrey)

4.2.1.1 Literature Review of Real and Synthetic Bathroom Greywater Quality. The published literature was reviewed for detailed composition data on real bathroom greywaters. Articles focusing on greywater were gathered through Web of

Science using topic search terms of ‘graywater,’ ‘greywater,’ ‘gray water,’ and ‘grey water.’ All searches were limited to research articles published from 1998 to October 2016. The searches yielded 1,018 research articles. Each paper was then individually screened to verify that the water quality data reported was for real greywater from showers, baths, and/or bathroom sinks only; for example, data on synthetic greywaters, greywater including laundry or kitchen wastewater, or greywater where the source was ambiguous were excluded. If multiple articles sampled greywater from the same building, only one was included. This yielded 48 datasets from 42 peer-reviewed articles. Original data for an additional greywater (Section 4.2.3) was included for a total of 49 different real bathroom greywater datasets (Table C.1). The following 20 water quality parameters were compiled from these data (as available): calcium, chlorine, COD, EC, magnesium, nitrate, pH, phosphate, potassium, sodium, solids (total, total dissolved, total suspended, and volatile suspended), sulfate, total ammonium nitrogen, total nitrogen, total phosphorus, TOC, and turbidity. Each parameter’s median, 25th percentile, and 75th percentile values were calculated based on the data’s distribution. The composition of existing synthetic greywater intended to simulate bathroom greywater[159–163] were compared to the percentiles of the compiled real bathroom greywater.

4.2.1.2 Recipe Development. Two main criteria for SynGrey were that its chemical composition was representative of bathroom greywater (i.e., each water quality parameter was in the 25th to 75th percentile range of the compiled real bathroom greywaters) and that it was composed of controlled substances for reproducibility (i.e., no commercial bathroom products were used due to proprietary ingredients or unknown ingredient quantities). Ingredients were selected using the following water quality parameters: COD (soluble, particulate, biodegradable, and recalcitrant fractions), solids (dissolved, suspended, volatile, and fixed), surfactants, nutrients (nitrogen, phosphorus), inorganics (calcium, chloride, magnesium, sodium), and turbidity.

To determine the concentrations of ingredients in consideration, first, the mass relationships between each ingredient and each water quality parameter (except pH and EC, which were determined experimentally) were determined by using each ingredient's molecular formula. Otherwise, the contribution of an ingredient to each parameter was predicted based on the literature or experimentally determined.

Second, ingredient concentrations were changed to attain the desired parameter values using an iterative optimization process. Specifically, the sum of squared error (SSE) between the expected values of SynGrey and the median values of the compiled real bathroom greywaters was minimized for 18 water quality parameters (all of the 20 parameters except pH and EC). The SSE used error values normalized by the real greywaters' respective median values so that numerically high parameters would not dominate. This optimization process also included the constraint that each water quality parameter of SynGrey had to be between the respective 25th and 75th percentile values of the compiled real greywaters.

Third, the recipe resulting from the optimization process was then prepared in the lab in 3.9 L batches in amber glass containers. Each batch was mixed for 2 hours at 20 ^{0}C. Finally, the pH and EC were checked experimentally for each iteration of the recipe. It was found that EC fell within the 25th to 75th percentile range for all iterations. When the pH fell outside the 25th to 75th percentile range, the calcium carbonate was adjusted until the pH was in the target range, and then the ingredient optimization process was repeated to account for the change in calcium concentration. This iterative process was stopped once all the 20 water quality parameters of SynGrey matched that of the complied real greywater (i.e., were within the 25th to 75th percentile ranges).

4.2.2 Analytical Methods

Volatile suspended solids (VSS) were determined according to Standard Methods[176] with 1µm type A/E glass fiber filters. COD, total nitrogen, ammonia, nitrate, total phosphorus, and phosphate were analyzed with Hach TNTplus vial tests (Loveland, CO, USA). Samples for soluble COD (sCOD) and dissolved organic carbon (DOC) were pre-filtered with 0.45 µm nitrocellulose filters. DOC and TOC were determined using a Shimadzu TOC-V_{SCH} analyzer (Kyoto, Japan). Turbidity was measured with a Hach 2100N Turbidimeter (Loveland, CO, USA). Electrical conductivity (EC) was measured with a Hach Conductivity/TDS Meter (Loveland, CO, USA). Total chlorine residual was measured by the N,N diethyl-1,4 phenylenediamine sulfate (DPD) method with a Hach Pocket Colorimeter (Loveland, CO, USA).

4.2.3 Real Bathroom Greywater Sampling

The real bathroom greywater used for treatment experiments in this study was collected from the showers and bathroom sinks of approximately 180 students in a university residence hall in Boulder, CO, USA. It was referred to as residence hall (RH) greywater. The raw greywater was sampled as 3.9 L grab samples in glass for adsorption, chlorination, and biodegradation, and 14 L grab samples in plastic for coagulation. The sampling line was flushed for over a minute before each sample was collected. Each real greywater and synthetic greywater sample was stored at 4 ^{0}C and used within 24 hours.

4.2.4 Treatability Comparisons and Validation

The impact of four water and wastewater treatment technologies—chlorination, biodegradation, adsorption, and coagulation—were experimentally evaluated for both SynGrey and the RH greywater. These technologies were selected to test whether SynGrey matched real greywater not just in composition, but also in treatability for a wide range of chemical and biological mechanisms of interest to greywater researchers. Chlorination represents a disinfection technology while biodegradation, adsorption, and coagulation represent various approaches to remove organic matter. Coagulation also represents a method for removing particulate matter. Chlorination, adsorption, and coagulation treatability experiments were carried out at an ambient lab temperature of 20 ^{0}C.

4.2.4.1 Chlorination. Total chlorine demand and decay kinetics were determined as total chlorine residuals have been found to provide disinfection and prevent regrowth in bathroom greywater and are resilient to influent ammonium fluctuations [177]. Greywater samples were completely mixed and distributed into nine 125 mL amber bottles without headspace. Each bottle had an initial dose of 40 mg/L Cl_2 (added as liquid sodium hypochlorite) and was sacrificially used to test the chlorine residual at time intervals of 0.5, 1, 2, 4, 8, 24, 48, 72, and 120 hours. Ambient temperature was 20 ^{0}C. Each experiment (including all time points) was replicated using 15 samples each of RH greywater and SynGrey.

The measured chlorine residuals were used to determine parameters of the parallel first-order decay model (Equation 1)[178] using nonlinear curve fitting in Excel. This model was found to be the most appropriate for total chlorine decay in greywater.[178] The model assumes a portion of the chlorine decays immediately through reactions with reducing agents present in the sample. Of the remaining chlorine residual, a fraction exponentially decays rapidly (i.e., over the course of hours), and the rest exponentially decays slowly (i.e., over the course of days). Total chlorine residuals at each time interval and all model parameters were statistically compared using Student's t-tests with a 95% confidence level ($p<0.05$). Normality was checked with normal probability plots to check that Student's t-test was the appropriate approach for statistical comparison.

Equation 1

$$C(t) = (C_{added} - C_w) \cdot x \cdot e^{-k_1 t} + (C_{added} - C_w) \cdot e^{-k_2 t}$$

Where $C(t)$ is the chlorine concentration at a given time (t, in hours), C_{added} is the initial dose (mg/L Cl_2), C_w is the concentration of the chlorine that decays immediately (mg/L Cl_2), x is the fraction of chlorine that decays rapidly, k_1 is the rate constant for the rapidly decaying chlorine (hr^{-1}), and k_2 is the rate constant for the slowly decaying chlorine (hr^{-1}).

4.2.4.2 Biodegradation. Aerobic respirometry was used to determine and compare the biodegradability and specific oxygen uptake rate (SOUR).[179] Oxygen uptake was measured at one minute intervals with a headspace oxygen batch reactor (Challenge AER-800 Respirometer, Springdale, AK, USA). Eight 500 mL sample bottles were run simultaneously, maintained at 25 ^{0}C, and continuously stirred (700 rpm). Nitrification inhibitor (Formula 2533™) was used at a concentration of 533 mg/L, which is recommended for biochemical oxygen demand tests.[180] Each bottle had the same constant volume, with 214 mL of inoculant and 286 mL of greywater and/or deionized water. The inoculant was return activated sludge from the Boulder Wastewater Treatment Facility. The food to microorganism (F:M) ratio was 0.01 mg substrate soluble COD/mg VSS to have negligible biomass growth and determine extant kinetics.[181] Controls (inoculant only, with deionized water added to maintain volume and VSS concentration) were run in duplicate. To control for the RH greywater biomass activity, a bottle with RH greywater only was monitored for oxygen uptake for one hour prior to initiating the experiment to verify that any aerobic biodegradation was negligible relative to the inoculated samples. RH greywater and SynGrey samples were both run in triplicate. The initial sCOD of the residence greywater sample was 60 mg/L, and the mean sCOD of the SynGrey was 80 mg/L. Therefore, the SynGrey was diluted (215 mL synthetic greywater with 71 mL deionized water) so that the initial sCOD in each bottle would be within ±10%.

Cumulative oxygen uptake (mg O_2) for each sample was calculated after 80 minutes of reaction time after subtracting the controls' average cumulative oxygen uptakes. The readily biodegradable COD fraction was calculated as the cumulative oxygen uptake divided by the initial sample sCOD (assuming negligible hydrolysis). Specific oxygen uptake rate (mg O_2/hr/mg VSS) was calculated by dividing the change in oxygen uptake in 1 minute time intervals (smoothed with an 11-minute central moving average) by the 0.5 L reactor volume and VSS concentration.

4.2.4.3 Adsorption. Adsorption of DOC onto activated carbon (AC) was determined using batch reactors with a Phipps & Bird stirrer. The AC was commercially available bituminous-based Norit 1240. It was ground to the diameter of commercial powdered AC (i.e., passing through a 45 µm (325 mesh) sieve) to provide a basis for estimating the performance of full-scale powdered or granular AC columns. Sample volumes of 0.5 L and a 120 rpm mixing rate were used. A contact time of 2 hours was used; preliminary tests with 2 g/L AC and contact times of 2, 4, 8, and 24 hours revealed that insignificant additional adsorption occurred after 2 hours (i.e., less than 6% additional DOC removal from 2 to 24 hours). AC adsorption was tested on two samples each of RH greywater and SynGrey. For the first samples, the AC doses were 0, 1, 2, 4, 8, and 16 g/L; this range resulted in a plateau of DOC removal at the high doses. For the next samples, the AC doses were 0, 1, 2, 4, and 8 g/L, with replication at the 4 g/L dose. Before AC addition, samples were pre-filtered with 1.2 µm glass fiber filters to simulate pre-treatment with physical filtration and prevent biodegradation from interfering with adsorption results.[174]

4.2.4.4 Coagulation. TOC and turbidity removal by coagulation, flocculation, and sedimentation were tested with bench-scale jar tests on two samples each of RH greywater and SynGrey. Six alum (aluminum sulfate, Al2(SO4)3·16H2O) doses of 0, 20, 40, 80, 160, and 320 mg/L were used. The jar volume was 2 L, and the alum stock solution concentration was 20 g/L. Alum doses were added to each jar at the same time. Jars were mixed in a procedure simulating rapid mix, coagulation, 2-stage flocculation, and sedimentation (Table C.2). The samples were then filtered with 1.2

µm glass fiber filters to simulate physical filtration. TOC and turbidity values were measured for each jar before and after coagulation, and turbidity again after filtration.

4.3 Results & Discussion

4.3.1 Literature Review of Existing Synthetic and Real Bathroom Greywaters

The 25th and 75th percentiles for 20 water quality parameters were determined based on the data compiled on 49 real greywaters (Figure C.1 and Table C.3). Real bathroom greywater values (i.e., criteria) for a few key parameters include: 112 to 346 mg/L COD; 1.0 to 7.2 mg/L ammonia as N; 38 to 99 mg/L TSS; 31 to 96 NTU turbidity; 7.2 to 7.6 pH; and 0.19 to 3.0 mg/L phosphate as P (Figure 4.1). When comparing existing synthetic bathroom greywaters to all 20 real greywater composition criteria, it was found that previous synthetic greywaters were not representative of real greywater (Figure C.1). None of the existing synthetics had measurements or enough information to calculate concentrations for all 20 criteria, so the number of the values known for each synthetic that matched the respective criteria value, for the 7 previous synthetics, ranged from 14% matching to 33% matching, with most around 20% matching. So most synthetics did not have compositions that that fell between the 25th and 75th percentiles of the recently reviewed real bathroom greywaters for the majority of reported water quality parameters.

Each synthetic did not match the real greywater composition data for different reasons, especially since each reported water quality data using different metrics, such as some reported organic matter concentrations using the conventional wastewater metric of COD and others used the conventional drinking water metric of TOC. For example, one synthetic bathroom greywater (Synthetic2 in Figure 4.1 and Figure C.1)[163] was generally less contaminated than the real bathroom greywaters. This recipe had COD (42 mg/L), total nitrogen (5 mg/L N), total phosphorus (0.047 mg/L P), magnesium (5.02 mg/L), and potassium (3.96 mg/L) concentrations all below the 25th percentile. Furthermore, this study compared the synthetic and real greywaters' SOURs and found that the synthetic greywater SOUR was 20% to 144% (61% average) higher, depending on the nutrients added.[163] Another synthetic bathroom greywater (Synthetic3 in Figure 4.1 and Figure C.1) was found to have comparable BOD and DOC removal as real greywater during nanofiltration.[161] However, this synthetic greywater composition was above the 75th percentile for COD (454 mg/L) but below the 25th percentile for turbidity (24 NTU), EC (188 μS/cm), and pH (6.76). The current study experimentally found the pH of this synthetic to be much lower, around 4.6, and this low pH may have been responsible for the synthetic greywater causing harm to periwinkle plants when used to irrigate a green roof.[169] The ingredient 100 mg/L of lactic acid was likely the cause of the very low pH. Another synthetic (Synthetic 6 in Figure 4.1 and Figure C.1)[160] also had a pH value (6.16) below the 25th percentile but TDS (563 mg/L) and ammonia (9.6 mg/L N) concentrations above the respective 75th percentile values. Also, this recipe had a phosphate (36 mg/L P) concentration that was orders of magnitude above any reported real bathroom greywater due to the use of a phosphate buffer. Yet another recipe (Synthetic1 in Figure 4.1 and Figure C.1),[159] which was designed to test treatment systems' ability to meet the National Sanitation Foundation (NSF) 350 standard for indoor reuse,[182] also did not match real greywater compositions when evaluating the recipe's midpoint values for each reported water quality parameter. This recipe had EC (400 μS/cm) and total nitrogen (6 mg/L N) values that were below the 25th percentile of the compiled real greywater, while TSS (120 mg/L), COD (325 mg/L), TOC (100 mg/L), and total phosphorus (5 mg/L P) were above the 75th percentile values. Also, the entire range for total phosphorus (3 to 7 mg/L P) for was over twice the 75th percentile value of 1.5 mg/L P for real greywater. While high values for organic matter and solids can be seen as conservative (i.e., more likely to cause overdesign than insufficient treatment), the discrepancies in terms of nutrients could cause unrepresentative behaviour during biological treatment.[163] The lack of representative compositions between existing synthetics and real greywater is also expected to result in unrepresentative treatability studies. Therefore, a new synthetic greywater was designed and then experimentally validated.

4.3.2 SynGrey Composition

Table 4.1 shows the 15 ingredients and concentrations of SynGrey. Overall, the recipe used a minimal number of common ingredients (e.g.,[158,161,162]). Yeast extract (biodegradable, soluble COD), cellulose (particulate COD), and surfactants were used to provide COD. Three surfactants were used to represent common personal care products used in showers and to represent various surfactant categories: cocoamidopropyl betaine (CAPB) is a zwitterionic surfactant common in body wash;

Table 4.1. SynGrey recipe developed by matching 20 water quality parameters between this recipe and 49 real bathroom greywaters. The yeast extract used was 'yeast extract for technical purposes.' Most ingredients, in particular ingredients contribution to solids (total, total dissolved, total suspended, and volatile suspended) concentrations.

Ingredient	Concentration (mg/L)	Water Quality Parameter
Ammonium chloride crystalline	12.2	ammonium, chloride
Calcium carbonate anhydrous	2.1	calcium, pH
Calcium chloride dihydrate	63.5	calcium, chloride
Cellulose	52.2	COD, turbidity
Cocamidopropyl betaine (CAPB)	4.0	zwitterionic surfactant
Hydroxyethylcellulose ethylate (Polyquaternium-10)	4.0	cationic surfactant
Kaolin	35.6	turbidity
Magnesium sulfate anhydrous powder	110	magnesium, sulfate
Potassium chloride crystalline	7.5	potassium, chloride
Sodium bicarbonate	29.5	sodium, pH
Sodium chloride	120	sodium, chloride
Sodium dodecyl sulfate (SDS)	15	anionic surfactant
Sodium nitrate	4.0	sodium, nitrate
Sodium sulfate	100	sodium, sulfate
Yeast extract	49.0	COD, total nitrogen, ammonium, total phosphorus, phosphate

hydroxyethylcellulose ethoxylate (polyquaternium-10) is a cationic surfactant common in hair conditioner; and sodium dodecyl sulfate (SDS) is an anionic surfactant common in shampoo. The yeast extract was the main source of phosphorus and nitrogen, with ammonium chloride and sodium nitrate providing additional nitrogen. Kaolin, a common clay mineral ,[162] was the primary source of inorganic particulates and turbidity, and the cellulose also provided additional turbidity. Magnesium sulfate, potassium chloride, calcium chloride, and sodium sulfate provided additional inorganic ions. The pH was buffered using calcium carbonate and sodium bicarbonate.

Experimentally, turbidity contributions were: 0.69 NTU per mg/L kaolin, 0.18 NTU per mg/L cellulose, and 0.016 NTU per mg/L yeast extract. Yeast extract was estimated to be 40% organic carbon, 5% potassium, 0.2% chloride, and 0.13% magnesium based on literature;[183–185] it was experimentally determined to be 10% nitrogen, 0.8% ammonia, 1.8% phosphorus, and 1% phosphate and to contribute 0.81 mg COD per mg yeast extract. The total surfactant concentration was set to 23 mg/L since total surfactant concentrations have been measured between 15 and 31 mg/L for real bathroom greywaters.[186–188] SDS was set to 15 mg/L, which is within the range measured in real bathroom greywater.[189] The remaining two surfactants did not have previously measured concentrations and were set to 4 mg/L each. This CAPB concentration translates to 13 mg/L of commercially available 31% stock solution.[190,191]

SynGrey was more similar to the compiled real greywaters than the existing synthetic greywaters (Figure 4.1 and Figure C.1). SynGrey had 159 mg/L COD, 3.6 mg/L ammonia as N, 67 mg/L TSS, 39 NTU turbidity, 7.43 pH, and 0.48 mg/L phosphate as P, which all fell within the 25th to 75th percentile ranges for the compiled real greywaters (Figure 4.1). Also, SynGrey fell within this range for the other 14 parameters (Table C.3 and Figure C.1). SynGrey has COD:N:P ratio of 100:5.6:0.6, which is similar to the typical COD:N:P ratio of real bathroom greywater (25th to 75th percentile of 100:3.1:0.4 to 100:8.3:1.3 based on the data in Table C.1). Both the SynGrey and typical real bathroom greywater would be nutrient limited compared to the ideal COD:N:P ratio of 100:20:1.[163]

When compared to the RH greywater, SynGrey and the RH greywater were similar and had average COD, sCOD, turbidity, ammonia, DOC, and TSS values that were less than 25% different. The COD:sCOD ratio of the RH greywater and SynGrey were comparable at 2.3 and 2.0, respectively, which were also similar to the COD:sCOD of the other real greywaters, which ranged from 1.4 to 2.9 (Table C.4).[192,193] Additionally, the COD:DOC ratios of the RH greywater and SynGrey were comparable at 7.1 and 6.9, respectively, which were comparable to the COD:DOC ratio of 7.2 for another real greywater.[194]

When compared to typical surface water and municipal wastewater, bathroom greywater was found to be distinct with water quality parameters that fell between both of these waters. Typical medium strength wastewater has 508 mg/L COD, 20 mg/L ammonia as N, and 195 mg/L TSS.[195] Average values for typical drinking water influents are 2.8 mg/L TOC (assuming a maximum possible COD/TOC ratio of 5.3, then the maximum organics would be 15 mg/L COD), 12 NTU turbidity, and 0.14 mg/L ammonia as N.[76] Bathroom greywater water quality parameters, when considering the 25th to 75th percentile range, were all lower than wastewater but higher than surface water for organics, nutrients, solids, and turbidity (Figure C.2). Since bathroom greywater is a distinct category of water, technologies conventionally associated with both wastewater and drinking water treatment were considered to determine the most effective treatment options.

4.3.3 SynGrey Experimental Validation and Greywater Treatability

The RH greywater used for comparison in the treatment validation tests was generally representative of real bathroom greywaters from the literature, with average values of 196 mg/L COD (n=35), 4.7 mg/L ammonia as N (n=20), 57 mg/L TSS (n=8), 34 NTU turbidity (n=77), pH 7.0 (n=60), and 0.25 mg/L phosphate as P (n=3). The RH greywater mean values fell within the 25th to 75th percentile range of compiled real greywaters for all key parameters, including turbidity (34 NTU for the RH greywater, which was 14% lower than the literature greywater median), TSS (57 mg/L, 2% lower), COD (196 mg/L, 7% higher), TOC (42 mg/L, 10% lower), and ammonia (4.7 mg/L N, 74% higher) (Figure C.2). However, the RH greywater had an average pH of 7.0 and EC of 214 μS/cm, both of which were below the respective 25th percentile values. These two values were lower because the tap water in the RH comes from a low alkalinity surface water, while many of the compiled real greywaters had tap water from groundwater sources, which tend to have more inorganic ions and higher alkalinity.[196] Overall, the RH greywater was found to be representative of typical greywaters and appropriate for treatability experiments and comparisons with the new synthetic greywater.

4.3.3.1 Chlorination. The total chlorine decay for the RH greywater (n= 15) and SynGrey (n= 15) is shown in Figure 4.2. Both greywaters were statistically similar at all contact times tested, based on Student's t-tests with 95% confidence (Table C.5). Overall, these results indicate that SynGrey could be a useful substitute for real bathroom greywater in chlorination studies and that chlorination of raw greywater, such as for odor control, will require high chlorine doses. The parallel first-order decay model (Equation 1) yielded a good fit for both waters; R-squared values were between 0.935 and 0.999 for the 15 RH greywater samples and between 0.876 and 0.987 for the 15 SynGrey samples. Four chlorine decay kinetic parameters were calculated and the values are shown in Table 4.2 for the RH greywater and SynGrey, as well as for a real bathroom greywater from a literature study performed in Spain.[164]

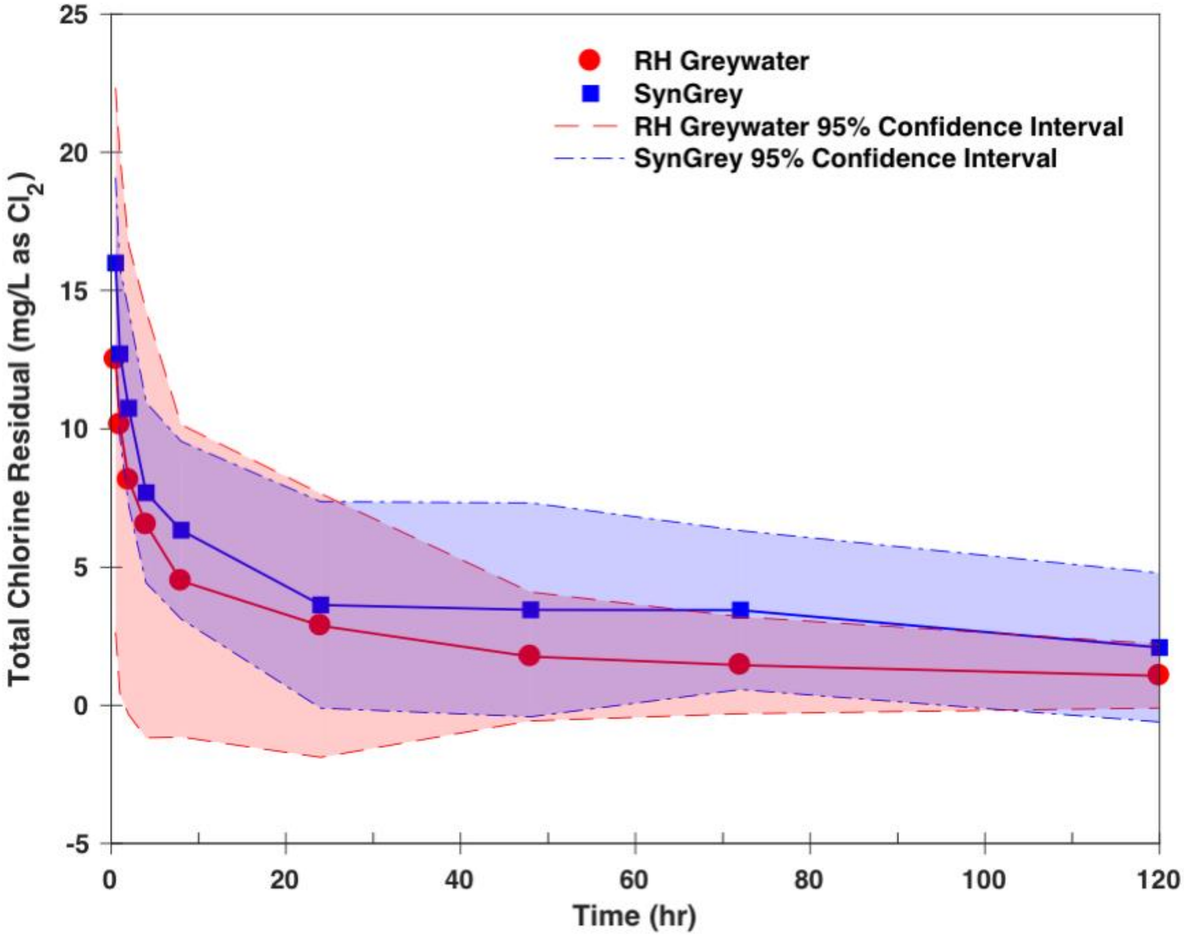


Figure 4.2. Total chlorine residuals and 95% confidence intervals (based on Student's t-tests, p-values listed in Table C.5) for the RH Greywater (red circle) and SynGrey (blue square) at 0.5, 1, 2, 4, 8, 24, 48, 72, and 120 hours.

The kinetic parameter values for SynGrey were found to be statistically similar to those for both real greywaters (Table 4.2). Specifically, the values for all four kinetic parameters were statistically similar between SynGrey and RH greywater. The values of three of the four kinetic parameters were statistically the same between SynGrey and the greywater from Spain. The fraction decaying rapidly parameter was statistically different, with the SynGrey fraction of 0.71 being higher than the greywater from Spain fraction of 0.34. Differences in this parameter could be due to different ammonium concentrations, which were not reported for the real greywater from Spain. Different ammonium amounts lead to different ratios of free and

Table 4.2. The chlorine decay kinetic parameters were calculated using the parallel first-order decay model and experimental on 15 samples each for RH greywater and SynGrey. Values reported in the literature for an additional real bathroom greyewater from Spain were also included (ref. 163) and were calculated using the parallel first-order decay model and 14 samples. Kinetic values are reported as mean ± standard deviation values. Student's t-tests were used to statistically compare all three greywaters. Superscript letters indicate statistical similarity ($p > 0.05$); kinetic values with the same superscript letter are statistically similar.

Parallel First-order Decay Model Parameter	Residence Hall Greywater	Synthetic Greywater	Spain Real Bathroom Greywater
Immediate chlorine demand, C_W (mg/L Cl_2)	23 ± 6^{a}	19 ± 8^{ab}	9 ± 2^{b}
Fraction decaying rapidly, x (%)	73 ± 16^{a}	71 ± 11^{a}	34 ± 6^{b}
Rapid decay rate constant, k_1 (hr^{-1})	0.9 ± 1.1^{a}	0.72 ± 0.63^{a}	1.3 ± 0.4^{a}
Slow decay rate constant, k_2 (hr^{-1})	0.016 ± 0.010^{a}	0.013 ± 0.013^{a}	0.05 ± 0.02^{a}

combined chlorine residual, and combined chlorine generally decays slower than free chlorine.[164]

The greywater from Spain had immediate chlorine demand and rapidly decaying fraction values that were significantly lower than the RH greywater values, while the other two parameter values were statistically similar. The immediate chlorine demand parameter was found to strongly correlate with soap concentration.[164] Differences in this parameter may be due to different soap concentrations since the greywater from Spain included wastewater from only showers while the RH included wastewater from showers and sinks. Overall, the SynGrey was similar to both real greywaters, even though there were some differences in source waters.

The chlorine dose used for treatment depends on the treatment objectives (e.g., regulatory specifications for chlorine residual or log reduction of pathogens) and can be calculated using each greywater's chlorine decay kinetic parameters (Table 4.2). For example, if the goal is to prevent pathogen regrowth in a toilet for at least 4 days, then a 1-hour total chlorine residual around 2.75 mg/L Cl_2 could be used,[177] resulting in chlorine doses of 23, 28, and 13 mg/L for SynGrey, RH greywater, and greywater from Spain, respectively. Greywater reuse standards for non-potable reuse based solely on log reduction of pathogens have been proposed to replace standards requiring effluent organic matter targets.[197] While meeting such targets with chlorination alone would be possible, the raw greywater chlorine doses required would be much higher than the doses used for drinking water treatment, which are generally 2.1 to 7.8 mg/L as Cl_2.[198] High chlorine doses can lead to high disinfection byproduct formation,[198] which could result in human disinfection byproduct exposure such as by ingestion of greywater-irrigated crops[199] as well as lead to high financial and environmental costs.[200] Therefore, reducing chlorine demand by organic matter removal before chlorination should be an important priority for greywater treatment to reduce costs, ensure proper disinfection, and minimize disinfection byproduct formation.

4.3.3.2 Biodegradability. The biodegradability as measured by the SOUR experiments was found to be similar between SynGrey and RH greywater. Figure 4.3 shows that the SOUR of SynGrey peaked sooner and was slightly higher than the SOUR of the RH greywater. The peak SOURs for the RH greywater and SynGrey were 0.31 d^{-1} and 0.39 d^{-1}, respectively. These values were compared to another real greywater from the literature;[163] in that study a

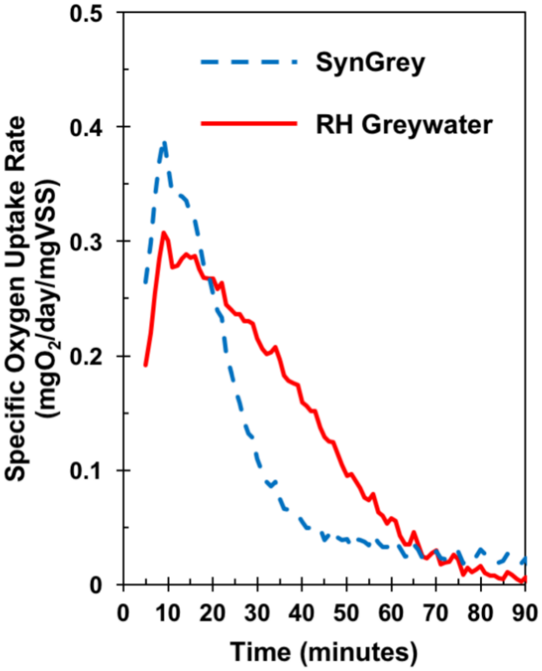


Figure 4.3. Specific oxygen uptake rate (SOUR) of RH Greywater and SynGrey. Each line represents the average of three replicates where the average SOUR of two controls have been subtracted. The dashed blue line represents SynGrey, and the solid red line represents RH Greywater.

real greywater from the United Kingdom (UK) was supplemented with macronutrients and micronutrients to evaluate the impact on oxygen uptake and COD removal. The lowest SOUR for the UK greywater was when only copper was added as a micronutrient, and this combination had an oxygen uptake rate of 0.4 d^{-1}, which was similar to the values for the SynGrey and RH greywater. However, when nitrogen and phosphorus were added to the UK greywater, the SOUR was notably higher at 1.0 d^{-1}.[163] This suggests that the biodegradation of the RH greywater and SynGrey could also be enhanced with nutrient addition since both were expected to have nitrogen and phosphorus concentrations lower than nutrient balanced UK greywater.

Biodegradability is also affected by biomass acclimation.[181] The SOUR results were obtained using wastewater sludge as inoculant, and since about 36% of wastewater flows are bathroom greywater,[195] the wastewater sludge should have contained microorganisms acclimatized to compounds found in bathroom greywater. However, acclimation to greywater only could further improve organic matter removal efficiencies. When compared to the biodegradability of greywaters reported in the literature, there is also an expected improvement to biodegradation with longer residence times (i.e., to support hydrolysis) as well as nutrient addition.[163,180]

The RH greywater and SynGrey were both found to be aerobically biodegradable, and they had similar amounts of readily biodegradable COD. The readily biodegradable fraction was calculated by dividing the cumulative oxygen uptake by the initial sample sCOD or COD. The cumulative oxygen uptake is equal to the area under the curve in Figure 4.3 ($mgO_2/mgVSS$) multiplied by the VSS of the inoculant (mgVSS/L). On average, the SynGrey's readily biodegradable fraction of total COD was 40% and that of the sCOD was 80%. The RH greywater sample's readily biodegradable fraction of total COD was 43% and that of the sCOD was 71%. The RH greywater sample for this experiment had more soluble COD than average, so around 30% readily biodegradable COD was expected given the RH greywater average COD:sCOD ratio. This value was very similar to another real greywater from Turkey as reported in the literature; that greywater had about 29% readily biodegradable COD.[180] The RH greywater biodegradability values also show that more soluble COD results in higher biodegradation; therefore, supporting hydrolysis can improve COD removal. The greywater from Turkey was found to be about 94% biodegradable, which included both readily and slowly biodegradable COD.[180] As a comparison, domestic wastewater COD was found to be around 70 to 80% biodegradable,[180,181,195] so biological treatment for greywater can be very promising for organics removal. Also, the biodegradability of SynGrey was representative of real greywater and could be a useful substitute for real bathroom greywater in studies of biological treatment.

4.3.3.3 Adsorption. Figure 4.4 shows the DOC removal by AC from RH

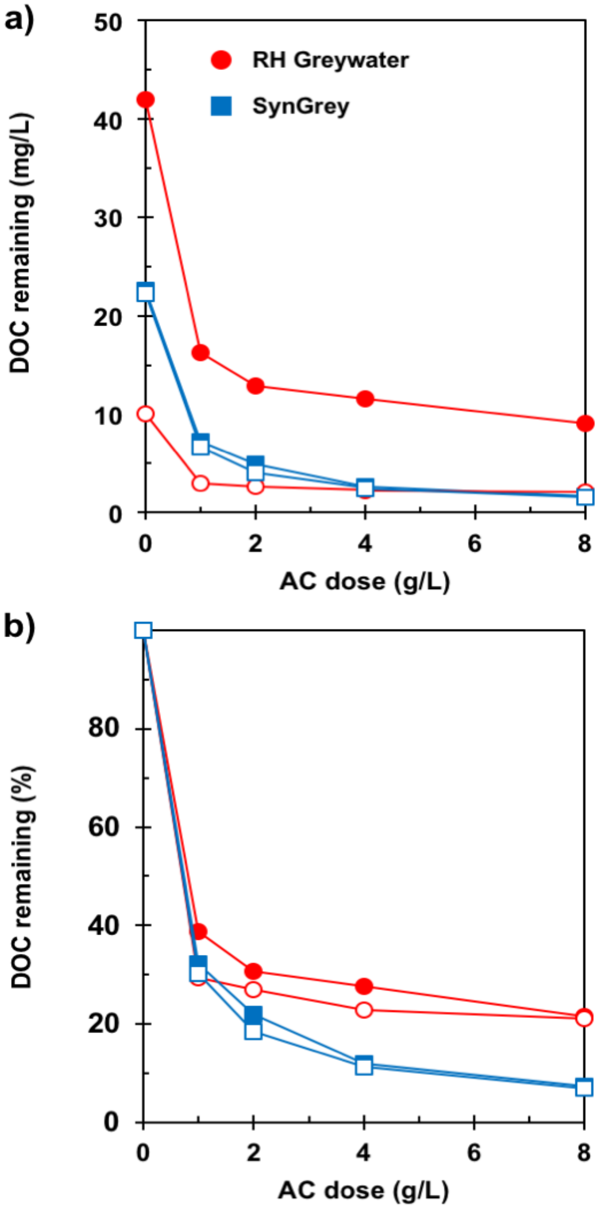


Figure 4.4. Dissolved organic carbon (DOC) remaining (a) as mg L^{-1} and (b) as percent after activated carbon (AC) adsorption. Initial DOC was 42.6 mg/L for RH Greywater sample 1 (filled red circle) and 10.7 mg/L for RH Greywater sample 2 (hollow red circle), 22.6 mg/L for SynGrey sample 1 (filled blue square), and 23.0 mg/L for SynGrey sample 2 (hollow blue square). Replicate samples were from different days.

greywater and SynGrey. The first RH greywater sample had an initial 42.6 mg/L DOC and 7.1 pH, and the second sample had an initial 10.7 mg/L DOC and 7.5 pH. Despite the large difference in initial DOC values, the RH greywater samples had very similar percent DOC removals (less than 10% different for any AC dose tested) (Figure 4.4b). This was unexpected as initial DOC concentration has been shown to impact adsorption.[201] The greatest DOC removal was 83% at a dose of 16 g/L AC, with an average 66% DOC removal achieved at 1 g/L AC.

For SynGrey, the first sample had an initial 22.6 mg/L DOC and 7.6 pH, and the second sample had an initial 23.0 mg/L DOC and 7.4 pH. Both samples had similar DOC removals at each AC dose (±4% difference). The greatest DOC removal was 94% at a dose of 16 g/L AC and the average DOC removal at 1 g/L AC was 69%. While DOC removal at each AC dose was similar between SynGrey and RH greywater (±14% difference), DOC removal was greater for the SynGrey at higher doses, which indicated that it may have a lower non-adsorbable fraction (Figure 4.4b). Replicates of the same samples at 4 g/L had the same DOC removal within ±2% for both RH greywater and SynGrey.

Overall, greywater DOC removal required very high AC doses. For example, a typical AC dose for taste and odor removal from drinking water is 10 to 30 mg/L[201] and for organic micropollutant removal from wastewater effluent is 70 mg/L.[33] However, 1000 mg/L AC was needed to remove the majority of greywater DOC (Figure 4.4). Even at 8 g/L AC, which achieved 80% removal, adsorption alone can only meet the stringent non-potable reuse standard of ≤10 mg/L effluent BOD[182] if the initial DOC was less than 15 mg/L DOC (assuming an average greywater BOD:DOC ratio of 3.3:1).[202] Since greywater initial DOC values were typically much higher, around 45±28 mg/L (Table C.3), adsorption must be coupled with other organic matter removal mechanisms to reliably meet these targets. For example, activated carbon has been tested as a polishing step after sand filtration,[174] and biochar, a similar adsorbent, has been tested as polishing step after wetland treatment.[45]

4.3.3.4 Coagulation. Alum coagulation was more effective for turbidity than for TOC removal, and it was most effective for the RH greywater. Alum coagulation and sedimentation achieved 93 to 98% removal of turbidity from the RH greywater (Figure 4.5a) with doses in the range of 40 to 160 mg/L, achieving less than 5 NTU for both samples. Turbidity removal from the RH greywater was not highly sensitive to alum dose in the range 40 to 160 mg/L. Flocs were very filterable, such that 1.2 µm filtration after alum doses of 80 to 160 mg/L achieved less than 1 NTU of turbidity (Figure 4.5b). Maximum TOC removal ranged from 37 to 46% (Figure C.4).

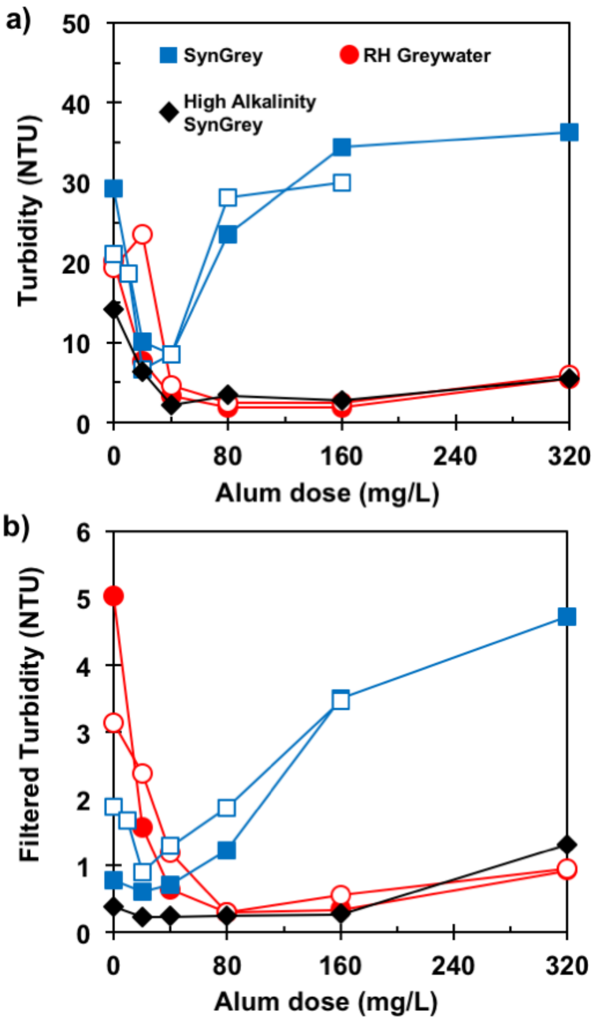


Figure 4.5. Alum coagulation removal of: (a) turbidity and (b) filtered turbidity. Waters evaluated were: RH Greywater (red circles), SynGrey (blue squares), and high alkalinity SynGrey (black diamonds). Hollow and filled symbols indicate replicate samples of each greywater from different days. The high alkalinity SynGrey has the same composition as in Table 4.1 except the calcium carbonate concentration was 10.8 mg/L and the sodium bicarbonate concentration was 151 mg/L.

However, alum coagulation was not as effective at turbidity or TOC removal from SynGrey. Maximum SynGrey turbidity removal was about 80% at alum doses of 20 to 40 mg/L, and no alum dose achieved less than 5 NTU (Figure 4.5a). Also, the optimal coagulation dose for the synthetic greywater was lower and narrower (Figure 4.5). SynGrey TOC removal by coagulation and flocculation was negligible relative to sedimentation alone (Figure C.4) and was insufficient to meet the BOD target of NSF 350 indoor reuse standard[182] without additional processes (based on typical BOD:TOC ratios). However, coagulation followed by 1.2 µm filtration could meet the NSF 350 standard's turbidity target of ≤2 NTU average. Overall, greywater alum doses were notably larger than the U.S. drinking water treatment median alum dose of 18 mg/L,[65] and they were not enough to achieve the organic matter removal required by stringent reuse standards. Other studies have found that even higher alum doses were needed for optimal coagulation performance.[203,204]

The effluent turbidity and filtered turbidity of SynGrey increased at alum doses of 80 mg/L and greater (Figure 4.5b). This phenomenon was largely due to the formation of fine precipitate particulates formed between the yeast extract and the alum (Figure C.5). To minimize this precipitation, the alkalinity of the SynGrey recipe was increased from 19 to 87 mg/L as $CaCO_3$ by increasing the calcium carbonate and sodium bicarbonate concentrations. This higher alkalinity SynGrey behaved much more like the RH greywater in terms of turbidity and filtered turbidity removal. It had a minimum turbidity of 2.2 NTU at 40 mg/L alum (Figure 4.5a) and minimum filtered turbidity of 0.23 NTU at 20 mg/L alum (Figure 4.5b). The rise in turbidity in the high alkalinity SynGrey at alum doses of 80 mg/L or greater matched the slight resuspension that occurred in the RH greywater. Overall, increasing the alkalinity of the SynGrey recipe allowed it to better represent real greywater in terms of turbidity removal by coagulation.

4.4 Conclusions

In this study the treatability of a real and synthetic bathroom greywater for commonly applied treatment processes was evaluated. A literature review of bathroom greywater quality was conducted, and the results served as a baseline for the development of a recipe for a new, representative synthetic greywater, SynGrey, that matched both the median composition of 49 real greywaters for 20 water quality parameters and the treatability of a real bathroom greywater.

- Chlorination of SynGrey and the RH greywater yielded similar decay kinetics, which were well-fit by a parallel first-order decay model. Chlorine doses necessary to achieve a sustained chlorine residual in raw greywater were very high relative to that for typical surface waters. Organic matter removal prior to chlorination, to reduce chlorine demand, may be economically prudent.
- The RH greywater and SynGrey yielded very similar peak specific oxygen uptake rates, around 0.35 d^{-1}, and readily biodegradable total COD fractions around 40%. Biological COD removal is expected to remove even more organic matter with extended residence times and acclimation.
- Adsorption with activated carbon yielded similar DOC removal results for both SynGrey and the RH greywater with the non-adsorbable DOC fraction in the range of 10 to 20%. Relative to surface water, high doses were required to get significant removals, such as 1 g/L to remove over 50% DOC. Further organic matter removal will require combination with other treatment processes to meet stringent reuse regulations.
- At economical alum doses, 40 mg/L, coagulation of the RH greywater and SynGrey yielded effective turbidity removal, < 5 NTU and <10 NTU, respectively. Increasing the alkalinity to a range similar to most surface waters increased the turbidity removal of the SynGrey to <5 NTU. However, coagulation was less effective for TOC removal; 37 to 46% for the RH greywater and less than 5% for SynGrey. Also, the dose range for effective turbidity removal was much narrower for SynGrey.
- SynGrey was found to be representative of bathroom greywater. It matched the median composition of 50 real bathroom greywaters more closely than previous

recipes and had similar treatability as the RH greywater, specifically for chlorine decay and organic matter removal by aerobic biodegradation and sorption.

CHAPTER 5

THE EVALUATION OF ACTIVATED CARBON AND NOVEL BIOCHAR SORBENTS AS TREATMENT APPROACHES FOR GREYWATER REUSE

Abstract

Population growth and climate change are exacerbating water scarcity. The reuse of greywater from showers, baths, and bathroom sinks could reduce residential water demand. Activated carbon (AC) is an established sorbent for drinking water treatment, but its applicability for greywater treatment is not well-established. Biochar is an emerging, low-cost, alternative to AC, produced by pyrolyzing organic feedstocks, and its applicability for greywater treatment is unknown. The objectives of this study were to (1) compare the performance of biochar and AC for removing dissolved organic carbon (DOC) from greywater and (2) determine whether AC or biochar can satisfy greywater reuse regulations alone or in combination with the processes coagulation, aeration, and rainwater blending. Among five biochars tested, a wood-based biochar produced at ~850 °C was the most effective for greywater treatment. Activated carbon removed more DOC than this biochar on all greywater samples, at all doses, and after all pretreatments. Aeration was a more effective pretreatment than coagulation. Following aeration, AC could reach treatment targets for irrigation and toilet flushing reuse with doses of 0.25 g/L and 1 g/L respectively. DOC removal by AC from blends of greywater and rainwater could be predicted with mass balance. From most to least, removal by sorption followed the order UV absorbance, DOC, and free chlorine demand.[§]

[§] Sorption with biochar for stormwater and wastewater effluent has been evaluated previously[33] with promising environmental implications (Chapter 3). The following chapter represents the first evaluation of biochar sorption of microfiltered, coagulated, aerated, or rainwater-blended bathroom greywater. The synthetic bathroom greywater SynGrey (Chapter 4) was included to further verify its experimental validity and to enhance the reproducibility of this work.

5.1 Introduction

Water scarcity is a severe global challenge. Approximately 4 billion people live under local severe water scarcity for at least one month each year and 0.5 billion people experience local severe water scarcity every month of the year.[1] Greywater reuse is a key strategy for reducing water demand and thus alleviating water scarcity. Greywater is wastewater from showers, baths, bathroom sinks, laundry, or kitchen but not toilets or urinals. Categories of greywater (i.e., kitchen, laundry, or bathroom), have distinctive water quality characteristics in terms of organics, nutrients, and pH.[154] "Light greywater" or "bathroom greywater" is greywater from showers, baths, and bathroom sinks, and is generally the most abundant category of greywater and least contaminated in terms of organics.[38,154] Decentralized reuse of bathroom greywater could fully meet the water demand for toilet flushing, and thus reduce residential water demand by 30-40% and urban water demand by 10-25%.[39] Furthermore, life cycle assessments have found that decentralized greywater reuse could be more environmentally sustainable than centralized wastewater reuse or desalination due to lower energy requirements.[40] However, the relative environmental sustainability of greywater reuse will depend on the treatment processes selected.[166]

Despite the potential of greywater reuse to alleviate water scarcity, decentralized greywater reuse presents technical, operational, regulatory and financial challenges due to economies of scale. To address these issues, greywater reuse treatment technologies must be low-cost and simple to operate. Furthermore, to protect public health, greywater systems should be redundant, reliable under influent fluctuations, and resilient to temporary shutdown or failure.[197] Greywater regulations vary by jurisdiction, but current greywater regulations for both irrigation and toilet flushing generally include a limit for effluent organic matter.[38] However, flexible, risk-based regulations focusing on log reduction targets for pathogens have been proposed.[197] Under such a framework, the usefulness of a treatment technology for greywater reuse would depend on its ability to reduce pathogens or its ability to increase the efficiency of disinfection processes such as chlorination or UV.

Previous research on greywater treatment has focused on membrane bioreactors, direct membrane filtration, and constructed wetlands.[38] However, economic evaluation indicates that greywater treatment with membrane bioreactors and direct membrane filtration would cost 4.40 and 4.81 euro/m^3 respectively, well above the typical cost of tap water in Europe or the United States.[41,42] Constructed wetlands are a promising approach for greywater treatment, but require significant land area which may be prohibitive in many cases. For example, a previous study found that an 8 m^2 constructed wetland successfully treated 103 L/day of bathroom and laundry greywater to less than 10 mg/L biochemical oxygen demand (BOD).[44] However, based on typical flows in the USA, this system would require over 5 m^2 of surface area per person to meet toilet flushing demand.[195]

Sorption, such as with activated carbon, has several advantages over biological treatment in the context of greywater reuse. Biological systems are vulnerable to toxic shock and require acclimation time, which limits effectiveness during start-up or under wide influent fluctuation. Studies have also indicated that greywater is nutrient limited,[163] reducing the rate (and therefore expanding the physical footprint) of biological treatment. Greywater also often has a high chemical oxygen demand (COD) to BOD ratio, indicating low maximum removal by biological processes alone.[205] In contrast, sorbent performance would be resilient to toxic shock, influent fluctuation, or nutrient limitation. While sorbents may be exhausted relatively quickly due to the high dissolved organic carbon (DOC) in raw greywater, sorption could also serve as secondary treatment or a polishing step, increasing contaminant removal and adding redundancy, resilience, and reliability to the system.

Previous studies on sorption for bathroom greywater treatment are limited. Most studies testing granular activated carbon for greywater treatment have used laundry greywater[206–209] or mixed greywater including kitchen water.[173,210,211] Both of these categories of greywater tend to have more organic matter than bathroom greywater,[154] and laundry greywater tends to have higher pH than bathroom greywater (Table D.1 and Table D.2). Four studies have tested granular activated for sorption of sand-filtered bathroom greywater.[174,212–214] These studies found that treatment with activated carbon resulted in substantial removal of organic matter. A system in Malaysia[213] achieved less 10 mg/L BOD, though the bathroom greywater influent had BOD of around 50 mg/L, which is below the 25th percentile (Table D.2). A similar system in Greece achieved a final BOD of 25 mg/L,[215] while two other systems would have achieved 11 to 13 mg/L BOD based on a typical COD:BOD ratio of 2.2 (Table D.2).[174] These studies had effluent turbidity of 6 NTU or more,[174,212–214] which exceeds typical international standards requiring 2 NTU for toilet flushing or unrestricted irrigation.[38,63,174,182,216] So for these reuse applications, additional treatment (i.e., coagulation or membrane filtration) to further reduce turbidity would have been required. Furthermore, the high cost of activated carbon (around $4.60 per kg at scales appropriate for decentralized treatment)[217] motivates the investigation of lower cost sorbents.

Biochar can serve as a low-cost alternative to activated carbon in water treatment. Biochar is generated through the pyrolysis of organic waste materials such as biosolids, timber waste or cow bone.[33,218] The effectiveness of biochar for sorption varies based on factors such as feedstock[33] and pyrolysis temperature.[219] Furthermore, the various types of biochar differ in their effective for removing different contaminants; for example, more hydrophobic biochars are better for removing hydrophobic organics, while biochars with more oxygen-containing functional groups are better for removing polar organics.[220] Therefore, it is necessary to screen multiple biochars for a given water treatment application. Previous studies have tested biochar as a biological support media for intermittent filtration of kitchen greywater in developing countries.[221] However, only one study has tested biochar as a sorbent for greywater treatment, specifically as a polishing step after a constructed wetland.[45] In both cases, a single biochar was tested. There have been no previous studies on sorption with activated carbon or biochar on microfiltered, coagulated, aerated, or rainwater-diluted bathroom greywater.

Coagulation is another physico-chemical approach for greywater treatment. Like sorption, coagulation avoids many of the drawbacks associated with biological treatment. Bathroom greywater coagulation has been tested with the coagulants ferric chloride,[202,203,222,223] alum,[46,202–204] and polyaluminum chloride.[203,223] Minimum turbidities after bathroom greywater coagulation range from 2 to 5 NTU with ferric chloride and 2 to 8 NTU with alum.[46,202,204,222] The coagulant dose to achieve minimum turbidity has ranged from 7 to 12 mg-Al/L for alum and 22 to 55 mg-Fe/L for ferric chloride.[46,204,222,223] Total organic carbon (TOC) or DOC removal by coagulation is reported in the range of 40% to 60% for bathroom greywaters.[46,202,222] Higher coagulants doses of alum are required for greywaters including kitchen greywater, and lower percent removals of COD and total suspended solids have been reported for greywaters including laundry greywater.[173] The effectiveness of coagulation for greywater treatment appears to vary at different locations. However, water quality characteristics that relate to the effectiveness of coagulation, such as alkalinity and especially specific UV absorbance (SUVA), are not consistently reported.[77] Since coagulation achieves high removal of turbidity, but only moderate removal of organic matter, coagulation may be most effective in combination with other processes that remove organic matter. Coagulation and carbon-based sorption can be synergistic in combination because coagulation is most effective at removing high molecular weight, aromatic compounds,[224] and activated carbon is capable of removing low molecular weight, low-SUVA (non-aromatic) compounds.[225]

Rainwater harvesting and greywater reuse have often been compared in terms of their water savings, environmental sustainability, and cost effectiveness.[226–229] The reuse of both rainwater and greywater has been proposed to maximize water savings,[226,229] especially considering that the proportion of greywater reuse could be increased during dry seasons when less rainwater is available. Blending rainwater and greywater in a combined storage tank would have lower capital cost than storing rainwater and greywater separately.[229] Only one experimental study has been published on treatment of blended greywater and rainwater.[209] However, that study used a relatively uncontaminated bathroom and laundry greywater; the pH, COD, ammonia, phosphate, and TDS were below the 25th percentile and the total coliforms, BOD, turbidity, and TSS were the lowest reported relative to other laundry greywaters in the literature (Table D.1). Furthermore, the total coliforms, BOD, and COD were below the 25th percentile and the turbidity, TSS, and ammonia were below the minimum reported for bathroom greywaters (Table D.2). Therefore, these low concentrations are not likely due to a relatively high ratio of bathroom to laundry greywater. The solids and organic matter in that greywater may have been low because the greywater was transported by lorry[209] from another location in warm, tropical climate, so the greywater may have settled and biodegraded en route to the lab.

To address these gaps in the literature, the objectives of this study were (1) screen biochars from a variety of feedstocks and production conditions to select the best biochar for greywater sorption, (2) compare the effectiveness of biochar and granular activated carbon for greywater sorption, (3) evaluate pretreatments (coagulation, rainwater dilution, and aeration) for meeting greywater reuse regulations in combination with sorption, and (4) investigate the impacts of sorption on greywater free chlorine demand and UV absorbance.

5.2 Methods

5.2.1 Analytical Methods

For rainwater, treated rainwater/greywater blends, and treated greywater samples with DOC <2 mg/L, DOC was measured with a Sievers M5310 C Laboratory TOC Analyzer (Boston, MA, USA). For all other samples, TOC and DOC were measured with a Shimadzu TOC-V_{SCH} analyzer (Kyoto, Japan). Turbidity was measured in duplicate with a Hach 2100N Turbidimeter (Loveland, CO, USA). Alkalinity was determined by the bromocresol green-methyl red method with a Hach digital titrator. Ultraviolet absorbance at 254 nm (UVA_{254}) was measured with a Hach DR 6000 spectrophotometer with a 10-mm sample cell. pH was measured with a Thermo Scientific Orion Star A211 pH Meter (Lafayette, CO, USA). Dissolved oxygen (DO) was measured with a Hach HQ440d Laboratory Multi-Parameter Meter. Electrical conductivity (EC) was measured with a Hach conductivity/TDS meter. Chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), and ammonia were measured with Hach TNTplus kits. DOC, sCOD, and UVA_{254} samples were prepared by filtration with 0.45 μm nitrocellulose membranes. Free chlorine residual was measured with the N,N diethyl-1,4 phenylenediamine sulfate (DPD) method with a Hach pocket colorimeter. Moisture content of sorbents was determined according to ASTM method D2867.[230] Apparent density was determined according to AWWA standard B600.[119]

5.2.2 Greywater Sampling

Raw greywater was collected from a collection network draining the showers and washbasins of approximately 180 students in a university residence hall in Colorado. Raw greywater was stored at 4 °C in 3.9-L amber glass or 20-L plastic carboys. Key greywater characteristics (turbidity, pH, TOC, DOC, UVA_{254}) were measured immediately after sampling. These characteristics were measured again at the start of each experiment. The DOC of the greywater sometimes declined significantly in storage despite refrigeration. Therefore, the key characteristics listed above were measured again at the start of each experiment, and the experimental results were only analyzed and presented if these characteristics had changed by less than 20% from the first measurement.

Seven greywater batches (A through G) from different sampling days but the same location were used for experiments in this study (Table 5.1). Prior to the onset of this study, greywater was monitored at this location to establish typical water quality values. Beginning with batch C, the greywater sample was only used for experiments if the TOC and DOC fell within the interquartile range of greywater samples from this sampling location (Table C.3). Furthermore, the greywater samples were only used if the turbidity and UVA_{254} fell within the 95% confidence interval for this sampling location. Otherwise, the greywater sample was considered unrepresentative and discarded.

Compared to bathroom greywater in the literature (Table D.2), the greywater in this study was typical (i.e., within the interquartile range) for DOC, pH and turbidity (Table 5.1). The mean greywater TOC in this study was 39 mg/L which is less than 10% below the literature interquartile range of 42 to 75 mg/L, and above the TOC reported in three previous studies.[171,231,232] The UVA_{254} of bathroom greywater has only been reported in three studies, with a range of 0.11 to 0.282 1/cm,[233,234] and the greywater in this study fell within that range. However, the EC of this greywater was very low at 212 μS/cm compared to the literature interquartile range of 479 to 983 μS/cm. Therefore, the greywater samples used in this study could be considered typical except for having low EC. Due to the variability of real greywater among sites and over time, synthetic greywater was also used during the biochar screening experiments.

5.2.3 Materials

Five biochars were selected for screening from a range of feedstocks and productions conditions. “800 °C Furnace Wood” and “900 °C Furnace Wood” were pyrolyzed at University of Colorado Boulder from pine pellets in a closed ceramic crucible in a laboratory furnace for 2 hours at 800 °C and 900 °C respectively. “Full-scale Wood” was generated by Confluence Energy, LLC and Biochar Solutions, Inc., in a full-scale pyrolysis facility where pine wood chips were exposed to a temperature gradient from 400 to 1200 °C (“Low-Capacity Wood Biochar in Chapter 5). “Bone” was produced from the bones of beef cows at a 1 ton/day pilot facility by Confluence Energy, LLC. The bones were heated to a highest holding temperature of approximately 700 °C with a total run time of around 8 hours. “FD-TLUD Wood” was produced at North Carolina State University from a blend of hardwood and softwood pellets in a 55-gallon forced draft top-lit updraft (FD-TLUD) gasifier at approximately 850 °C. The activated carbon used was coal-derived, commercially available Norit 1240 granular activated carbon. All sorbents were ground with mortar and pestle to ≤45 μm (≤325 mesh) particle diameter, the typical diameter of commercial powdered activated carbon. A ground commercial granular activated was used instead of a commercial powdered activated carbon so that the results would be more valid for estimating the performance of bed mode sorption with granular sorbents.

5.2.4 Biochar Screening

Screening to select the best biochar for greywater sorption was carried out using batch reactors with a Phipps & Bird stirrer. The jar volume was 0.5 L and the mixing rate was 120 rpm. Sorbent doses were weighed to within ±1%. The screening included six jars with one control and five biochars (Section 5.2.3). A dose of 2 g/L was used for all biochars in the screening. Samples for DOC and UVA_{254} were extracted via syringe at 2, 4, and 8 hours. Experimental replicates were carried out with a different greywater sample for the highest performing biochar and with activated carbon doses of both 2 and 4 g/L. Preliminary tests found significant DOC reduction in the control due to biological activity. Chaillou et al.[174] also observed this phenomenon in a jar test with granular activated carbon and sand-filtered greywater. Wll greywater samples were filtered with 1.2 µm glass fiber filters immediately prior to the sorption jar tests. This procedure led to stable DOC in the control jar (±4% after 8 hours). These screening jar tests were repeated with both real bathroom greywater and the SynGrey synthetic greywater recipe (Chapter 4).[46]

Table 5.1. Greywater batch characteristics. “Kinetics” refers to experiments with a fixed dose and multiple time points to select a contact time for further experiments (Sections 5.2.4 and 5.3.1). “Sorption” refers to experiments comparing activated carbon and the best biochar for greywater treatment with filtration as the only pretreatment (Sections 5.2.5 and 5.3.2). “Selection” refers to screening biochars at a set dose to select the best biochar for further experiments. Batch C was used for coagulant dose selection and coagulation followed by sorption (Sections 5.2.6.1 and 5.3.3.1). Batch D was used to compare simultaneous versus sequential coagulation and sorption (Section D.2.3.1). “Rainwater blend” refers to experiments with greywater blended with rainwater (Sections 5.2.6.2 and 5.3.3.2). “Aeration” refers to experiments were greywater was aerated prior to sorption (Sections 5.2.6.3 and 5.3.3.3). “Cl Demand” refers to experiments on the effective of treatment on chlorine demand (Sections 5.2.7 and 5.3.4). “Mean±SD” is the mean and standard deviation of these eight batches. [a]Activated carbon and FD-TLUD Wood only (Figure D.1). [b]All biochars (Figure 5.2).

Batch	A	B	C	D	E	F	G	Mean±SD
Dates used	10/17/16	10/19/16	7/19/17-7/31/17	9/19/17-9/25/17	10/5/17-10/8/17	10/11/17-10/15/17	10/24/17-10/29/17	
Experiments	Kinetics[a]	Sorption	Selection Kinetics[b] Sorption Coagulation	Sorption Rainwater blend Coagulation	Sorption	Sorption Aeration	Cl Demand	
pH	6.9	7.1	7.8	6.9	7.4	6.8	7.6	7.2±0.4
EC (µS/cm)	300	270	160	170	-	190	190	212±56
Turbidity (NTU)	33	37	68	30	36	40	23	38±14
TOC (mg/L)	46	49	38	38	33	37	30	39±7
DOC (mg/L)	30	43	29	27	30	29	26	31±6
UVA254 (1/cm)	-	-	0.086	0.175	0.189	0.145	0.158	0.151±0.040
SUVA (L/mg/m)	-	-	0.30	0.64	0.63	0.51	0.60	0.53±0.14

5.2.5 Biochar to Activated Carbon Comparison

After the best preforming biochar had been determined (Section 5.2.4), dose response jar tests were used to determine the biochar and activated carbon doses required to achieve target DOC removal. The jar volume was 0.5 L and the mixing rate was 120 rpm. As in the biochar screening jar tests, filtration with 1.2-µm glass fiber filters was used to prevent interference from biological activity. A contact time of 2 hours was selected because negligible additional sorption occurred after 4 or 8 hours in the biochar screening experiments. Immediately after the 2-hour contact time, the sorbents were removed from solution with 0.45-µm nitrocellulose membrane filters. For the first dose response experiment, the sorbent dose range was 1 to 16 g/L. A plateau in removal occurred at the highest doses, so the sorbent dose range was revised downward in subsequent experiments to 0.25 to 2 g/L. There was at least one experimental replicate included for every ten jars. Sorbents were dosed as-received. The moisture contents of both activated carbon and FD-TLUD Wood were less than 10%.

5.2.6 Pretreatment

Figure 5.1 shows the three pretreatment approaches used prior to sorption: coagulation, rainwater blending, and aeration. For the experiments with rainwater blending, filtration was used to prevent biological interference as described above. Filtration was not used prior to the experiments with coagulation because coagulated greywater was found to have stable DOC for over two hours at 20 °C. For the experiments with aeration, filtration was not used because the goal was to enhance biological activity.

5.2.6.1 Coagulation. Coagulation, flocculation, and sedimentation of greywater were evaluated with bench-scale jar tests to the select the optimal dose of alum ($Al_2(SO_4)_3 \cdot 16H_2O$). The alum doses were 0, 10, 20, 30, 40, 60, 80, and 120 mg/L,

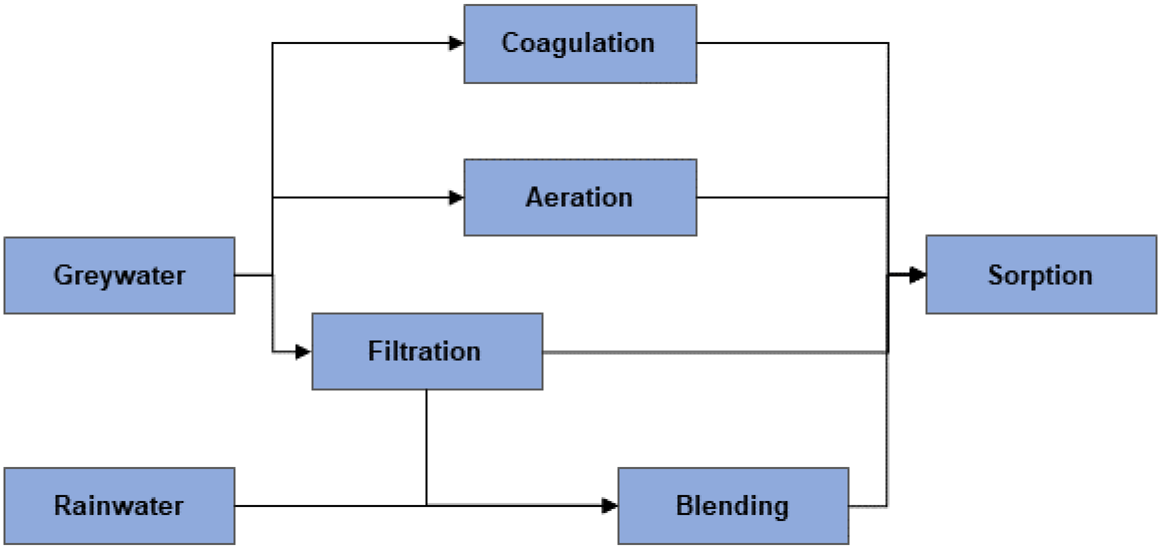


Figure 5.1. Process flow diagram showing pretreatments evaluateded prior to sorption.

with an experimental replicate at the 40 mg/L dose. The jar volume was 1 L, and the alum stock solution concentration was 20 g/L. The mixer speed was initially 290 rpm to simulate a rapid mix process. Alum addition to each jar was simultaneous. After 1 minute of rapid mix, the mixer speed was reduced to 55 rpm and then 20 rpm for 10 minutes each to simulate a 2-stage flocculation process. Sixty minutes of sedimentation followed the flocculation process. The samples from the settled water were then analyzed for TOC, DOC, turbidity, UVA_{254}, and pH. The optimal alum dose was selected based on maximum turbidity and TOC removal, and a plateau of DOC and UVA_{254} removal. Eight jars with volume of 2 L were then coagulated with the selected optimal dose and the mixing regime described above. The top 1 L of each jar was then decanted, combined in a clean 10 L plastic carboy, stirred, and used immediately for sorption jar tests as described above.

5.2.6.2 Rainwater Blending. Rainwater was collected from the roof of the Sustainability, Energy, and Environment Laboratory at University of Colorado Boulder during a 23 mm rain event.[235] This facility has ceramic roofing tiles and the rainwater was collected after the storm had been raining for over an hour. Therefore, this rainwater would be considered non-first flush.[236] The rainwater was characterized immediately and stored at 4 °C in a 20 L carboy. Within 24 hours, 4 L of the rainwater and 4 L of filtered greywater were blended in a clean 10 L plastic carboy. The 50:50 blend of rainwater and filtered greywater was then used for sorption jar tests as described above.

5.2.6.3 Aeration. Open jars of raw greywater were stirred with a Phipps & Bird stirrer to facilitate oxygen transfer from the air. The jars were square (9.5 cm X 9.5 cm) and filled to a volume of 0.5 L. The mixing rates were 0, 12 and 120 rpm and the ambient temperature was 20 °C. Residence times were 2, 4, 8, and 24 hours. An experimental replicate was included at 120 rpm and 2 hours. Aerated jars were measured for TOC, DOC, DO, COD, sCOD, pH, and UVA_{254}. The best combination of residence time and mixing rate was selected. Half liter jars of raw greywater were then aerated under these conditions and then immediately used for sorption jar tests as described above.

5.2.7 Chlorine Demand Reduction

To evaluate the impact of sorption on greywater disinfection, chlorine demand was determined for raw and treated samples of greywater batch H. The treatments applied to greywater batch H were: sorption, coagulation, coagulation followed by sorption, aeration, and aeration followed by sorption. An experimental replicate was included for coagulation followed by sorption. Coagulation was conducted with the jar test protocol described in Section 5.2.6.1 with an alum dose of 30 mg/L. Sorption was conducted with the jar test protocol described in Section 5.2.5 with an activated carbon dose of 1 g/L. Greywater was aerated as described in Section 5.2.6.3 with a 12-rpm mixing speed and a 24-hour contact time. Chlorine demand was determined according to Uniform Formation Conditions, with temperature 20±1 °C, pH 8.0±0.2, contact time 24±1 hours, and free chlorine residual 1.0±0.4 mg/L as Cl_2.[57]

5.3 Results and Discussion

5.3.1 Biochar Screening

In the biochar screening experiment, negligible additional sorption was observed after 2 hours (Figure 5.2. Thus, 2 hours was selected as the focus for analysis and the contact time for further experiments. Preliminary experiments with 2 g/L activated carbon also found negligible additional sorption at contact times longer than 2 hours (Figure D.1).

As shown in Figure 5.2 for 2 hours of contact time, the FD-TLUD Wood biochar was by far the best biochar with 51% DOC removal, while the other biochars had comparable DOC removals ranging 20% to 30%. A similar rank order was found for UVA_{254} removal (Figure D.2). The UVA_{254} results showed a wide range of response compared to those for DOCs, with FD-TLUD Wood achieving 70% removal of UVA_{254}, and Full-Scale Wood achieving negligible removal. Therefore, since UVA_{254} is a quicker and lower cost measurement than DOC, it could be used for rapid screening of many greywater sorbents. SynGrey (Chapter 3) had the same rank order of DOC

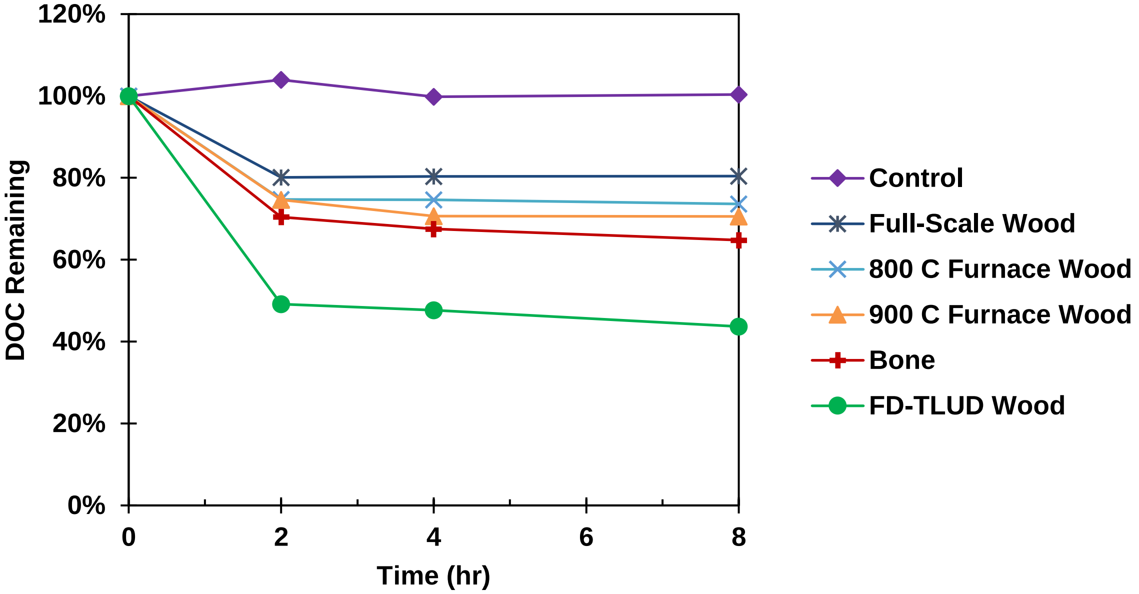


Figure 5.2. Biochar screening for DOC removal from real, filtered greywater. All sorbent doses were 2 g/L.

removal as the real greywater, so SynGrey would also be valid for screening greywater sorbents (Figure D.3). Wood biochars produced under similar conditions as FD-TLUD Wood have been found to be the best biochar for sulfamethoxazole removal from stormwater, wastewater effluent and surface water,[33] and for total trihalomethane removal from simulated surface water.[101] Therefore, FD-TLUD Wood could be considered an established, high performing biochar. Based on the results of the screening tests, FD-TLUD Wood was used for all subsequent comparisons to activated carbon.

5.3.2 Biochar versus Activated Carbon Comparison

The activated carbon removed more DOC than did the FD-TLUD Wood at all doses and on all greywater batches tested (Figure D.4). Five greywater batches were tested with both activated carbon and FD-TLUD Wood at sorbent doses of 1 and 2 g/L. At 1 g/L, FD-TLUD Wood removed 34±7% of DOC and activated carbon removed 58±12% of DOC. At 2 g/L, FD-TLUD Wood removed 43±8% of DOC and activated carbon removed 65±10% of DOC. Based on a paired t-test, activated carbon achieved statistically significantly greater percent DOC removal than FD-TLUD Wood at both doses (p-values of 0.03 and 0.0003 respectively). With FD-TLUD Wood, the DOC remaining tended to plateau around 5 mg/L or 20% above the minimum DOC remaining with activated carbon. This higher plateau indicates that there was a higher nonsorbable fraction with FD-TLUD Wood than with activated carbon. Due to this high plateau or nonsorbable fraction, the higher removals achieved with activated carbon were not possible with any dose of FD-TLUD Wood. The sorbability of each greywater batch varied. For example, 1 g/L activated carbon removed 46% to 73% of DOC depending on the greywater batch. No significant correlation was found between DOC removal and initial DOC or specific UV absorbance (SUVA).

While activated carbon removed significantly more DOC than FD-TLUD Wood, it did not remove sufficient DOC to reliably meet current regulatory targets without pretreatment. Regulations for greywater reuse vary by jurisdiction, but treatment targets including 10 mg/L BOD for toilet flushing and 25 mg/L BOD for irrigation are used in multiple countries and US states.[38,197] A typical BOD:DOC ratio of 3:1 has been measured in bathroom greywater (Table D.2),[202] so these treatment targets equate to approximately 8 mg/L DOC and 3 mg/L DOC respectively. The median raw DOC of greywater from the sampling location in this study is 29 mg/L (n=35). Thus, DOC removals of approximately 70% and 90% would be required to reach irrigation and toilet flushing treatment targets respectively. Activated carbon would require doses of greater than 2 g/L to reach the irrigation treatment target reliably, and neither sorbent could reach the toilet flushing target. Since sorption alone with activated carbon or FD-TLUD Wood would not be feasible for these treatment targets, pretreatments to use in combination with sorption were explored (Figure 5.1).

5.3.3 Pretreatment

5.3.3.1 Coagulation. As shown in Figure 5.3, the optimal dose for coagulating greywater was 2.6 mg/L as Al (30 mg/L alum). This dose achieved maximum removal of TOC and turbidity and a plateau of removal for DOC and UVA_{254}. Previous studies have reported higher optimal doses of 12 to 24 mg/L as Al, respectively.[202,204] The higher optimal doses in previous studies may be due to higher alkalinity. One of these previous studies did not report alkalinity, but the other reported an alkalinity of 289 mg/L as $CaCO_3$, which is much higher than the alkalinity of the greywater in this study, 44 mg/L as $CaCO_3$.

Maximum turbidity removal by alum coagulation was high at 94%, but DOC removal was low, around 20%. This DOC removal by coagulation was poor relative to surface waters, which may be related to the low SUVA of the greywater. In surface waters, lower SUVA is associated with lower DOC removal by coagulation.[61] The SUVA of this greywater sample was 0.30 L/mg/m, while the typical range of SUVA in

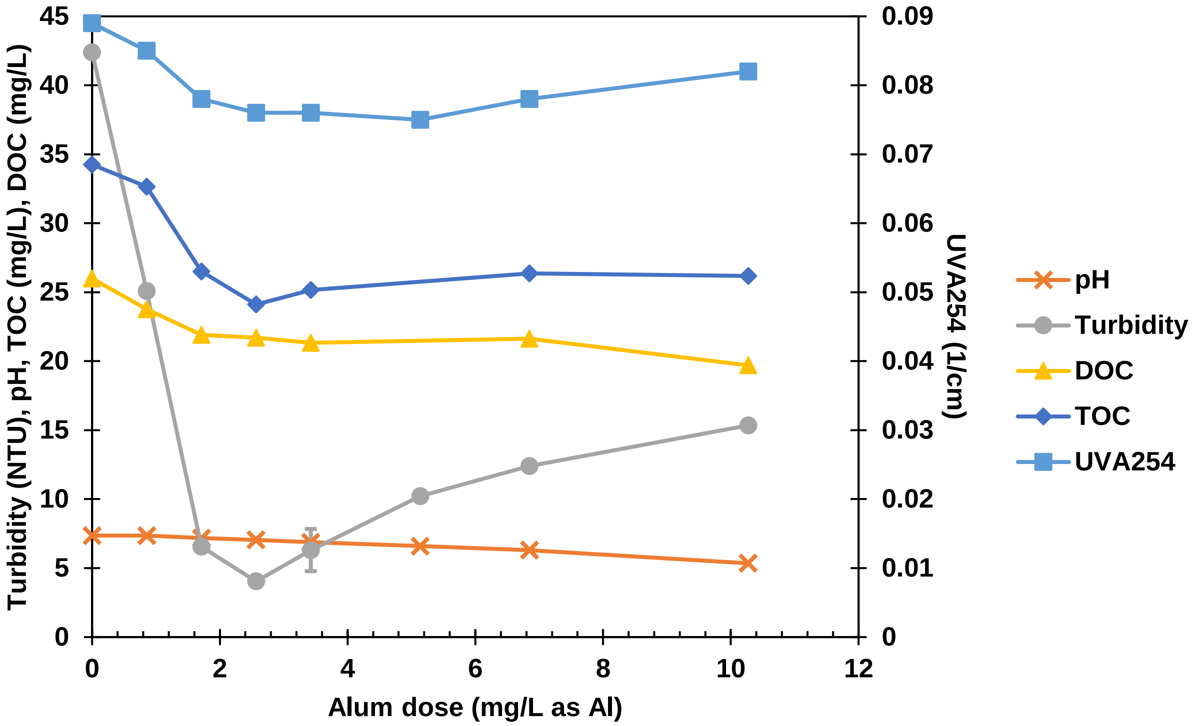


Figure 5.3. Coagulation of greywater. Error bars show range of experimental replicates for turbidity. Replicates were within ±7% for TOC, DOC, UVA_{254}, and pH.

surface water is 1.4 to 6.1 L/mg/m.[61] DOC removal from greywater by coagulation was not predicted well by the Coagulation Model (standard error = 29%).[61]

In the filtered greywater sample, 2 g/L of activated carbon was required to reach the irrigation treatment target (70% removal of DOC), but after coagulation with 30 mg/L alum, the required activated carbon dose was only about 0.75 g/L (Figure 5.4). However, sorption with FD-TLUD Wood after coagulation approached, but did not achieve the irrigation treatment target, and neither sorbent could reach the toilet flushing target. Similar percent removals by sorption were observed at each dose in the filtered and coagulated greywater samples. Therefore, coagulation and sorption were neither synergistic nor competing.

DOC and UVA_{254} removal were within ±10% regardless of whether the coagulant and sorbent were added sequentially or simultaneously (Figure D.5). Tests with sorption followed by coagulation found that 15 mg/L alum was sufficient to

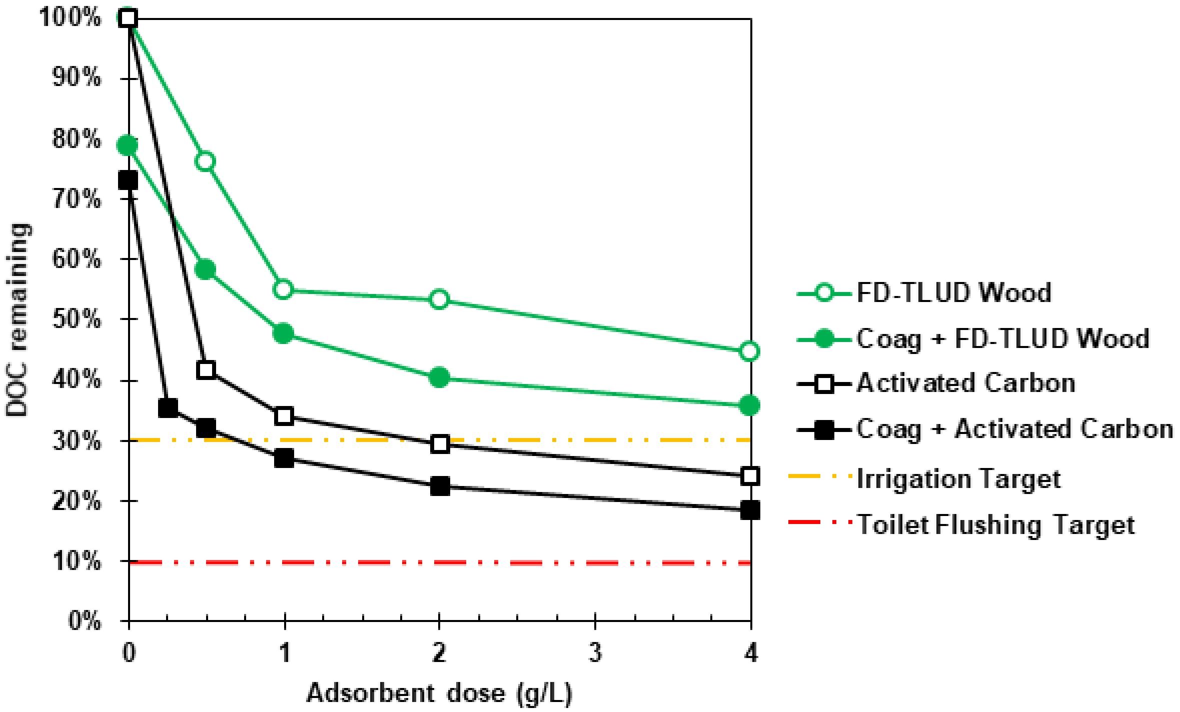


Figure 5.4. Removal of DOC from greywater with and without coagulation pretreatment at 30 mg/L alum ("Coag"). The orange and red lines represent the estimated DOC removals necessary for regulatory compliance for irrigation and toilet flushing, respectively. Experimental replicates at the 2 g/L dose were within ±10%.

remove 1 g/L of powdered activated carbon such that the turbidity was below 2 NTU, a common treatment target in greywater regulations (Figure D.6).[38,63,174,182,216] However, alum doses as high as 60 mg/L alum were insufficient to reduce the turbidity of greywater with 1 g/L FD-TLUD Wood to below 2 NTU. The difference in removal by coagulation between the two powdered sorbents may have been related to apparent density; the apparent density of the activated carbon was 640 g/cc,[237] and that for biochar in this study was 450 g/cc. The difference in removal by coagulation may also have been related to particle size distribution, since only a top sieve (i.e., maximum diameter of 45 µm) was applied to the powdered sorbents. By Stoke's Law, lower density and smaller particle diameter contribute to slower settling velocity.[196]

5.3.3.2 Rainwater Blending. The sorbents caused similar percent removals of DOC from rainwater-blended greywater as from the pure greywater, indicating that the percent removal of the greywater DOC is independent of initial concentration (Figure 5.5). The characteristics of the rainwater were 2 mg/L TOC, 2 mg/L DOC, 0.019 1/cm UVA_{254}, 7.7 pH, and 1 NTU turbidity. The DOC of the rainwater was <10% that of the greywater, so 50% blending with rainwater effectively divided the initial DOC of the greywater in half. Expected DOC concentrations in the sorbed, blended greywater were calculated be taking the average of the rainwater DOC and the DOC of the sorbed, unblended greywater at each sorbent dose. This expected DOC is what the final DOC would be if the rainwater blending step had taken place after sorption. Thus, the results indicate that it would be unimportant whether the greywater is blended with rainwater before or after sorption.

Furthermore, these results indicate that if the typical dose-response curve of the greywater is known, modeling the final DOC of blended greywater by mass balance is simple and accurate. That is, the final DOC of sorbed, blended greywater

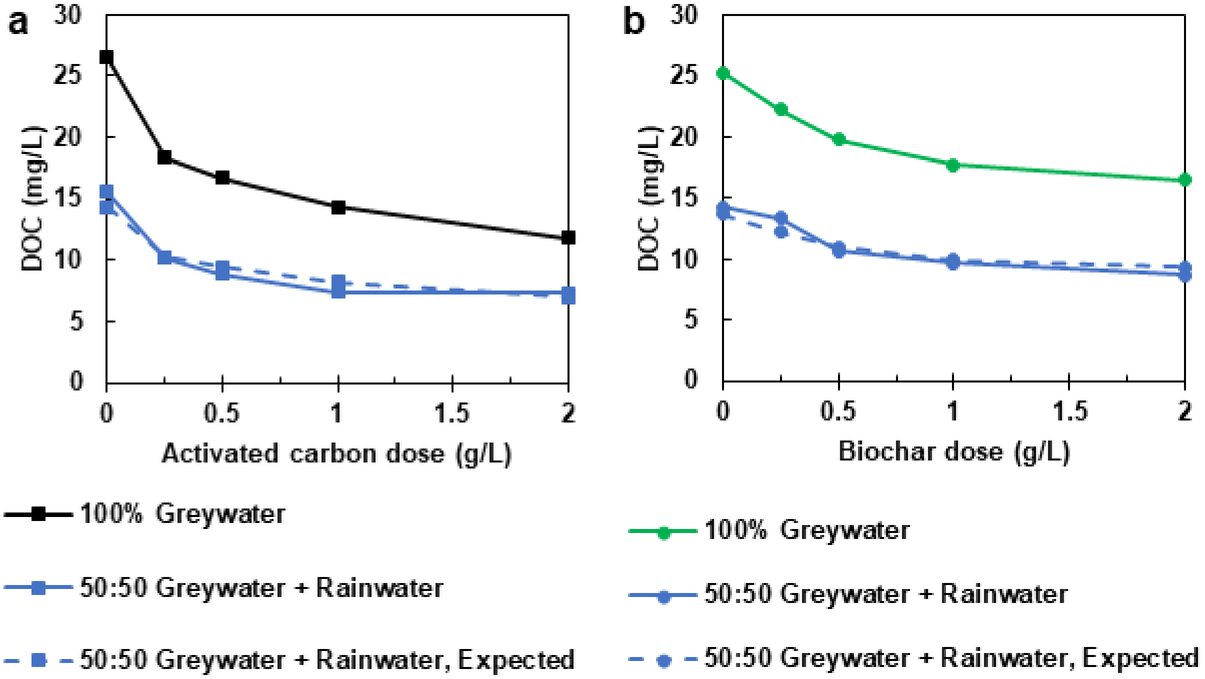


Figure 5.5. DOC removal from greywater by (a) activated carbon and (b) FD-TLUD Wood with and without 50% blending with rainwater. "Expected" refers to the calculated concentration of DOC if the rainwater blending had occurred after sorption instead of prior.

could be calculated by taking the weighted average of the DOC of the rainwater and the DOC of the sorbed pure greywater, even if the blending ratio fluctuated seasonally. Greywater Batch D, which was used for the rainwater blending experiments, was relatively challenging to sorb. However, based on this modeling approach and the average results from five greywater samples (Figure D.4), using 1 g/L activated carbon would require a 34% blend with rainwater to reach the irrigation target, or 90% blend with rainwater to meet the toilet flushing target. Using 1 g/L FD-TLUD Wood would require much higher rainwater ratio: 61% to reach the irrigation target, or 99% to reach the toilet flushing target.

However, there are limitations to this model. Previous research has found that percent removal of contaminants by sorption is independent of initial concentration only within certain ranges.[50] Across a wider range (i.e., orders of magnitude), greater percent removal of contaminants is expected at lower initial concentrations. Also, with a higher proportion of rainwater, or with first flush rainwater with higher DOC, the characteristics and sorbability of the rainwater DOC would begin to dominate. Sorption jar tests were not conducted on the rainwater sample in this study because the rainwater DOC was already below treatment targets and near the limit of quantitation.

5.3.3.3 Aeration. DOC removal was greatest in the jar with 12 rpm mixing speed and 24-hour residence time (Figure D.7); therefore, these conditions were selected for the aeration pretreatment experiment. Removal of TOC, COD, sCOD, and UVA_{254} were also similar or greater with a mixing speed of 12 rpm than with a mixing speed of 120 rpm (Figure D.7). Aerating raw greywater by stirring caused a significant drop in DOC over time (Figure D.7), but DOC was stable in stirred jars of filtered greywater (Figure 5.2 and Figure D.1). Therefore, the primary mechanism for DOC removal in aerated greywater was aerobic biodegradation, not volatilization. In the unstirred jars, DO fell to 0.9 mg/L, but in the 12 rpm jars, the DO was maintained above 3 mg/L (Figure D.7). While a mixing speed of 120 rpm maintained the DO at an even higher concentration, it did not cause a higher rate of removal compared to 12 rpm. Thus, stirring at 12 rpm was sufficient to maintain the DO at a high enough concentration to prevent oxygen from becoming limiting. A typical half-saturation constant of oxygen in wastewater is 0.1 mg/L,[181] and a similar half-saturation constant of oxygen in greywater would explain why a low mixing speed was sufficient.

Aeration was the most effective pretreatment before sorption. Aeration by stirring at 12 rpm mixing speed for 24 hours removed 45% of DOC from greywater. Without aeration, the activated carbon dose required for the irrigation target (70% DOC removal) was approximately 0.8 g/L, based on linear interpolation between the 0.5 g/L and 1 g/L doses (Figure 5.6). After aeration, the necessary dose of activated carbon for the irrigation target was approximately 0.15 g/L. Furthermore, the toilet flushing target (90% DOC removal) could be reached with aeration followed by an

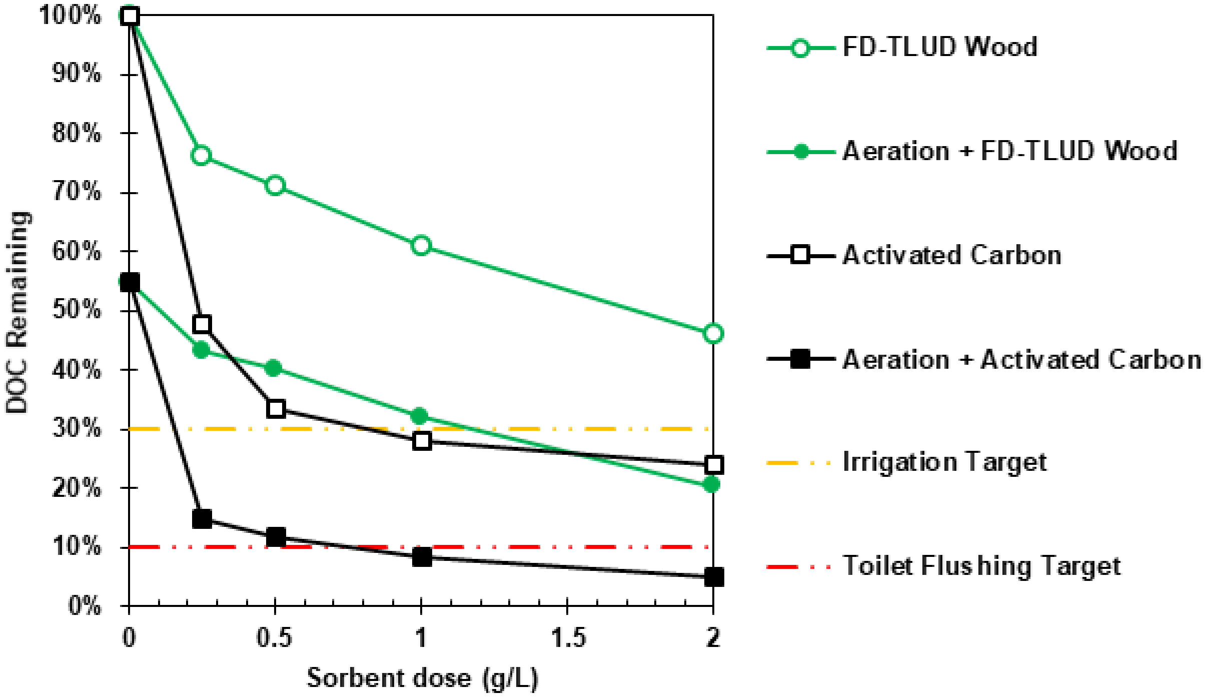


Figure 5.6. DOC removal from greywater by aeration and sorption. Aeration + FD-TLUD Wood and Aeration + Activated Carbon were stirred at 12 rpm for 24 hours prior to the addition of the respective sorbents.

activated carbon dose of approximately 0.75 g/L; this was the only treatment scenario which reached the toilet flushing target. Aeration followed by FD-TLUD Wood reached the irrigation target at a dose of approximately 1.2 g/L, or about eight times the required activated carbon dose. Therefore, FD-TLUD Wood would need to cost about an eight as much per mass to be cost-competitive with activated carbon in this scenario.

The aeration methods used in this study represent a simple, low cost approach to aerobic biological treatment, but the performance of aeration could improve with biomass retention, nutrient addition, or thermal insulation. For example, moving bed bioreactors increase the biomass in the system through the use free floating carriers that accumulate biofilm.[238] A previous study found that nutrient addition increased the rate of greywater biodegradation.[163] However, in practice, nutrient addition would add cost and complexity to the treatment system, and high levels of biological treatment is possible without it. In this study, aeration was conducted at 20 °C, the ambient temperature of the laboratory. However, the average temperature of raw greywater from the sampling location was 31 °C, at which temperature the biological degradation rate would likely be higher. For example, a previous study achieved over 90% removal of TOC and COD from mixed greywater with an aerobic sequencing bioreactor maintained at 32 °C.[239] Faster biodegradation due to biomass retention, nutrient addition, or thermal insulation would also cause faster oxygen consumption, so a greater mixing speed or air bubbling may be required.

5.3.4 Chlorine Demand

The reduction in free chlorine demand was less than that for DOC in all treatments tested. Coagulation with 30 mg/L alum had little impact on greywater batch G, the sample used for chlorination experiments; DOC was removed by only 8%, and chlorine demand was removed by only 5% (Figure 4.7). In terms of free chlorine demand reduction, coagulation was not useful as a pretreatment for sorption;

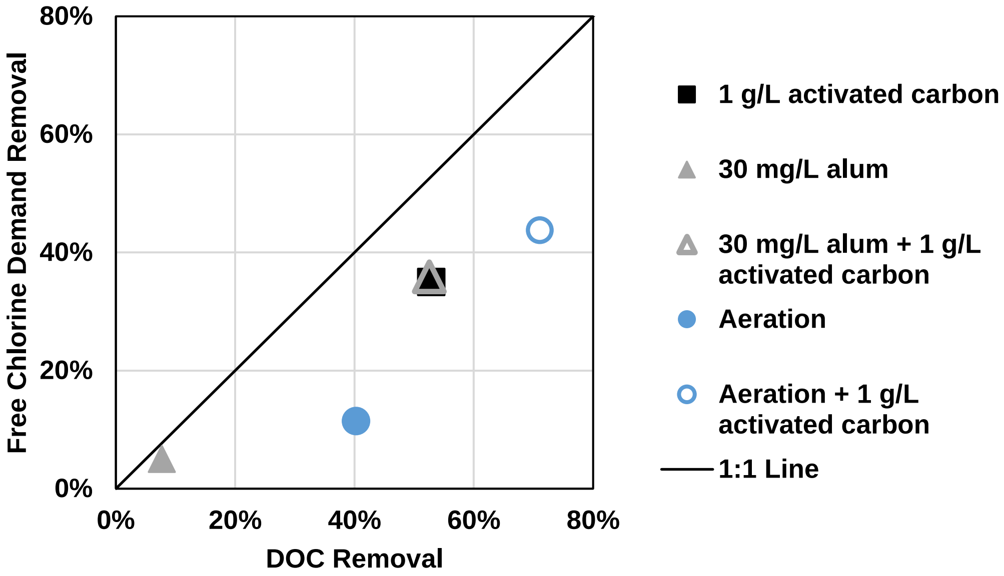


Figure 5.7. Comparison of free chlorine demand removal and DOC removal from greywater batch G by activated carbon, coagulation with alum, and aeration. Experimental replicates of 30 mg/L alum + 1 g/L activated carbon were within 2% in terms of final DOC, UVA254, and free chlorine demand.

the chlorine demand reduction for coagulation followed by sorption with 1 g/L activated carbon was negligibly higher than the free chlorine demand reduction of sorption alone. Aeration had the greatest difference in removals: DOC removal was 40%, but free chlorine demand removal was only 11%. Aeration followed by sorption with 1 g/L activated carbon removed 71% of DOC, sufficient for the irrigation treatment target, but the free chlorine demand was reduced by less than half.

The challenge in reducing free chlorine was partly due to the ammonia in the greywater. Greywater batch H had 2.37 mg/L ammonia as N; this is close to the median ammonia for this sampling location (2.5 mg/L ammonia as N), and the median ammonia concentration of bathroom greywater in the literature (2.7 mg/L ammonia as N).[46] The free chlorine demand due to this ammonia was approximately 18 mg/L as Cl_2, or 18% of the overall free chlorine demand, 101 mg/L as Cl_2. Aeration reduced the ammonia concentration by 34%, but coagulation and sorption had negligible impact. Even after adjusting for the free chlorine demand due to ammonia, free chlorine demand was still removed to a lesser extent than DOC. This finding indicates that the organic compounds in greywater that are most reactive with free chlorine also tend to be relatively recalcitrant to coagulation, sorption, and aerobic biodegradation.

5.3.5 UV Absorbance

Due to the expense meeting such a high chlorine demand, UV inactivation may be more promising for greywater disinfection than free chlorine. Greywater batch G had a free chlorine demand of 101 mg/L as Cl_2, orders of magnitude above the typical free chlorine demand of surface water, 2.1 to 7.8 mg/L as Cl_2.[198] In contrast, studies on UV disinfection of greywater have met treatment goals with doses ranging from 10 to 69 mJ/cm^2, which are comparable to UV doses used in drinking water treatment.[175,240,241] Furthermore, the free chlorine demand of the greywater was challenging to remove; free chlorine demand was always reduced to a lesser extent than DOC. In contrast, UVA_{254} was readily removed by sorption; UVA_{254} was reduced to a greater extent than DOC in all jars with activated carbon and most jars with FD-TLUD Wood. Reducing UVA_{254} (i.e., increasing UV transmittance) improves the efficiency of UV disinfection because it increases the effective UV dose for a given irradiance at the water surface.[242] The average initial UV transmittance of the greywater was 71±7%. Sorption with 1 g/L activated carbon was sufficient to increase UV transmittance to 98% or greater. After aeration, 0.25 g/L activated carbon was sufficient to increase UV transmittance to 98%. Turbidity can also interfere with UV disinfection,[243] but would be removed by the same coagulation or filtration step used to removed powdered sorbents from solution.

UVA_{254} removal correlated well with DOC removal. Including all data for activated carbon and FD-TLUD Wood at 2 hours of contact time without pretreatment (n=36), DOC remaining (mg/L) and UVA_{254} remaining (1/cm) were linearly correlated with an R^2 of 0.75 (Figure 5.8). The slope was 94±9 cm*mg/L with

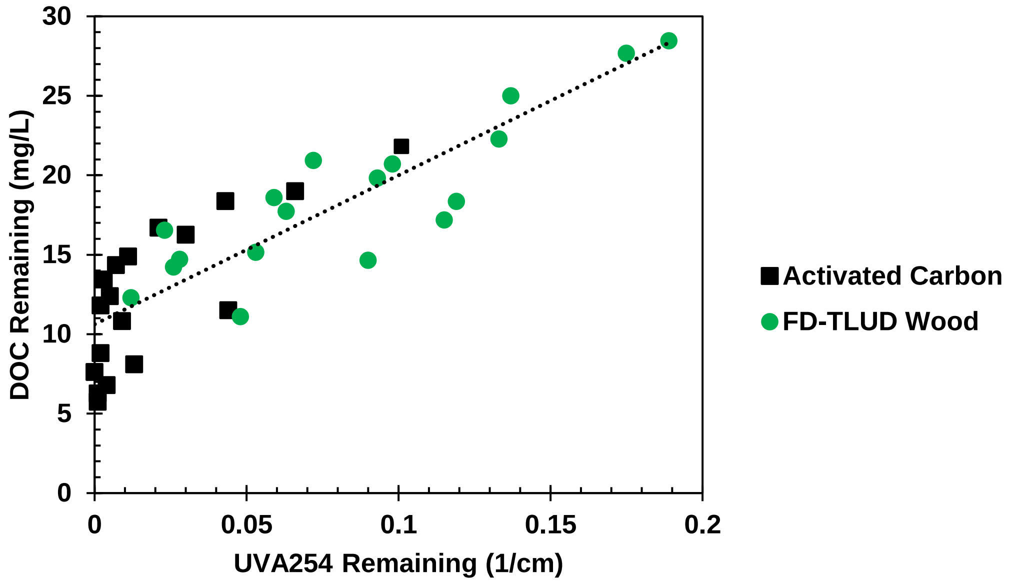


Figure 5.8. Correlation between UVA_{254} and DOC remaining after sorption by activated carbon (black squares) and biochar (green circles). The slope and intercept of the linear correlation (dashed black line) were 94±9 cm*mg/L and 10.6±0.7 mg/L respectively. All contact times were 2 hours. Data is included for greywater batches C through G.

an intercept of 10.6±0.7 mg/L. Linear regression of the percent DOC and percent UVA_{254} remaining resulted in a slightly similar R^2 of 0.72, because this approach avoided error due to fluctuation in the initial DOC and UVA_{254} (Figure D.8). The intercept of 10.6 mg/L DOC (or 40% when correlating the percent remaining) indicates that there is a portion of the greywater DOC that is recalcitrant to sorption and that does not absorb UV radiation at a wavelength of 254 nm. This portion of greywater DOC may include surfactants such as sodium dodecyl sulfate and cocoamidopropyl betaine. These surfactants are highly soluble and do not include aromatic groups or conjugated double bonds, functional groups associated with UVA_{254}. Including data for activated carbon and biochar sorption after pretreatment (n=61), the R^2 was also high at 0.69, and the slope was statistically similar to the regression for sorption only, but the intercept was statistically significantly lower at

8.2±0.6 mg/L DOC (Figure D.9). This lower intercept indicates that some of the fraction of DOC that is recalcitrant to sorption was removed by pretreatment.

UVA_{254} could be monitored in-line at the treatment system effluent. In-line monitoring would increase the reliability of a greywater treatment system and could cost less than regular lab testing. If the UVA_{254} were above a threshold, an alert could be sent to the operator or the degree of treatment could increase automatically, such as by increasing the dose of coagulant or sorbent or increasing the residence time in a bioreactor or sorption column. However, since the intercept of the correlation was 10.6±0.7 mg/L (or 8.2±0.6 mg/L with pretreatment), any detectable UVA_{254} would indicate that the treatment target had already been exceeded been exceed for toilet flushing and may have been exceeded for irrigation.

5.4 Conclusion

Five biochars were screened and FD-TLUD Wood was selected as the most effective for DOC removal from bathroom greywater. However, activated carbon removed significantly more DOC than FD-TLUD Wood at all doses. Neither sorption nor any of the pretreatments explored would consistently meet current regulations on their own, but certain combinations of processes were promising. For example, aeration was found to be the most effective pretreatment prior to sorption. Aeration followed by sorption with 0.25 g/L activated carbon achieved over 70% DOC removal, sufficient for irrigation reuse, and aeration followed by sorption with 1 g/L activated carbon achieved of 90% DOC removal, sufficient for toilet flushing reuse. Aeration followed by 1.2 g/L FD-TLUD Wood also met the irrigation target. Coagulation was less effective than aeration for greywater DOC removal, though coagulation followed by activated carbon could reach the irrigation target. UVA_{254} was reduced more than DOC, but chlorine demand was reduced less.

The results of this study indicate that biochar is less effective relative to activated carbon for greywater treatment on a mass sorbent basis. Activated carbon removed more DOC than biochar at all doses, on all greywater batches, and after all pretreatments. A higher fraction of the greywater DOC was nonsorbable with the biochar as with the activated carbon. While an established high performing biochar was used in this study, further improvements in biochar technology such as double-heating[244] may make biochar more competitive for greywater treatment in the future. However, biochar is significantly less expensive than activated carbon on a mass basis, so comparisons in a practical setting should be done on a cost to treat basis.

CHAPTER 6

CONCLUSIONS

The work presented in this dissertation evaluated data gaps in the literature on the use of alternative source waters. This dissertation utilized bench-scale treatment methods and modeling approaches to address the research needs for the use of sorption and conventional drinking water treatment (CDWT) in reuse. This chapter first summarizes the key findings of this dissertation, organized by alternative source water. Lastly, an overview is provided of (1) the successes and limitations of the treatment technologies tested, (2) advantages and disadvantages of the alternative source waters tested, and (3) the contributions of this work and recommendations for future research.

6.1 Stormwater

It was found that CDWT was highly effective for stormwater treatment, with maximum turbidity removal of 1 to 2 logs and maximum TOC removal of 16% to 66%. In stormwaters from grassy or mixed-use drainage basins, significant TOC and turbidity removal was achieved with alum doses comparable to those used in surface water treatment. Therefore, this work proved that CDWT can play an important role in stormwater reuse. However, stormwater quality and treatability varied greatly depending on drainage basin characteristics and precipitation conditions. For example, two stormwater samples from the same location but under different precipitation conditions differed by orders of magnitude in both initial and treated water quality. Therefore, this study demonstrated that stormwater reuse projects should include careful selection and management of the drainage basin, and the ability to divert contaminated stormwater from unfavorable precipitation conditions.

6.2 Wastewater Effluent

While wastewater effluents needed little or no addition of coagulant to meet turbidity standards for surface water reservoir augmentation, CDWT was needed for organic matter removal. DOC removal by coagulation from wastewater effluents was similar to low-SUVA surface waters. However, the organic matter removal by coagulation would be insufficient to meet DBP regulations after chlorination, so advanced treatment or significant blending would be required. DOC removal from a blend of wastewater effluent and surface water was accurately predicted by a coagulation model developed for drinking water source waters and by taking the weighted average of the treated quality of the unblended waters. These results: (1) show which secondary treatments systems result in wastewater effluent that is most suitable for reuse (2) enable engineers to predict DOC removal from blended and unblended wastewater effluent, and (3) assist engineers in determining the degree of advanced treatment or dilution required for safe, sustainable wastewater reuse. In terms of the range from cleanest to most contaminated and model predictions, wastewater effluent was more predictable and reliable than stormwater. Increasing storage or equalization could further enhance the relative reliability of wastewater effluent.

Using life cycle assessment, biochar was found to be a more environmentally sustainable alternative to activated carbon in the context of micropollutant removal from wastewater effluent. The relative sustainability of biochar for tertiary wastewater treatment depends on adsorption capacity and feedstock. For example, moderate capacity wood biochar (requiring approximately twice as much mass as activated carbon to achieve the same treatment target) was more environmentally sustainable in eight of ten impact categories, but low capacity wood biochar (requiring approximately nine times as much mass as activated carbon to achieve the same treatment target) was more environmentally sustainable in only five of ten impact categories, indicating significant environmental tradeoffs. Furthermore, biosolids biochar was environmentally inferior to both activated carbon and wood biochar, primarily due to higher energy required for drying before pyrolysis. This research motivates the development of biochars with even greater adsorption capacity for contaminants of concern in wastewater effluent and directs researchers to focus on the most environmentally sustainable biochar feedstocks. This research also motivates experimental and life cycle assessment studies of biochar versus activated carbon for other treatment applications.

6.3 Greywater

A thorough literature review was conducted on the ranges of real bathroom greywater characteristics, and all previous synthetic greywaters were found to fall outside of most of these ranges. This finding demonstrated the need for new, more representative synthetic greywater. SynGrey was designed to fall between the 25th and 75th percentiles of real bathroom greywater for 20 water quality parameters. Experiments with biodegradation, coagulation, sorption, and chlorination where then conducted to further characterize and compare the treatability of both real bathroom greywater and SynGrey. SynGrey closely matched behavior of real bathroom greywater in biodegradation, sorption, and chlorination. SynGrey will serve as a tool to enhance the reproducibility and accessibility of greywater treatment research, and the treatment results from this study can be used for the selection of the most appropriate treatment process combinations for greywater reuse.

Compared to biochar, activated carbon removed more DOC from greywater on a mass basis. Biochar did not meet the treatment targets for toilet flushing (90% removal of DOC) even after pretreatment. However, biochar could meet the treatment target for irrigation (70% removal of DOC) after aeration with a dose of approximately 1.2 g/L. Activated carbon could reach the treatment target for irrigation after aeration with a dose of approximately 0.15 g/L. Therefore, the biochar would need to cost approximately an eighth as much as activated carbon to be cost-competitive in this scenario. This research will motivate the development of higher performing biochars for bulk organic matter removal, or direct researchers to focus on more competitive applications for biochar sorption.

6.4 Overview

Overall, CDWT caused high turbidity removal in both stormwater and greywater. Relative to surface water, removal of TOC by CDWT was wide-ranging for stormwater, low for greywater, and moderately low for wastewater effluent. However, the calculated cytotoxicity of measured DBPs was not significantly reduced by CDWT in most alternative source water samples. Biochar could be a sustainable alternative to activated carbon for tertiary wastewater treatment; however, further improvements to biochar are needed before biochar would be an effective alternative to activated carbon for greywater reuse. Both coagulation and sorption would be insufficient as standalone processes but have important roles to play in sustainable reuse, particularly as pretreatments before advanced treatment or disinfection.

In terms of both the range from most to least contaminated and the accuracy of the models tested, wastewater effluent is more reliable or consistent than stormwater. Additional storage or equalization of wastewater effluent could further enhance this relative reliability. For both wastewater effluent and stormwater, DBPs are a critical challenge and blending or advanced treatment would be required. Greywater is more suited for decentralized than centralized reuse. However, it would require expensive or multi-component treatment systems to achieve current regulations for turbidity and organic matter.

The findings in this thesis will (1) enable decision-makers to select the most appropriate alternative source water for their communities, (2) encourage the inclusion of but not sole reliance upon existing CDWT infrastructure in reuse treatment trains, (3) aid engineers in the selection and design of treatment processes for potable and non-potable reuse, and (4) direct researchers towards the most sustainable feedstocks and applications for biochar. Overall, this research has filled key gaps in the reuse literature. It will direct scientists and engineers to pursue the most promising applications for coagulation and sorption, and towards finding solutions to the most critical ongoing challenges for safe, sustainable water reuse. Future research on further improvements to biochar and a greater understanding of DBP formation in alternative source waters is especially encouraged.

REFERENCES

1 M. M. Mekonnen and A. Y. Hoekstra, *Sci. Adv.*, 2016, **2**, e1500323–e1500323.

2 S. L. Postel, *Ecol. Appl.*, 2000, **10**, 941–948.

3 W. Shi, M. Wang and W. Guo, *J. Geophys. Res. Ocean.*, 2014, **119**, 3313–3326.

4 D. Lauwaet, N. P. M. van Lipzig, K. Van Weverberg, K. De Ridder and C. Goyens, *Q. J. R. Meteorol. Soc.*, 2012, **138**, 707–719.

5 W. D. Williams, *Environ. Conserv.*, 2002, **29**, 154–167.

6 S. E. Bunn and A. H. Arthington, *Environ. Manage.*, 2002, **30**, 492–507.

7 UN Water and FAO, *Coping With Water Scarcity-Challege of the Twenty-First Century*, United Nations, New York, 2007.

8 L. Changming, Y. Jingjie and E. Kendy, *Water Int.*, 2001, **26**, 265–272.

9 S. Contreras-B. and M. L. Lozano-V., *Conserv. Biol.*, 2016, **8**, 379–387.

10 J. Rice and P. Westerhoff, *Environ. Sci. Technol.*, 2015, **49**, 982–989.

11 J. Rice, S. H. Via and P. Westerhoff, *J. Am. Water Works Assoc.*, 2015, **107**, E571–E581.

12 J. Rice and P. Westerhoff, *Nat. Geosci.*, 2017, **10**, 587–591.

13 C. J. Vörösmarty, C. J. Vo and P. Green, *Science (80-.).*, 2007, **284**, 284–289.

14 S. N. Gosling and N. W. Arnell, *Clim. Change*, 2016, **134**, 371–385.

15 A. E. Ercin and A. Y. Hoekstra, *Environ. Int.*, 2014, **64**, 71–82.

16 Y. Jiang, *J. Environ. Manage.*, 2009, **90**, 3185–3196.

17 R. R. Trussell, H. A. Anderson, E. G. Archuleta, J. Crook, J. E. Drewes, D. D. Fort, C. N. Haas, B. M. Haddad, D. B. Huggett, S. Jiang, D. L. Sedlak, S. A. Snyder, M. H. Whittaker and D. Whittington, *Water Reuse: Potential for Expanding the Nation's Water Supply Through Reuse of Municipal Wastewater*, The National Academies Press, Washington, DC, 2012.

18 E. Amoueyan, S. Ahmad, J. N. S. Eisenberg, B. Pecson and D. Gerrity, *Water Res.*, 2017, **119**, 252–266.

19 R. M. Chaudhry, K. A. Hamilton, C. N. Haas and K. L. Nelson, *Int. J. Environ. Res. Public Health*, 2017, **14**, 1–20.

20 A. Hurlimann and S. Dolnicar, *Water Res.*, 2010, **44**, 287–297.

21 I. Michael, L. Rizzo, C. S. McArdell, C. M. Manaia, C. Merlin, T. Schwartz, C. Dagot and D. Fatta-Kassinos, *Water Res.*, 2013, **47**, 957–995.

22 T. Zeng, M. J. Plewa and W. A. Mitch, *Water Res.*, 2016, **101**, 176–186.

23 M. G. Muellner, E. D. Wagner, K. Mccalla, S. D. Richardson, Y. T. Woo and M. J. Plewa, *Environ. Sci. Technol.*, 2007, **41**, 645–651.

24 M. Inyang and E. R. V. Dickenson, *Chemosphere*, 2017, **184**, 168–175.

25 Y. Alfiya, E. Friedler, J. Westphal, O. Olsson and Y. Dubowski, *Sci. Total Environ.*, 2017, **601–602**, 397–404.

26 M. Park, T. Anumol, K. D. Daniels, S. Wu, A. D. Ziska and S. A. Snyder, *Water Res.*, 2017, **119**, 21–32.

27 E. J. Marti, E. R. V. Dickenson, R. A. Trenholm and J. R. Batista, *J. Am. Water Work. Assoc.*, 2017, **109**, 273–285.

28 K. V. Plakas, A. J. Karabelas and A. A. Georgiadis, *Water Sci. Technol.*, 2016, **73**, 1532–1540.

29 P. McArdle, J. Gleeson, T. Hammond, E. Heslop, R. Holden and G. Kuczera, *Water Sci. Technol.*, 2011, **63**, 16–24.

30 Orange City Council, Blackmans Swamp Creek Stormwater Harvesting Scheme, http://www.orange.nsw.gov.au/site/index.cfm?display=147115, (accessed 17 September 2017).

31 J. R. Vogel and T. L. Moore, *Water Environ. Res.*, 2016, **88**, 1918–1950.

32 Y. Han, S.-L. Lau, M. Kayhanian and M. K. Stenstrom, *Water Environ. Res.*, 2006, **78**, 2377–2388.

33 K. K. Shimabuku, J. P. Kearns, J. E. Martinez, R. B. Mahoney, L. Moreno-Vasquez and R. S. Summers, *Water Res.*, 2016, **96**, 236–245.

34 D. Page, J. Vanderzalm, P. Dillon, D. Gonzalez and K. Barry, *Water. Air. Soil Pollut.*, , DOI:10.1007/s11270-016-3021-x.

35 I. M. Brodie, *J. Water Reuse Desalin.*, 2012, **2**, 13.

36 J.-H. Kang, Y. Li, S.-L. Lau, M. Kayhanian and M. K. Stenstrom, *J. Environ. Eng.*, 2007, **133**, 426–434.

37 J. J. Sansalone and J. Y. Kim, *Water Res.*, 2008, **42**, 909–922.

38 Y. Boyjoo, V. K. Pareek and M. Ang, *Water Sci. Technol.*, 2013, **67**, 1403–1424.

39 E. Friedler and M. Hadari, *Desalination*, 2006, **190**, 221–234.

40 T. Opher and E. Friedler, *J. Environ. Manage.*, 2016, **182**, 464–476.

41 P. Humeau, F. Hourlier, G. Bulteau, A. Massé, P. Jaouen, C. Gérente, C. Faur and P. Le Cloirec, *Water Sci. Technol.*, 2011, **63**, 2949–2956.

42 Raftelis Financial Consultants Inc. and AWWA, in *2012 Water and Wastewater Rate Survey*, AWWA, 2013, pp. 1–9.

43 Z. L. T. Yu, A. Rahardianto, M. K. Stenstrom and Y. Cohen, *J. Am. Water Works Assoc.*, 2016, **108**, E392–E404.

44 C. Ramprasad, C. S. Smith, F. A. Memon and L. Philip, *Ecol. Eng.*, 2017, **106**, 55–65.

45 Y. M. Patil and G. R. Munavalli, *Ecol. Eng.*, 2016, **95**, 492–500.

46 K. A. Thompson, R. S. Summers and S. M. Cook, *Environ. Sci. Water Res. Technol.*, 2017, **3**, 1120–1131.

47 E. C. Wert, S. Gonzales, M. M. Dong and F. L. Rosario-Ortiz, *Water Res.*, 2011, **45**, 5191–5199.

48 Intergovernmental Panel on Climate Change, *IPCC Special Report: Emission Scenarios*, 2000.

49 D. Gerrity, S. Gamage, D. Jones, G. V. Korshin, Y. Lee, A. Pisarenko, R. A. Trenholm, U. von Gunten, E. C. Wert and S. A. Snyder, *Water Res.*, 2012, **46**, 6257–6272.

50 K. K. Shimabuku, J. M. Paige, M. Luna-Aguero and R. S. Summers, *Environ. Sci. Technol.*, 2017, **51**, 10031–10040.

51 I. Michael-Kordatou, C. Michael, X. Duan, X. He, D. D. Dionysiou, M. A. Mills and D. Fatta-Kassinos, *Water Res.*, 2015, **77**, 213–248.

52 J. J. Mosher, G. M. Vartanian and G. Tchobanoglous, *Potable Reuse Research*

Compilation: Synthesis of Findings, Fountain Valley, CA, 2016.
53 N. Tran, P. Drogui, J. F. Blais and G. Mercier, *Sep. Purif. Technol.*, 2012, **95**, 16–25.
54 J. W. Hatt, E. Germain and S. J. Judd, *Water Res.*, 2011, **45**, 6471–6478.
55 W. C. Sonzogni, G. Chesters, D. R. Coote, J. C. Konrad, D. N. Jeffs, R. C. Ostry and J. B. Robinson, *Environ. Sci. Technol.*, 1980, **14**, 148–153.
56 P. L. Brezonik and T. H. Stadelmann, *Water Res.*, 2002, **36**, 1743–1757.
57 R. S. Summers, S. M. Hooper, H. M. Shukairy, G. Solarik and D. Owen, *J. / Am. Water Work. Assoc.*, 1996, **88**, 80–93.
58 D. Munch and D. Hautman, *Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents , and halogenated pesticides/ herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection*, Cincinnati, OH, 1995.
59 D. J. Munch, J. W. Munch and A. M. Pawlecki, *Method 552.2: Determination of Haloacetic Acids in Drinking Water By Liquid-Liquid Extraction, Derivatization and Gas Chromatography With Electron Capture Detection*, Cincinnati, OH, 1995.
60 E. D. Wagner and M. J. Plewa, *J. Environ. Sci.*, 2017, **58**, 64–76.
61 M. Edwards, *J. / Am. Water Work. Assoc.*, 1997, **89**, 78–89.
62 T. Tseng and M. Edwards, *J. Am. Water Work. Assoc.*, 1999, **91**, 159–170.
63 USEPA, *Guidelines for Water Reuse*, USEPA, Washington, DC, OH, 2012.
64 Partnership for Safe Water, *Partnership for Safe Water Guidelines for Phase IV Application for the 'Excellence in Water Treatment' Award*, Denver, CO, 2011.
65 S. J. Randtke, R. C. Hoehn, W. R. Knocke, A. M. Dietrich, B. W. Long and N. Wang, in *Annual Conference - Water Quality*, 1994, pp. 737–777.
66 D. B. Booth and C. R. Jackson, *J. Am. Water Resour. Assoc.*, 1997, **33**, 1077–1090.
67 L. H. Kim, M. Kayhanian, K. D. Zoh and M. K. Stenstrom, *Sci. Total Environ.*, 2005, **348**, 1–18.
68 The Council of the European Union, *Off. J. Eur. Communities*, 1998, **L330**, 32–54.
69 USEPA, National Primary Drinking Water Regulations, https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations, (accessed 29 December 2017).
70 E. Sawade, R. Fabris, A. Humpage and M. Drikas, *J. Water Health*, 2016, **14**, 183–191.
71 S. W. Krasner, T. C. F. Lee, P. Westerhoff, N. Fischer, D. Hanigan, T. Karanfil, W. Beita-Sandí, L. Taylor-Edmonds and R. C. Andrews, *Environ. Sci. Technol.*, 2016, **50**, 9583–9591.
72 K. R. Dailey, K. A. Welch and W. B. Lyons, *Appl. Geochemistry*, 2014, **47**, 25–35.
73 A. K. Hohner, L. G. Terry, E. B. Townsend, R. S. Summers and F. Rosario, *Environ. Sci. Water Res. Technol.*, 2017, **3**, 18–20.

74 World Health Organization, *Guidelines for Drinking-water Quality*, WHO Press, Geneva, Switzerland, 4th edn., 2011.

75 USEPA, Secondary Drinking Water Standards: Guidance for Nuisance Chemicals, https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals, (accessed 29 July 2017).

76 M. J. McGuire, J. L. Mclain and A. Obolensky, *Information Collection Rule Data Analysis*, WRF and AWWA, Denver, CO, 2002.

77 J. A. Korak, F. L. Rosario-Ortiz and R. S. Summers, *Environ. Sci. Water Res. Technol*, 2015, **1**, 493–506.

78 D. M. Mcknight, E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe and D. T. Andersen, *Limnol. Ocean.*, 2001, **46**, 38–48.

79 S. W. Krasner, P. Westerhoff, B. Chen, B. E. Rittmann, S.-N. Nam and G. Amy, *Environ. Sci. Technol.*, 2009, **43**, 2911–2918.

80 L. G. Terry, University of Colorado Boulder, 2017.

81 L. Rizzo, C. Manaia, C. Merlin, T. Schwartz, C. Dagot, M. C. Ploy, I. Michael and D. Fatta-Kassinos, *Sci. Total Environ.*, 2013, **447**, 345–360.

82 L. Kovalova, D. R. U. Knappe, K. Lehnberg, C. Kazner and J. Hollender, *Environ. Sci. Pollut. Res.*, 2013, **20**, 3607–3615.

83 R. Mailler, J. Gasperi, Y. Coquet, S. Deshayes, S. Zedek, C. Cren-Oliv??, N. Cartiser, V. Eudes, A. Bressy, E. Caupos, R. Moilleron, G. Chebbo and V. Rocher, *Water Res.*, 2014, **72**, 315–330.

84 P. Bayer, E. Heuer, U. Karl and M. Finkel, *Water Res.*, 2005, **39**, 1719–1728.

85 J. Jin, M. Kang, K. Sun, Z. Pan, F. Wu and B. Xing, *Sci. Total Environ.*, 2016, **550**, 504–513.

86 S. S. Mayakaduwa, P. Kumarathilaka, I. Herath, M. Ahmad, M. Al-Wabel, Y. S. Ok, A. Usman, A. Abduljabbar and M. Vithanage, *Chemosphere*, 2016, **144**, 2516–2521.

87 D. Shan, S. Deng, T. Zhao, B. Wang, Y. Wang, J. Huang, G. Yu, J. Winglee and M. R. Wiesner, *J. Hazard. Mater.*, 2016, **305**, 156–163.

88 M. B. Ahmed, J. L. Zhou, H. H. Ngo and W. Guo, *Sci. Total Environ.*, 2015, **532**, 112–126.

89 K. Sun, K. Ro, M. Guo, J. Novak, H. Mashayekhi and B. Xing, *Bioresour. Technol.*, 2011, **102**, 5757–5763.

90 S. Shackley, A. Clare, S. Joseph, B. A. McCarl and H.-P. Schmidt, in *Biochar for Environmental Management*, eds. J. Lehmann and S. Joseph, Routledge, New York, 2nd edn., 2015, pp. 813–852.

91 Alibaba.com, 325 Mesh Powdered Activated Carbon Factory Price, alibaba.com, (accessed 12 February 2016).

92 J. F. Peters, D. Iribarren and J. Dufour, *Environ. Sci. Technol.*, 2015, **49**, 5195–5202.

93 L. Miller-Robbie, B. A. Ulrich, D. F. Ramey, K. S. Spencer, S. P. Herzog, T. Y. Cath, J. R. Stokes and C. P. Higgins, *J. Clean. Prod.*, 2015, **91**, 118–127.

94 R. Ibarrola, S. Shackley and J. Hammond, *Waste Manag.*, 2012, **32**, 859–868.

95 K. G. Roberts, B. A. Gloy, S. Joseph, N. R. Scott and J. Lehmann, *Environ.*

Sci. Technol., 2010, **44**, 827–833.
96 Q. Liu, B. Liu, P. Ambus, Y. Zhang, V. Hansen, Z. Lin, D. Shen, G. Liu, Q. Bei, J. Zhu, X. Wang, J. Ma, X. Lin, Y. Yu, C. Zhu and Z. Xie, *GCB Bioenergy*, 2016, **8**, 148–159.
97 K. Homagain, C. Shahi, N. Luckai and M. Sharma, *J. For. Res.*, 2015, **26**, 799–809.
98 A. Clare, S. Shackley, S. Joseph, J. Hammond, G. Pan and A. Bloom, *GCB Bioenergy*, 2015, **7**, 1272–1282.
99 N. D. Berge, L. Li, J. R. V Flora and K. S. Ro, *Waste Manag.*, 2015, **43**, 203–217.
100 W. Ouyang, X. Zhao, M. Tysklind and F. Hao, *Water Res.*, 2016, **92**, 156–163.
101 J. P. Kearns, K. K. Shimabuku, R. B. Mahoney, D. R. U. Knappe and R. S. Summers, *J. Water Sanit. Hyg. Dev.*, 2015, **5**, 359–372.
102 B. Chen, D. Zhou and L. Zhu, *Environ. Sci. Technol.*, 2008, **42**, 5137–5143.
103 M. Ahmad, S. S. Lee, X. Dou, D. Mohan, J. K. Sung, J. E. Yang and Y. S. Ok, *Bioresour. Technol.*, 2012, **118**, 536–544.
104 T. Mattila, J. Grönroos, J. Judl and M. R. Korhonen, *Process Saf. Environ. Prot.*, 2012, **90**, 452–458.
105 M. Sparrevik, H. Lindhjem, V. Andria, A. M. Fet and G. Cornelissen, *Environ. Sci. Technol.*, 2014, **48**, 4664–4671.
106 M. Sparrevik, J. L. Field, V. Martinsen, G. D. Breedveld and G. Cornelissen, *Environ. Sci. Technol.*, 2013, **47**, 1206–1215.
107 M. Wepf, 100 Water Treatment Plants must be Upgraded, https://www.news.admin.ch/message/index.html?lang=en&print_style=yes&msg-id=58567, (accessed 28 June 2016).
108 The International Standards Organisation, *Environmental management — Life cycle assessment — Principles and framework*, ISO, Geneva, 2nd edn., 2006, vol. 2006.
109 D. W. Kolpin, E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton, *Environ. Sci. Technol.*, 2002, **36**, 1202–1211.
110 K. Chen and J. L. Zhou, *Chemosphere*, 2014, **95**, 604–612.
111 M. J. García-Galán, S. González Blanco, R. López Roldán, S. Díaz-Cruz and D. Barceló, *Sci. Total Environ.*, 2012, **437**, 403–412.
112 P. Westerhoff, Y. Yoon, S. Snyder and E. Wert, *Env. Sci Technol*, 2005, **39**, 6649–6663.
113 C. J. Corwin and R. S. Summers, *J. Am. Water Works Assoc.*, 2012, **104**, 43–44.
114 P. Gao, Y. Ding, H. Li and I. Xagoraraki, *Chemosphere*, 2012, **88**, 17–24.
115 R. Hirsch, T. Ternes, K. Haberer and K. L. Kratz, *Sci. Total Environ.*, 1999, **225**, 109–118.
116 A. Bhandari, L. I. Close, W. Kim, R. P. Hunter, D. E. Koch and R. Y. Surampalli, *Pract. Period. Hazardous, Toxic, Radioact. Waste Manag.*, 2008, **12**, 275–281.
117 J. Levine, 2015.

118 ASTM International, *D2035-13 Standard Practice for Coagulation-Flocculation Jar Test of Water*, ASTM International, Conshohocken, PA, 2013.
119 AWWA, *AWWA B600-10 Powdered Activated Carbon*, AWWA, Denver, CO, 2010.
120 EarthShift, *US-EI Database.*, EarthShift, Huntington, VT, 2014.
121 Blonk Consultants, *Agri-footprint*, Blonk Consultants, Gouda, The Netherlands, 2015.
122 J. Bare, *Clean Technol. Environ. Policy*, 2011, **13**, 687–696.
123 Google Maps, Calgon Carbon, www.google.com/maps/search/calgon+carbon/, (accessed 11 March 2016).
124 Z. K. Chowdhury, R. S. Summers, W. P. Garret, B. J. Leto, K. O. Nowack and C. J. Corwin, *Activated Carbon: Solutions for Improving Water Quality*, Denver, CO, 2013.
125 Norit Americas Inc., *Standard Activated Carbon Injection System Specification*, Marshall, TX, 2007.
126 Solimar Pneumatics, *Silo Fluidizer*, Minneapolis, MN, 2014.
127 FRC Systems International LLC, *Sludge Dewatering Belt Press*, Cummings, GA, 2015.
128 P. Sannigrahi, A. J. Ragauskas and G. A. Tuskan, *Biofuels, Bioprod. Biorefining*, 2010, **4**, 209–226.
129 A. Demirbas, *Prog. Energy Combust. Sci.*, 2004, **30**, 219–230.
130 G. Cornelissen, N. R. Pandit, P. Taylor, B. H. Pandit, M. Sparrevik and H. P. Schmidt, *PLoS One*, 2016, **11**, 1–16.
131 M. Sparrevik, G. Cornelissen, M. Sparrevik, C. Adam, V. Martinsen, G. Cornelissen and G. Cornelissen, *Biomass and Bioenergy*, 2015, **72**, 65–73.
132 Shanhai Clirik Manufacturing, Activated Carbon Crushing Plant/Grinding Plant, www.crusher-plant.net/industry_news/Activated-carbon-crushing-plant.html, (accessed 9 December 2017).
133 Sylvis, *The Biosolids Emissions Assessment Model (BEAM): A Method for Determining Greenhouse Gas Emissions from Canadian Biosolids Management Practices*, New Westminster, 2009.
134 Greenhouse Gas Technology Center, *Technology Assessment Report Aqueous Sludge Gasification Technologies*, USEPA, 1.5., 2012.
135 Boulder Wastewater Treatment Facility, *2011 Annual Report*, Boulder, CO, 2012.
136 D. Sullivan, C. Cogger and A. Bary, *Pacific Northwest Ext.*, 2007, 1–18.
137 H. Wang, L. Wang and A. Shahbazi, *J. Clean. Prod.*, 2015, **87**, 511–519.
138 A. Demirbas, *J. Hazard. Mater.*, 2009, **167**, 1–9.
139 N. Nipattummakul, I. I. Ahmed, S. Kerdsuwan and A. K. Gupta, *Int. J. Hydrogen Energy*, 2010, **35**, 11738–11745.
140 A. Hanief, D. Matiichine, A. E. Laursen, I. V. Bostan and L. H. McCarthy, *J. Environ. Qual.*, 2015, **0**, 0.
141 A. Hospido, T. Moreira, M. Martín, M. Rigola and G. Feijoo, *Int. J. Life Cycle Assess.*, 2005, **10**, 336–345.

142 K. McClellan and R. U. Halden, *Water Res.*, 2010, **44**, 658–668.
143 A. K. Venkatesan and R. U. Halden, *J. Hazard. Mater.*, 2013, **252–253**, 413–418.
144 A. K. Venkatesan and R. U. Halden, *Water Res.*, 2014, **55**, 133–142.
145 A. Hospido, M. Carballa, M. Moreira, F. Omil, J. M. Lema and G. Feijoo, *Water Res.*, 2010, **44**, 3225–3233.
146 S. E. Hale, H. P. H. Arp, D. Kupryianchyk and G. Cornelissen, *Chemosphere*, 2016, **144**, 65–74.
147 G. Rodriguez-Garcia, M. Molinos-Senante, A. Hospido, F. Hernández-Sancho, M. T. Moreira and G. Feijoo, *Water Res.*, 2011, **45**, 5997–6010.
148 A. Y. Hoekstra, M. M. Mekonnen, A. K. Chapagain, R. E. Mathews and B. D. Richter, *PLoS One*, 2012, **7**, e32688.
149 T. R. Ault, J. E. Cole, J. T. Overpeck, G. T. Pederson and D. M. Meko, *J. Clim.*, 2014, **27**, 7529–7549.
150 Asian Development Bank, *Thinking about Water Differently*, Asian Development Bank, Mandaluyong City, Phillipines, 2013.
151 H. Kjerstadius, S. Haghighatafshar and Å. Davidsson, *Environ. Technol.*, 2015, **36**, 1707–1720.
152 A. Peter-Fröhlich, L. Pawlowski, A. Bonhomme and M. Oldenburg, *Water Sci. Technol.*, 2007, **56**, 239–249.
153 A. Bertrand, R. Aggoune and F. Maréchal, *Appl. Energy*, 2017, **192**, 110–125.
154 F. Li, K. Wichmann and R. Otterpohl, *Sci. Total Environ.*, 2009, **407**, 3439–3449.
155 L. Domenech and D. Saurí, *Resour. Conserv. Recycl.*, 2010, **55**, 53–62.
156 Z. L. T. Yu, A. Rahardianto, J. R. DeShazo, M. K. Stenstrom and Y. Cohen, *Water Environ. Res.*, 2013, **85**, 650–662.
157 T. Tal, A. Sathasivan and K. C. B. Krishna, *J. Water Sustain.*, 2011, **1**, 127–137.
158 M. Negahban-Azar, S. E. Sharvelle, Y. Qian and A. Shogbon, *Environ. Sci. Process. Impacts*, 2013, **15**, 713–760.
159 NSF International, *NSF Standard for Wastewater Treatment Systems - Onsite residential and commercial graywater treatment systems for subsurface discharge*, NSF International, Ann Arbor, MI, Draft 1., 2010.
160 F. Nazim and V. Meera, *Bonfring Int. J. Ind. Eng. Manag. Sci.*, 2013, **3**, 111–117.
161 F. Hourlier, A. Masse, P. Jaouen, A. Lakel, C. Gerente, C. Faur and P. Le Cloirec, *Environ. Technol.*, 2010, **31**, 215–223.
162 S. N. Abed and M. Scholz, *Environ. Technol.*, 2016, **3330**, 1–16.
163 B. Jefferson, J. E. Burgess, A. Pichon, J. Harkness and S. J. Judd, *Water Res.*, 2001, **35**, 2702–2710.
164 J. G. March and M. Gual, *Desalination*, 2009, **249**, 317–322.
165 S. Toze, *Desalination*, 2006, **187**, 41–51.
166 F. A. Memon, Z. Zheng, D. Butler, C. Shirley-Smith, S. Lui, C. Makropoulos and L. Avery, *Environ. Monit. Assess.*, 2007, **129**, 27–35.

167 G. P. Winward, L. M. Avery, T. Stephenson and B. Jefferson, *Water Res.*, 2008, **42**, 483–491.
168 R. H. K. Al-Isawi, S. A. A. A. N. Almuktar and M. Scholz, *Environ. Monit. Assess.*, 2016, **188**, 287.
169 S.-E. E. Ouldboukhitine, G. Spolek and R. Belarbi, *Ecol. Eng.*, 2014, **67**, 60–66.
170 Y. Al-Zu'bi, *J. food, Agric. Environ.*, 2008, **6**, 408–410.
171 Y. Alfiya, O. Damti, A. Stoler-Katz, A. Zoubi, A. Shaviv and E. Friedler, *Water Sci. Technol.*, 2012, **65**, 757–764.
172 J. Henkel, M. Lemac, M. Wagner and P. Cornel, *Water Res.*, 2009, **43**, 1711–1719.
173 G. Antonopoulou, A. Kirkou and A. S. Stasinakis, *Sci. Total Environ.*, 2013, **454–455**, 426–432.
174 K. Chaillou, C. Gérente, Y. Andrès and D. Wolbert, *Water. Air. Soil Pollut.*, 2011, **215**, 31–42.
175 E. Friedler, A. Yardeni, Y. Gilboa and Y. Alfiya, *Water Sci. Technol.*, 2011, **63**, 931–940.
176 L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Eds., *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, WEF, Baltimore, MD, 20th edn., 1998.
177 K. M. Ekeren, B. A. Hodgson, S. E. Sharvelle and S. K. De Long, *Desalin. Water Treat.*, 2016, **57**, 1–13.
178 J. G. March, M. Gual and J. Ramonell, *Desalination*, 2005, **181**, 267–273.
179 J. C. Young and R. M. Cowan, in *Respirometers for Environmental Science and Engineering Applications*, 2003.
180 S. M. Hocaoglu, G. Insel, E. U. Cokgor, A. Baban and D. Orhon, *J. Chem. Technol. Biotechnol.*, 2010, **85**, 1241–1249.
181 C. P. L. Grady, G. T. Daigger, N. G. Love and C. D. M. Filipe, *Biological Wastewater Treatment*, IWA Publishing, Boca Raton, FL, 3rd edn., 2011.
182 T. Bruursema, *Plumb. Syst. Des.*, 2011, 15–22.
183 E. K. Holwerda, K. D. Hirst and L. R. Lynd, *J. Ind. Microbiol. Biotechnol.*, 2012, **39**, 943–947.
184 C. L. Grant and D. Pramer, *J. Bacteriol.*, 1962, **84**, 869–870.
185 BD Biosciences, *BD Bionutrients ™ Technical Manual - advanced Bioprocessing*, BD Biosciences, Sparks, MD, 3rd edn., 2006.
186 C. Santasmasas, M. Rovira, F. Clarens and C. Valderrama, *Resour. Conserv. Recycl.*, 2013, **72**, 102–107.
187 N. Shamabadi, H. Bakhtiari, N. Kochakian and M. Farahani, *Energy Procedia*, 2015, **74**, 1337–1346.
188 S. A. Prathapar, A. Jamrah, M. Ahmed, S. Al Adawi, S. Al Sidairi and A. Al Harassi, *Desalination*, 2005, **186**, 177–186.
189 C. Ramprasad and L. Philip, *Chem. Eng. J.*, 2016, **284**, 458–468.
190 M. A. Liebert, *J. Am. Coll. Toxicol.*, 1991, **10**, 33–52.
191 HERA Substance Team, *Human and Environmental Risk Assessment on*

ingredients of household cleaning products Cocamidopropyl betaine (CAPB), 2005.

192 E. Friedler, R. Kovalio and N. I. Galil, *Water Sci. Technol.*, 2005, **51**, 187–194.

193 M. A. López-Zavala, *Water Sci. Technol.*, 2007, **55**, 39–45.

194 E. Friedler, *Environ. Technol.*, 2004, **25**, 997–1008.

195 G. Tchobanoglous, H. D. Stensel, R. Tsuchihashi and F. Burton, *Wastewater Engineering: Treatment and Resource Recovery*, McGraw-Hill Education, New York, NY, 5th edn., 2014.

196 T. D. Reynolds and P. A. Richards, *Unit Operations and Processes in Environmental Engineering*, CENGAGE Learning, Stamford, CT, 2nd edn., 1996.

197 S. Sharvelle, N. Ashbolt, E. Clerico, R. Hultquist, H. Leverenz and A. Olivieri, *Risk-Based Framework for the Development of Public Health Guidance for Decentralized Non-Potable Water Systems*, Prepared by the National Water Research Institute for the Water Environment & Reuse Foundation, Alexandria, VA, 2017.

198 S. Chowdhury, P. Champagne and P. J. McLellan, *Sci. Total Environ.*, 2009, **407**, 4189–4206.

199 E. Pehlivanoglu-Mantas, E. L. Hawley, R. A. Deeb and D. L. Sedlak, *Water Res.*, 2006, **40**, 341–347.

200 C. H. Jones, E. G. Shilling, K. G. Linden and S. M. Cook, *Environ. Sci. Technol.*, 2017, **52**, 2998–3007.

201 R. S. Summers, D. R. U. Knappe and V. L. Snoeyink, in *Water Quality and Treatment*, Amer. Water Works Assoc., McGraw-Hill, New York, NY, 6th edn., 2010.

202 M. Pidou, L. Avery, T. Stephenson, P. Jeffrey, S. A. Parsons, S. Liu, F. A. Memon and B. Jefferson, *Chemosphere*, 2008, **71**, 147–155.

203 D. M. Ghaitidak and K. D. Yadav, *J. Water, Reuse Desalin.*, 2016, **6**, 108–124.

204 D. M. Ghaitidak and K. D. Yadav, *Desalin. Water Treat.*, 2015, **55**, 913–925.

205 B. Jefferson, A. Palmer, P. Jeffrey, R. Stuetz and S. Judd, *Water Sci. Technol.*, 2004, **50**, 157–164.

206 I. Ciabattia, F. Cesaro, L. Faralli, E. Fatarella and F. Tognotti, *Desalination*, 2009, **245**, 451–459.

207 S. Šostar-Turk, I. Petrinić and M. Simonič, *Resour. Conserv. Recycl.*, 2005, **44**, 185–196.

208 L. Ward, M. Page, J. Jurevis, A. Nelson, M. Rivera, M. Hernandez, M. Chappell and J. Dusenbury, *J. Water Reuse Desalin.*, 2015, **5**, 212–239.

209 J. Y. C. Leong, M. N. Chong and P. E. Poh, *J. Clean. Prod.*, 2018, **172**, 81–91.

210 A. Y. Katukiza, M. Ronteltap, C. B. Niwagaba, F. Kansiime and P. N. L. Lens, *J. Environ. Manage.*, 2014, **146**, 131–141.

211 L. Hernández-Leal, H. Temmink, G. Zeeman and C. J. N. Buisman, *Water Res.*, 2011, **45**, 2887–96.

212 C. Noutsopoulos, A. Andreadakis, N. Kouris, D. Charchousi, P. Mendrinou, A. Galani, I. Mantziaras and E. Koumaki, *J. Environ. Manage.*, ,

DOI:10.1016/j.jenvman.2017.05.094.
213 K. S. Oh, P. E. Poh, M. N. Chong, D. Gouwanda, W. H. Lam and C. Y. Chee, *J. Environ. Chem. Eng.*, 2015, **3**, 1146–1151.
214 M. S. Zipf, I. G. Pinheiro and M. G. Conegero, *J. Environ. Manage.*, 2016, **176**, 119–127.
215 C. Noutsopoulos, A. Andreadakis, N. Kouris, D. Charchousi, P. Mendrinou and A. Galani, *J. Environ. Manage.*
216 J. Jong, J. Lee, J. Kim, K. Hyun, T. Hwang, J. Park and Y. Choung, *Desalination*, 2010, **250**, 568–572.
217 EnviroSupply & Service Inc., 20X50 prewashed coal activated carbon - 55 lb bag, https://envirosupply.net/shop/activated-carbon/liquid-filtration/20x50-prewashed-coal/20x50-prewashed-coal-activated-carbon-55-lb-bag.html, (accessed 8 March 2018).
218 T. L. Yami, J. Du, L. R. Brunson, J. F. Chamberlain, D. A. Sabatini and E. C. Butler, *Int. J. Life Cycle Assess.*, 2015, **20**, 1277–1286.
219 J. P. Kearns, D. R. U. Knappe and R. S. Summers, *Environ. Eng. Sci.*, 2015, **32**, 912–921.
220 M. Ahmad, A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S. S. Lee and Y. S. Ok, *Chemosphere*, 2014, **99**, 19–23.
221 S. S. Dalahmeh, C. Lalander, M. Pell, B. Vinnerås and H. Jönsson, *J. Appl. Microbiol.*, 2016, **121**, 1427–1443.
222 E. Friedler, I. Katz and C. G. Dosoretz, *Desalination*, 2008, **222**, 38–49.
223 D. M. Ghaitidak and K. D. Yadav, *Desalin. Water Treat.*, 2015, **54**, 2410–2421.
224 S. J. Randtke, *J. / Am. Water Work. Assoc.*, 1988, **80**, 40–56.
225 H. K. Shon, S. Vigneswaran, I. S. Kim, J. Cho and H. H. Ngo, *Water Res.*, 2004, **38**, 1933–1939.
226 E. Ghisi, R. F. Rupp and Y. Triska, *Resour. Conserv. Recycl.*, 2014, **87**, 137–144.
227 J. Chang, W. Lee and S. Yoon, *J. Clean. Prod.*, 2017, **141**, 728–736.
228 L. C. Proença, E. Ghisi, D. D. F. Tavares and G. M. Coelho, *Resour. Conserv. Recycl.*, 2011, **55**, 960–965.
229 E. Ghisi and D. F. Ferreira, *Build. Environ.*, 2007, **42**, 2512–2522.
230 ASTM International, 2017, D2867.
231 Y. Boyjoo, M. Ang and V. Pareek, *Int. J. Photoenergy*, , DOI:10.1155/2012/578916.
232 M. Lamine, L. Bousselmi and A. Ghrabi, *Desalination*, 2007, **215**, 127–132.
233 T. Zeng and W. A. Mitch, *Environ. Sci. Technol.*, 2015, **49**, 13158–13167.
234 E. Friedler and Y. Gilboa, *Sci. Total Environ.*, 2010, **408**, 2109–2117.
235 NOAA, Climate Data Online Search, https://www.ncdc.noaa.gov/cdo-web/search, (accessed 16 November 2017).
236 Y. Mason, A. A. Ammann, A. Ulrich and L. Sigg, *Environ. Sci. Technol.*, 1999, **33**, 1588–1597.
237 K. A. Thompson, K. K. Shimabuku, J. P. Kearns, D. R. U. Knappe, R. S. Summers and S. M. Cook, *Environ. Sci. Technol.*, 2016, **50**, 11253–11262.

238 M. C. Chrispim and M. A. Nolasco, *J. Clean. Prod.*, 2017, **142**, 290–296.
239 L. H. Leal, H. Temmink, G. Zeeman and C. J. N. Buisman, *Water*, 2010, **2**, 155–169.
240 S. E. Beck, R. A. Rodríguez, A. Salveson, N. Goel, S. Rhodes, P. Kehoe and K. G. Linden, *J. Environ. Eng.*, 2013, **139**, 1137–1145.
241 Malcom Pirnie Inc., Carollo Engineers P.C., Cadmus Group Inc., K. G. Linden and J. P. Malley, *Ultraviolet disinfection guidance manual for the final long term 2 enhanced surface water treatment rule*, USEPA, Washington, DC, 2006.
242 J. R. Bolton and K. G. Linden, *J. Environ. Eng.*, 2003, **129**, 209–215.
243 C. Farrell, F. Hassard, B. Jefferson, T. Leziart, A. Nocker and P. Jarvis, *Sci. Total Environ.*, 2018, **624**, 638–647.
244 B. G. Greiner, K. K. Shimabuku and R. S. Summers, *Environ. Sci. Water Res. Technol.*, 2018, **4**, 169–174.
245 NOAA, Climate Data Online Search, https://www.ncdc.noaa.gov/cdo-web/search, (accessed 9 June 2017).
246 H. C. Kim and T. J. Wallington, *Environ. Sci. Technol.*, 2013, **47**, 14358–14366.
247 A. P. Davis, M. Shokouhian and S. Ni, *Chemosphere*, 2001, **44**, 997–1009.
248 W. Feng, B. E. Hatt, D. T. McCarthy, T. D. Fletcher and A. Deletic, *Environ. Sci. Technol.*, 2012, **46**, 5100–5108.
249 USEPA, National Primary Drinking Water Regulations, https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations, (accessed 29 July 2017).
250 Z. L. Yang, B. Y. Gao, Q. Y. Yue and Y. Wang, *J. Hazard. Mater.*, 2010, **178**, 596–603.
251 Calgon Carbon Corporation, Calgon Carbon, www.calgoncarbon.com, (accessed 9 December 2017).
252 C. D. Cooper and F. C. Alley, *Air Pollution Control: A Design Approach*, Waveland Press, Inc., Long Grove, IL, 4th edn., 2011.
253 Baker-Rullman Mfg., Rotary Drum Dryers, www.baker-rullman.com/Dehydration/, (accessed 10 December 2017).
254 T. J. Morgan, A. George, A. K. Boulamanti, P. Álvarez, I. Adanouj, C. Dean, S. V. Vassilev, D. Baxter and L. K. Andersen, *Energy and Fuels*, 2015, **29**, 1669–1685.
255 R. C. Dewar, *Tree Physiol.*, 1991, **8**, 239–258.
256 C. Sigmon, 2015.
257 G. Tian, T. C. Granato, A. E. Cox, R. I. Pietz, C. R. Carlson and Z. Abedin, *J. Environ. Qual.*, 2009, **38**, 61.
258 G. Tian, C. Y. Chiu, A. J. Franzluebbers, O. O. Oladeji, T. C. Granato and A. E. Cox, *Appl. Soil Ecol.*, 2015, **85**, 86–93.
259 J. P. Kearns, L. S. Wellborn, R. S. Summers and D. R. U. Knappe, *Water Res.*, 2014, **62**, 29–28.
260 B. Boundy, S. W. Diegel, L. Wright and S. C. Davis, *Biomass Energy Data Book*, U.S. Department of Energy, Washington, DC, 4th edn., 2011.

261 K. A. Spokas, *Carbon Manag.*, 2010, **1**, 289–303.
262 W. Saw, H. McKinnon, I. Gilmour and S. Pang, *Fuel*, 2012, **93**, 473–478.
263 M. . Almeida, D. Butler and E. Friedler, *Urban Water*, 1999, **1**, 49–55.
264 A. D. Alsulaili and M. F. Hamoda, *Water Sci. Technol.*, 2015, **72**, 1973–1980.
265 R. Birks and S. Hills, *Environ. Monit. Assess.*, 2007, **129**, 61–69.
266 I. Bodnar, A. Szabolcsik, E. Baranyai, A. Uveges and N. Boros, *Environ. Eng. Manag. J.*, 2014, **13**, 2717–2724.
267 D. Christova-Boal, R. E. Eden, S. McFarlane, D. ChristovaBoal, R. E. Eden and S. McFarlane, *Desalination*, 1996, **106**, 391–397.
268 E. Eriksson, K. Auffarth, A. M. Eilersen, M. Henze and A. Ledin, *Water SA*, 2003, **29**, 135–146.
269 A. M. Ghrair, O. A. Al-Mashaqbeh and S. B. Megdal, *Clean - Soil, Air, Water*, 2015, **43**, 351–359.
270 M. Gual, A. Moià and J. G. March, *Desalination*, 2008, **219**, 81–88.
271 F. Hourlier, A. Massé, P. Jaouen, A. Lakel, C. Gérente, C. Faur and P. Le Cloirec, *Water Sci. Technol.*, 2010, **62**, 1544–1550.
272 A. Jamrah, A. Al-Omari, L. Al-Qasem and N. A. Ghani, *Water Int.*, 2006, **31**, 210–220.
273 A. Jamrah, A. Al-Futaisi, S. Prathapar and A. Al Harrasi, *Environ. Monit. Assess.*, 2008, **137**, 315–327.
274 B. Jefferson, A. L. Laine, T. Stephenson and S. J. Judd, *Water Sci. Technol.*, 2001, **43**, 211–218.
275 J. Laaffat, N. Ouazzani and L. Mandi, *Process Saf. Environ. Prot.*, 2015, **95**, 86–92.
276 Y. Maiga, D. Moyenga, B. C. Nikiema, K. Ushijima, a H. Maiga and N. Funamizu, *Environ. Technol.*, 2014, **35**, 3020–7.
277 J. G. March and M. Gual, *Water Environ. Res.*, 2007, **79**, 828–32.
278 J. G. March, M. Gual and F. Orozco, *Desalination*, 2004, **164**, 241–247.
279 C. Merz, R. Scheumann, B. El Hamouri and M. Kraume, *Desalination*, 2007, **215**, 37–43.
280 E. Nolde, *Urban Water*, 1999, **1**, 275–284.
281 G. Ramon, M. Green, R. Semiat and C. Dosoretz, *Desalination*, 2004, **170**, 241–250.
282 Z. Ronen, A. Guerrero and A. Gross, *Chemosphere*, 2010, **78**, 61–65.
283 C. Santos, F. Taveira-Pinto, C. Y. Cheng and D. Leite, *Desalination*, 2012, **285**, 301–305.
284 S. Surendran and A. D. Wheatley, *Water Environ. J.*, 1998, **12**, 406–413.
285 X. Y. Teh, P. E. Poh, D. Gouwanda and M. N. Chong, *J. Clean. Prod.*, 2015, **99**, 305–311.
286 G. P. Winward, L. M. Avery, R. Frazer-Williams, M. Pidou, P. Jeffrey, T. Stephenson and B. Jefferson, *Ecol. Eng.*, 2008, **32**, 187–197.
287 T. P. Abegunrin, G. O. Awe, A. Y. Sangodoyin, O. E. Onofua and O. M. Oguntoye, *Int. J. Curr. Microbiol. Appl. Sci.*, 2017, **6**, 4489–4500.
288 L. M. Casanova, C. P. Gerba and M. Karpiscak, *J. Environ. Sci. Health. A.*

Tox. Hazard. Subst. Environ. Eng., 2001, **36**, 395–401.

289 J. Guilbaud, A. Massé, Y. Andrs, F. Combe and P. Jaouen, *Resour. Conserv. Recycl.*, 2010, **55**, 148–154.

290 S. Jiawkok, S. Ittisupornrat, C. Charudacha and J. Nakajima, *Water Environ. J.*, 2013, **27**, 229–237.

291 H. C. Kim, X. Shang, J. H. Huang and B. A. Dempsey, *J. Memb. Sci.*, 2014, **456**, 167–174.

292 L. T. Kist, C. Albrecht and Ê. L. Machado, *Clean - Soil, Air, Water*, 2008, **36**, 775–780.

293 R. K. Misra and A. Sivongxay, *J. Hydrol.*, 2009, **366**, 55–61.

294 R. K. Misra, J. H. Patel and V. R. Baxi, *J. Hydrol.*, 2010, **386**, 95–102.

295 S. Mozia, M. Janus, P. Brozek, S. Bering, K. Tarnowski, J. Mazur and A. W. Morawski, *Environ. Sci. Pollut. Res.*, 2016, **23**, 19145–19155.

296 J. B. Rose, G. S. Sun, C. P. Gerba and N. A. Sinclair, *Water Res.*, 1991, **25**, 37–42.

297 X. Shang, H. C. Kim, J. H. Huang and B. A. Dempsey, *Sep. Purif. Technol.*, 2015, **147**, 44–50.

298 A. Sumisha, G. Arthanareeswaran, Y. Lukka Thuyavan, A. F. Ismail and S. Chakraborty, *Ecotoxicol. Environ. Saf.*, 2015, **121**, 174–179.

299 Z. L. Yu, B. R. Bill, M. K. Stenstrom and Y. Cohen, *Ecol. Eng.*, 2015, **82**, 311–322.

300 M. Á. López Zavala and E. E. Estrada, *Water*, 2016, **8**, 214.

301 S. Sharvelle, L. A. Roesner, Y. Qian, M. Stromberger and M. N. Azar, *Long-term study on landscape irrigation using household graywater - experimental study*, 2012.

302 L. Ringqvist, A. Holmgren and I. Öborn, *Water Res.*, 2002, **36**, 2394–2404.

303 O. R. Al-Jayyousi, *Desalination*, 2003, **156**, 181–192.

304 J. B. Rose, M. M. Karpiscak, K. E. Foster, K. J. DeCook, C. P. Gerba and R. Brittain, in *Proceedings Water Reuse Symposium IV*, AWWA Research Foundation, Denver, Colo., 1988, pp. 1391–1398.

305 I. Brook, T. Malchi and S. Nir, *Desalin. Water Treat.*, 2015, **53**, 2184–2192.

306 P. David, G. Bulteau, P. Humeau, C. Gerente and Y. Andres, *Environ. Technol.*, 2013, **34**, 3087–3094.

307 A. Gross, O. Shmueli, Z. Ronen and E. Raveh, *Chemosphere*, 2007, **66**, 916–923.

308 C. Y. Yun, D. G. Kim, W. Y. Kim, D. J. Son, D. Chang, J. H. Kim, Y. S. Bae, H. S. Bae, Y. Sunwoo, M. S. Kwak and K. H. Hong, *Int. J. Electrochem. Sci.*, 2014, **9**, 1522–1536.

309 N. Atanasova, M. Dalmau, J. Comas, M. Poch, I. Rodriguez-Roda and G. Buttiglieri, *J. Environ. Manage.*, 2017, **193**, 503–511.

310 B. F. Bakare, S. Mtsweni and S. Rathilal, *J. Water Reuse Desalin.*, 2017, **7**, 520–528.

311 B. Hodgson, Colorado State University, 2012.

312 G. Ramon, M. Green, R. Semiat and C. Dosoretz, *Desalination*, 2004, **170**,

241–250.
313 E. Friedler, R. Kovalio and A. Ben-Zvi, *Environ. Technol.*, 2006, **27**, 653–663.
314 E. Girensunlu and B. B. Baykal, *Water Sci. Technol. Water Supply*, 2016, **16**, 1659–1667.
315 J. Laaffat, N. Ouazzani and L. Mandi, *Process Saf. Environ. Prot.*, 2015, **95**, 86–92.
316 M. Lamine, D. Samaali and A. Ghrabi, *Desalin. Water Treat.*, 2012, **46**, 182–187.
317 C. Santos, F. Taveira-Pinto, C. Y. Cheng and D. Leite, *Desalination*, 2012, **285**, 301–305.
318 X. Y. Teh, P. E. Poh, D. Gouwanda and M. N. Chong, *J. Clean. Prod.*, 2015, **99**, 305–311.
319 K. M. Ekeren, B. A. Hodgson, S. E. Sharvelle and S. K. De Long, *Desalin. Water Treat.*, 2016, **57**, 1–13.
320 E. Newcomer, C. Boyd, L. Nyirenda, E. Opong, S. Marquez and R. Holm, *Water Sci. Technol. Water Supply*, 2017, **17**, 1088–1096.

APPENDIX A

SUPPLEMENTARY INFORMATION

For

CONVENTIONAL DRINKING WATER TREATMENT OF ALTERNATIVE SOURCE WATERS

A.1 Surface Water and Stormwater Sampling

Table A.1. Time and location of surface water and stormwater sampling. Precipitation data for these storm events came from NOAA’s Climate Data Online database.[245] n/a means not applicable. *Suburban Pond Outlet StmW* was a composite sample collected over a six-hour period.

Sample	Precip. Type	Precip. Amount (mm)	Lat.	Long.	Date	Time
Surface Water-1	n/a	n/a	40^{0}04’17” N	105^{0}13’27” W	1/13/17	n/a
Surface Water-2	n/a	n/a	40^{0}04’17” N	105^{0}13’27” W	3/23/17	n/a
Industrial StmW	Rain	4.1	39^{0}43’12” N	105^{0}00’30” W	4/20/17	16:45
Highway StmW	Rain	4.1	39^{0}43’14” N	105^{0}00’30” W	4/20/17	17:15
Parking Lot StmW-1	Snow	193	40^{0}00’31” N	105^{0}14’32” W	2/23/17	13:00
Parking Lot StmW-2	Snow	198	40^{0}00’31” N	105^{0}14’32” W	4/3/17	23:00
Field StmW	Rain	18.5	40^{0}00’40” N	105^{0}15’58” W	3/26/17	15:00
Campus Manhole StmW	Snow	356	40^{0}00’29” N	105^{0}15’35” W	1/9/17	13:00
Suburban Pond Outlet StmW	Rain	56.2	New York, USA		5/5/17	n/a
Campus Pond StmW	None	n/a	40^{0}00’28” N	105^{0}15’34” W	2/19/10	-

A.2 Additional Initial Water Quality Data

Table A.2. Initial Water Quality, continued: metals. All units µg/L. [a]Would require removal to meet the US EPA Primary Standard. [b]Would require removal to meet the US EPA Secondary Standard. [c]Would require removal to meet the WHO Guideline.

	Ag	Al	As	Ba	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Se	Th	U	Zn
US EPA Primary Standard			10	2000	5	100	1300			15	6	50	2		
US EPA Secondary Standard	100	200					1000	50							5000
WHO Guideline		200	10	700	3	50	2000	100	70	10	20	40		30	
Surface Waters															
Surface Water-1	<1	91	0.91	51.0	1.56	16	3	0.2	5.5	0.35	<2.44	4.66	0.01	0.71	4
Surface Water 2	<1	139	0.56	45.8	<0.09	19	6	1.0	8.0	<0.05	<2.44	1.14	0.02	1.27	1
Stormwaters															
Parking Lot StmW-1	<1	949[b,c]	3.27	18.9	0.12	26	30	10.1	3.7	0.76	<2.44	1.21	0.15	0.34	14
Parking Lot StmW-2	<1	365[b,c]	0.34	11.6	DL	10	8	2.6	1.2	0.17	<2.44	<0.26	0.04	0.06	6
Highway StmW	<1	568[b,c]	3.68	84.4	0.42	22	39	147[b]	14.4	1.11	4.39	4.97	0.10	0.14	1558
Industrial StmW	<1	443[b,c]	9.07	108	0.10	36	34	292[b]	20.3	2.76	<2.44	3.83	0.08	0.20	49
Campus Manhole StmW	<1	40	4.02	46.4	0.15	14	23	0.8	6.9	0.09	<2.44	5.32	0.01	0.31	21
Field StmW	<1	35	0.71	35.1	DL	27	19	2.1	11.3	0.05	<2.44	4.15	0.01	0.36	33
Suburban Pond Outlet StmW	<1	35	0.80	25.4	<0.012	15	12	0.5	3.9	<0.02	<0.78	<0.51	0.01	0.03	1
Wastewater Effluents															
BOD-Removal WWeff	<1	9	5.74	8.8	<0.09	112[a,c]	16	47.1	16.2	0.07	<2.44	11.0	0.00	2.86	13
N-Removal Filter WWeff	<1	8	0.83	15.6	0.030	17	13	8.8	16.6	<0.02	<0.78	7.98	0.00	1.10	28
N-Removal Bardenpho WWeff	<1	8	0.80	38.4	<0.09	29	26	1.4	10.4	0.49	<2.44	3.42	0.00	0.17	55
P-Removal Johannesburg WWeff	<1	28	2.86	53.3	<0.09	40	10	30.6	22.3	0.06	<2.44	4.76	0.00	2.11	21
P-Removal A2O WWeff	<1	18	0.40	34.2	0.031	32	13	9.3	6.6	<0.02	<0.78	2.78	0.00	0.04	71

Four stormwaters (*Parking Lot StmW-1*, *Parking Lot StmW-2*, *Highway StmW*, and *Industrial StmW*) exceeded the US EPA Secondary Standard for aluminum (50-200 μg/L) by 80% or more (Table A2).[75] These stormwaters were all from paved watersheds with vehicles. The high concentration of aluminum in these stormwaters may be related to the growing use of aluminum alloys in lightweight vehicles to increase fuel efficiency.[246] Most literature about metals in stormwater focuses on the metals that are most toxic to aquatic ecosystems such as lead, copper, cadmium, and zinc.[247] Less work has been done on metals such as iron and aluminum that could pose social sustainability challenges due to taste and color in a potable reuse context.[247,248] Nevertheless, a study in Australia also found aluminum levels in stormwater to be above aesthetic guidelines.[29] Further study is needed to understand the state (particulate or dissolved, ionic or metallic) and removal of aluminum in stormwaters from watersheds with roads or parking lots.

Only one of the alternative source waters exceeded a US EPA Primary Standard for a metal. *BOD-Removal WWeff* had a chromium concentration of 112 μg/L, exceeding the US EPA Primary Standard of 100 μg/L by a 12% margin.[249] A slight dilution with surface water would be sufficient to reduce this concentration below the standard. For example, *Surface Water-2* had a chromium concentration of 19 μg/L, so a 13% dilution would be required.

Table A.3. Initial Water Quality, continued: nutrients. Nutrients are as reported by the utility on the closest sampling day.

	Nitrate + Nitrite (mg/L as N)	Nitrate (mg/L as N)	Nitrite (mg/L as N)	Ammonia (mg/L as N)	Total Phosphorus (mg/L as P)	Phosphate (mg/L as P)
BOD-Removal WWeff	-	<0.2	-	42.6	-	2.2
N-Removal Filter WWeff	19.9	19.7	0.20	1.23	-	2.64
N-Removal Bardenpho WWeff	-	-	-	-	-	-
P-Removal Johannesburg WWeff	-	-	-	-	-	-
P-Removal A2O WWeff	5.56	-	-	<1.3	0.019	-

A.3 Additional Treatment Data

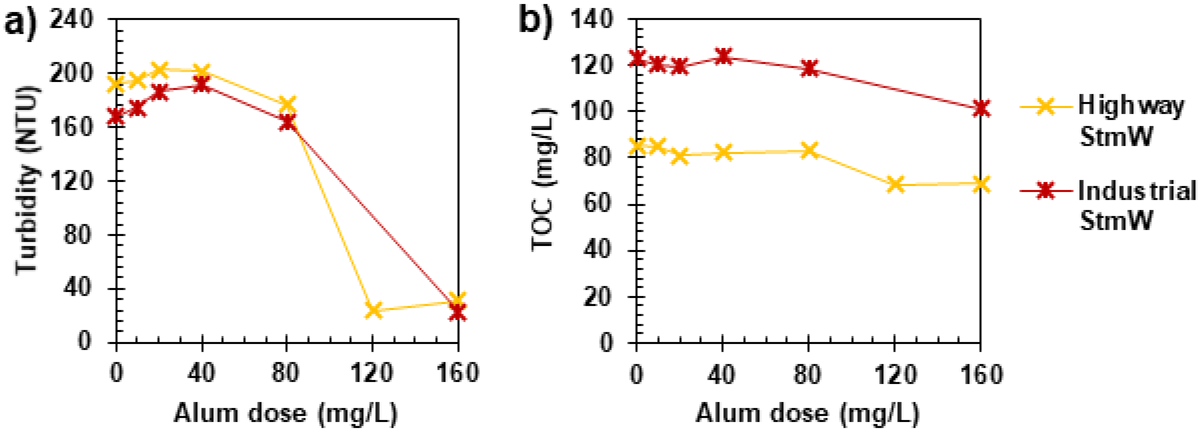


Figure A.1. Turbidity (a) and TOC (b) removal by coagulation from *Highway StmW* and *Industrial StmW*.

At the same dose of alum or ferric chloride in mg/L, ferric chloride achieved greater DOC removal but less turbidity removal. Ferric chloride has approximately twice as many moles of ferric ion per mass as alum has moles of aluminum ion per mass. Considering the results on a molar basis, ferric chloride achieved comparable DOC removal but much less turbidity removal.

Treating *Parking Lot StmW-1* with ferric chloride was similar to alum in terms of DOC modeling (Figure A.2). DOC removal from *Parking Lot StmW-1* by alum was predicted well by the Coagulation Model at all doses (R^2 of 0.97 and standard error 8%). DOC removal from this stormwater by ferric chloride was also well predicted by the Coagulation Model (R^2 of 0.92 and standard error 17% with 10 to 160 mg/L), especially at low doses (R^2 of 0.89 and standard error 6% with 10 to 80 mg/L). Counter to the trend with alum, the Coagulation Model underestimated—rather than overestimated—DOC removal by ferric chloride at the highest dose. Ferric chloride had greater DOC removal than alum at 160 mg/L (66% and 49%, respectively). This difference may indicate that *Parking Lot StmW-1* had a lower nonsorbable fraction with ferric chloride than with alum, which is the trend observed in surface

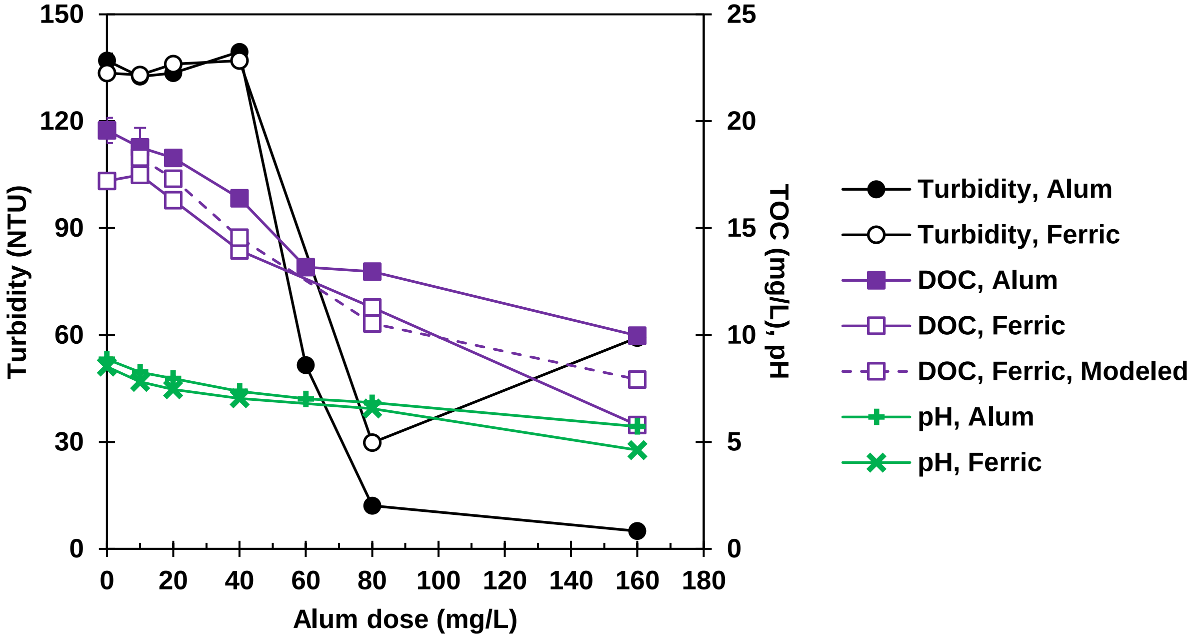


Figure A.2. Turbidity and DOC removal from *Parking Lot StmW-1* with alum or ferric chloride. "DOC, Ferric, Modeled" is the DOC removal by ferric chloride predicted by the Coagulation Model. Error bars show the range of replicates at 0 and 10 mg/L alum.

waters.[61] However, using the ferric chloride specific version of the Coagulation Model only slightly improved predictive accuracy for DOC removal from *Parking Lot StmW-1* (R^2 of 0.92 standard error 14% with 10 to 160 mg/L ferric chloride).

For *N-Removal Bardenpho WWeff*, ferric chloride caused comparable TOC removal and worse turbidity removal than alum (Figure A.3). These results show similar trends as the ferric chloride and alum comparison for *Parking Lot StmW-1*. The Coagulation Model was extremely accurate for TOC removal from the *N-Removal Bardenpho WWeff* using ferric chloride, with R^2 of 0.97 and standard error of 4%. Since DOC typically accounts for 90-95% of TOC in surface water,[61] this model is considered acceptably accurate for TOC, and has been validated for TOC at full-scale drinking water facilities.[62] Since particulate organic carbon is more readily removed than DOC by coagulation, this model tends to slightly overpredict removal when applied to TOC.[61]

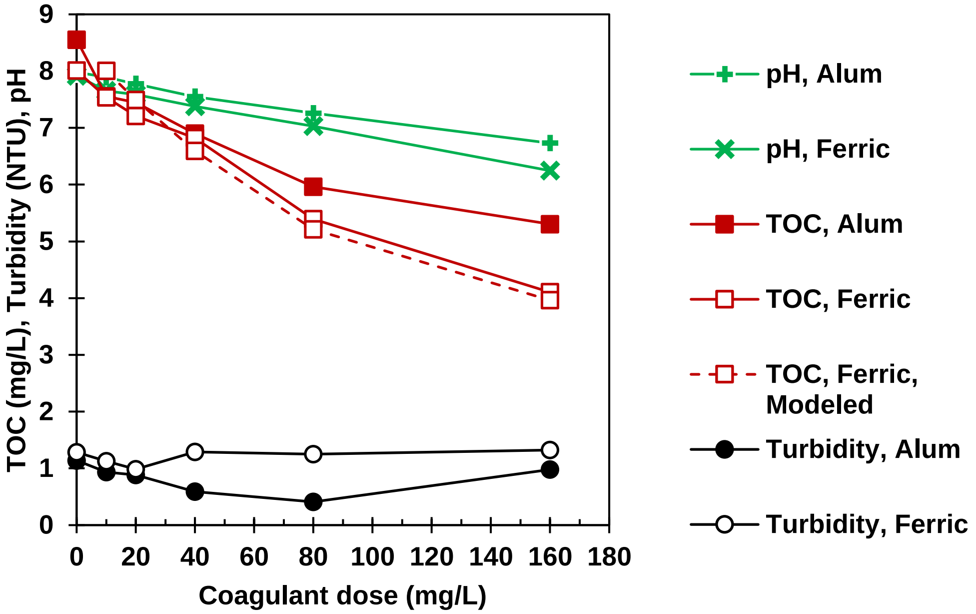


Figure A.3. Turbidity and TOC removal from *N-Removal Bardenpho WWeff* with alum or ferric chloride. "TOC, Ferric, Modeled" is the DOC removal by ferric chloride predicted by the Coagulation Model. Error bars show the range of replicates at 0 and 10 mg/L alum.

A.4 Disinfection Byproducts and Toxicity

Table A.4. DBP yields and max TOC to meet TTHM and HAA5 MCLs. *HAA6.

Sample		TTHM/ TOC (μg/mg)	HAA5/ TOC (μg/mg)	HAA9/ TOC (μg/mg)	HAN4/ TOC (μg/mg)	MAX TOC for TTHM Compliance (mg/L)	MAX TOC for HAA5 Compliance (mg/L)
10 surface waters,[57] mean±SD	Coag	28±1	21±3*			2.9	2.9
Surface Water-1	Raw	21	15	18	0.89	3.8	3.9
	Coag	17	12	15	1.05	4.7	5.2
Parking Lot StmW-1	Raw	32	25	26	0.74	2.5	2.4
	Coag	24	14	15	1.27	3.3	4.4
Parking Lot StmW-2	Raw	26	21	22	1.44	3.1	2.8
	Coag	8	11	11	0.38	9.9	5.6
Field StmW	Raw	30	23	29	1.66	2.7	2.6
	Coag	16	8	11	1.61	5.0	7.9
Campus Manhole StmW	Raw	47	43	64	2.05	1.7	1.4
	Coag	35	14	32	3.24	2.3	4.3
Suburban Pond Outlet StmW	Raw	63	99	102	0.88	1.3	0.6
	Coag	33	30	34	1.32	2.4	2.0
N-Removal Filter WWeff	Raw	25	30	34	2.36	3.2	2.0
	Coag	23	22	30	2.70	3.5	2.7
N-Removal Bardenpho WWeff	Raw	30	28	34	1.80	2.7	2.2
	Coag	27	22	28	2.04	3.0	2.7
P-Removal Johannesburg WWeff	Raw	24	26	32	1.69	3.3	2.3
	Coag	12	17	25	1.79	6.4	3.5
P-Removal A2O WWeff	Raw	23	23	27	1.57	3.6	2.6
	Coag	13	20	25	1.65	6.0	3.0
Stormwaters, mean±SD (n=5)	Raw	40±14	42±30	49±31	1.4±0.5	2.2±0.7	2.0±0.8
	Coag	23±10	15±8	21±10	1.6±0.9	4.3±3.0	4.5±2.1
Wastewater Effluents, mean±SD (n=4)	Raw	25±3	27±3	32±3	1.9±0.3	3.2±0.3	2.3±0.2
	Coag	19±6	20±2	27±2	2.0±0.4	4.7±1.5	3.0±0.3

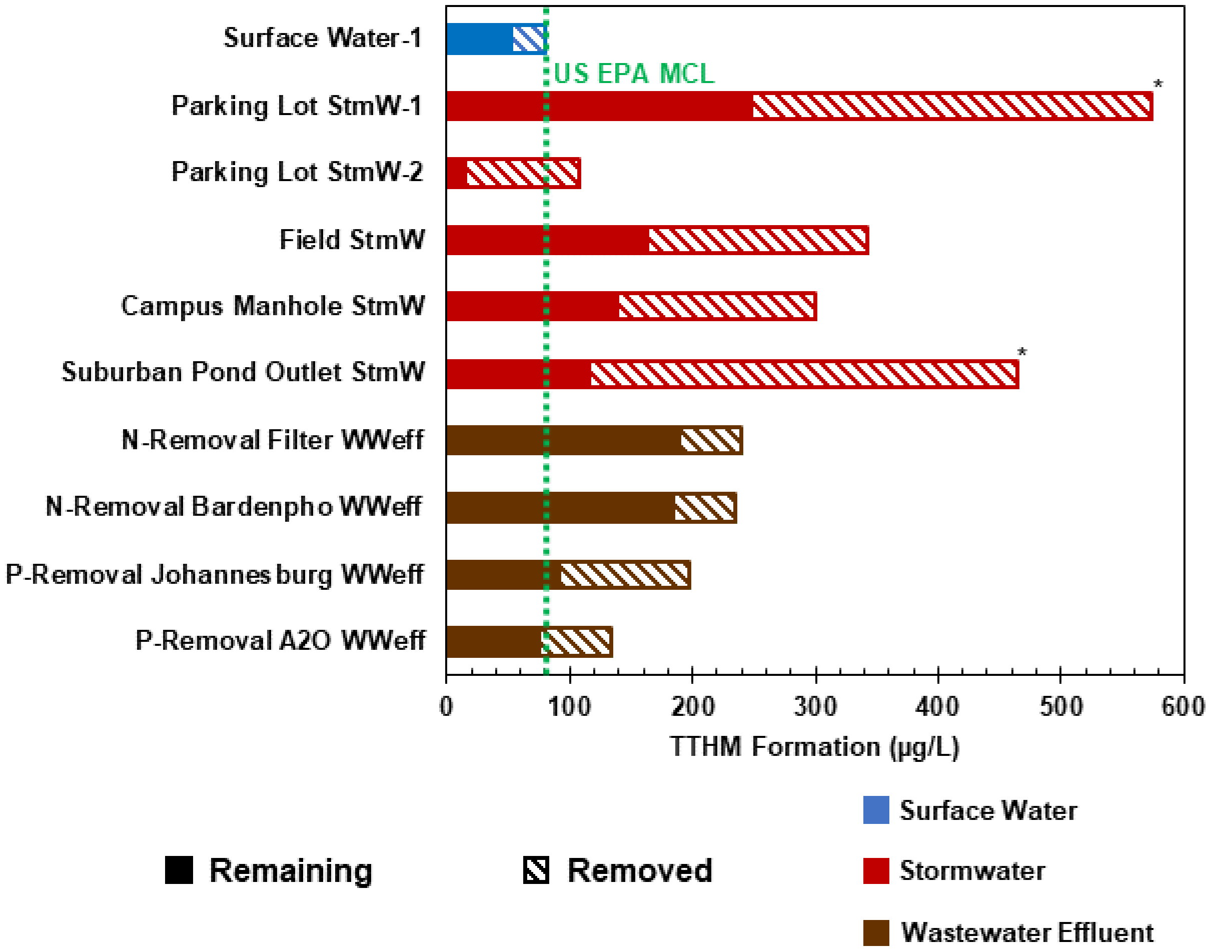


Figure A.4. TTHM formation under UFC conditions. The total bar length (solid plus hashed) represents initial DBP formation, the solid bar represents DBP formation in treated water, and the hashed bar represents reduction by coagulation. All samples were coagulated with 40 mg/L alum except for *Parking Lot StmW-1*, which was coagulated with 80 mg/L alum. *Raw *Parking Lot StmW-1* and raw *Suburban Pond Outlet StmW* had chloroform concentrations of 526 μg/L and 423 μg/L, respectively, which are above the calibrated range of the method (>250 μg/L). These extrapolated values for chloroform are included in the TTHM values in this figure.

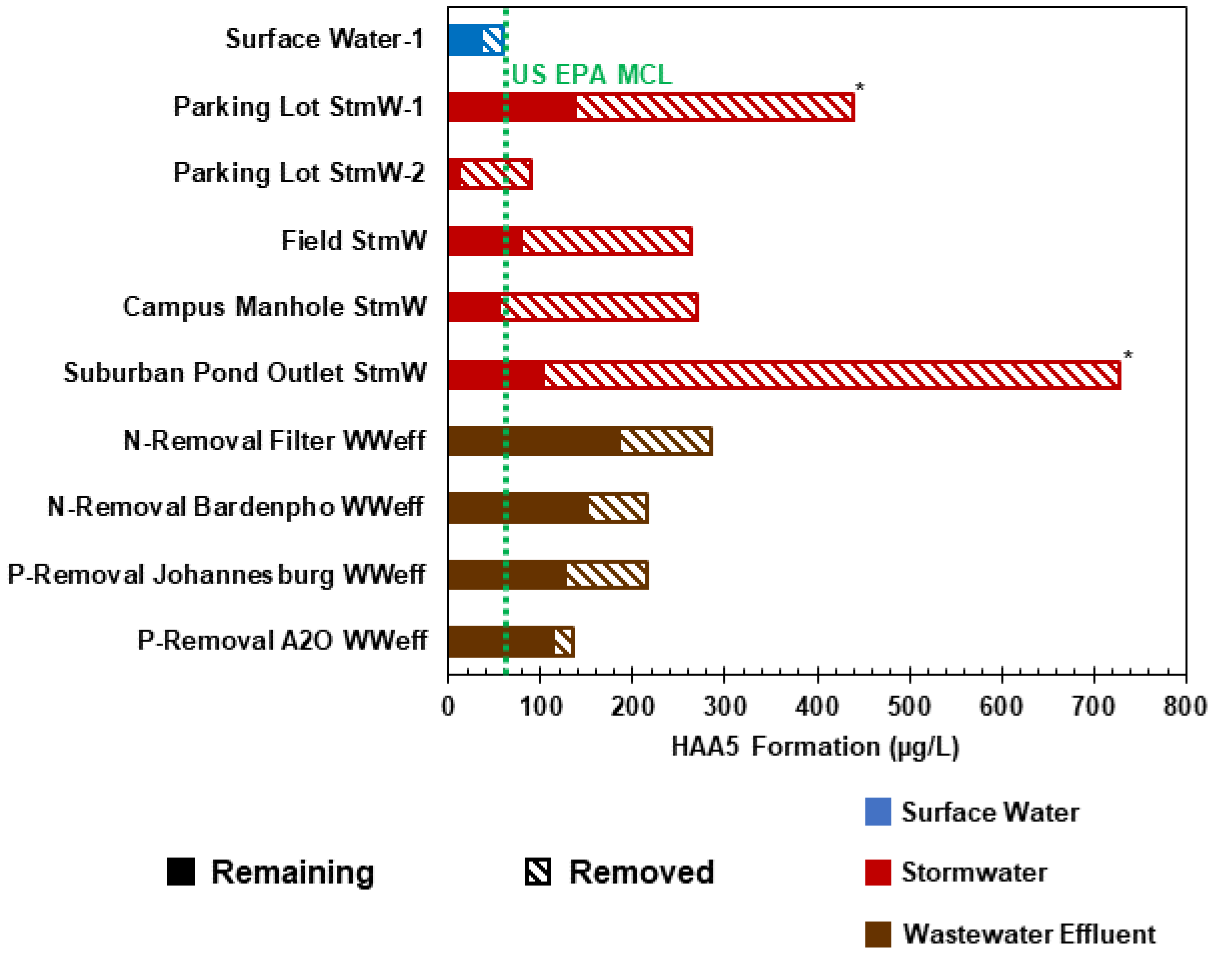


Figure A.5. HAA5 formation under UFC conditions. The total bar length (solid plus hashed) represents initial DBP formation, the solid bar represents DBP formation in treated water, and the hashed bar represents reduction by coagulation. All samples were coagulated with 40 mg/L alum except for Parking Lot StmW-1, which was coagulated with 80 mg/L alum. *Raw *Parking Lot StmW-1* had a trichloroacetic acid concentration of 256 μg/L, and Raw *Suburban Pond Outlet StmW* had a trichloroacetic acid concentration of 454 μg/L and a dichloracetic acid concentration of 260 μg/L. These values are above the calibrated range of the method (>250 μg/L). These extrapolated values are included in the total HAA5 values in this figure.

Figure A.6. Calculated cytotoxicity of measured DBPs in (a) surface water and wastewater effluents and (b) stormwaters. “Coag” refers to samples coagulated with 40 mg/L alum, except for *Parking Lot StmW-1* which was coagulated with 80 mg/L alum.

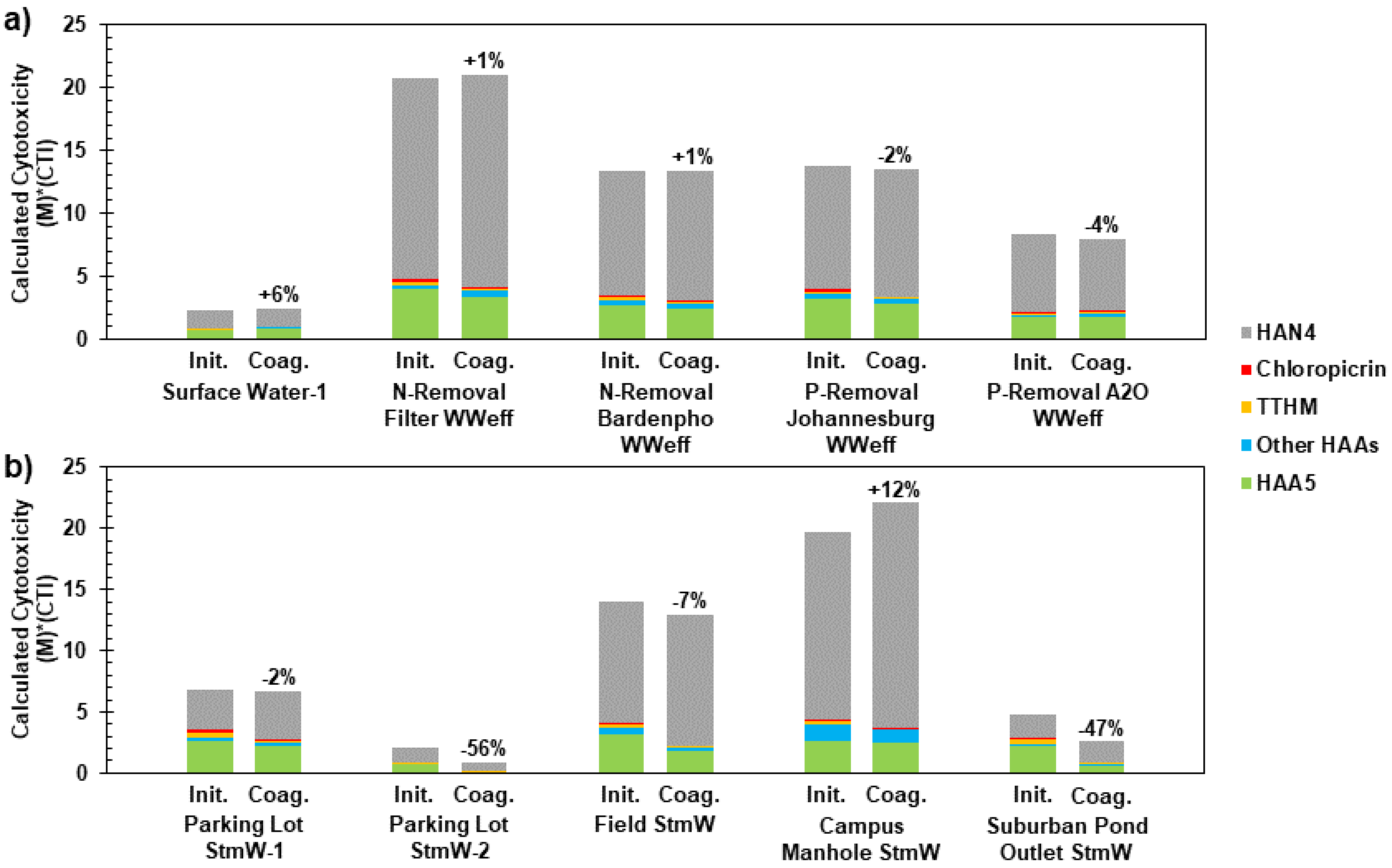


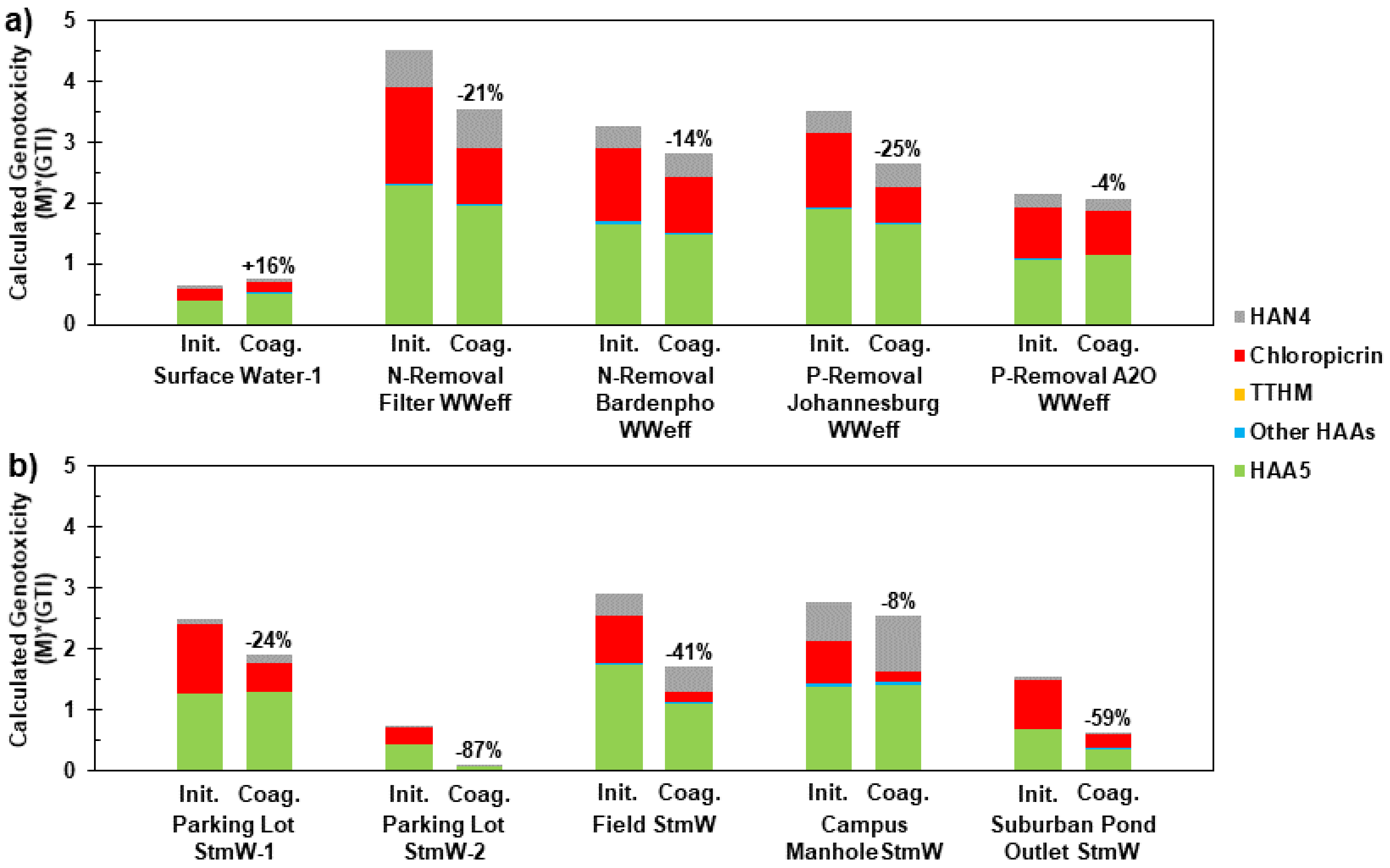
Table A.5. Reduction of DBP formation under UFC conditions. For DBP formation categories with analytes that were over the range of the method, extrapolated values are in parenthesis.

Sample		TOC (mg/L)	UVA_{254} (1/cm)	Cl Demand (mg/L as Cl_2)	TTHM (µg/L)	HAA5 (µg/L)	HAA9 (µg/L)	HAN4 (µg/L)
Surface Water-1	Raw	3.8	0.061	2.67	80.6	58.2	68.6	3.37
	Coag.	3.1	0.033	2.41	52.3	36	45.7	3.24
	% Removal	18%	46%	10%	35%	38%	33%	4%
Parking Lot StmW-1	Raw	17.7	0.549	20.3	299 (574)	432 (438)	452 (459)	13.1
	Coag.	10.2	0.24	9.87	247	138	155	12.9
	% Removal	43%	56%	51%	57%	69%	66%	1%
Parking Lot StmW-2	Raw	4.194	0.136	8.25	108	89.8	93	6.04
	Coag.	3.229	0.060	3.40	15.7	11.6	19	4.05
	% Removal	23%	56%	59%	85%	87%	80%	33%
Field StmW	Raw	11.4	0.203	21.3	342	264	328	18.9
	Coag.	10.19	0.141	13.8	164	77.6	116	16
	% Removal	11%	31%	35%	52%	71%	65%	13%
Campus Manhole StmW	Raw	6.4	0.193	13.5	301	271	407	13.1
	Coag.	4.0	0.080	8.28	139	55.3	129	12.9
	% Removal	37%	59%	39%	54%	80%	68%	1%
Suburban Pond Outlet StmW	Raw	7.337	0.245	15.6	292 (465)	514 (728)	535 (750)	6.45
	Coag.	3.482	0.054	4.19	116	103	117	4.58
	% Removal	53%	78%	73%	75%	86%	84%	29%
N-Removal Filter WWeff	Raw	9.61	0.185	26.7	240	285	327	22.7
	Coag.	8.288	0.151	24.0	190	184	250	22.4
	% Removal	14%	18%	10%	21%	35%	24%	1%
N-Removal Bardenpho WWeff	Raw	7.79	0.155	14.7	235	216	261	14
	Coag.	6.90	0.122	12.1	185	151	195	14.1
	% Removal	11%	21%	18%	21%	30%	25%	-1%
P-Removal Johannesburg WWeff	Raw	8.288	0.128	15	198	215	266	14
	Coag.	7.324	0.113	10.9	91.2	127	180	13.1
	% Removal	12%	12%	27%	54%	41%	32%	6%
P-Removal A2O WWeff	Raw	5.955	0.106	9.71	134	136	160	9.34
	Coag.	5.617	0.097	9.22	74.9	114	141	9.24
	% Removal	6%	8%	5%	44%	16%	12%	1%

Table A.6. Bromine Incorporation Factor (BIF) for alternative waters before and after coagulation.

	TTHM (0 to 3)			Dihalogenated HANs (0 to 2)			Trihalogenated HAAs (0 to 3)			Dihalogenated HAAs (0 to 2)		
	Raw	Coag.	Diff.	Raw	Coag.	Diff.	Raw	Coag.	Diff.	Raw	Coag.	Diff.
Surface Water-1	0.15	0.19	0.04	0.37	0.38	0.01	0.19	0.31	0.13	0.13	0.18	0.05
Parking Lot StmW-1	0.08	0.11	0.03	0.13	0.18	0.05	0.04	0.15	0.11	0.04	0.09	0.05
Parking Lot StmW-2	0.10	0.16	0.05	0.056	0.053	-0.003	0.03	0.24	0.21	0.04	0.49	0.46
Field StmW	0.23	0.33	0.10	0.43	0.56	0.14	0.25	0.46	0.21	0.14	0.36	0.22
Campus Manhole StmW	0.33	0.83	0.50	0.91	1.17	0.26	0.42	1.12	0.70	0.28	0.72	0.44
Suburban Pond Outlet StmW	0.09	0.19	0.10	0.18	0.31	0.13	0.02	0.10	0.08	0.03	0.13	0.10
N-Removal Filter WWeff	0.30	0.34	0.04	0.71	0.76	0.05	0.10	0.31	0.21	0.17	0.23	0.06
N-Removal Bardenpho WWeff	0.24	0.29	0.05	0.72	0.74	0.02	0.20	0.28	0.08	0.16	0.20	0.05
P-Removal Johannesburg WWeff	0.27	0.36	0.09	0.72	0.80	0.08	0.23	0.39	0.15	0.17	0.25	0.08
P-Removal A2O WWeff	0.25	0.33	0.08	0.66	0.60	-0.06	0.16	0.21	0.06	0.15	0.19	0.04

Figure A.7. Calculated genotoxicity of measured DBPs in (a) surface water and wastewater effluents and (b) stormwaters. “Coag” refers to samples coagulated with 40 mg/L alum, except for Parking Lot StmW-1 which was coagulated with 80 mg/L alum.



A.5 Blending

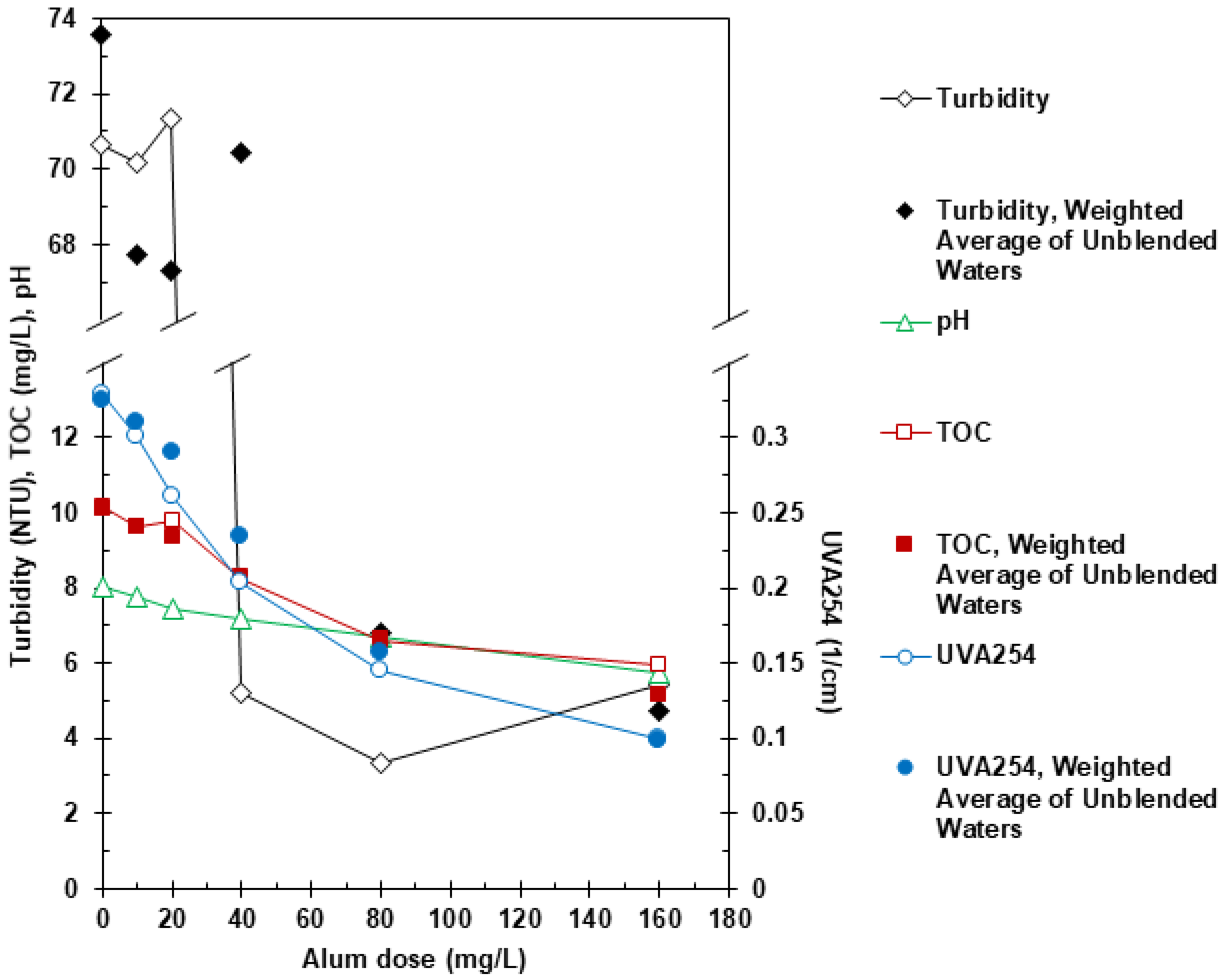


Figure A.8. Turbidity, DOC, and UVA_{254} removal by alum coagulation from a 50:50 blend of *Parking Lot StmW-1* and *Surface Water-1*. "Weighted Average of Unblended Waters" refers to the weighted average of unblended *Parking Lot StmW-1* and unblended *Surface Water-1* at each alum dose. Experimental replicates at 40 mg/L alum were within ±2% or ±1 NTU.

A.6 Modeling Treatment Performance

Table A.7. R^2 and standard error (%) of the Coagulation Model for organic carbon removal from unblended stormwaters and wastewater effluents at coagulant dose ranges of 10 to 160 mg/L and 10 to 80 mg/L. Organic carbon was measured as DOC unless otherwise indicated.

Source Waters	Coagulant	10 to 160 mg/L		10 to 80 mg/L	
		R^2	Standard Error (%)	R^2	Standard Error (%)
Highway StmW	Alum	-2.12	29%	-0.58	12%
Industrial StmW	Alum	-1.73	15%	-0.85	5%
Parking Lot StmW-1	Alum	0.92	8%	0.93	5%
Parking Lot StmW-1	Ferric chloride	0.92	14%	0.89	6%
Parking Lot StmW-2	Alum	-1.29	25%	0.46	15%
Field StmW	Alum	-3.48	17%	-2.59	10%
Campus Manhole StmW	Alum	0.47	16%	0.81	9%
Suburban Pond Outlet StmW	Alum	0.32	47%	0.20	52%
Campus Pond StmW*	Alum	-1.53	16%	-1.56	11%

*TOC

Table A.8. Characteristics of the two samples from the *N-Removal Bardenpho WWeff* sampling location.

	Aug. 2016	Mar. 2017
DOC (mg/L)	6.32	8.23
UVA_{254} (1/cm)	0.132	0.155
SUVA (L/mg/m)	2.1	1.9
pH	7.5	7.8
Alkalinity (mg/L as $CaCO_3$)	110	99
Turbidity (NTU)	1.28	1.74

Table A.9. Nonsorbable fraction, R^2, and standard error of the general and site-specific Coagulation Model for samples of wastewater effluent and stormwater collected from the same wastewater treatment facility or stormwater drain on different days. For the site-specific Coagulation Model, the nonsorbable fraction was optimized to minimize standard error for the chronologically first sample from each sampling location. Model parameters other than the nonsorbable fraction were held constant.

Sample Location	Sample Date	Coagulation Model	Nonsorbable Fraction (%)	R^2	Standard Error (%)
N-Removal Bardenpho WWeff	Aug. 2016	General	43%	0.43	14%
		Site-specific	57%	0.93	4%
	Mar. 2017	General	44%	0.79	7%
		Site-specific	57%	0.92	4%
Parking Lot StmW	Feb. 2017	General	39%	0.92	8%
		Site-specific	44%	0.94	4%
	Apr. 2017	General	36%	-1.29	25%
		Site-specific	44%	-0.46	19%

Parking Lot StmW-2 had an increase in DOC at 160 mg/L alum (Figure A.9). This increase may be due to resuspension or suboptimal pH[250] (4.7 at that dose). The Coagulation Model was incapable of predicting this increase, regardless of modifications to the nonsorbable fraction. This fact contributed to the low accuracy of the Coagulation Model for *Parking Lot StmW-2* regardless of whether a site-specific nonsorbable fraction was calibrated based on *Parking Lot StmW-1*.

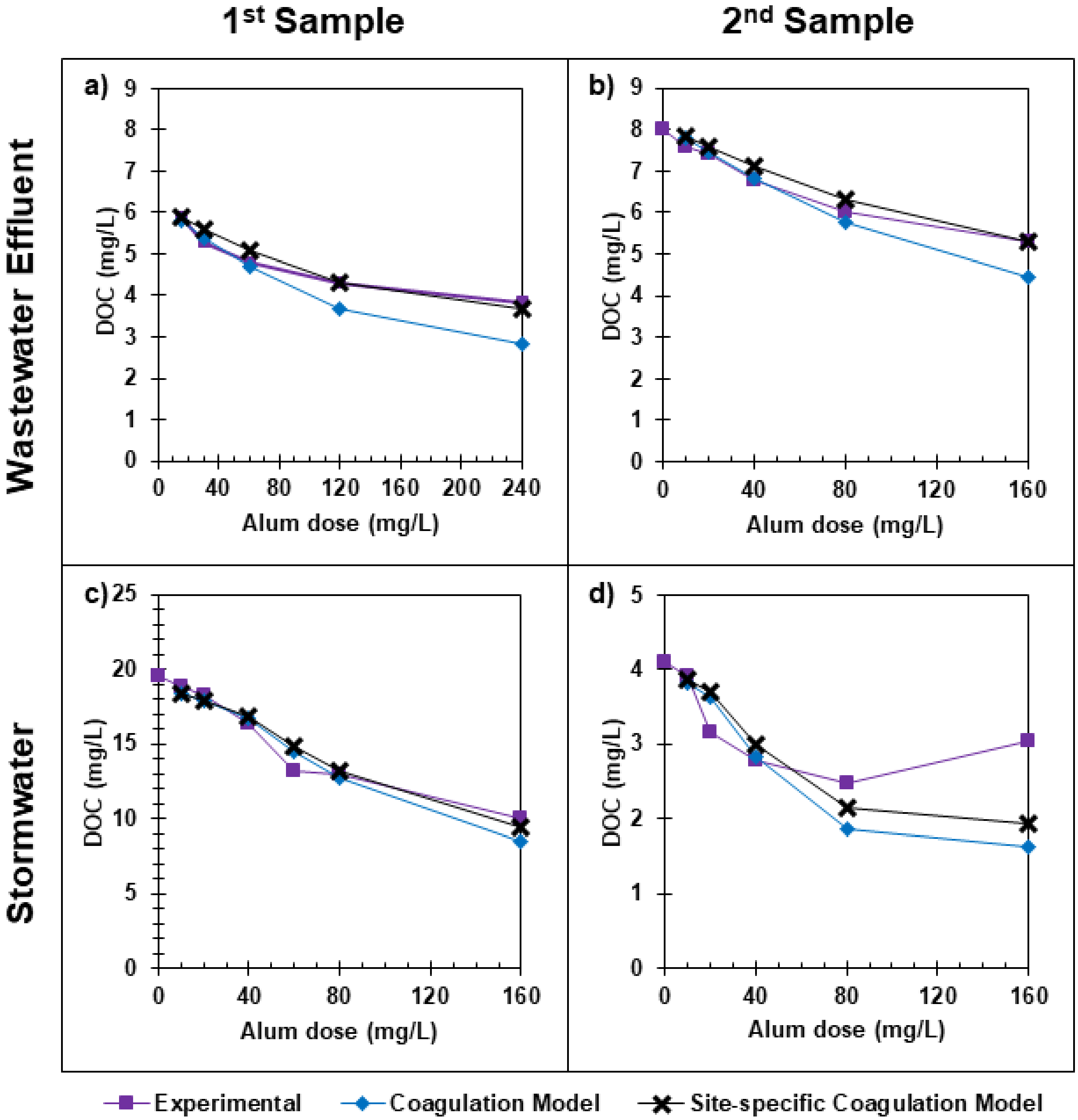


Figure A.9. Predicting DOC removal with the general Coagulation Model and a calibrated site-specific Coagulation Model from (a) *N-Removal Bardenpho WWeff* (August 2016 sample) (b) *N-Removal Bardenpho WWeff* (March 2017 sample) (c) *Parking Lot StmW-1* (February 2017 sample) and (d) *Parking Lot StmW-2* (April 2017 sample).

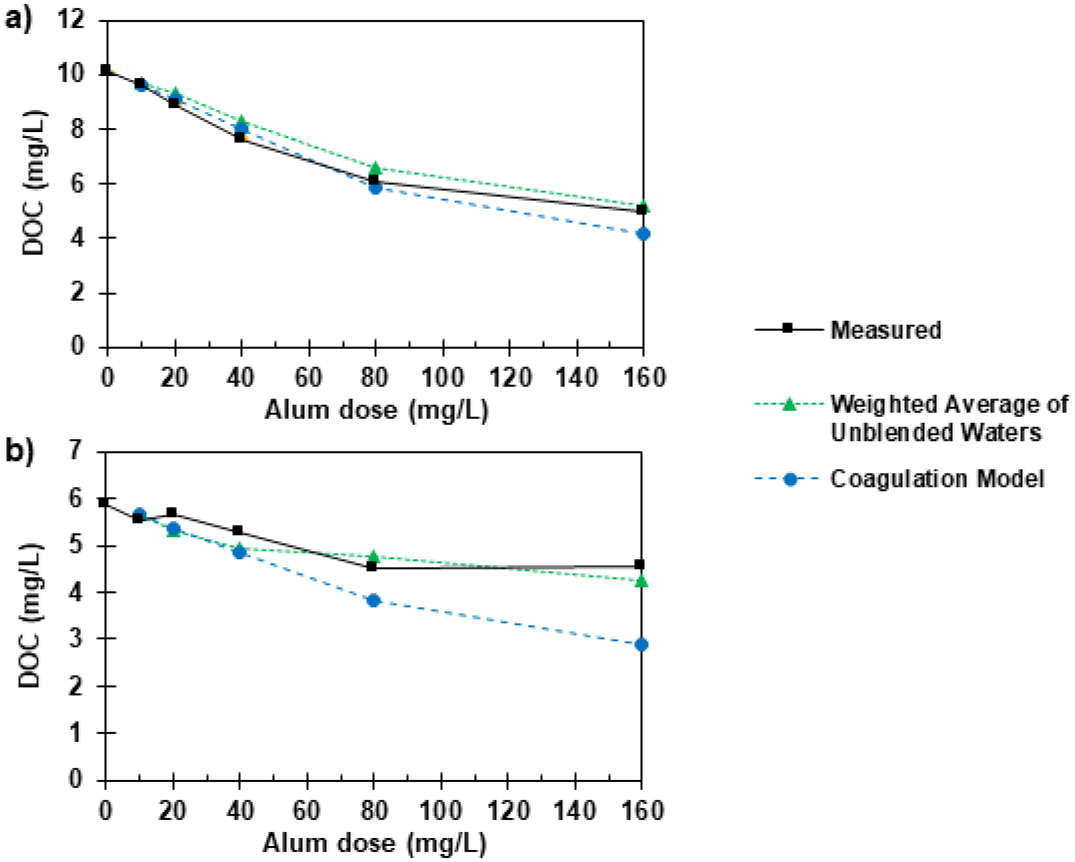


Figure A.10. **Two methods (the Coagulation Model and the Weighted Average of Unblended Waters) for predicting DOC removal from two blends of stormwater with surface water: (a) 50%** ***Parking Lot StmW-1*** **+ 50%** ***Surface Water-1*** **(b) 50%** ***Field StmW*** **+ 50%** ***Surface Water-2.***

Table A.10. Predicting Turbidity, TOC, DOC, and UVA_{254} with Weighted Average of Unblended Waters.

	Parking Lot StmW-1 + Surface Water-1		Field StmW + Surface Water-2		N-Removal Bardenpho WWeff + Surface Water-1	
	R^2	Standard Error (%)	R^2	Standard Error (%)	R^2	Standard Error (%)
Turbidity	0.35	494%	-0.70	39%	0.68	32%
TOC	0.83	8%	0.92	3%	0.89	5%
DOC	0.94	6%	0.70	5%	0.94	4%
UVA_{254}	0.89	9%	0.99	2%	0.98	4%

Turbidity was the least well predicted parameter for the wastewater effluent blend, with R^2 of 0.68 and standard error of 32%. Turbidity removal from the 50:50 blend of *Parking Lot StmW-1* and *Surface Water-1* was not well simulated by the Weighted Average of Unblended Waters (Figure A.5 and Table A.10). The difference was most apparent at the 40 mg/L alum dose, at which the turbidity in the blend was reduced from 80 NTU to 5.2 NTU, but the turbidity in the unblended *Parking Lot StmW-1* was only reduced from 148 NTU to 140 NTU. Rather than diluting the post-coagulation turbidity of the *Parking Lot StmW-1* by a factor of two, blending with surface water appears to have reduce the dose required for high turbidity removal from around 80 mg/L alum to 40 mg/L alum. The Weighted Average of Unblended Waters was also inaccurate for the turbidity of the 50:50 blend of *Field StmW* and *Surface Water-2* (Table A.10). However, the Weighted Average of Unblended Waters was accurate for UVA_{254} and TOC in this blend with R^2 of 0.99, and 0.92, respectively (Table A.10).

APPENDIX B

SUPPLEMENTARY INFORMATION

For

ENVIRONMENTAL COMPARISON OF BIOCHAR AND ACTIVATED CARBON FOR TERTIARY WASTEWATER TREATMENT

B.1 Abbreviations and TRACI category descriptions

Table B.1. Commonly used abbreviations and definitions.

PAC	Powdered Activated Carbon
MCWB	Moderate Capacity Wood Biochar
LCWB	Low Capacity Wood Biochar
MCBB	Moderate Capacity Biosolids Biochar
MCBB+ MCWB	Moderate Capacity Biosolids Biochar supplemented with Moderate Capacity Wood Biochar
MCBB+Low Impact PAC	Moderate Capacity Biosolids Biochar supplemented with Low Impact PAC
LFWB	Lab Furnace Wood Biochar
LFBB	Lab Furnace Biosolids Biochar
HHV	Higher heating value
WWTF	Wastewater treatment facility
mc	Moisture content
LCI	Life Cycle Inventory
TRACI	Tool for the Reduction and Assessment of Chemical Impacts

B.1.1 TRACI Impact Categories

Information about each impact category used in the TRACI[122] methodology is summarized below:

- *Ozone depletion* refers to decreasing the concentration of stratospheric ozone, which provides protection from skin cancer and cataracts.
- *Global warming* refers to the rise in the Earth's global average surface temperature.
- *Smog* refers to the formation of ground-level ozone, created by chemical reactions between nitrogen oxides (NOx) and volatile organic compounds (VOCs) in sunlight.
- *Acidification* is the increasing concentration of hydrogen ion (H+) in a local environment.
- *Eutrophication* refers to enrichment of an aquatic ecosystem with nutrients (nitrates, phosphates) that accelerate an undesirable accumulation of algal biomass.

- *Carcinogenics* and *non-carcinogenics* refer to relative human toxicological impacts, separated into carcinogenic and non-carcinogenic effects such as the effects of benzene and toluene, respectively.
- *Respiratory effects* deals with a subset of the criteria pollutants, i.e., particulate matter and precursors to particulates.
- *Ecotoxicity* captures the direct impacts of chemical emissions from industrial systems on the health of plant and animal species.
- *Fossil fuel depletion* refers to the consumption of oil, coal, and natural gas in MJ equivalents.

B.2 PAC Scenario Methods

B.2.1 Production Sites

The PAC production sites considered were four different Calgon Carbon Corporation locations in Santa Fe Springs, CA; Houston, TX; Catlettsburg, KY; and Pittsburgh, PA.[251] For each site, state-specific electricity emissions were used in the LCI data. The hauling of PAC from a production site to a WWTF was modeled with semi-trailer trucks, with a carrying capacity of 3.5-20 metric tonnes. The distance between each site and Boulder, CO was estimated using Google Maps™.

B.2.2 Storage

The required number of silos was calculated assuming a weekly (once every 7 days) adsorbent delivery frequency; this was an uncertainty parameter (see Table B.3). Silos were assumed to be cylindrical with 4.76 mm (3/16 inch) wall thickness.[125] The dosing infrastructure was assumed similar between all scenarios and negligible relative to the silo's steel mass. Each silo had an air fluidizer system to keep the PAC dry and loose. It was assumed that each silo had sixteen air fluidizers, which was based on visual inspection.[124] The electricity requirements for these fluidizers were estimated based on data for commercially available systems;[126] it was assumed that each fluidizer was blowing 55 m^3/hr^5 of air at 1.1 bar.[126] Also, a 50% efficiency for the air pump was assumed; this was an uncertainty parameter (see Table B.3). The power consumption was calculated using the following equation:[252]

Equation B 1

$$\dot{\omega} = \frac{1}{\eta} \frac{\gamma}{\gamma - 1} P_1 Q_1 \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right]$$

where:

ω is power (kW)

η is efficiency

γ is the ratio of heat capacities at constant pressure (C_p) and volume (C_V);

for air, $\gamma = C_p/C_V = 1.4$

P_1 is initial absolute pressure (kPa)

P_2 is final absolute pressure (kPa)

Q_1 is volumetric flow at inlet conditions (m^3/s)

B.2.3 Disposal

After settling, the coagulated adsorbent was dewatered to 22.5% solids with a belt filter press. This percent was selected as the midpoint of the typical range for dewatered sludge cake after a belt filter press (20-25%).[195] Commercially available data for belt filter presses[127] was used to estimate the electricity and stainless steel requirements for dewatering. The dewatered coagulated adsorbent was then hauled by semi-trailer truck from the Boulder WWTF to the nearest municipal landfill (19.6 km).

B.3 Wood Biochar Scenario Methods

B.3.1 Full-scale Facility

The following operational data about wood biochar and wood pellet co-production facility was based on full-scale operations.[117] The facility was assumed to run 24 hours per day, 5.5 days per week, and 50 weeks per year. The production process starts with the woodchips being dried to 8% moisture content in a 1 MW triple pass rotary dryer. The heat for the dryer comes from pyrolysis gas combustion except for startup, at which time woodchips are burned for approximately 2 hours each week. The dried woodchips are then split, with approximately 95% being pelletized (out of scope) and 5% conveyed by air to the pyrolysis chamber. The residence time in the pyrolysis chamber is approximately 45 minutes. The dried woodchips are augured through the pyrolysis system and exposed to a temperature gradient ranging from 400 to 1200°C. The infrastructure for biochar pyrolysis includes fans, tubes, rotary airlocks, conveyors, and the pyrolysis chamber itself. The pyrolysis yield under the above conditions is 0.29 kg non-ground biochar per kg of 8% mc woodchips, or 0.31 kg non-ground biochar per kg dry (0% mc) woodchips. The energy recovered from pyrolysis gas combustion is 27.8 MJ of heat energy/kg non-ground biochar. Therefore, the pyrolysis gas is sufficient to operate the dryer for the woodchips being dried for pyrolysis; also, extra energy is produced, which is used to dry the woodchips that will be turned into pellets. The total drying electrical energy consumption was estimated based on commercially available dryers[253] that matched the throughput of the full-scale facility. The drying electricity energy allocated to biochar was estimated by assuming only 5% of the total electrical energy was for biochar (because only 5% of the woodchip mass being dried was converted to biochar), which was 340 MJ electricity per tonne of non-ground wood biochar.

B.3.2 MCWB Generation

Moderate capacity wood biochar ($dose_{75}$ = 150 mg/L) was produced in the lab under the following conditions (details in [33]). Pine pellets were placed in a laboratory-scale, 1-gallon top-lit updraft gasifier (TLUD) and a small fraction of the pellets where ignited (<0.1%). A fan was placed underneath the TLUD to create an atmosphere higher in oxygen, which resulted in a peak temperature of 850^0C and a duration of ~20 minutes. The laboratory scale TLUD simulates the full-scale system because the only energy source was thermal decomposition of the pine pellets.

B.3.3 Pyrolysis Gas

Biochar pyrolysis gas energy available after combustion was estimated using:

Equation B 2

$$E_{pyrolysis\ gas} = \eta_{overall} * [(HHV_{feedstock} - Y * HHV_{biochar}) * m_{feedstock}]$$

where:

$E_{pyrolysis\ gas}$ is the total energy recovered (after losses) from pyrolysis gas (MJ)

$\eta_{overall}$ is the overall energy conversion efficiency

$HHV_{feedstock}$ is the higher heating value of the feedstock (MJ/kg feedstock)

Y is the pyrolysis mass yield (kg non-ground biochar/kg feedstock)

$HHV_{biochar}$ is the higher heating value of the biochar (MJ/kg biochar)

$m_{feedstock}$ is the mass of feedstock (kg)

The heat content of the feedstock minus the heat content of the biochar is the maximum amount of energy that could be captured in the form of pyrolysis gas. However, much of this energy was assumed to be lost due to conversion losses, gas combustion due to furnace operation (maintaining the temperature), fugitive gas emissions, etc. Individually, these losses are difficult to quantify, so an overall efficiency ($\eta_{overall}$) was used. For the low capacity wood biochar from the full-scale facility, $\eta_{overall}$ was calculated as 74.5%; this value is an uncertainty parameter for moderate capacity wood biochar and moderate capacity biosolids biochar (see Table B.3). The HHV of wood was an uncertainty parameter (see Table B.3). The HHV of wood biochar was calculated using it elemental content (Table B.2) and an equation derived by Demirbas (Equation B 1).[129] The HHV for low and moderate capacity wood biochars were calculated as 31.3 and 31.7 MJ/kg, respectively.

Equation B 3

$$HHV = 33.5(\%C) + 142.3(\%H) - 15.4(\%O) - 14.5(\%N)$$

where:

HHV is higher heating value (MJ/kg)
%C is percent carbon by mass
%H is percent hydrogen by mass
%O is percent oxygen by mass
%N is percent nitrogen by mass

Peters et al.[92] estimated the air emission from the combustion and treatment of poplar biochar pyrolysis gas. The units on that data were converted to mass of emission per mass of woodchip mass lost, by using that study's pyrolysis yield. These data were used to represent wood biochar, and specifically the pine wood biochar used in the current study, since pine and poplar have similar elemental composition and heating values.[92,128,254] The full-scale facility[117] and the simulated facility in Peters et al.[92] both had air quality control with thermal oxidation and cyclones. While the direct emission of the treated air are included in the model, the energy and material inputs for air quality control processes were not to maintain the same system boundary used for the activated carbon LCI.

B.3.4 Biochar Grinding

The full-scale facility currently sells wood biochar in ≤3mm and ≤6mm sizes. Therefore, further grinding would be required for PAC-style adsorbent applications. The electrical energy consumption of these grinder models is around 0.25 MJ/kg non-ground biochar, which was based on commercially available grinding units.[132] The grinding was assumed to take place at the biochar facility so that the WWTF would not need to invest the capital for an on-site adsorbent grinder.

B.3.5 Carbon Sequestration

Carbon sequestration due to wood biochar production (i.e., part of the wood's biogenic carbon was sequestered because it was turned into inert carbon and stored as biochar instead of remaining in the natural carbon cycle) was calculated by multiplying the mass of ground biochar by the biochar percent carbon and by a factor that accounts for the biochar carbon's recalcitrance. This recalcitrance factor is an uncertainty parameter (see Table B.3). While tree harvesting initially results in a loss of carbon stored in the forest ecosystem, these ecosystems gradually return to equilibrium carbon storage over the course of decades.[255] The rate at which the forest ecosystem returns to equilibrium depends on factors such as climate, tree species, and logging techniques.[255] This model assumed sustainable forestry practices such that, over a 40-year timeframe, tree harvesting for woodchips results in negligible net change to the quantity of carbon stored in the forest; therefore, avoided carbon sequestration from woodchip harvesting was not included.

B.4 Biosolids Biochar Scenario Methods

B.4.1 On-site Biochar Production

The Boulder WWTF uses a Modified Ludzack-Ettinger process for liquid treatment. Primary and waste activated sludge are thickened and mixed before being anaerobically digested at mesophilic temperatures. Biogas is converted to energy using a combined heat and power unit. The sludge available for biochar production was based on the final mass of the dewatered, digested sludge so that all scenarios had the same energy recovery due to anaerobic digestion. The total mass available for biochar production was 1,406 dry tonnes in 2014.[256] For either digested or pre-digested sludge streams, not enough feedstock material was available to produce the biosolids biochar needed for 75% SMX removal. The total amount of moderate capacity biosolids biochar (dose_{75} = 150 mg/L) that could be produced from digested sludge was 428 tonnes ground biochar per year, which allowed for the treatment of only 16.5% of the wastewater effluent flow. Since biosolids pyrolysis was assumed to take place onsite at the WWTF, biochar delivery hauling was negligible.

B.4.2 Biosolids Drying

Heat and electrical energy required for biosolids drying was calculated according to the Biosolids Emissions Assessment Model (BEAM).[133] The initial moisture content of the biosolids was 77.4%, based on data from the Boulder WWTF.[256] The moisture content of the dried biosolids was estimated as 7.5%, which is average value achieved by current technologies;[195] this moisture content was an uncertainty parameter (see Table B.3). The energy for drying biosolids was based on these moisture contents, biosolids mass, and the energy requirement assumptions of 4.5 MJ heat per kg of water removed and 214 kWh per metric tonne of dry biosolids.[133]

B.4.3 Pyrolysis Gas

Equation B 2 shows the calculation for pyrolysis gas energy recovery. The best guess overall efficiency was the same as wood biochar, 74.5%; this value is an uncertainty parameter (see Table B.3). The HHV of biosolids was assumed to be 18.8 MJ/kg[21]; this value is also an uncertainty parameter (see Table B.3). The HHV of biosolids biochar was calculated using the moderate capacity biosolids biochar's elemental contents (see Table B.2 and Equation B 3). The energy recovered from pyrolysis gas energy was used to dry the biosolids. For our base case assumptions, moderate capacity biosolids biochar pyrolysis gas provided 82% and natural gas provided 18% of the heat for the dryer.

Air emissions from pyrolysis gas combustion were based on the air emissions data from a full-scale biosolids pyrolysis facility.[134] The air quality control units for this gasification plant were thermal oxidation, cyclones, a baghouse with lime injection, and a wet scrubber. While the direct emission of the treated air are included in the model, the energy and material inputs for air quality control processes were not to maintain the same system boundary used for the activated carbon LCI. Had air quality control processes been included, the impacts from air pollution control would have been greater for biosolids biochar than for wood biochar since wood biochar only requires thermal oxidation and cyclones.[92,117]

B.4.4 Fertilizer

The quantity of artificial fertilizer needed to substitute the avoided biosolids land application was calculated using the elemental content of Boulder WWTF biosolids (7.34% N and 2.21% P dry weight)[256] and assumptions about the amount of those nutrients that are plant available nutrients for typical biosolids (35% plant available nitrogen and 40% plant available phosphorus).[136] The transportation distance to the land application site from the Boulder WWTF and from the regional fertilizer storehouse were assumed roughly equal, and therefore that hauling was not included in the scope of this model.

B.4.5 Carbon Sequestration

Carbon sequestration due to biosolids biochar was calculated by multiplying the mass of ground biochar by the biochar carbon content and a factor to account for the biochar carbon recalcitrance. Both the biosolids biochar carbon content and recalcitrance are uncertainty parameters (see Table B.3). Biosolids land application also results in carbon sequestration due to the residence time of biosolids carbon in the soil, and the increased soil microbial growth due to improved soil properties.[257] Artificial fertilizers do not result in the same degree of carbon sequestration from soil microbial growth.[258] A factor of 0.22 kg CO2 eq./kg cumulative dry biosolids mass was used to estimate carbon sequestration from biosolids land application;[257] this is an uncertainty parameter (Table B.3).

B.5 Adsorbent Elemental Composition and Properties

Table B.2 summarizes the main properties of each adsorbent used in this study. The PAC was a widely used, high performing, bituminous coal-based activated carbon (Calgon WPH).[33] The low capacity wood biochar (LCWB) was generated in a full-scale pyrolysis facility where pine woodchips were exposed to a temperature gradient from 400 to 1200^{0}C.[117] The moderate capacity wood biochar (MCWB) was produced from pine wood pellets in a 1-gallon TLUD gasifier under high draft (850^{0}C) conditions.[33] The lab furnace wood (LFWB) and biosolids (LFWB) biochars were produced using a laboratory furnace under similar conditions to each other (850^{0}C for 8 hours) and had the same SMX adsorption capacity in tertiary wastewater (dose$_{75}$=300 mg/L).[33] The moderate capacity biosolids biochar (MCBB) was modelled by estimating adsorbent properties based on the relationships between the lab furnace wood and biosolids biochars, and between the lab furnace wood biochar and moderate capacity wood biochar (described below).

Table B.2. Adsorbent Elemental Compositions and Properties. All values were measured excluding MCBB, which was based on the MCWB values and to reflect the relationship between the LFWB and LFBB as described below. NA is not applicable. [a]Assumed same as corresponding lab furnace biochar. [b]Estimated based on trends of yield vs. temperature (as described below).[33,146,259] [c]Estimated based on its assumed ash mass (same as biosolids) and the composition of LFBB (described below).

Property	**PAC**	**Low Capacity Wood Biochar (LCWB)**	**Moderate Capacity Wood Biochar (MCWB)**	**Moderate Capacity Biosolids Biochar (MCBB)**	**Lab Furnace Wood Biochar (LFWB)**	**Lab Furnace Biosolids Biochar (LFBB)**
Carbon	NA	85.4%	94%	22.8%[c]	93.1%	20.7%
Hydrogen	NA	4.8%	0.54%	0.2%[c]	0.9%	0.3%
Nitrogen	NA	0.5%	0.12%	1.1%[c]	0.1%	0.8%
Oxygen	NA	7.6%	2.5%	3.5%[c]	4.1%	5.2%
Ash	NA	1.7%	3.1%	72.4%[c]	1.8%	73.0%
Pyrolysis Yield (kg non-ground biochar/kg dry feedstock)	NA	31%	26%[b]	34%[c]	25%	34%
Dose$_{75}$ (mg/L)	70	600	150	150	300	300
Apparent Density (kg/m^3)	641	670[a]	670[a]	911[a]	670	911

B.5.1 Pyrolysis Yield

The pyrolysis yields of lab furnace wood and biosolids biochars were determined by massing dry material before and after pyrolysis. Pyrolysis yield of the low capacity wood biochar was reported through personal correspondence.[117] The pyrolysis yields for moderate capacity wood biochar was estimated as 26% based on the full-scale LCWB and differences in operational temperature. The pyrolysis yield for moderate capacity wood biochar was estimated as 26% by adjusting the LCWB's yield according to temperature trends from experimental data;[33,146,259] this yield is an uncertainty parameter (Table B.3). The moderate capacity biosolids biochar pyrolysis yield was estimated using the following equations (Equation B 4 to Equation B 7). For these equations, the main assumptions were: (i) the ash mass during pyrolysis does not change (i.e., the mass of ash was the same in the biochar as in the feedstock, and therefore, the overall loss of solids was due to a decrease in ash free material); and (ii) differences between feedstocks are constant across production conditions (e.g., the wood to biochar relationship of yields are the same regardless of production condition, furnace and TLUD, since the production condition has the greatest influence on yield). Since the moderate capacity biosolids biochar pyrolysis yield (Equation B 4) and ash content (Equation B 7) depend on each other's values, they were simultaneously solved for iteratively.

Equation B 4

$$Y_{MCBB} = \frac{Y_{AFM,MCBB}}{1 - \%Ash_{f,MCBB} + \%Ash_{f,MCBB} * Y_{AFM,MCBB}}$$

where:

Y_{MCBB} is pyrolysis yield for moderate capacity biosolids biochar (kg biosolids biochar/kg dry biosolids).

$Y_{AFM,MCBB}$ is yield of ash free matter (AFM) of moderate capacity biosolids biochar (kg biosolids biochar AFM/kg dry biosolids AFM) (Eqn S5).

$\%Ash_{f,MCBB}$ is the final ash content (ash content of the biosolids biochar)

Equation B 5

$$Y_{AFM,MCBB} = \left(\frac{Y_{AFM,LFBB}}{Y_{AFM,LFWB}} \right) Y_{AFM,MCWB}$$

where:

$Y_{AFM,MCBB}$ is yield of ash free matter of moderate capacity biosolids biochar (kg biosolids biochar AFM/kg biosolids AFM).

$Y_{AFM,MCWB}$ is yield of ash free matter of moderate capacity wood biochar (kg wood biochar AFM/kg wood AFM).

$Y_{AFM,\ LFBB}$ is yield of ash free matter of lab furnace biosolids biochar (kg biosolids biochar AFM/kg biosolids AFM).

$Y_{AFM,LFWB}$ is yield of ash free matter of lab furnace wood biochar (kg wood biochar AFM/kg wood AFM).

Equation B 6

$$Y_{AFM} = \frac{AFM_f}{AFM_i} = \frac{Y - Y * \%Ash_f}{1 - Y * \%Ash_f}$$

where:

Y_{AFM} is yield of ash free matter (kg biochar AFM/kg dry feedstock AFM); calculated for MCWB, LFBB, LFWB using experimental data.

AFM_f is the final biochar AFM fraction (1- $\%Ash_f$) (percent mass basis).

AFM_i is the initial feedstock AFM fraction (1- $\%Ash_i$) (percent mass basis).

$\%Ash_f$ is the final biochar ash content (percent mass basis).

Y is biochar pyrolysis yield (kg biochar/kg dry feedstock).

Equation B 7

$$\%Ash_{f,MCBB} = \frac{\%Ash_{i,MCBB}}{Y_{MCBB}}$$

where:

$\%Ash_{f,MCBB}$ is the moderate capacity biosolids biochar final ash content (percent mass basis).

Y_{MCBB} is pyrolysis yield for moderate capacity biosolids biochar (kg biosolids biochar/kg dry biosolids).

$\%Ash_{i,MCBB}$ is the moderate capacity biosolids biochar's feedstock initial ash content (percent mass basis) (assumed 25%, calculated from LFBB ash content using Eqn. S7 and is within the range of typical biosolids ash contents).[134]

B.5.2 Elemental Composition

The elemental composition of each biochar (except MCBB) was determined with a CHN Elemental Analyzer (Perkin-Elmer model 2400) (described in [33]). The elemental composition of moderate capacity biosolids biochar was estimated using Equation S8 which assumes that the relative differences in elemental content between feedstocks and biochars are the same for wood and biosolids at a given production condition:

Equation B 8

$$x_{MCBB} = \left[\frac{\left(\frac{x_{LFBB}}{AFM_{LFBB}}\right)}{\left(\frac{x_{LFWB}}{AFM_{LFWB}}\right)}\right] * \left(\frac{x_{MCWB}}{AFM_{MCWB}}\right) * AFM_{MCBB}$$

where:

x is elemental content for C, N, H, or O elements (percent mass basis).

AFM_b is the biochar AFM fraction (1- $\%Ash_b$) (percent mass basis).

Subscripts denote biochar: moderate capacity biosolids biochar (MCBB), moderate capacity wood biochar (MCWB), lab furnace biosolids biochar (LFBB), and lab furnace wood biochar (LFWB).

B.6 Uncertainty and Sensitivity Analysis Methods

B.6.1 Silo Storage Capacity

The minimum silo storage capacity was used to calculate the number of silos required to store the adsorbent volume. The storage capacity depended on the frequency of adsorbent delivery, which considered amount of truck traffic, possibility of weekend deliveries, etc. Seven days was selected as the base case to allow for a week's worth of adsorbent, no weekend deliveries, and a feasible number of silos (for a 7-day capacity, PAC required 1 silo and the moderate and low capacity biochars required 2 and 6 silos, respectively).

B.6.2 Air Fluidizer Operation

The air fluidizers must be running while the adsorbent is being dosed from the silo to ensure a loose, steady stream of adsorbent; therefore, the air fluidizer system was assumed to be running in at least one silo at all times. However, the operation of air fluidizers in silos that are not actively being used for dosing and are being used only for storage was uncertain. This uncertainty parameter allowed one silo's air fluidizer to be running at all times while extra silo's had the system operating 0-100% of the time throughout the functional unit. For the base case, the conservative assumption of all silos having air fluidizers running all the time was used, which increased the impact for the biochar scenarios (all had multiple silos) but did not impact PAC (only 1 silo).

B.6.3 Air Fluidizer Pump Efficiency

This refers to the air fluidizer system in the silos used to keep the adsorbent dry and friable. The base case of 50% efficiency was based on the value cited for a typical air compressing pump.[252] The parameter's uncertainty range of 40-60% was chosen to assess sensitivity to this parameter by ranging the expected value by 10%.

Table B.3. All values and their explanations for the uncertainty parameters. Base case (BC) values were used for the main results. Low and high values were used for the Monte Carlo analysis, assuming a uniform probability distribution.

#	Uncertainty Parameter	Low Value	High Value	Base Case Value	Basis
1	Silo Storage Capacity (days)	1	7	7	Daily to weekly delivery frequency; BC was conservative
2	Air Fluidizer Operation (% time)	0%	100%	100%	Full possible range; BC was conservative
3	Air Fluidizer Pump Efficiency	40%	60%	50%	BC was typical value;[167] range was ±10% BC
4	Biochar Grinding Yield	80%	95%	87.5%	Range of existing grinders,[120] BC as average
5	MCWB Pyrolysis Yield	26%	31%	26%	High was LCWB full-scale yield;[104] low and BC were high value adjusted using literature trends[60,134,174]
6	Wood HHV (MJ/kg)	18.6	21.1	19.85	Typical values for softwood;[175] BC was average
7	MCWB Overall Energy Conversion Efficiency	65.1%	74.5%	74.5%	BC and high value were same $\eta_{overall}$ as full-scale;[104] low was same energy per feedstock heat content as full-scale
8	Wood Biochar Recalcitrant Carbon (% mass)	98.6%	99.99%	99.3%	Based on relationship between O:C and C half-life;[176] BC was average
9	MCBB Pyrolysis Yield	32%	36%	34%	BC estimated using Equation D 4 to Equation D 7; range was ±2% BC
10	Dried Biosolids Moisture Content	5%	10%	7.5%	Typical values for current technology;[52] BC was average
11	Biosolids Drying Thermal Energy (MJ/Mg water removed)	3.5	4.5	4.5	Typical values for low[168] and high,[121] BC was conservative
12	Biosolids HHV (MJ/kg)	18.2	19.7	18.8	Typical values for range,[122] BC was average
13	MCBB Overall Energy Conversion Efficiency	69.1%	92.1%	74.5%	Low and high calculated to achieve cited energy recovery (as %feedstock HHV),[127] BC from full-scale data[104]
14	MCBB Carbon Content (% mass)	20.3%	25.3%	22.8%	BC estimated using Equation D 8, range was ±2.5% BC based on range between three biosolids biochar doses
15	Biosolids Land Application Carbon Sequestration (kg CO2 eq./kg dry solids)	0.08	0.37	0.22	Typical values,[172] BC was average
16	Biosolids biochar recalcitrant Carbon (% mass)	87.3%	98.6%	93.0%	Based on relationship between O:C and C half-life;[176] BC was average

B.6.4 Biochar Grinding Yield

This parameter accounts for the biochar mass lost due to grinding (yield = 1 - % mass lost). For both wood and biosolids biochar, the grinding mass yield was assigned the typical mass yield range of industrial activated carbon grinders, which is 80-95%.[132] The average value from this range was used for the base case. The grinding for PAC was included in the PAC generation LCI data.

B.6.5 MCWB pyrolysis yield

This parameter accounts for the mass of dry feedstock lost during pyrolysis (yield units of kg non-ground biochar per kg dry woodchips are represented as a percent). The pyrolysis yield for the moderate capacity wood biochar was not available for full-scale operation, so the maximum value was assumed to be the same as the full-scale low capacity wood biochar (31%).[117] Since pyrolysis yield is generally lower for higher temperature, which results in higher capacity biochars, it was expected that the moderate capacity wood biochar would have a lower yield at the full-scale than the lower capacity biochar.[33,146,259] Therefore, the low value for this uncertainty parameter was set to 5% less than the full-scale system yield (i.e., 26%). This 5% was based on lab-scale experimental data that showed wood biochars with adsorption capacities much higher (150 mg/L dose_{75}) and much lower (1700 mg/L dose_{75}) than the full-scale wood biochar (600 mg/L dose_{75}) had pyrolysis yields that were 10% apart. The low value was also used for the base case since it is expected to be more representative due to the impact of temperature on yield. The range of pyrolysis mass yields in this study is similar to pyrolysis mass yields for biochars with lignocellulosic feedstocks in other LCAs (26%-35%).[92,94,95,97,98,104,105]

B.6.6 Wood HHV

The uncertainty range used typical HHVs of softwood (18.6 and 21.1 MJ/kg dry wood),[260] since pine was the experimental feedstock and is a softwood. The base case was the average of this range (19.85 MJ/kg dry wood). This value is used to estimate energy recovery (Equation B 3).

B.6.7 MCWB Overall Energy Conversion Efficiency

There are two ways of defining the overall efficiency of a pyrolysis system: the pyrolysis gas energy divided by the heat content of the feedstock, or the pyrolysis gas energy divided by difference between the heat content of the feedstock and the heat content of the biochar multiplied by the yield (Equation B 2). For this study, the later definition of efficiency was used. Using the later definition of efficiency, a lower yield char will produce more energy in an equally efficient facility because less of the heat content of the feedstock has been stored in the biochar and more of the heat content of the feedstock is available for capture as pyrolysis gas energy. The full-scale, low capacity wood biochar had an efficiency of 38% based on the first definition or 74.5% based on the definition used for calculations in this model. For the base case and high estimate, moderate capacity biochar was assumed to have the same $\eta_{overall}$ as the full-scale, low capacity wood biochar, 74.5%. For the low estimate, moderate capacity wood biochar was assumed to produce the same amount of pyrolysis gas energy per heat content of feedstock as the full-scale, low capacity wood biochar (i.e., the other definition of efficiency was used). Using this value, an $\eta_{overall}$ of 65.1% was calculated for the moderate capacity wood biochar.

B.6.8 Wood Biochar Recalcitrant Carbon

The amount of carbon sequestration due to biochar production depends on the timeframe recalcitrance of the carbon. Based on the MCWB's and LCWB's O:C ratios, the range of carbon half-lives would be 1,000-100,000 years, based on another study's derived relationship between O:C and half-life.[261] After the functional unit timeframe of 40 years, these half-lives would result in 98.6-99.99% of carbon remaining sequestered for wood biochar. The base case value is the average of this range.

B.6.9 MCBB Pyrolysis Yield

The moderate capacity biosolids biochar pyrolysis yield was estimated using Equation B 4 to Equation B 7. The estimated yield was 34%, and this value was the base case value. The parameter's uncertainty range of 32-36% was chosen to assess sensitivity to this parameter by ranging the expected value by 2%.

B.6.10 Dried Biosolids Moisture Content

One of the most common approaches for drying biosolids at WWTFs are rotary dryers, and current commercially-available systems can dry biosolids to 5-10% final moisture content.[195] The base case was the average value (7.5%).

B.6.11 Biosolids Drying Thermal Energy

The high value for thermal energy requirements of drying biosolids was the value used in the Biosolids Emission Assessment Model (BEAM) model v1.1 (4.5 MJ of heat/Mg water removed when drying biosolids).[133] The low value is based on the stated requirements of commercially-available triple pass rotary dryers (3.5 MJ/Mg).[253] The base case uses the more conservative typical value (4.5 MJ/Mg).

B.6.12 Biosolids HHV

The uncertainty range was based on three biosolids HHV measurements (19.7, 18.6, and 18.2 MJ/kg).[134] The base case was the average of this range (18.8 MJ/kg). This value is used to estimate energy recovery (Equation B 3).

B.6.13 MCBB Overall Energy Conversion Efficiency

This parameter, η_{overall}, was used to calculated energy recovery from moderate capacity biosolids biochar pyrolysis (Equation B 3). Previous studies have found that energy recovered from biosolids pyrolysis gas can range from 60-80% of the biosolids HHV, depending on temperature.[262] Therefore, the η_{overall} values needed to achieve this cited range were calculated (69.1-92.1%). The base case is the value calculated form the full-scale wood biochar facility data (74.5%).[117]

B.6.14 MCBB Carbon Content

The carbon content of moderate capacity biosolids biochar (22.8%) was estimated using Equation B 8. The elemental contents of very low capacity ($dose_{75}$= 600 mg/L) biosolids biochar and low capacity biosolids biochar ($dose_{75}$= 1700 mg/L) were estimated using Equation B 8 based on very low and low capacity wood biochar (W-ND-625^{0}C and W-A-Biochar in [33]). The carbon contents for the very low and low capacity biosolids biochars were calculated as 25.7% and 19.6%, respectively. The range between the three biosolids biochar's carbon contents was 2.5%, which was used as the uncertainty range.

B.6.15 Biosolids Land Application Carbon Sequestration

The low, high, and mean carbon sequestration factors were 0.06, 0.37, and 0.22 kg CO_2 eq./kg dry biosolids, respectively. These values are based on the range and mean of carbon sequestration factors in soils reported by Tian et al.[257]

B.6.16 Biosolids Biochar Recalcitrant Carbon

The carbon recalcitrance of biosolids biochar was determined using the MCBB's O:C ratio and the relationship derived by Spokas.[261] From these, the half-life of biochar carbon in soil would be between 100 and 1,000 years. After the functional unit timeframe of 40 years, these half-lives would result in 87.3-98.6% of carbon remaining in the soil. The base case value is the average of this range.

B.6.17 Wood Biochar Pyrolysis Air Emissions

Four datasets of pyrolysis gas air emissions were selected from the literature (see Table B.4). Peters et al.[92] was selected as the base case for biochar air emissions because of similarities between the modeled system and the real facility in Kremmling, CO. Both the modeled system and the facility in Kremmling, CO were large-scale (>1,000 tonne/yr of dry feedstock), high-tech facilities in developed countries with air treatment with cyclones.[92,117] The other three studies empirically measured air emissions from small- to medium-scale biochar production in developing countries with various low-cost methods to capture and use the pyrolysis gas but no cyclones.[106,130,131] For each air emission dataset, the TRACI environmental impacts per kg biochar were assessed separately using SimaPro (Table B.5). The maximum and minimum impact in each impact category were selected as the high and low values for the uncertainty assessment, respectively. None of the literature air emission datasets had impacts in the ozone depletion or fossil fuel depletion categories.

Table B.4. Wood biochar pyrolysis air emission data (kg emission/kg non-ground biochar) and uncertainty scenarios.

Scenario #	1[92]	2[130]	3[131]	4[106]
Type	Modeled	Experimental	Experimental	Experimental
CO2, biogenic	3.01E+00	4.30E+00	3.02E+00	
CO, biogenic	3.03E-10	5.40E-02	1.22E-01	9.37E-02
VOC		6.00E-03	6.65E-03	3.17E-02
CH4		3.00E-02	1.97E-02	3.70E-03
SO2	5.88E-04			
NO2	4.52E-05			
NO	6.78E-04			
NOx		4.00E-04	7.30E-04	4.80E-03
H	4.45E-11			
Cl	1.08E-09			
HCl	1.23E-04			
TSP	4.97E-05			
PM10		1.10E-02	5.50E-03	6.60E-03
Al	3.11E-08			
B	1.87E-08			
Ca	1.31E-05			
Cd	4.18E-08			
Fe	9.33E-08			
K	4.36E-06			
M	1.52E-06			
Mn	5.29E-08			
Na	5.29E-08			
P	9.95E-07			
Zn	1.12E-07			
Cu	4.04E-08			
Pb	4.36E-09			

Table B.5. Pyrolysis Gas Air Emissions Uncertainty Parameters. Calculated from pyrolysis air emissions datasets from four studies[92,106,130,131] using TRACI methodology.[122]

#	Uncertainty Parameter	Low Value	High Value	Base Case Value	Basis
17	Global warming (kg CO2 eq/kg non-ground biochar)	0.00E+00	7.50E-01	0.00E+00	Full possible range from 4 scenarios; BC was most representative
18	Smog (kg O3 eq/kg non-ground biochar)	1.76E-02	2.33E-01	1.76E-02	Full possible range from 4 scenarios; BC was most representative
19	Acidification (kg SO2 eq/kg non-ground biochar)	2.80E-04	3.36E-03	1.45E-03	Full possible range from 4 scenarios; BC was most representative
20	Eutrophication (kg N eq/kg non-ground biochar)	1.77E-05	2.13E-04	4.96E-05	Full possible range from 4 scenarios; BC was most representative
21	Carcinogenics (CTUh/kg non-ground biochar)	0.00E+00	9.19E-12	9.19E-12	Full possible range from 4 scenarios; BC was most representative
22	Non carcinogenics (CTUh/kg non-ground biochar)	0.00E+00	3.69E-09	3.69E-09	Full possible range from 4 scenarios; BC was most representative
23	Respiratory effects (kg PM2.5 eq/kg non-ground biochar)	4.76E-05	2.53E-03	4.76E-05	Full possible range from 4 scenarios; BC was most representative
24	Ecotoxicity (CTUe/kg non-ground biochar)	0.00E+00	2.98E-03	2.98E-03	Full possible range from 4 scenarios; BC was most representative

B.7 Life Cycle Inventory (LCI) Data

Table B.6. LCI data description and citations for material and energy inputs. [a]Process was modified to include "Electricity mix, California/US US-EI U" for low-impact PAC and "Electricity mix, Kentucky/US US-EI U" for high-impact PAC in place of the default electricity mix. [b]Data was converted from cubic meters to kg using a dry density of 169 kg/m3 (density value is from unit process data description for "Woodchips, softwood, from industry, u=40%, at plant").[120]

LCA Input	**Unit Process from Agri-footprint Database**[121]
PAC	Activated carbon, at plant/RER Mass[a]
LCA Input	**Unit Process from US-EI 2.2**[120]
Alum	Aluminium sulphate, powder, at plant/US
Colorado electricity	Electricity mix, Colorado/US
Galvanized sheet steel	Galvanized steel sheet, at plant NREL/RNA U
Hauling	Transport, lorry 3.5-20t, fleet average/US*
Natural gas heat energy	Natural gas, combusted in industrial boiler NREL/US U
Nitrogen fertilizer	Urea, as N, at regional storehouse/US
Phosphorus fertilizer	Single superphosphate, as P2O5, at regional storehouse
Stainless steel	Chromium steel 18/8, at plant/US
Woodchip heat energy	Woodchips, from industry, softwood, burned in furnace 1000kW/US*
Woodchip	Woodchips, softwood, from industry, u=40%, at plant

Table B.7. Total amounts and types of material and energy inputs for each scenario to achieve the functional unit. (n/a is not applicable).

Input	Unit	High Impact PAC	Low Impact PAC	Low Capacity Wood Biochar	Moderate Capacity Wood Biochar	MCBB+ MCWB	MCBB + Low Impact PAC
PAC	kg	4.84E+07	4.84E+07				4.04E+07
Hauling	tkm	1.07E+08	8.53E+07	1.13E+08	2.88E+07	2.56E+07	8.61E+07
Colorado Electricity	MJ	1.02E+08	1.02E+08	1.15E+09	3.39E+08	3.76E+08	2.64E+08
Galvanized sheet steel	kg	5.26E+03	5.26E+03	3.30E+04	1.10E+04	1.16E+04	1.27E+04
Alum	kg	6.91E+06	6.91E+06	6.91E+06	6.91E+06	6.91E+06	6.91E+06
Stainless steel	kg	2.91E+03	2.91E+03	1.50E+04	4.01E+03	4.01E+03	2.91E+03
Woodchips	kg			2.54E+09	7.59E+08	6.32E+08	
Woodchip combustion	MJ			-1.09E+10	-3.74E+09	-3.13E+09	
Nitrogen fertilizer	kg					1.47E+06	1.47E+06
Phosphorus fertilizer	kg					5.04E+05	5.04E+05
Natural gas combustion	MJ					1.57E+08	1.57E+08

Table B.8. Direct air emissions due to the release of treated and combusted pyrolysis gas in the low and moderate capacity wood biochar scenarios. These emissions are in addition to the life cycle emissions form the materials and energy used (Table B.7).

Emission	Low Capacity Wood Biochar	Moderate capacity Wood Biochar	Unit
Sequestration			
Carbon sequestered, CO_2 eq	1.34E+09	3.54E+08	kg
Emissions to Air			
Carbon dioxide (biogenic)	8.14E+08	2.61E+08	kg
Carbon monoxide (biogenic)	8.20E-02	2.63E-02	kg
Sulfur dioxide	1.59E+05	5.10E+04	kg
Nitrogen dioxide	1.22E+04	3.92E+03	kg
Nitrogen monoxide	1.83E+05	5.88E+04	kg
Hydrogen	1.20E-02	3.86E-03	kg
Chlorine	2.92E-01	9.36E-02	kg
Hydrogen chloride	3.33E+04	1.07E+04	kg
Particulates	1.34E+04	4.31E+03	kg
Al	8.41E+00	2.70E+00	kg
B	5.06E+00	1.62E+00	kg
Ca	3.54E+03	1.14E+03	kg
Cd	1.13E+01	3.62E+00	kg
Fe	2.52E+01	8.09E+00	kg
K	1.18E+03	3.78E+02	kg
Mg	4.11E+02	1.32E+02	kg
Mn	1.43E+01	4.59E+00	kg
Na	1.43E+01	4.59E+00	kg
P	2.69E+02	8.63E+01	kg
Zn	3.03E+01	9.71E+00	kg
Cu	1.09E+01	3.50E+00	kg
Pb	1.18E+00	3.78E-01	kg

Table B.9. Direct air emissions due to the release of treated and combusted pyrolysis gas in the moderate capacity biosolids biochar supplemented with moderate capacity wood biochar scenario. These emissions are in addition to the life cycle emissions form the materials and energy used (Table B.7).

	MCBB+MCWB	Unit
Sequestration		
Carbon sequestered, CO2 eq.	2.96E+08	kg
Emissions to Air		
Carbon dioxide (biogenic)	2.95E+08	kg
Carbon monoxide (biogenic)	2.18E+08	kg
Sulfur dioxide	1.25E+03	kg
Nitrogen dioxide	4.26E+04	kg
Nitrogen monoxide	3.27E+03	kg
Hydrogen	4.91E+04	kg
Chlorine	3.22E-03	kg
Hydrogen chloride	3.17E+02	kg
Particulates	9.99E+03	kg
Al	3.60E+03	kg
B	2.25E+00	kg
Ca	1.35E+00	kg
Cd	9.48E+02	kg
Fe	3.03E+00	kg
K	6.75E+00	kg
Mg	3.16E+02	kg
Mn	1.10E+02	kg
Na	3.83E+00	kg
P	3.83E+00	kg
Zn	7.20E+01	kg
Cu	8.11E+00	kg
Pb	3.02E+00	kg
Dioxin	3.22E-06	kg
Mercury	9.00E-01	kg
NOx	6.05E+04	kg

Table B.10. Direct air emissions due to the release of treated and combusted pyrolysis gas in the moderate capacity biosolids biochar supplemented with low impact PAC scenario. These emissions are in addition to the life cycle emissions form the materials and energy used (Table B.7).

	MCBB + Low Impact PAC	**Unit**
Sequestration		
Carbon sequestered, CO2 eq	7.46E+05	kg
Emissions to Air		
Cadmium	8.16E-03	kg
Carbon monoxide (biogenic)	1.02E+03	kg
Dioxin	3.22E-06	kg
HCl	3.17E+02	kg
Lead	9.24E-02	kg
Mercury	9.00E-01	kg
Nox	6.05E+04	kg
PM	1.08E+03	kg
SO2	1.25E+03	kg

B.8 Results

Figure B.1. Overview of relative impacts in all 10 TRACI impact categories for all six adsorbent scenarios. Each scenario's value in a category was normalized to the low impact PAC value in that category.

B.8.1 Process Contribution by TRACI category

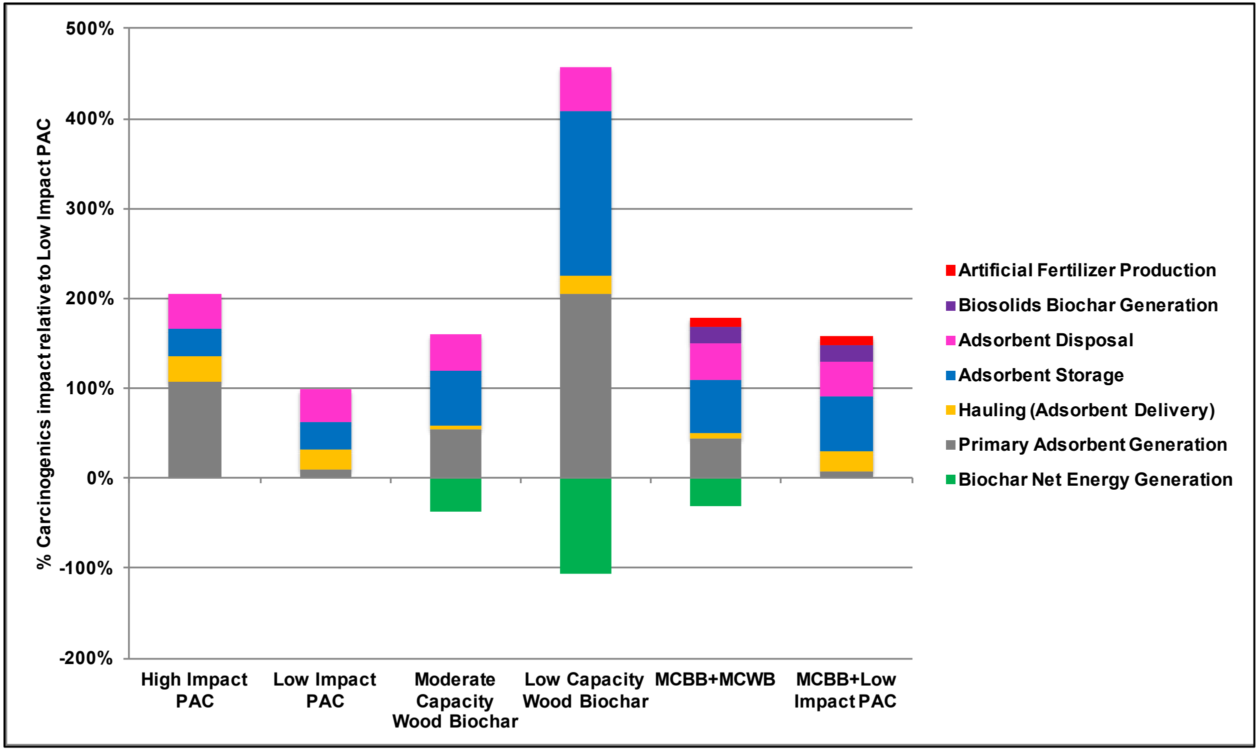


Figure B.2. Process contributions to *Eutrophication*.

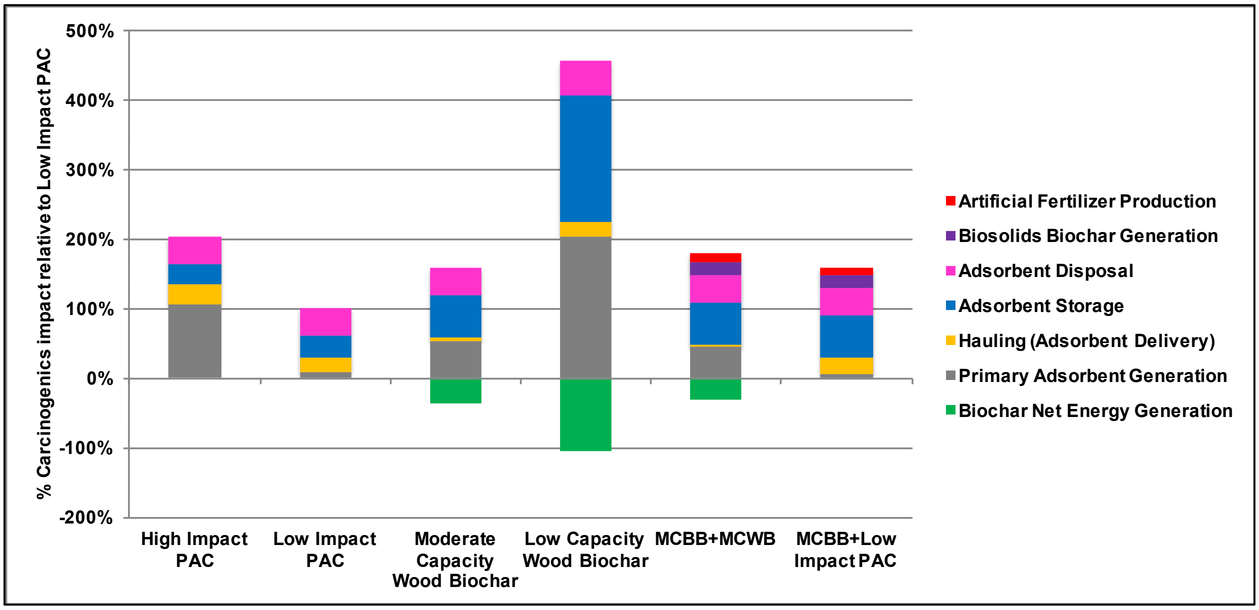


Figure B.3. Process contributions to Carcinogenics.

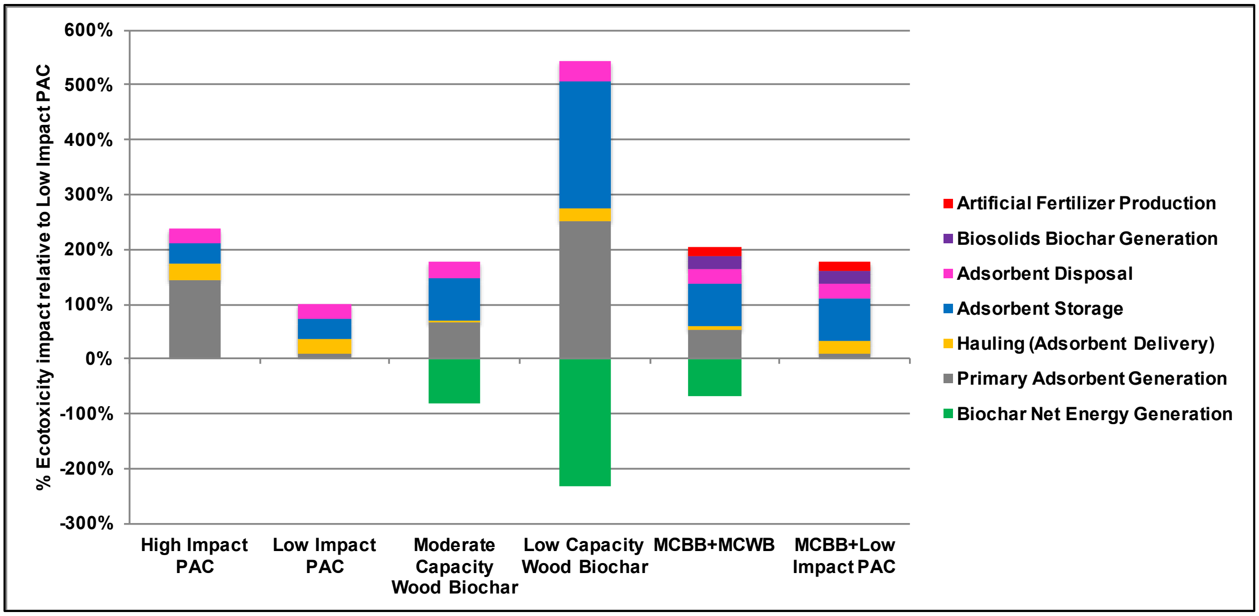


Figure B.4. Process contributions to *Ecotoxicity*.

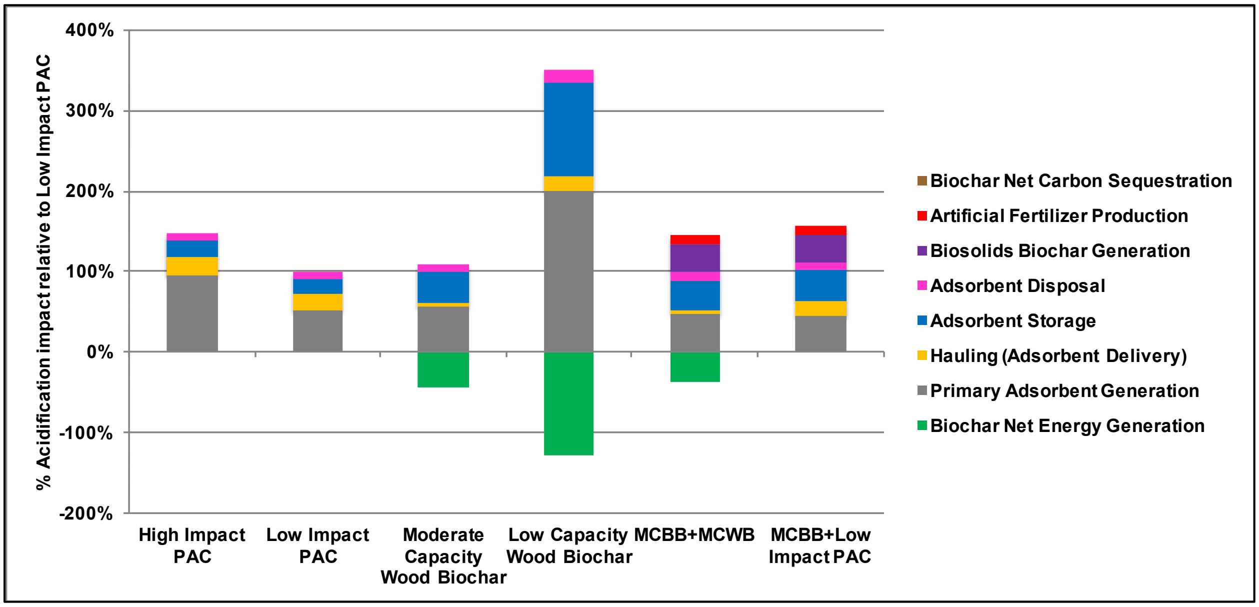


Figure B.5. Process contributions to *Acidification*.

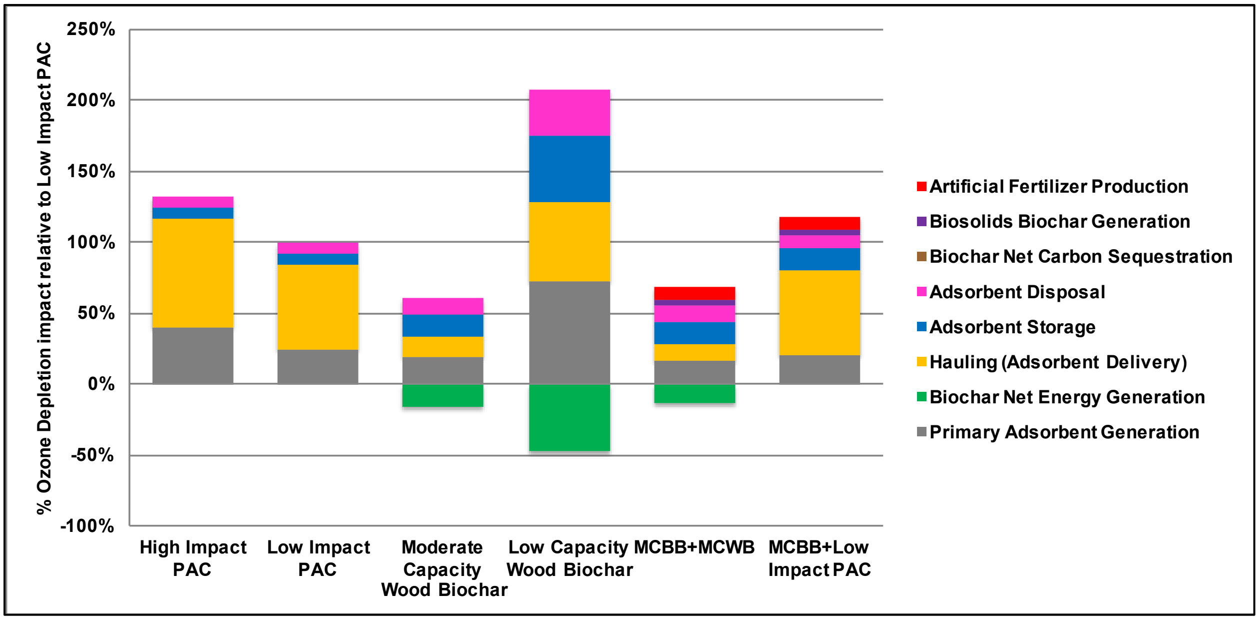


Figure B.6. Process contributions to *Ozone Depletion*.

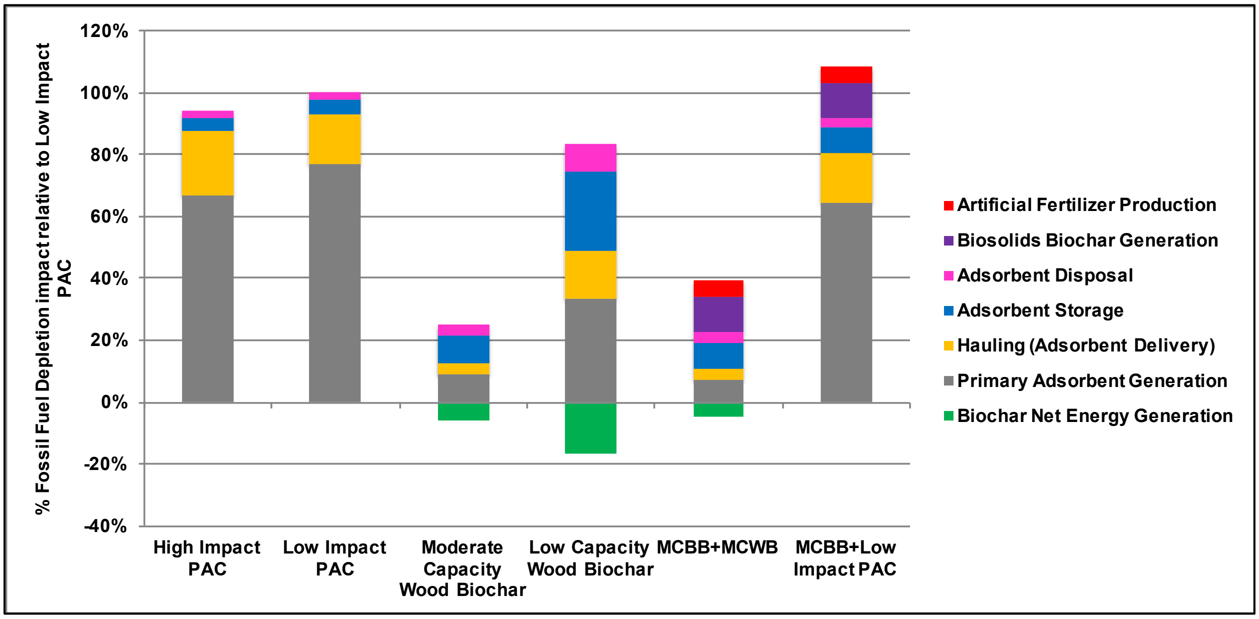


Figure B.7. Process contributions to *Fossil Fuel Depletion*.

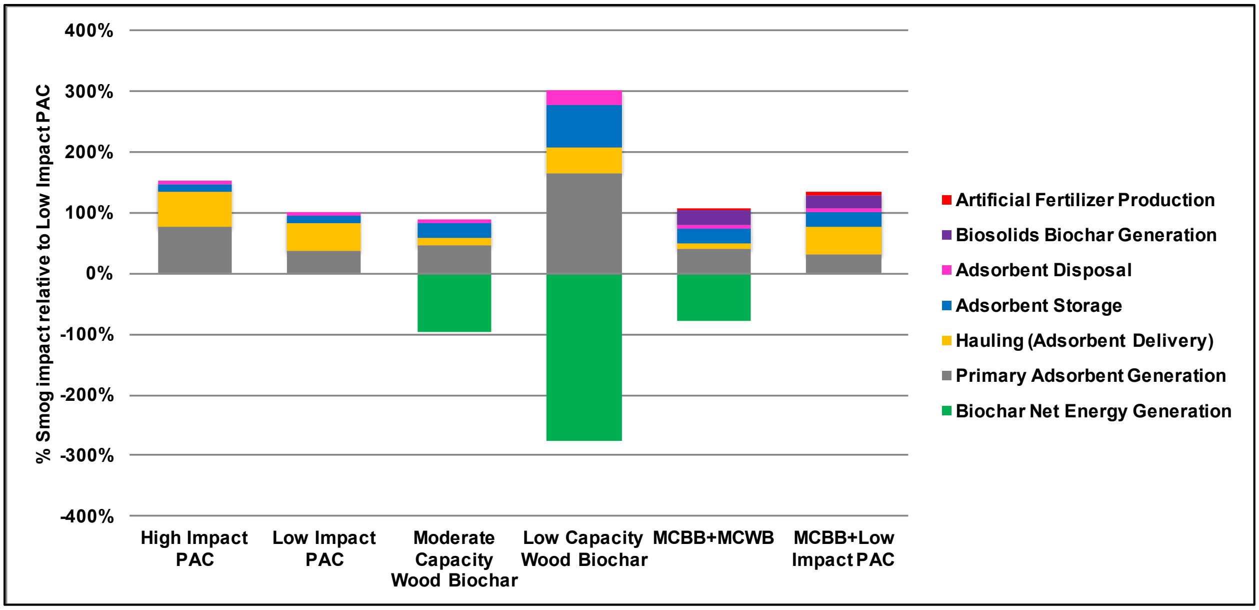


Figure B.8. Process contributions to *Smog*.

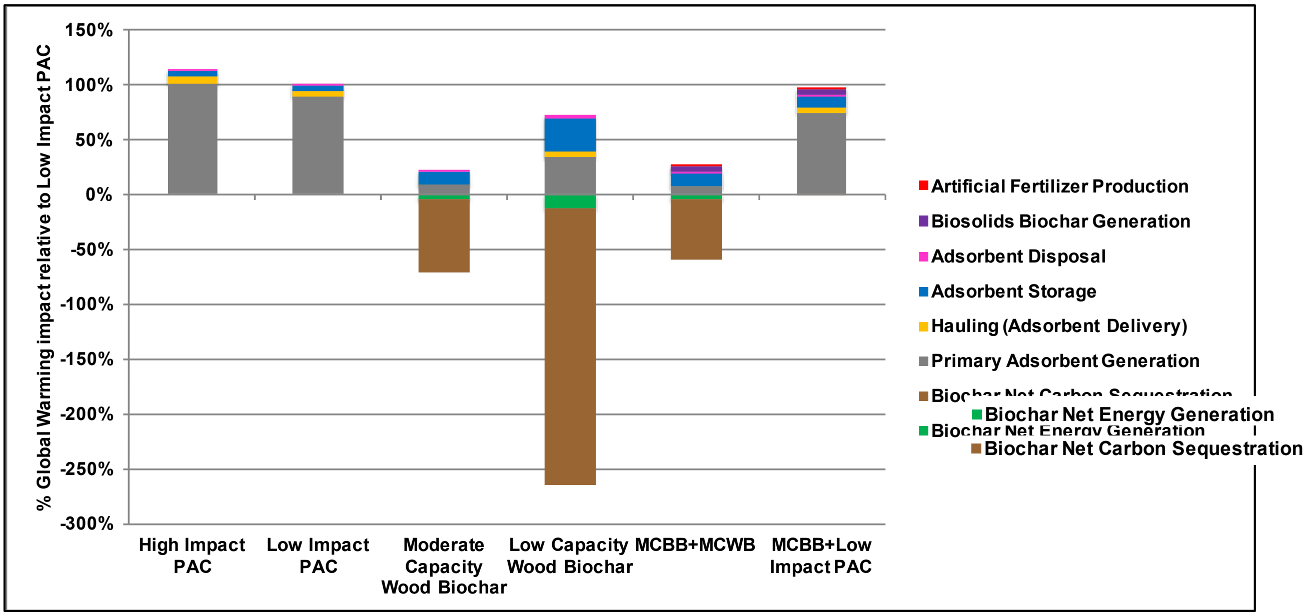


Figure B.9. Process contributions to *Global Warming*.

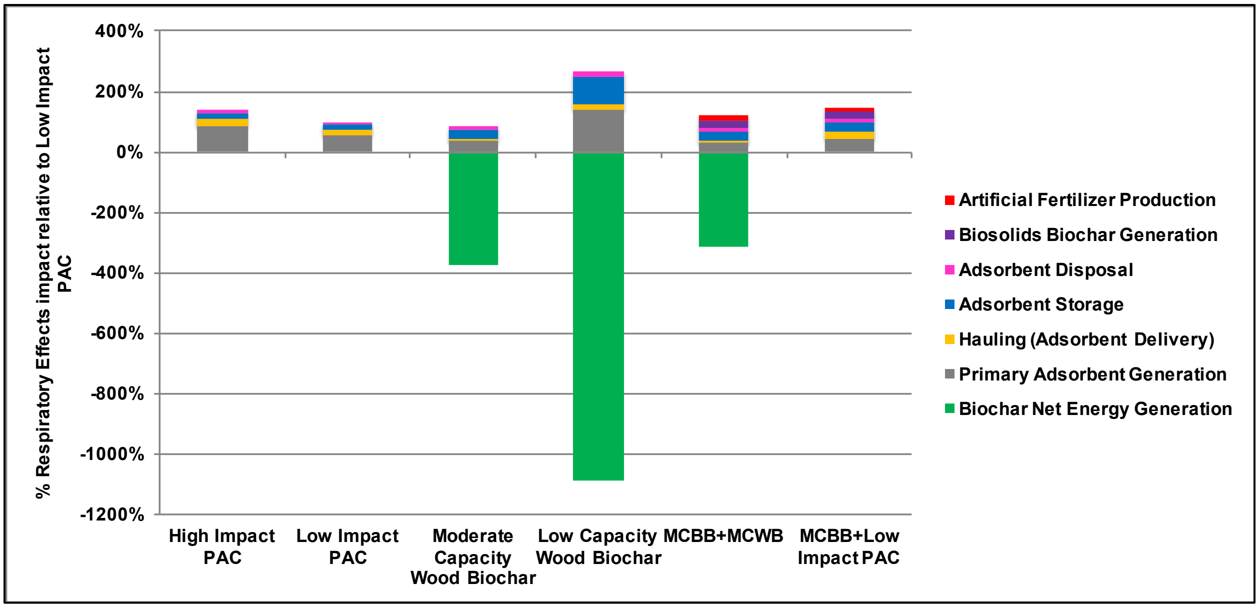


Figure B.10. Process contributions to *Respiratory Effects.*

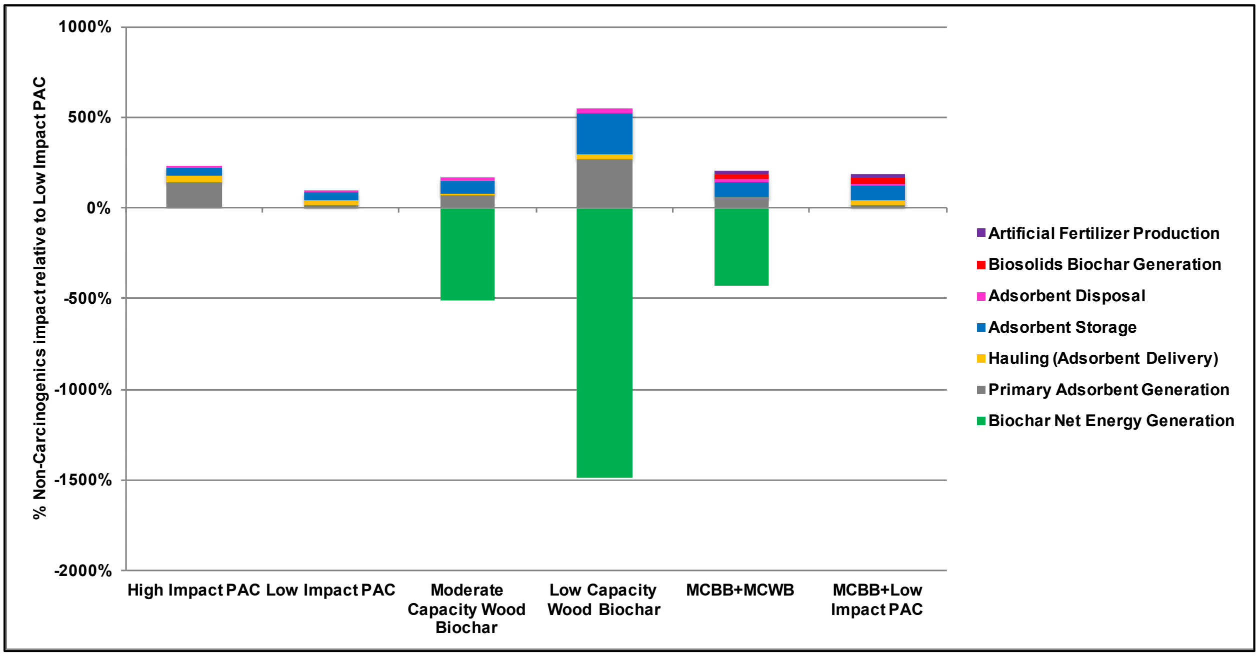


Figure B.11. Process contributions to *Non-carcinogenics.*

B.8.2 Uncertainty Results

Of the all the uncertainty parameters (Table B.3 and Table B.5), only Pyrolysis Gas Air Emissions, Fluidizer Pump Efficiency, Grinder Mass Yield, and MCWB Pyrolysis Mass Yield were strongly correlated ($|\rho|\geq0.8$) with at least one impact category, in at least one scenario (Table B.11). Acidification, global warming, respiratory effects, and smog were sensitive to their respective pyrolysis gas air emissions impacts for both the MCWB and LCWB scenarios. Non-carcinogenics in the MCWB scenario and both non-carcinogenics and respiratory effects in the MCBB+MCWB scenario were sensitive to *the MCWB pyrolysis yield*. Non-carcinogenics were sensitive to *biochar grinding yield* in the scenario LCWB. Both *MCWB pyrolysis yield* and *biochar grinding yield* have a large impact on energy recovery (and pyrolysis gas production) which resulted in the offset of woodchip combustion for heat energy in those three scenarios. Higher yields reduced the offset of woodchip combustion for energy, and the offset of woodchip combustion air emissions had a large contribution to the non-carcinogenics and respiratory effects categories (as discussed in the main paper).

All 10 environmental impact categories were sensitive to *air fluidizer pump efficiency* in the low-impact PAC and high-impact PAC scenarios. Higher efficiencies resulted in less energy consumption and therefore smaller environmental impacts. This uncertainty parameter correlation is so large because this was the only uncertainty parameter that impacted either of these PAC scenarios. There were a total of three parameters. The second was silo storage capacity, but the uncertainty range (1-7 days) did not change the number of silos needed. Since only one silo was needed, the third uncertainty parameter representing the time an air fluidizer was running had no impact on the PAC results either.

Table B.11. Correlation coefficients from the Monte Carlo analysis for uncertainty parameters that had strong correlations.

#	Uncertainty Parameter	Scenario	Impact Category	Correlation Coefficients
3	Air Fluidizer Pump Efficiency	Low-Impact PAC	ALL	-1.00
3	Air Fluidizer Pump Efficiency	High-Impact PAC	ALL	-1.00
4	Biochar Grinding Yield	LCWB	Non carcinogenics	0.80
5	MCWB Pyrolysis Yield	MCWB	Non carcinogenics	0.87
5	MCWB Pyrolysis Yield	MCBB+MCWB	Respiratory Effects	0.83
5	MCWB Pyrolysis Yield	MCBB+MCWB	Non carcinogenics	0.83
17	Pyrolysis gas air emissions - Global Warming	LCWB	Global Warming	0.94
17	Pyrolysis gas air emissions - Global Warming	MCWB	Global Warming	0.92
18	Pyrolysis gas air emissions - Smog	LCWB	Smog	1.00
18	Pyrolysis gas air emissions - Smog	MCWB	Smog	0.99
19	Pyrolysis gas air emissions - Acidification	MCWB	Acidification	0.82
23	Pyrolysis gas air emissions - Respiratory Effects	LCWB	Respiratory Effects	1.00
23	Pyrolysis gas air emissions - Respiratory Effects	MCWB	Respiratory Effects	0.97

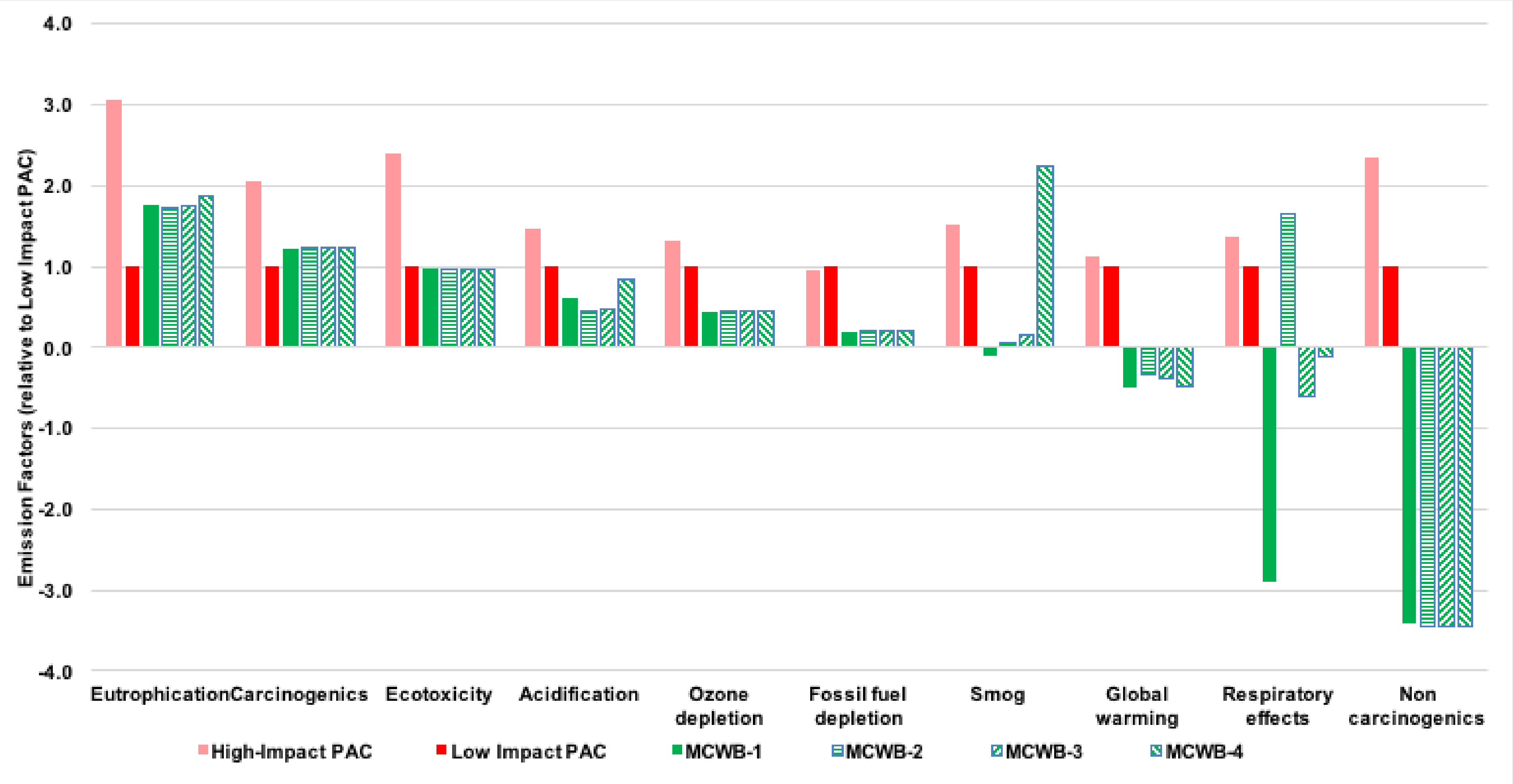


Figure B.12. Overview of relative impacts in all 10 TRACI impact categories for four scenarios of pyrolysis gas air emissions. MCWB-1 has large-scale, high-tech modeled pyrolysis gas air emissions with treatment by thermal oxidation and cyclones.[92] MCWB-2 has small-scale, experimental pyrolysis air emissions from a flame curtain kiln with no treatment.[130] MCWB-3 has small-scale, experimental pyrolysis air emissions from an Adam retort kiln with no treatment.[131] MCWB-4 has small-scale, experimental pyrolysis gas air emissions from a TLUD.[106]

B.8.3 Energy source for wood biochar energy offset

When considering the offset of heat from natural gas combustion instead of woodchip combustion, moderate capacity wood biochar still had lower environmental impacts compared to PAC (Figure B.13). In this scenario, moderate capacity wood biochar had lower environmental impacts than high impact PAC in all categories, and it had lower impacts than low impact PAC in six out of ten categories and net environmental benefits in the remaining four categories (global warming, acidification, respiratory effects, fossil fuel depletion).

B.8.4 Carbon Sequestration and WWTF Carbon Footprint Offset

The net amount of carbon sequestration (i.e., global warming impact) of the moderate capacity wood biochar scenario was found to be -261 gigagrams CO2 eq. After dividing by the functional unit time frame, the annual carbon sequestration expected was -6.5 gigagrams CO2 eq./yr. As a comparison, the carbon footprint of a typical WWTF was found from the literature. Rodriguez-Garcia at el.[147] determined the average global warming impact (i.e., carbon footprints) for six WWTFs in Spain that removed organic matter and nutrients before discharge to be 0.29 kg CO_2 equivalent per cubic meter of wastewater treated. This value included emissions from energy use and the production of chemicals as used for primary, secondary, and tertiary treatment of the liquid stream as well as sludge treatment and disposal. This value of 0.29 kg CO_2 eq./m^3 was used to represent a typical WWTF in the US with a reference flow of the functional unit (12.5 MGD or 1.73E+07 m^3/year), which resulted in a carbon footprint of 5.0 gigagrams CO2 eq./yr.

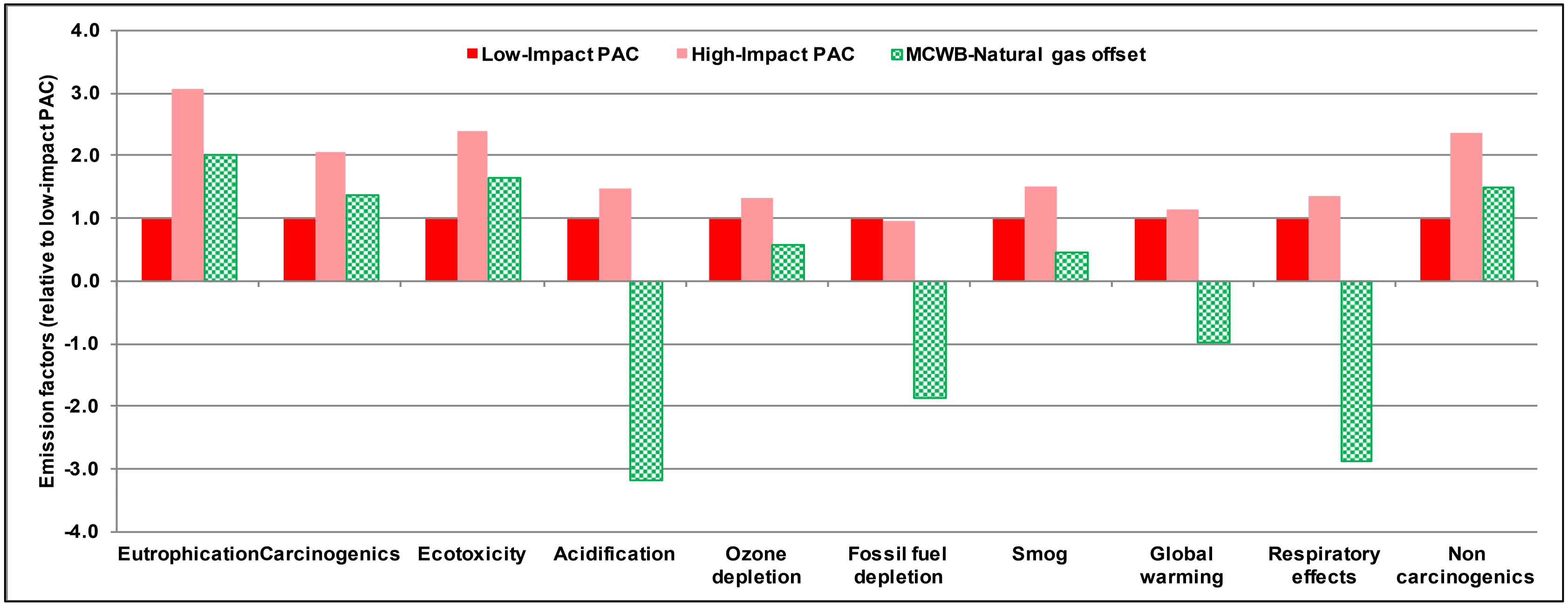


Figure B.13. Comparison of moderate capacity wood biochar offsetting natural gas from energy recovered during pyrolysis (MCWB-Natural Gas Offset), low-impact PAC, and high-impact PAC.

A comparison the two global warming impact values (6.5 Gg CO2 eq./yr offset due to biochar production and use *divided by* 5 Gg CO2 eq./yr emitted due to WWTF energy and chemical use) shows that the moderate capacity wood biochar scenario would offset all of the WWTF's carbon emissions and result in extra carbon sequestration; in other words, 130% of the emissions would be offset. The amount of carbon mitigation depends on the WWTF operations and location and on the amount of biochar being used (i.e., a lower dose of biochar would result in a lower offset or less carbon sequestration). However, even if a typical WWTF in the US is twice as carbon intensive as the cited value (e.g., due to higher carbon emitting electricity sources or greater energy use due to more stringent treatment requirements), the production and use of moderate capacity biochar would still have a significant offset of 65%, which is much better than the increase in carbon footprint exhibited by the low-impact PAC scenario. The use and production of low-impact PAC for SMX removal would resulted in 13 Gg CO2 eq./yr, which could more than triple the global warming impact of a WWTF.

B.9 Alternative Scenario #1: WWTF Location

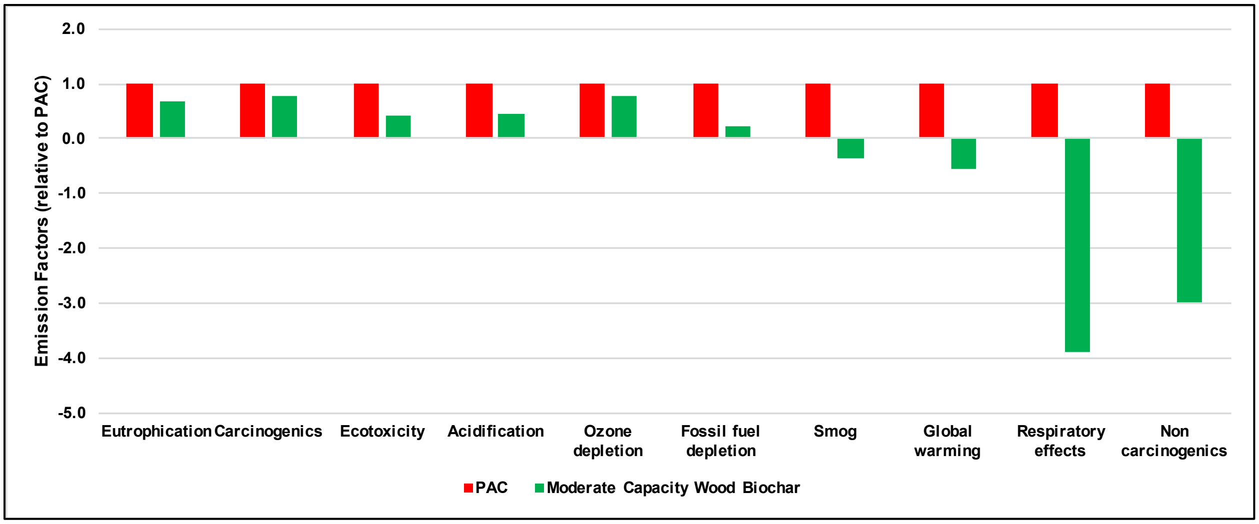


Figure B.14. The 10 TRACI impacts for PAC and moderate capacity wood biochar scenarios when <u>adsorbent delivery is 20 km</u> for both and all processes in the system boundary used the <u>US average electricity</u> production mix.

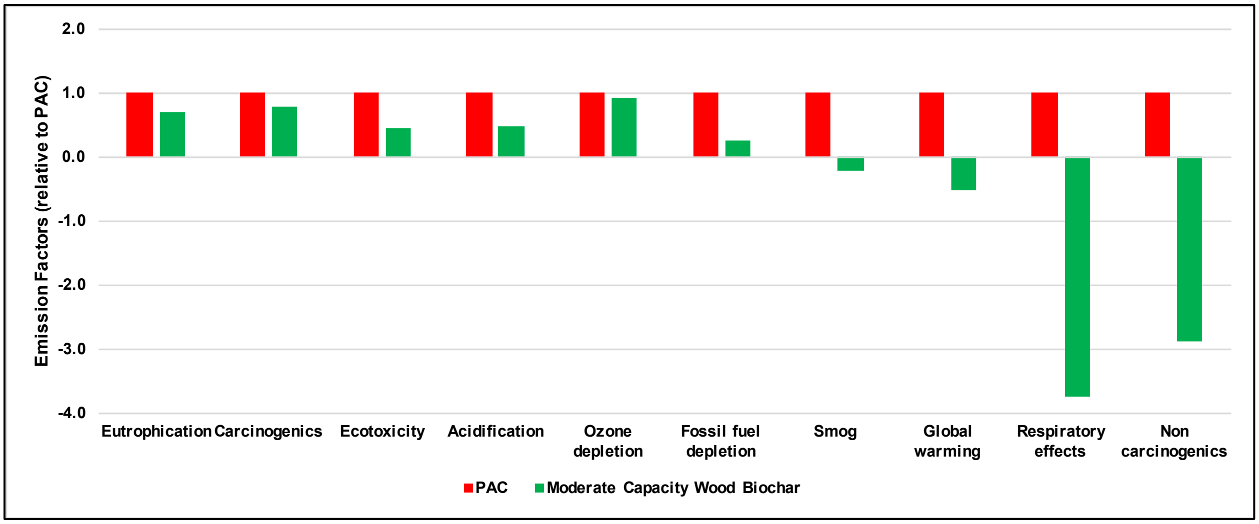


Figure B.15. The 10 TRACI impacts for PAC and moderate capacity wood biochar scenarios when <u>adsorbent delivery is 200 km</u> for both and all processes in the system boundary used the <u>US average electricity</u> production mix.

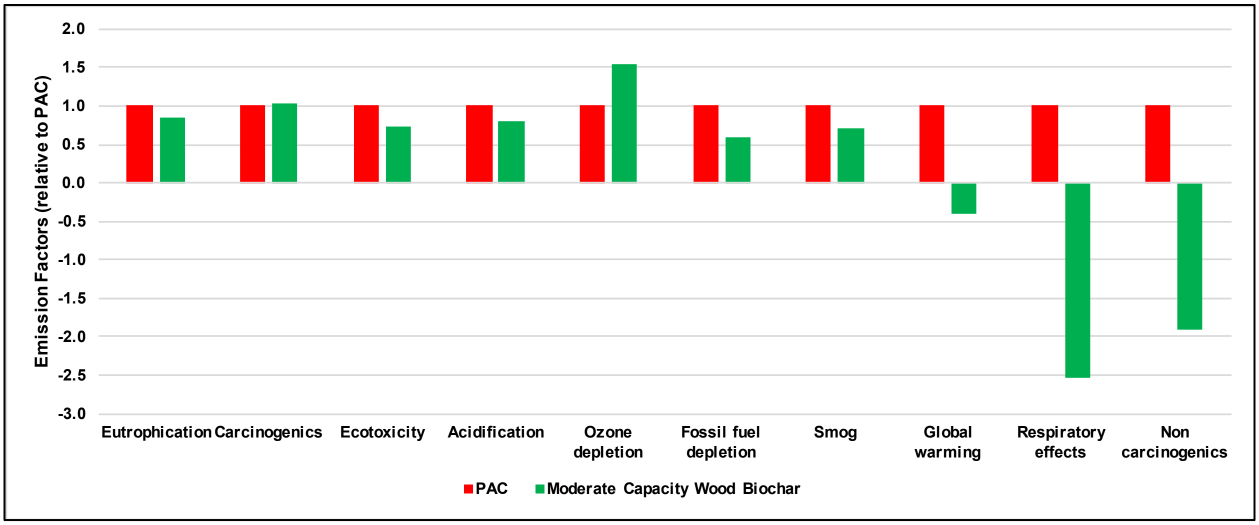


Figure B.16. The 10 TRACI impacts for PAC and moderate capacity wood biochar scenarios when adsorbent delivery is 2000 km for both and all processes in the system boundary used the US average electricity production mix.

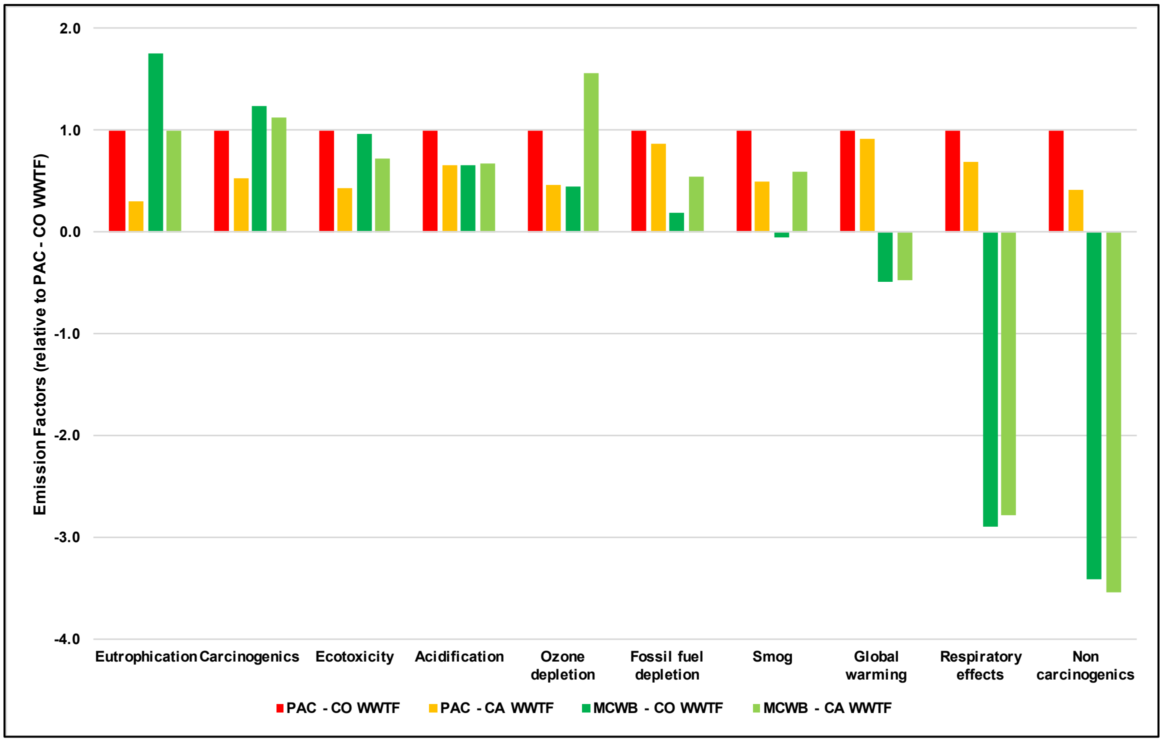


Figure B.17. Comparison wastewater treatment facility (WWTF) location on the impacts of PAC and moderate capacity wood biochar (MCWB). One WWTF location is in Colorado (CO) and one location is in California (CA). The CO WWTF scenarios used CO electricity for WWTF operation, and the CA WWTF used CA electricity. Both PAC scenarios used CA electricity for PAC production, and both biochar scenarios used CO electricity for biochar production. Delivery distance was based on those WWTF and adsorbent production locations and were 185 km within state and 1664 km for interstate delivery. (Note: The PAC – CO WWTF and MCWB – CO WWTF scenarios are same as Low-impact PAC and Moderate Capacity wood biochar Figure 3.2 and Figure B.1.)

B.10 Alternative Scenario #2: Adsorbent Dose

B.10.1 Adsorbent Dose and System Boundary

For this "dose alternative functional unit" analysis, a dose of 25 mg/L of MCBB was needed to treat the entire 12.5 MGD flow. The other adsorbent doses were reduced proportionally so that new doses were: 12 mg/L PAC and 25 mg/L MCWB. Also, the fate of biosolids for these scenarios was landfilling. As with the other functional unit, no hauling of biosolids to their final fate was included in the PAC or wood biochar scenarios. Since the hauling is not included in those scenarios, the offset of this hauling was included in the biosolids biochar scenario. Also, no artificial fertilizer production was included in the system boundary since the biosolids were not land applied and no replacement fertilizer was needed when they are pyrolyzed.

B.10.2 Results

Compared to wood biochar, the biosolids biochar (MCBB) scenario had greater environmental impacts than MCWB in nine categories and smaller impacts in only one category (ozone depletion). Compared to the PAC scenarios, the MCBB scenario had smaller environmental impacts than high-impact PAC in all except for two categories (acidification, respiratory effects), but it had greater environmental impact than low-impact PAC in seven categories (all except for ozone depletion, global warming, fossil fuel depletion). Overall, if the dose is small enough that biosolids can meet the treatment objective and if the biosolids fate is landfilling, biosolids biochar could be an environmentally preferred alternative to high-impact PAC. Therefore, the environmental decision between biosolids biochar and PAC would highly depend on the electricity production mix and hauling distance for the PAC. However, in all circumstances considered in this study, wood biochar would be more sustainable than a biosolids biochar with the same adsorption capacity.

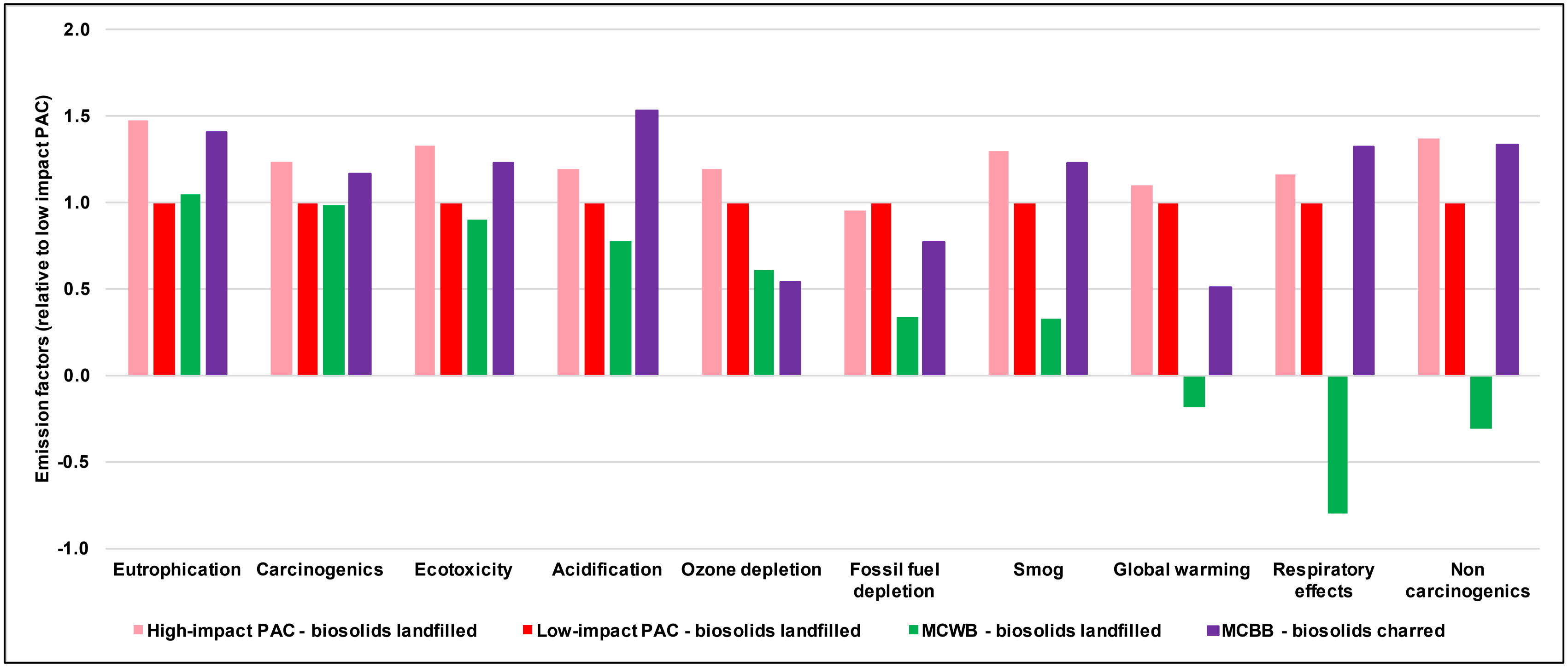


Figure B.18. Comparison of environmental impacts based on an alternative functional unit with reduced adsorbent dose and a biosolids fate of landfilling (instead of land application). The following scenarios were assessed: High-impact PAC with landfilled biosolids; Low-impact PAC with landfilled biosolids; Moderate capacity wood biochar (MCWB) with landfilled b biosolids; Moderate capacity wood biochar (MCBB) with charred biosolids.

APPENDIX C

SUPPLEMENTARY INFORMATION

For

DEVELOPMENT AND EXPERIMENTAL VALIDATION OF THE COMPOSITION AND TREATABILITY OF A NEW SYNTHETIC BATHROOM GREYWATER (SYNGREY)

C.1 Methods

Table C.1. Fifty real greywater compositions for 20 water quality parameters, as reported in the literature. GW type indicates source, which was any combination of showers (S), baths (B), or washbasins (WB). Values represent the mean measurement for each study; except, GW #8 were the median measurement, GW #10, #29, and #30 were the midpoint, and GW#47 were single measurements.

#	pH	Turbidity (NTU)	EC (µS/cm)	TS (mg/L)	TSS (mg/L)	VSS (mg/L)	TDS (mg/L)	COD (mg/L)	TOC (mg/L)	TN (mg/L N)	NH$_3$ (mg/L N)	NO$_3^-$ (mg/L N)	TP (mg/L P)	PO4$^-$ (mg/L P)	SO4$^-$ (mg/L)
1	7.24	28	1044		52	45		174	27	10.5		1.21		0.62	157
2					115		68	328			1.13	5.07		11.0	
3	7.14	10.9	443	165	16.1		140	50					0.218		
4	7.2	26.5	327		36.8			96.3					0.86		
5	7.45	25.5	544	470	67.8		413				1.67	0.85		3.86	
6	7.37								24.6						
7		150	468		125			399		9.48			0.424		
8	7.25	150	166		84						7.5		0.955		
9		32							44		8.4				
10	8.1				107			158.5		5	0.22	0.13	0.530		
11			1323	884		85		374	101		1			7	
12		33			43			158							
13	7.89	83.8	660	638	167		469	290			3			0.7	
14	7.91				58		806	86.1		12.2	7.2	0.226	1		222
15	6.8	38.8	921		32.2			72.7	41						
16	7.5	62			42.2			252							
17	7.42	35.2	890	659	94		565	77		10.9			1.12		
18	7.3	335		533	248		286	352.6	65.7			22.5			
19										5			1.37		
20					52.2			120.4							
21	7.47	101			100			451	72.6	8.73				0.11	
22	7.92		645		4.9			77.2		7.1			0.8		
23	7.6				33			102	32.6		6.7	0.2		3.5	
24	7.49		897												
25	7.62		571												
26	7.62	19.2			32.2			151	61.2						
27	7.6	20			42			171	58	11.4					
28	7.6	29	645					109			11.8	0	1.6	1	
29								150		7.5			0.4		
30								373							
31	7.36	143					355	194					1.33		
32		35						144		7.6	0.7	3.9		0.16	
33		42						575		16.4	1	7.5		0.42	
34	7.4	375	1400	683	353	133	330	294.3							
35	7.1	133	1500	817	505	347	312	58							
36	7.5	35.3	1600		29.8		599	170			2.7	0.67		0.03	58
37					216			370							
38	7.7	68	1267					302		23			3		
39	6.9			326	58	43		197			8.6		1.3		
40	6.3	55			70			291		22			4.1		
41	8.4	54			75			278		25			4.1		
42	7.6	92		631	76		559	424	104		1.56	0.9		1.63	
43	8.1	102		558	40		520	433	40		0.53	0.34			
44	6.13				81			445							
45	7.03	33.5	214		57	43		196	41.8		4.7		0.49	0.25	
46		19.6			29			87							
47					29			86	49						
48	6.52		237					374		11.6		0.69		0	17
59	7.7	35.8						146							

#	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^{-} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	GW Type	Citation
1	57	33		125	18.7	S, WB	[171]
2						S, WB, B	[263]
3			42.3			WB	[264]
4						S, B, WB	[265]
5	91.1	19	22.7	37.5	6.4	S, B	[266]
6						S	[231]
7						S, B, WB	[174]
8	5.7	1.85	13.5	12.7	3.35	B, S	[267]
9						S, WB	[177]
10	99.5	21.9		71.6	6.65	S, WB	[268]
11			207	126		B, S, WB	[194]
12						S, B, WB	[192]
13	17.5	25.8		105		S, WB, B	[223]
14	96.6	50.5	149	95.2		S, WB	[269]
15						S, WB	[270]
16						B, WB, S	[271]
17	59.9	23	147	110		S	[272]
18	16.0	53.1		181	39.9	S, WB	[273]
19	47.9	5.29			5.79	S, B, WB	[163]
20						S, B, WB	[274]
21						S, B, WB	[205]
22						WB	[275]
23						S	[232]
24						S	[276]
25						S	[276]
26						S	[277]
27						B, WB	[278]
28						S	[279]
29						B, S	[280]
30						S	
31			81			S, WB	[45]
32						S, B, WB	[202]
33						S	[202]
34	15.8	56.1		184	43.1	S	[188]
35	19.7	21		149	5.54	WB	[188]
36	79.6	47.6		106	10.4	S	[281]
37						S, WB	[282]
38						S, WB	[186]
39						S	[283]
40						S	[187]
41						B	[187]
42						B, S	[284]
43						WB	[284]
44						S, WB	[285]
45						S, WB	(This Study)
46						S, B, WB	[286]
47						WB, B, S	[167]
48			27.9			S	[193]
59						WB	[214]

Table C.2. Bench-scale coagulation jar test mixing conditions.

Simulated process	Mean velocity gradient, G (s^{-1})	Mixer speed (rpm)	Mixing time (min)
Rapid mix	600	290	1.0
Flocculation 1	50	55	10
Flocculation 2	10	20	10
Sedimentation	0	0	30

C.2 Results

C.2.1 Bathroom Greywater Quality Comparison

Table C.3. Distribution of water quality values expected for real bathroom greywater composition, as determined from 49 different real bathroom greywater compositions reported in the literature (Table C.1). The SynGrey values were measures experimentally except shaded cells which were calculated based on ingredients. SD is standard deviation.

Parameter	Real Bathroom Greywater Composition (distribution of values from literature data)				SynGrey
	Median	25th	75th	n	Mean±SD
pH	7.47	7.22	7.62	35	7.43±0.29
Turbidity (NTU)	38.8	30.5	96.3	31	39±7
EC (µS/cm)	653	462	1100	20	779±18
TS (mg/L)	631	502	671	11	609
TSS (mg/L)	58	37.6	98.5	34	67±17
TDS (mg/L)	441	326	561	12	521
VSS (mg/L)	67.8	44.0	109	7.00	44±14
COD (mg/L)	184	112	346	42	159±34
TOC (mg/L)	46.5	40.3	64.6	14	54.9
TN (mg/L)	10.7	7.58	13.3	16	8.9
Ammonia (mg/L N)	2.7	1.0	7.2	17	3.6±0.3
Nitrate (mg/L N)	0.77	0.25	3.23	14	0.66
TP (mg/L P)	1	0.53	1.37	17	0.88
Phosphate (mg/L P)	0.66	0.19	3.03	14	0.48
SO4 (mg/L)	108	47.8	173	4	156
Ca (mg/L)	52.5	17.1	82.5	12	18
Mg (mg/L)	24.4	20.5	48.3	12	22
Cl (mg/L)	61.7	26.6	148	8	116
Na (mg/L)	108	89.3	131	12	91
K (mg/L)	6.65	5.79	18.7	9	6

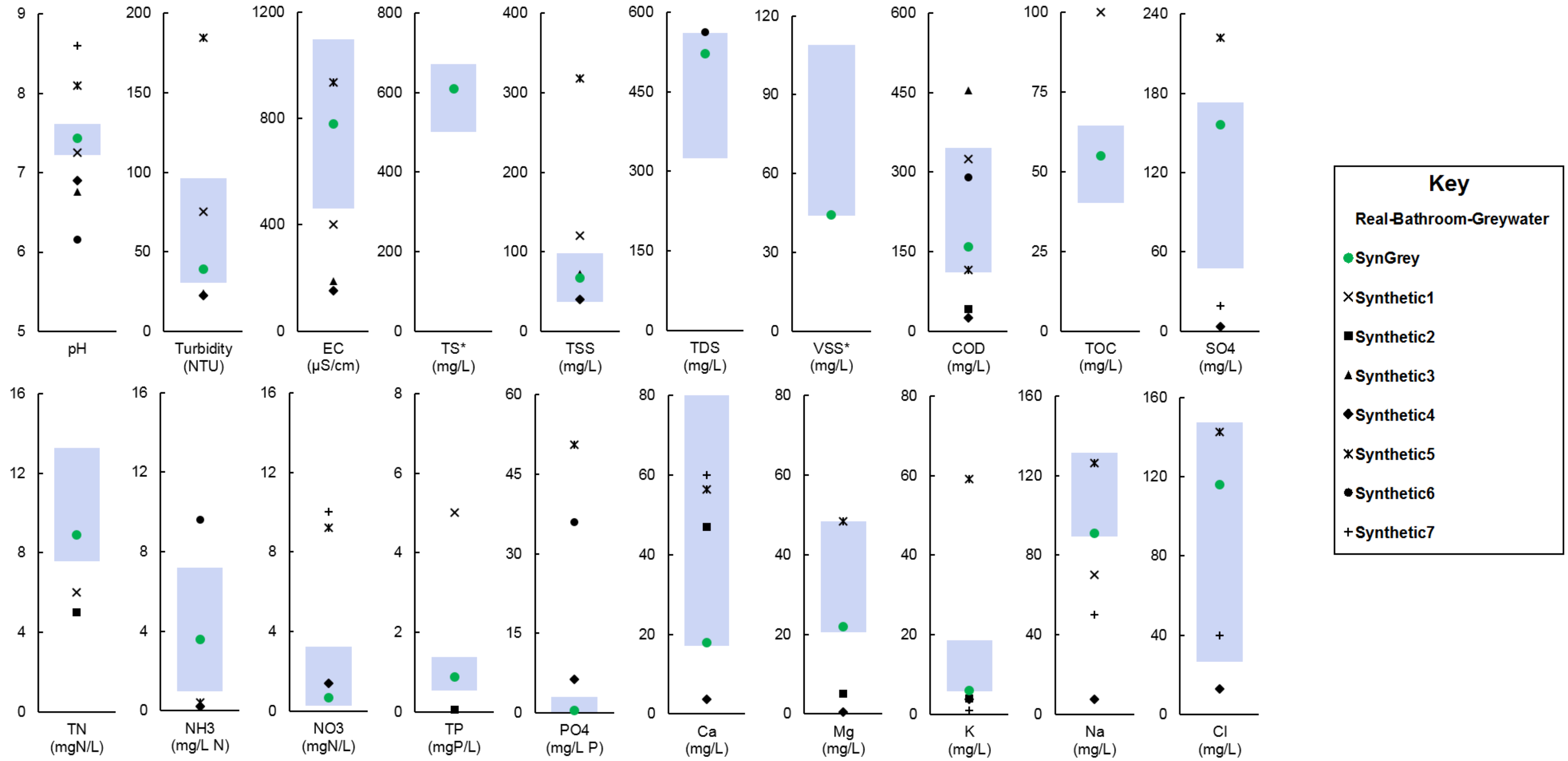


Figure C.1. Comparison of synthetic greywater recipes with the 25th to 75th percentile range of real bathroom greywaters (Table C.3) for 20 water quality parameters. Citations for the mean values for each synthetic recipes were: New Synthetic (SynGrey), 1 = 159, 2 = 163, 3 = 161, 4 = 162 low concentration, 5= 162 high concentration, 6 = 160, 7 = 164. For synthetic recipes 4 and 5, values for all ions, except nitrate and phosphate, were calculated based on ingredients since they were not measured experimentally. For synthetic recipe 1, commercial ingredients (shampoo, conditioner, etc.) are used, and an expect ranges of TSS, COD, etc. were given. This analysis used midpoints from those ranges. *None of the other synthetic recipes reported values for this parameter.

Table C.4. Average values for the ratios of total chemical oxygen demand (COD) to soluble COD (COD:sCOD) as reported for real bathroom greywaters in the literature (Table C.1).

GW#	COD (mg/L)	sCOD (mg/L)	COD:sCOD
10	148	86	1.7
11	423	250	1.7
12	158	110	1.4
13	211	108	2.0
37	170	106	1.6
49	374	129	2.9
Median			**1.9**

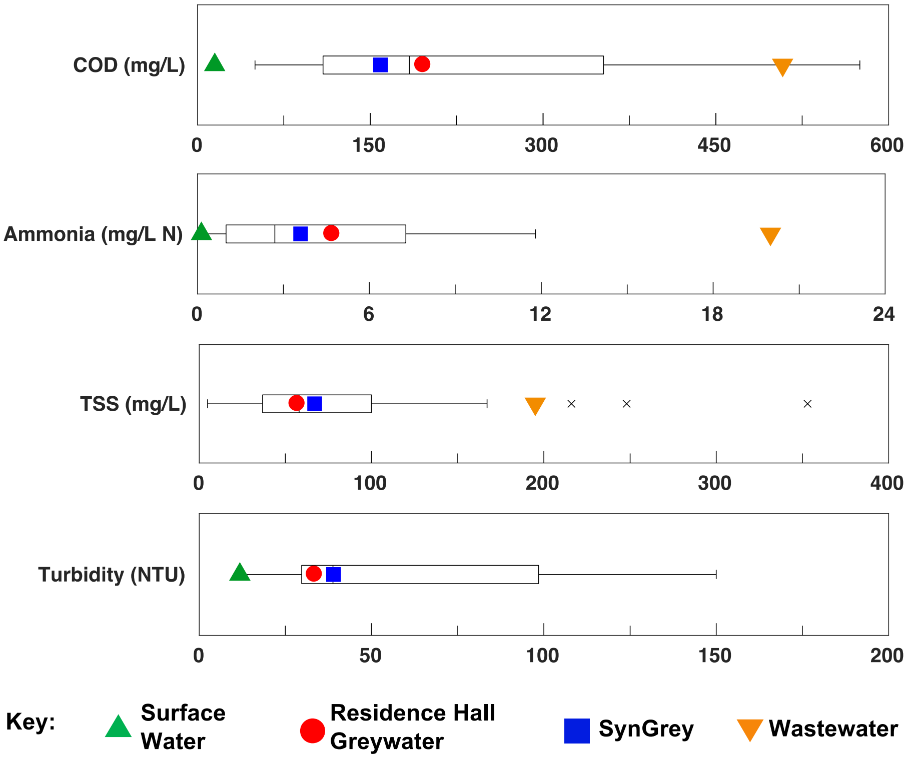


Figure C.2. Boxplots of real bathroom greywater literature data for COD (n=42), ammonia (n=17), TSS (n=34), and turbidity (n=31). Each boxplot has a different scale. Blue squares represent means of SynGrey for COD (n=12), ammonia (n=15), TSS (n=7), turbidity (n=19), pH (n=26), and phosphate (estimated). Red circles represent means of residence hall bathroom greywater for COD (n=35), ammonia (n=19), TSS (n=8), and turbidity (n=77). Data for the other 16 water quality parameters are in Table C.3 and Figure C.1.

C.2.2 Total Chlorine Demand and Decay Kinetics

Table C.5. Statistical comparison of total chlorine residuals (mg/L Cl_2). There were 15 samples of each greywater.

Time (hr)	RH Greywater	SynGrey	p-value
0.5	12.5±4.6	16±1.4	0.48
1	10.5±4.6	12.7±1.4	0.60
2	8.2±4	10.8±1.6	0.56
4	6.5±3.6	7.7±1.5	0.77
8	4.5±2.7	6.3±1.5	0.55
24	2.9±2.2	3.6±1.7	0.79
48	1.8±1.1	3.5±1.8	0.43
72	1.5±0.8	3.4±1.3	0.22
120	1.1±0.5	2.1±1.3	0.46

Table C.6. Chlorine demand values for both the RH Greywater and SynGrey. There were 15 samples of each water.

Chlorine demand	RH Greywater	SynGrey
1-hr Cl demand (mg/L Cl_2)	30.4±4.6[a]	28.1±1.5[a]
24-hr Cl demand (mg/L Cl_2)	37.7±2.2[a]	37.2±2.1[a]

In Table C.7, outliers, identified graphically using normal probability plots, were omitted to improve the normality of the data. The RH Greywater had one sample that was a statistical outlier, with high total chlorine residuals at 8 to 48 hours. SynGrey had three samples that were outliers due to low C_w values. All first-order chlorine decay model parameter values were statistically similar between SynGrey and the RH Greywater whether or not these outliers were included in the analysis (Table C.7 and Table C.2). However, omission of the outliers reduced the standard deviation of the SynGrey C_w such that it was no longer statistically similar to the additional real bathroom greywater value.[164]

Table C.7. Statistical similarity table of parameters of chlorine parallel first-order decay model, with outliers omitted. Values are reported as mean ± standard deviation. Same letters indicate statistical similarity (p>0.05).

Parallel First-order Decay Model Parameter	RH Greywater	SynGrey	Additional Real Bathroom Greywater
Number of samples	14	12	14
Immediate chlorine demand, Cw (mg/L)	23 ± 6^a	23 ± 2^a	9 ± 2^b
Fraction decaying rapidly, x (%)	$76 \pm 14\%^a$	$70 \pm 12\%^a$	$34 \pm 6\%^b$
Rapid decay rate, k1 (hr^{-1})	1.1 ± 0.9^a	0.43 ± 0.16^a	1.3 ± 0.4^a
Slow decay rate, k2 (hr^{-1})	0.016 ± 0.011^a	0.0093 ± 0.085^a	0.05 ± 0.02^a

C.2.3 Bathroom Greywater Biodegradability

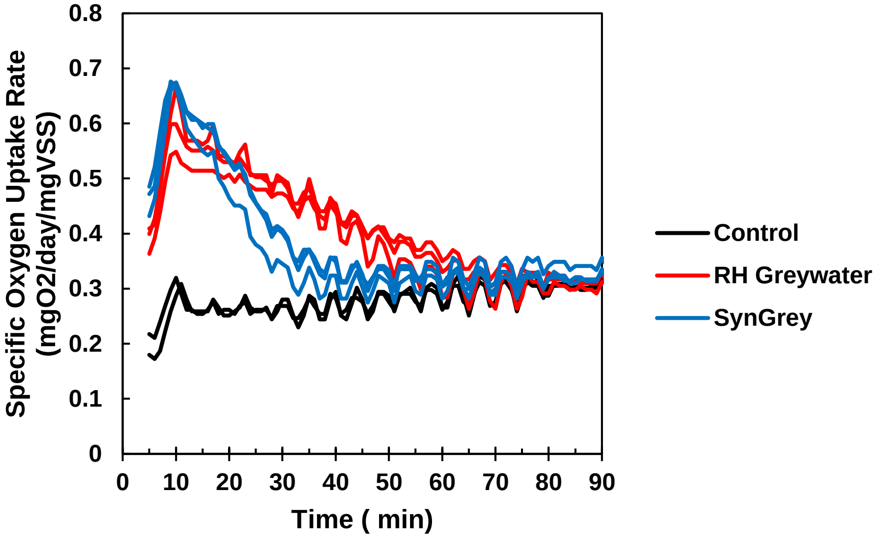


Figure C.3. All replicates of the SOUR experiment.

C.2.4 Bathroom Greywater Coagulation

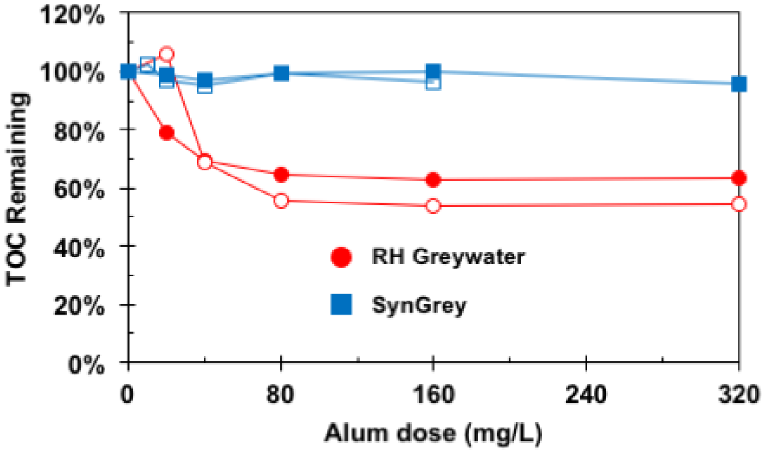


Figure C.4. Total organic carbon (TOC) removal during alum coagulation for the RH Greywater and SynGrey. Turbidity data is in Figure 4.5. TOC percent remaining is normalized by the control (0 mg/L alum jar). Hollow and filled symbols indicate replicate samples of each greywater on different days.

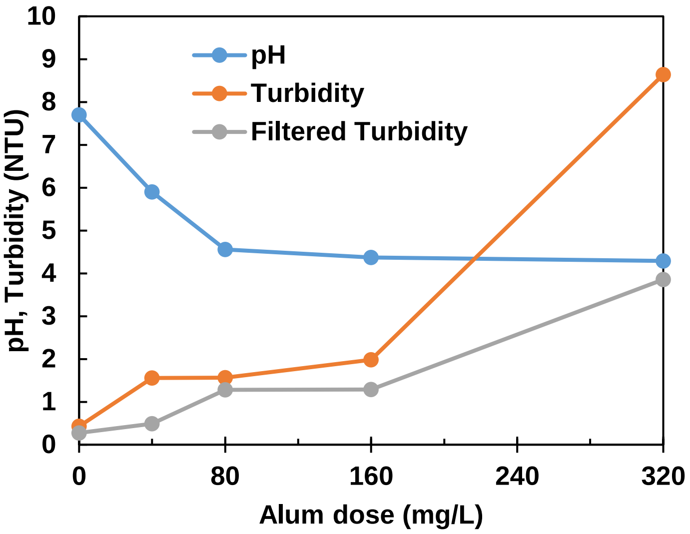


Figure C.5. Alum coagulation of a deionized water solution with 49 mg/L yeast extract and 31 mg/L of sodium bicarbonate.

Turbidity in SynGrey rose steeply from an alum doses of 40 mg/L to 80 mg/L, and continued to rise until the turbidity at 160 mg/L and 320 mg/L exceeded the turbidity at 0 mg/L by approximately 8 NTU (Figure 4.5a). The filtered turbidity at an alum dose of 20 mg/L was around 0.75 NTU and then at higher alum doses rose steadily to about 3.5 NTU at the 160 mg/L alum dose (Figure 4.5b). These rises in turbidity were greater than could be explained by charge reversal and resuspension alone. To explain this phenomenon, experiments were run with individual ingredients of SynGrey.

A solution was made of deionized water with 49 mg/L yeast extract (the same concentration as in SynGrey) and 31 mg/L sodium bicarbonate to reach an alkalinity of 18 mg/L, approximately equal to the alkalinity in the SynGrey. This solution was then dosed with alum (doses from 0 to 320 mg/L) and allowed to coagulate, flocculate, and settle with the same procedure and measurements used for all other samples (e.g., Section 5.2.4.4 and Table D.2). The effluent turbidity and filtered turbidity rose steadily in response to the alum addition. This rise in turbidity is expected to be caused by precipitation or complexation between the yeast extract and the alum. At the 320 mg/L alum dose, the effluent turbidity of the coagulated yeast extract solution was 8.6 NTU, and the filtered turbidity was 3.9 NTU. Based on these values, precipitate particles formed between the yeast extract and the alum can account for the majority of the rise in filtered turbidity seen during the SynGrey coagulation experiments. The rise in the total turbidity for SynGrey coagulation appears to a combination the formation of these alum-yeast extract particles as well as charge reversal and resuspension, which is expected to be mostly by kaolin. The modified SynGrey with higher alkalinity had a much less steep rise in turbidity and filtered turbidity from 40 to 320 mg/L alum doses (Figure 4.5), suggesting that high alkalinity can reduce or prevent this precipitation phenomenon.

APPENDIX D

SUPPLEMENTARY INFORMATION

For

THE EVALUATION OF ACTIVATED CARBON AND NOVEL BIOCHAR SORBENTS AS TREATMENT APPROACHES FOR GREYWATER REUSE

D.1 Greywater Quality

Table D.1. Review of laundry-only or combined laundry and bathroom greywater quality in the literature.

	(Leong et al. 2018)	Literature					
		Min.	25th	Median	75th	Max.	*n*
pH[187,188,207,209,233,266,272,273,284,287–302]	7.1	5.7	7.3	8.1	9.2	12.5	*30*
Turbidity (NTU)[187,188,209,238,266,272,273,284,288,289,291,292,296–300,303,304]	1.8	1.8	43	88	156	858	*23*
TSS (mg/L)[187,188,207,209,212,238,263,266,272,273,284,287–291,297–301,304–307]	3	3	38	129	281	705	*31*
TDS (mg/L)[188,209,266,272,273,284,287,291,299–301]	285	83	346	571	1118	2444	*15*
COD (mg/L)[187,188,207,209,212,238,263,272,273,284,289–292,295,297–301,303,306–308]	74	28	280	471	800	1815	*29*
BOD (mg/L)[187,188,207,209,212,238,266,272,273,284,287,288,290,292,295,299,301,303,304,307,308]	17	17	72	178	293	636	*23*
NH3-N (mg/L)[207,209,212,233,263,266,284,296,299,301,303,306,307]	0.4	0.3	0.8	2.5	6.7	18.6	*16*
PO4-P (mg/L)[209,212,263,266,284,296,299,301]	1.5	0.17	2.4	3.9	8.8	101	*11*
E. coli (CFU/100mL)[209]	0	0	-	-	-	1.1×10^3	*2*
Total coliforms (CFU/100mL)[209,284,288,304]	2.1×10^5	2.1×10^5	2.9×10^5	7.0×10^5	3.9×10^7	8.0×10^7	*5*

Table D.2. Review of bathroom-only (shower, bath, or handwashing) greywater quality in the literature.

	Min.	25th	Median	75th	Max.	*n*
pH[45,46,171,186–188,193,203,204,209,223,231–233,264–266,269–273,275–279,283–285,290,309–312]	6.1	7.1	7.5	7.6	9.2	*36*
EC (μS/cm)[45,171,174,186,188,193,194,203,204,223,264–266,270,272,273,275,276,279,309,310,312]	156	479	648	983	2000	*23*
Turbidity (NTU)[45,46,171,174,177,186–188,192,202–204,209,223,234,238,264–266,270–273,277–279,284,286,305,310–313]	3	29	39	82	375	*35*
TSS (mg/L)[46,163,167,171,174,186–188,192,194,203,204,209,223,232,238,263–266,269–273,277,278,281–286,290,305,309,311,313–316212]	5	35	58	98	353	*43*
TDS (mg/L)[45,188,203,204,209,223,264,266,269,272,273,281,284,311]	140	285	376	537	806	*14*
COD (mg/L)[45,46,163,167,171,174,186–188,192–194,202–204,209,212,223,232,234,238,263–265,269–273,277–279,281–286,290,309,310,313–316]	50	143	198	312	1426	*47*
BOD (mg/L)[45,167,174,186–188,192,194,202–204,209,212,223,232,234,238,264–266,269,271–273,279,281–286,290,309–311,313–316]	16	66	109	153	380	*41*
COD:BOD Ratio[45,167,174,186–188,202–204,209,212,223,232,238,264,265,271–273,279,282,284,286,290,309,310,312,315–318]	1.0	1.7	2.2	2.9	7.7	*35*
TOC (mg/L)[167,171,177,188,194,231,232,238,270,277,278,284,309,311]	25	42	49	75	109	*15*
DOC (mg/L)[174,194,202,233,266,271,311]	12	23	45	57	102	*8*
BOD:DOC Ratio[174,194,202,266,271,311]	0.9	2.9	3.3	4.7	5	*7*
UVA_{254} (1/cm)[233,234,311]	0.110	-	0.282	-	0.398	*3*
SUVA (L/mg/m)[233,311]	0.45	-	-	-	1.1	*2*
NH3-N (mg/L)[46,171,193,194,202–204,209,212,223,232,233,263,264,266,269,279,281,283,284,309,314,316,319]	0.5	0.9	2.4	5.7	9.7	*25*
PO4-P (mg/L)[46,171,193,194,202–204,209,212,223,232,263,266,279,281,284,309,314]	0	0.29	0.64	1.97	11.9	*19*
E. coli (CFU/100mL)[174,186,203,204,209,223,265,269,285,286,311,314,319,320]	5.0×10^{2}	1.7×10^{3}	2.4×10^{4}	2.4×10^{5}	2.1×10^{6}	*14*
Total coliforms (CFU/100mL)[167,209,265,270,277,284,285,305,314,316,319]	1.1×10^{4}	8.0×10^{5}	5.7×10^{6}	1.4×10^{7}	2.5×10^{8}	*12*

Table D.3. Greywater quality at the Colorado sampling location (February 16th, 2015 through October 24th, 2017).

	Min.	25th	Median	75th	Max.	*n*
pH	6.4	6.8	7.1	7.3	7.8	*64*
EC (μS/cm)	90	170	190	240	540	*60*
Turbidity (NTU)	4	19	30	43	150	*85*
TOC (mg/L)	6	24	37	46	196	*40*
DOC (mg/L)	6	17	29	34	93	*35*
UVA_{254} (1/cm)	0.043	0.080	0.122	0.181	0.521	*18*
SUVA (L/mg/m)	0.19	0.37	0.50	0.59	0.93	*14*

D.2 Results

D.2.1 Biochar Screening

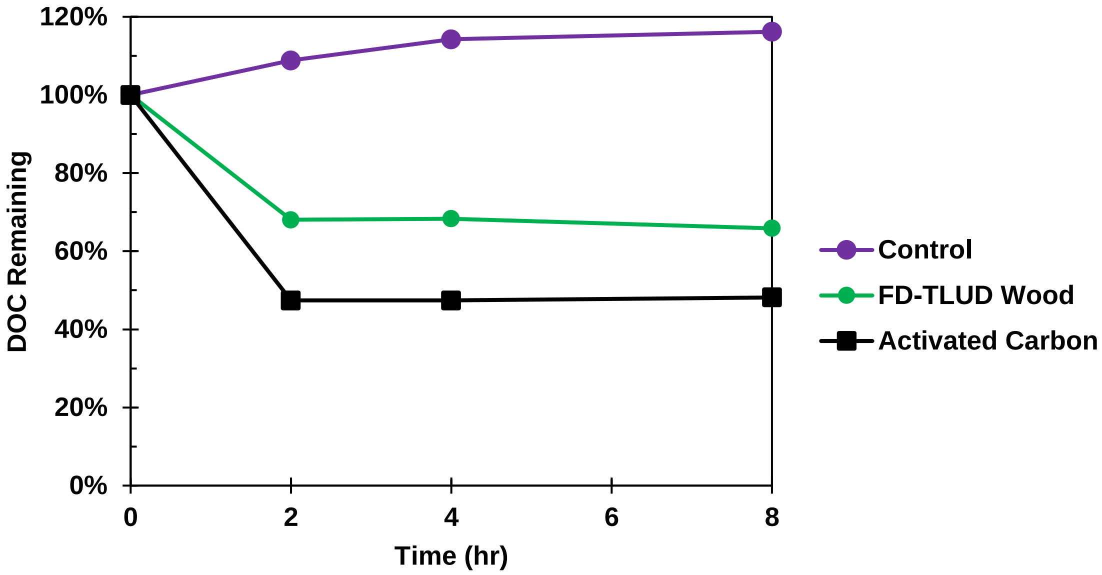


Figure D.1. DOC removal from greywater batch A. The sorbent doses were 2 g/L.

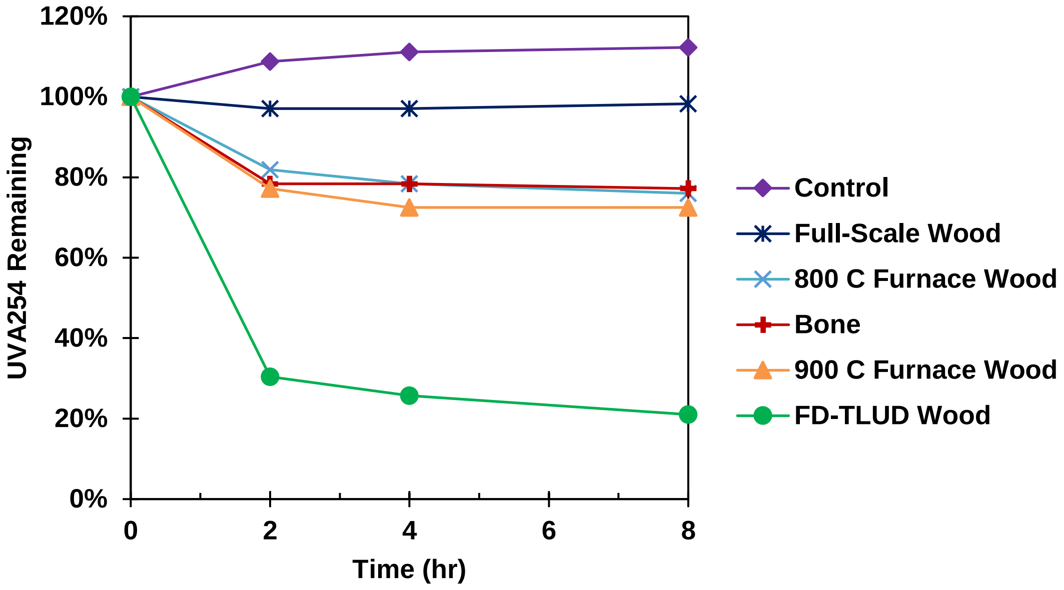


Figure D.2. UVA$_{254}$ removal from greywater batch C. All sorbent doses are 2 g/L.

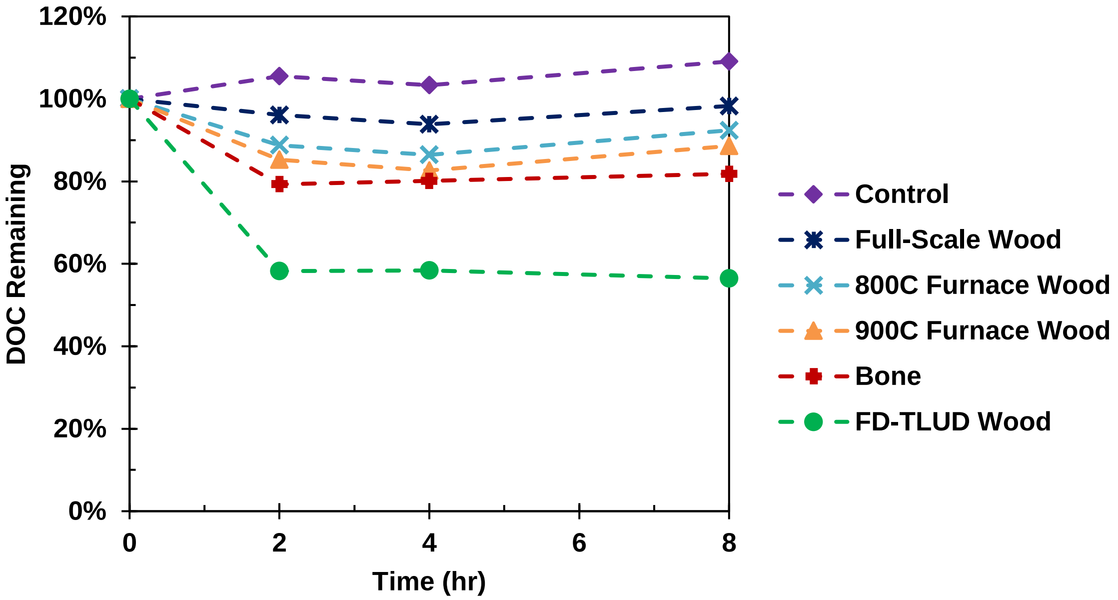


Figure D.3. DOC removal from SynGrey synthetic greywater.[46] All sorbent doses are 2 g/L.

D.2.2 Biochar versus Activated Carbon Comparison

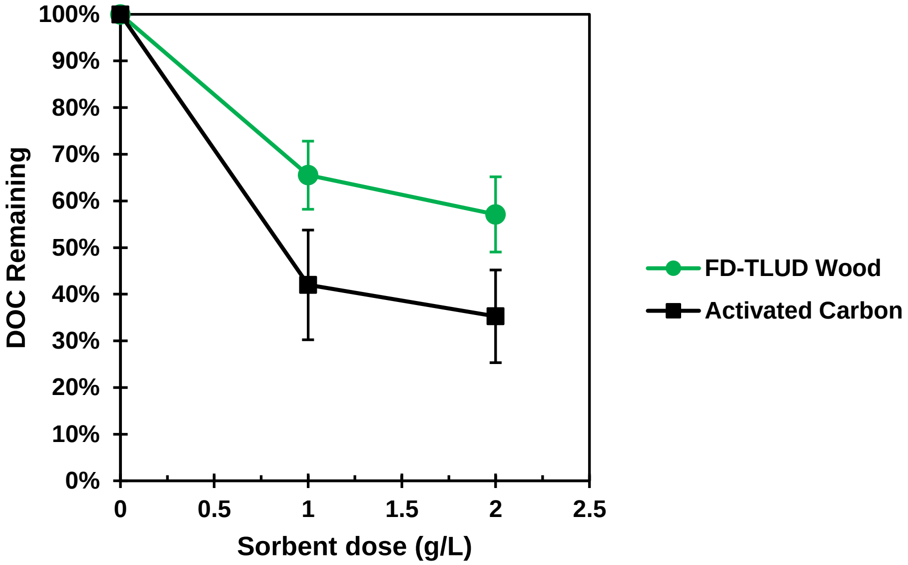


Figure D.4. Comparison of biochar and activated carbon for DOC removal from filtered greywater (n=5). Error bars show one standard deviation.

D.2.3 Pretreatment

D.2.3.1 Coagulation.

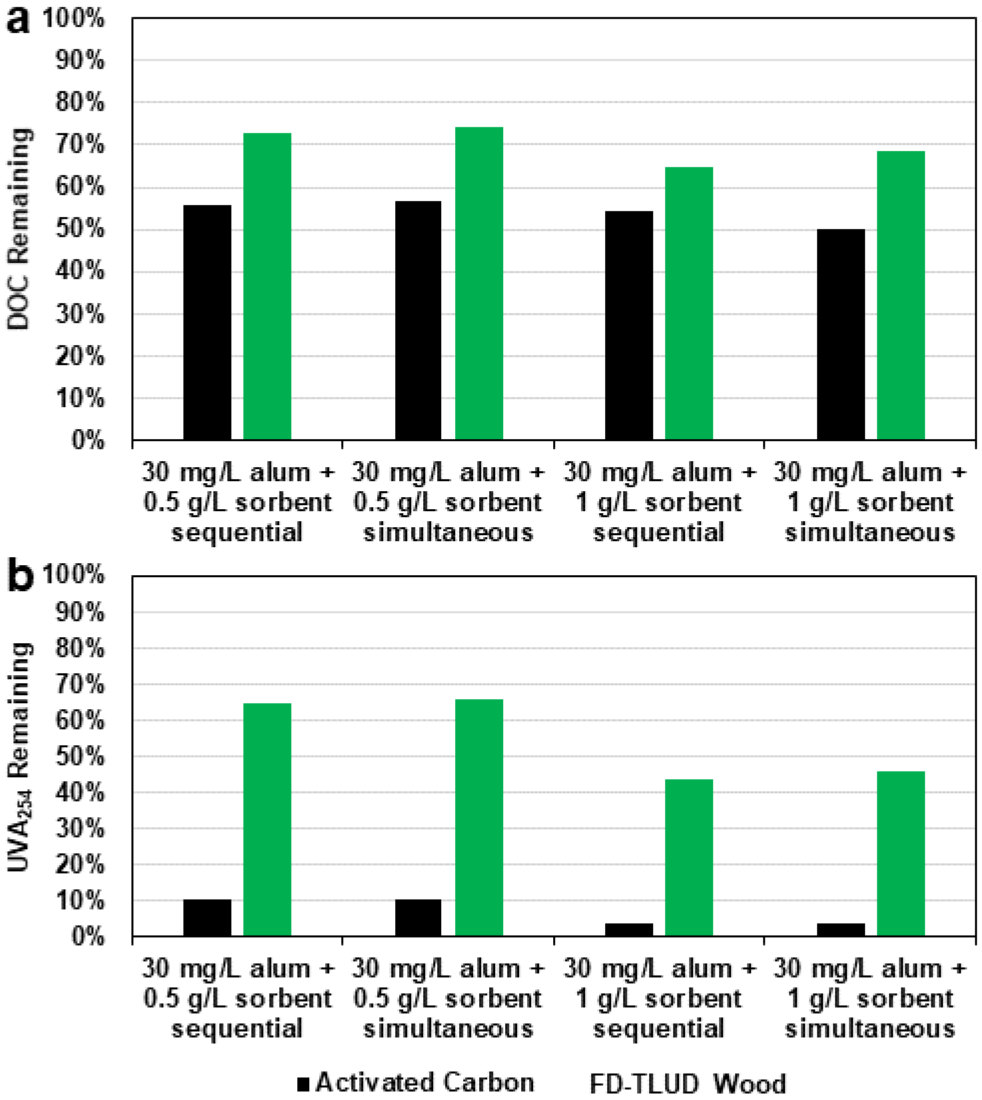


Figure D.5. DOC (a) and UVA_{254} (b) removal from greywater batch D by simultaneous or sequential coagulation and sorption. In sequential coagulation and sorption, 2 L jars were coagulated as described in Section 5.2.6.1. The top 1 L of each jar was then decanted, blended, and dispensed into 0.5 L jars, and then sorbed as described in Section 5.2.5. In simultaneous coagulation and sorption, the coagulant and sorbent were added simultaneous to 0.5 L jars, which were then stirred for 2 hours at 120 rpm.

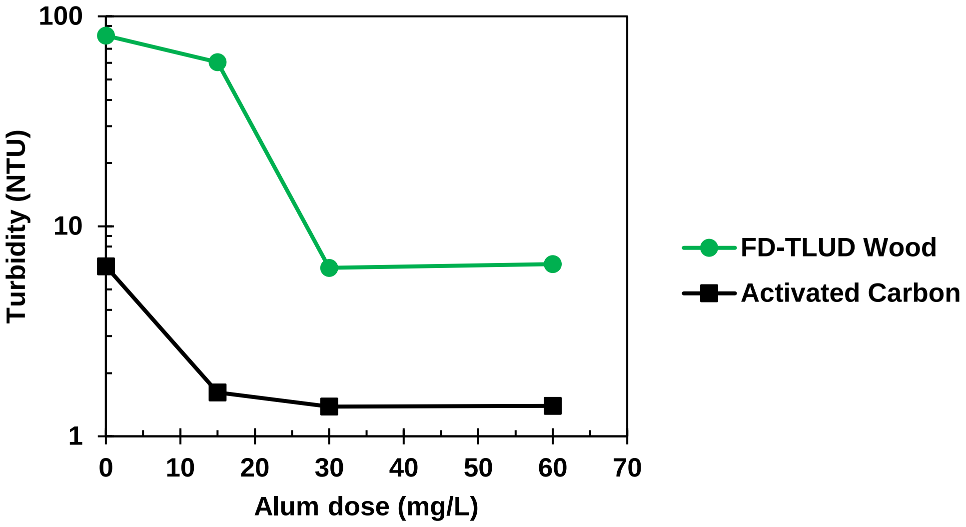


Figure D.6. Removal of powdered sorbents from greywater by coagulation. Activated carbon was coagulated from greywater batch D (initial turbidity = 30 NTU), while biochar was coagulated from greywater batch E (initial turbidity = 36 NTU). The 1 g/L of each sorbent was added to 1 L jars and stirred for 2 hours at 120 rpm, then coagulated as described in Section 5.2.6.1.

D.2.3.2 Aeration.

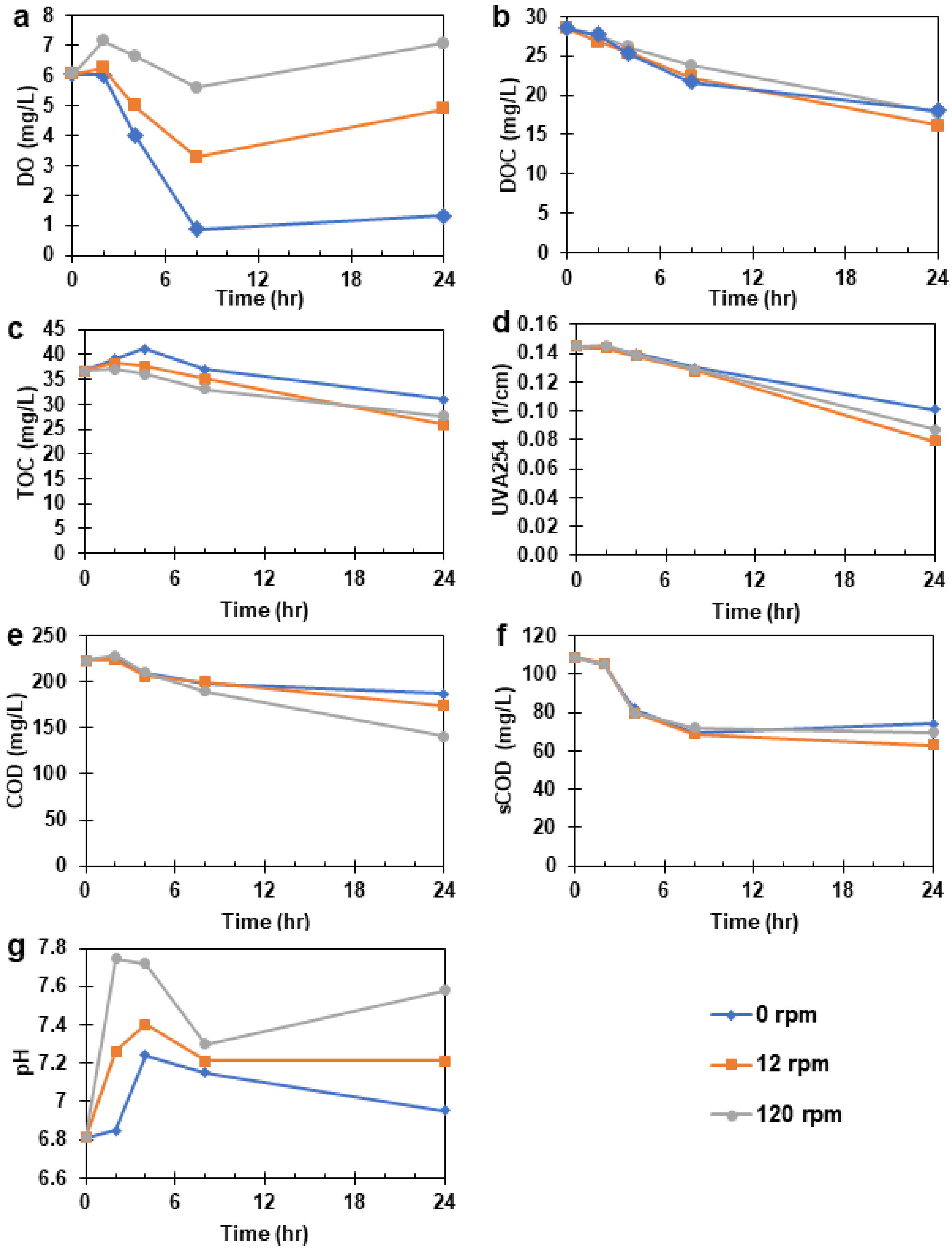


Figure D.7. Effect of mixing speed and residence time on (a) DO, (b) DOC, (c) TOC, (d) UVA_{254}, (e) COD, (f) sCOD, and (g) and pH in unfiltered greywater.

D.2.4 Correlations between UVA254 and DOC

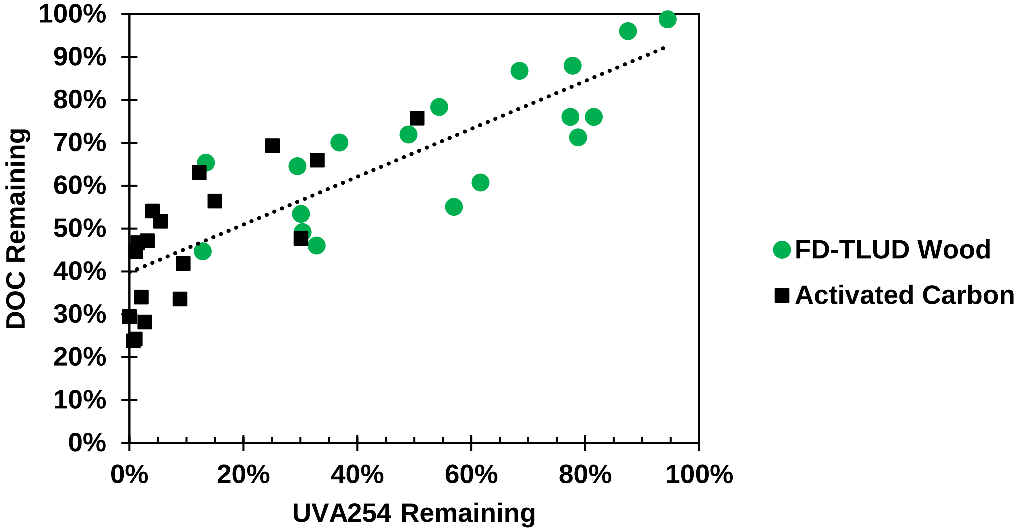


Figure D.8. Linear correlation between the percent remaining of DOC and the percent remaining of UVA254 after sorption with activated carbon (black squares) and biochar (green circles) (n=36). The R^2 is 0.72. The slope is 0.56±0.06 (unitless) and the intercept is 40±3%.

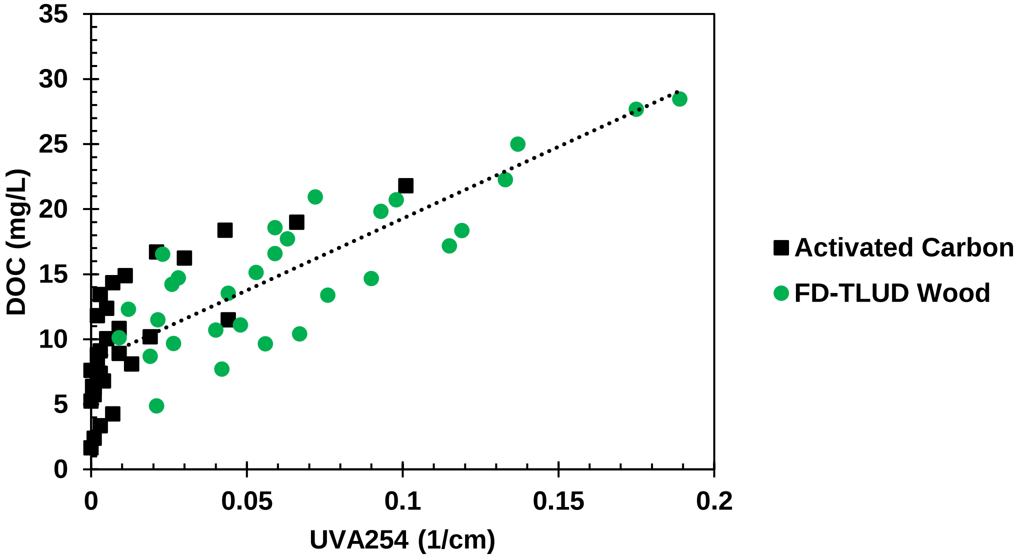


Figure D.9. Linear correlation between DOC and UVA254 remaining after sorption of raw, coagulated, aerated, or rainwater-diluted greywater after sorption with activated carbon (black squares) and biochar (green squares) (n=61). The R^2 is 0.69. The slope and intercept are 110±10 cm*mg/L and 8.2±0.6 mg/L respectively.