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Assessing Trace Organic Contaminant Removal Trends in Biologically Active Filters at Multiple Scales

By

Paige Marie Pruisner

Concurrent B.S./M.S., 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 requirements for the degree of Masters of Science Department of Civil, Environmental, and Architectural Engineering 2016 This thesis entitled:

Assessing Trace Organic Contaminant Removal Trends in Biologically Active Filters at Multiple Scales

written by Paige Marie Pruisner

has been approved for the Department of Civil, Environmental, and Architectural Engineering

R. Scott Summers (Chair)

Eric Dickenson

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

Pruisner, Paige Marie (M.S., Civil Engineering)

Assessing Trace Organic Contaminant Removal Trends in Biologically Active Filters at Multiple Scales Thesis directed by R. Scott Summers, Professor, Department of Civil, Environmental and Architectural Engineering, University of Colorado Boulder

Trace organic contaminants are becoming a water quality issue of increasing concern, especially in the context of potable water reuse scenarios. Biologically active filters (biofilters) have been evaluated for removal of some of these contaminants. The goals of this study were to 1) review the literature for trends in trace organic contaminant removal by biofiltration and 2) experimentally compare biofilter removal of trace organic contaminants at bench- and pilot-scale.

Information on operational parameters was gathered from multiple sources of biofiltration research. 1,400 removal data points on 200 compounds from 100 sources was refined by media type (granular activated carbon (GAC), sand, and anthracite) and empty bed contact time (EBCT) (between two and 30 minutes) to 850 data points on 150 compounds from 55 sources for quantitative analysis. Statistical analysis of 2-methylisoborneol and geosmin removal data reveals that removal increases with increasing EBCT for inert media types (sand, anthracite, etc.), while GAC media, with a high tendency to adsorb compounds, did not show significant differences in removal with EBCT. The consistently high removals achieved with GAC media imply another mechanism contributing to removal, likely adsorption.

Three bench-scale anthracite filters (media height = 25, 50, 100 cm, EBCT = 2 - 20 min) were evaluated for trace organic compound removal alongside one pilot-scale anthracite filter (media height = ~215 cm, EBCT = 10 min). Of 14 compounds measured, only two showed significant differences in removal between the bench- and pilot-scale filters. Experimental removal for five out of 14 compounds did not fall into the expected group based on the literature review, likely due to high variability in the data used. The disparities between the large-scale data generalizations and the removal achieved at different sites confirms the site-specific nature of biofiltration. The results presented in this study are consistent with the literature review analysis and a bench-scale experiment can replicate pilot-scale removal performance.

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CHAPTER 1 INTRODUCTION

MOTIVATION

A continued improvement in analytical techniques as led to the detection of many anthropogenic compounds in the parts per trillion (nanograms-per-liter) concentration range and lower in drinking water sources. These compounds are often termed trace organic contaminants. Effective removal of trace organic contaminants from drinking water is a widespread research topic, especially in the context of potential potable reuse applications, either de facto or planned. Many trace organic contaminants are pharmaceutical and personal care products (PPCPs), pesticides, flame retardants, or plasticizers. The public became more aware of the effects of pesticides due to their extensive application and noticeable effects on wildlife, publicized in Rachel Carson's Silent Spring, which criticized widespread use of the pesticide DDT in 1962 (Carson et al., 1962). Estrogen compounds and other hormones have also become more widely recognizable among the public due to impacts on male fish and sex ratios in fish populations (Purdom et al. 1994). Many contaminants are difficult to control because they are not completely removed from point sources, such as wastewater treatment facilities, and can also originate from nonpoint sources, such as agricultural and urban runoff (Köck-Schulmeyer et al. 2013; Wittmer et al. 2010). Furthermore, many contaminants are not removed by conventional drinking water treatment processes as they are not designed to specifically mitigate these contaminants (Pojana, Fantinati, and Marcomini 2011). Therefore, many of these compounds may end up in treated drinking water that is distributed to customers.

Filtration is mandated by the United States Environmental Protection Agency (U.S. EPA) for drinking water treatment systems in which the source water is either surface water or groundwater under the influence of surface water (United States Environmental Protection Agency 1989). The primary objective of filtration in drinking water treatment is to remove pathogenic microorganisms and particles that interfere with downstream inactivation. Biologically active filtration, or biofiltration, augments

standard filtration to remove contaminants through biodegradation. The goal of biological filtration is to utilize the microbial community within the filter to reduce contaminants and improve effluent water quality. To be a feasible treatment alternative, biofilter performance must consistently meet treatment needs and demonstrate high efficacy without sacrificing the primary filtration objective of removing pathogenic microorganisms. Biofiltration is an economical treatment method for contaminant control as it requires little, if any, additional capital and operating expenditures beyond that of normal filtration. In addition, it decreases microbial regrowth in distribution systems, prolonging the life of distribution infrastructure (Jones et al. 1998; van der Aa et al. 2012; Bouwer and Crowe 1988).

Most full-scale biofilters are created passively by the absence of a chlorine residual in the filter influent. Design parameters for biofiltration are relatively vague, although there has been a large body of research performed on factors that affect filtration (Zhu, Getting, and Bruce 2010). An evaluation of this information could reveal trends and gaps in knowledge that require further research. Pilot plant studies are a common method for producing this information, especially for specific source waters. However, pilot plant studies are usually large, expensive, and time consuming, requiring on-site work that can delay design projects. If a smaller, more mobile, and convenient experimental set up could replicate results from a pilot plant experiment, design experiments specific to a source water could be more manageable to perform. The goal of this study was to establish general operational trends that can be applied to biofiltration design and create a more manageable method of testing designs for a specific source water.

RESEARCH OBJECTIVES

The first objective of this study was to evaluate the current body of biofiltration literature results for general trends that can be applied to biofiltration design and operation. The second objective was to evaluate the potential of bench-scale experiments to replicate pilot-scale removal performance. Results from these experiments were compared to the trends found in the literature data.

THESIS ORGANIZATION

Chapter 2 provides a detailed literature review of microbiological factors and operational parameters that effect biofiltration. Chapter 3 evaluates the data collected through literature review for trends in operational parameters that may be used for designing biofilters. Chapter 4 describes the benchand pilot-scale studies and the possibility that these may be interchangeable, as well as how the experimental results compare to results from the literature review. Chapter 5 summarizes the findings of this study.

CHAPTER 2 LITERATURE REVIEW

INTRODUCTION

Biofiltration is achieved by allowing microorganisms to colonize the filter media and acclimate to the natural organic matter (NOM) and specific contaminants present in the feed water, which can then be metabolized by the microbial community. This decreases the concentration of the contaminant in the water as it moves through the filter. An overview of biodegradtion pathways and microbial communities is given in this section. Important operational parameters of interest for quantitative analysis are also described due to the large impact that those parameters have on biofilter performance and experimentation.

REMOVAL AND BIODEGRADATION PATHWAYS

Organisms derive energy for growth and maintenance from metabolizing substrate that serves as carbon source, electron donor, and/or electron acceptor (Madigan et al. 2014). The reduction potential is a measure of the tendency of a chemical species to gain electrons. The difference in reduction potentials between a reduction half reaction and an oxidation half reaction reflects the spontaneity of the overall reaction, with positive values indicating a spontaneous reaction. The spontaneous flow of electrons between two chemical species results in free energy. The difference in reduction potential, and resulting free energy, is higher for some half reaction pairs, such as the reaction with glucose as the electron donor oxidized to carbon dioxide and oxygen as the terminal electron acceptor reduced to water. However, this reaction can only occur under aerobic conditions. Other compounds can serve as the terminal electron acceptor under anaerobic or anoxic conditions, such as ferric, nitrate, or nitrite, although these have a lower reduction potential. In the context of the oxidation conditions and compound availability, redox pairs with a larger difference in reduction potential are preferentially utilized as electron donors and electron acceptors in microbial metabolism in order to maximize free energy.

The mechanism for contaminant metabolism by microorganisms in biofilters has generally been narrowed down to two pathways: direct catabolism or co-metabolism (Benner et al. 2013; Janke and Fritsche 1985; Rauch-Williams, Hoppe-Jones, and Drewes 2010). It is important to distinguish these two pathways because they occur under separate conditions with different efficiencies. The energetic needs of the microbial community relative to the concentration level of the contaminant determine the metabolic pathway by which the contaminant is degraded. The biodegradation pathway also affects the resulting metabolic by-products with impacts on the rest of the microbial community.

Compounds that are above the minimum required concentration and are metabolized to meet energetic needs are called primary substrates (Stratton, Namkung, and Rittmann 1983). The threshold concentration depends on the compound and microorganism (Stratton, Namkung, and Rittmann 1983). Compounds that are below the threshold concentration may also be metabolized, but do not provide energy for biofilm growth and maintenance. These compounds are called secondary substrates. Biodegradation of these compounds occurs by co-metabolism, in which the secondary substrate is incidentally metabolized while a primary substrate supplies energetic needs for the microbial community (Dalton and Stirling 1982).

Some microbial populations are specifically evolved to metabolize certain contaminants, making removal as primary substrate more likely. Contaminants are more likely to be catabolized as primary substrate when concentrations are higher than the nanogram-per-liter scale typically found in drinking water treatment applications. The contaminant is often mineralized as a result of metabolism as primary substrate. Mineralization end products include carbon dioxide, water, ammonium and other simple metabolites depending on the substrate (Benner et al. 2013). 17β-estradiol and estrone hormones can be used as the sole source of carbon and metabolized to non-estrogenic compounds by a *Sphingomonas* strain KC8 (Yu, Roh, and Chu 2007). Bacterial isolate M291-3 can use atrazine, a triazine herbicide, as its sole source of carbon and nitrogen under anoxic conditions in a glass bead column with a high initial concentration of 21.6 mg/L (Crawford et al. 1998). However, this level of atrazine contamination would

only occur in a highly impacted site, which would be an unlikely drinking water source. High concentrations of contaminants can initiate production of inducible enzymes capable of degrading the contaminant. *Pseudomonas putida* isolated from wastewater degrades caffeine through the inducible enzyme cytochrome P450 after a 14 hour delay lag time (Ogunseitan 2002). Most contaminants exist at low concentrations relative to other carbon sources in drinking water, such as background OM. Therefore, in most cases, it is assumed contaminants are metabolized as secondary substrate while the alternate carbon sources at higher concentrations are metabolized as primary substrate.

If the contaminant concentration is below the threshold for supporting growth and maintenance of the microbial community, then another carbon and/or energy source is required, typically background NOM present in the feed stream. This NOM is measured in water as total organic carbon (TOC), a fraction of which is biodegradable dissolved organic carbon (BDOC). In this situation, the alternate carbon source, such as BDOC, serves as the primary substrate to support growth and maintenance while the contaminant may be removed as secondary substrate (Stratton, Namkung, and Rittmann 1983).

Primary and secondary substrate concentrations need to be balanced in order to achieve maximum removal of the target micropollutant. If the contaminant concentration is high relative to the primary substrate concentration, degradation efficiency will decrease due to lack of primary substrate for energy supply or toxic effects of the contaminant. Atrazine removal from wastewater by anaerobic sludge was maximized at 300 mg/L of dextrose as primary substrate and 5 mg/L of atrazine, both moderate concentrations in the context of the study (Ghosh, Philip, and Bandyopadhyay 2005). Even though removal of contaminants through co-metabolism may be the ultimate goal, primary substrate concentrations are important to consider and may require optimization.

Contaminants can be degraded in a cascade of transformations involving metabolism and cometabolism. Some estrogen hormones are metabolized synergistically as primary and secondary substrate resulting in complete degradation. Fourteen strains of bacteria from eight different genera isolated from wastewater activated sludge can aerobically degrade 17β -estriol, but only the α -proteobacteria strain KC8 can metabolize 17β -estriol as a sole carbon source to non-estrogenic end products (Yu, Roh, and Chu 2007). 17α -ethinylestriol, more recalcitrant than 17β -estriol due to steric hindrance by the ethinyl group, can be co-metabolized by six strains from α , β , and γ -proteobacteria isolated from compost with 17β -estriol, estrone, and estriol as primary substrates (Pauwels et al. 2008). No other metabolites were detected in these batch tests, implying that total mineralization was achieved (Pauwels et al. 2008). The microbial community may require multiple organisms and multiple compounds supporting microbial biomass to achieve removal of the target compound.

Although microcontaminants can be metabolized as either primary or secondary substrate, they are much more likely to be secondary substrate due to the low nanogram-per-liter concentrations found in drinking water. Primary substrate concentrations can still factor into microcontaminant removal because the primary substrate supports the growth and maintenance of the biomass. These complex interactions involving multiple biodegradation pathways generally require a robust and diverse microbial community to achieve sufficient microcontaminant removal.

EFFECTS OF WATER QUALITY AND NUTRIENTS

pН

Changes in influent pH in the range commonly found in the environment or during drinking water treatment do not generally impact biomass concentration or removal capabilities of biofilters (Moll and Summers 1999). Each microbial population has a preferred range of acceptable pH, and most fall between 6 and 9. However, the composition of the microbial community may shift due to changes in pH. Biofilters with neutral influent waters have greater relative abundance of markers for Gram positive bacteria than those with more acidic or basic influent waters, while biofilters treating basic influent waters have greater relative bacteria (Moll and Summers 1999). pH does impact the speciation of compounds and removal of manganese by biofiltration. Although manganese oxidizing

bacteria (MOB) thrive in groundwater treatment applications, which typically have a pH greater than 7, MOB have been shown to effectively remove manganese at pH as low as 6.3 (Hoyland et al. 2014).

Temperature

Microbial populations have a distinct temperature range that is ideal. For example, the ideal temperature range for 2-methylisoborneol (MIB), geosmin, and microcystin degradation is 11 to 30° C (Ho, Sawade, and Newcombe 2012). Organic contaminant removal generally decreases at lower temperatures. Dehydrogenase enzyme activity was measured to be 70% higher in biofilters at temperatures greater than 12°C than in biofilters at 3°C, indicating a lower metabolic rate in colder biofilters (Fonseca, Summers, and Hernandez 2001). However, in the same experiment, biomass (measured as phospholipids) did not change with temperature (Fonseca, Summers, and Hernandez 2001). Biofilter effluent contaminant levels can spike when the influent water is below 10°C, indicating a lapse in removal and decrease in biological activity among ammonia-oxidizing bacteria (Kasuga et al. 2010). The temperature can have a profound impact on the microbial community and removal capacity of the biofilter. Biofilters operated at higher temperatures (20° C) have significantly more biomass at the top and bottom of the filter media than biofilters at lower temperatures (5° C), while biomass growth is reduced for higher temperature filters (35° C) (Moll et al. 1999). DOC removal at low temperatures (5° C) is also less than that achieved at higher temperatures $(20^\circ - 35^\circ \text{ C})$ (Moll et al. 1999). Temperature changes are fairly predictable on a seasonal basis and the biofilter is generally capable of compound removal within reasonable operating temperatures.

Nutrients: Carbon, Nitrogen, and Phosphorus

The ideal balance of carbon, nitrogen, and phosphorus was proposed to be approximately 100:10:1 (Redfield, Ketchum, and Richards 1963; Redfield 1934). If one of these nutrients is less available in these proportions, that nutrient will limit biomass growth. Although there has been research

since on the proportions of nutrients required to sustain biomass to update these values, the original ratio still serves as a general guideline.

Nitrogen is an essential nutrient for growth. However, excess nitrogen can inhibit biodegradation. When an alternate source of nitrogen is present, microorganisms will not degrade more recalcitrant nitrogen-based microcontaminants, such as atrazine. Bacteria isolated from cotton processing waste, initially unable to biodegrade atrazine in batch systems, may be prompted to biodegrade atrazine when ammonium nitrate levels are reduced from 35 mg/L to 1 mg/L (Feakin, Blackburn, and Burns 1994). At lower concentrations of ammonium nitrate, the bacteria may be using atrazine as a nitrogen source. The carbon to nitrogen ratio (C:N) can also influence biofilter operation, removal capacity, and microbial community distribution. For C:N less than four, nitrifying bacteria dominate the filter (Fdz-Polanco et al. 2000). For C:N greater than four, the filter is split between into two zones: heterotrophic bacteria removing TOC closer to the influent and nitrifying bacteria removing ammonia in the lower half of the filter (Fdz-Polanco et al. 2000). Whether carbon removal, ammonia removal, or both are desired, nitrogen is an important parameter that can dictate filter performance.

Phosphorus is most often limiting of the three Redfield Ratio nutrients. Phosphorus can be removed up to 97% through polyaluminum chloride and alum coagulation (Nishijima, Shoto, and Okada 1997). This could lead to phosphorus deficient biofiltration following these conventional water treatment processes. Microbial biomass in phosphorus-limited batch tests can increase by two orders of magnitude with the addition of just 1 μ g/L PO_4^{3-} (Lehtola, Miettinen, and Martikainen 2002). However, phosphorus amendment to enhance biofiltration removal is only effective in cases where phosphorus is limiting. If phosphorus is not limiting, dosing the biofilter with additional phosphorus can lead to an increase in heterotrophic bacteria in the effluent and no increase in total organic carbon (TOC) or assimilable organic carbon (AOC) removal in pilot-scale biological GAC filters (Vahala et al. 1998). Of the three main nutrients, phosphorus may be most often limiting, but adding more phosphorus does not automatically improve microcontaminant removal.

Micronutrients are required at lower concentrations than carbon, nitrogen, and phosphorus, but they can also limit contaminant removal if not present in high enough concentrations. The micronutrients iron and cooper, important components of the enzyme ammonia monooxygenase, can limit ammonia oxidation in anthracite biofilters fed with lake water (Wahman, Katz, and Speitel 2006; Arp and Stein 2003). Complete ammonia removal was achieved in the same system after addition of 200 μ g/L of iron and 15 μ g/L of copper (Wahman, Katz, and Speitel 2006). Even with adequate supply of carbon, nitrogen, and phosphorus, micronutrients required in smaller concentrations may still limit removal in biofilters.

Nutrient additions can increase biomass growth in biofilters, but only if that particular nutrient is limiting. Nutrient enhancement through additional dosing does not necessarily enhance removal if the biofilter is not in a nutrient-limited situation. Therefore, it is imperative to understand what concentrations of nutrients may or may not be reaching the biofilter in order to maintain a healthy filter biomass capable of microcontaminant removal.

MICROBIAL COMMUNITIES IN BIOFILTERS

An understanding of the microbial community is helpful for the optimization of biofilter performance. The health of the biomass is important to maintaining consistent contaminant removal. The microbial community is typically characterized through the biomass concentration, distribution, and interactions in the filter. The amount of biomass in the filter indicates the ability of microorganisms to attach to the media and proliferate. The location of the biomass within the filter affects exposure to necessary nutrients, electron acceptors, and electron donors and potentially harmful compounds, influencing which microorganisms can thrive. The community structure is ultimately determined by these parameters. Interactions between members of the microbial community can either enhance or inhibit compound removal.

The amount of live biomass in the filter is an important parameter that influences removal rates. The amount of biomass in the filter is dependent on media characteristics. Filter media with a greater

surface area, such as granular activated carbon (GAC), can host approximately six times more biomass on a weight basis in a drinking water filter pilot than media with less surface area, such as anthracite or sand (Wang et al. 2007; Wang, Summers, and Miltner 1995). Biomass is an important indicator of colonization, but cannot necessarily be directly correlated with compound metabolism and removal (Wang, Summers, and Miltner 1995). Biomass concentration is usually not dependent on contaminant concentration, since they are often metabolized as secondary substrate. Recently more success has been achieved relating activity measured by adenosine triphosphate (ATP) to biomass (Dowdell 2012; Magic-Knezev and van der Kooij 2004; Velten et al. 2007). When filter pre-chlorination is removed, aqueous ATP concentration can increase drastically, quadrupling from 50 to greater than 200 mg/mL for a fullscale anthracite-sand filter treating surface water in Nova Scotia, indicating natural colonization and increased biological activity (Stoddart and Gagnon 2015).

The amount and character of biomass changes based on the location in the filter, and therefore the compounds that are metabolized will vary with location as well. Assuming downflow operation, the upper layers of the filter receive the highest concentration of influent organic carbon and dissolved oxygen (DO) so biomass tends to have the highest concentration there (Wang, Summers, and Miltner 1995). As filter depth increases (and EBCT increases), the redox conditions in the filter change and biomass tends to decrease due to lack of substrate. Biomass distribution can be approximated using a first order exponential decay curve using EBCT to represent filter depth (Carlson and Amy 1998; Wang, Summers, and Miltner 1995). The distribution of the microbial community is important to consider, especially in the context of biological interactions where one microbial population degrades the byproducts of another. If microorganisms that are dependent on one another to metabolize a contaminant, such as geosmin, do not coincide within the filter structure, removal will not be ideal as demonstrated in batch studies (McDowall et al. 2009).

The biofilter contains a diverse microbial community. Biofilms are comprised of many types of microorganisms which may have competitive or synergistic relationships that impact target compound

removal. Competition for substrate and other resources, such as DO, impacts the microbial community structure in biofilters. Aerobic heterotrophs and anaerobic nitrifying microorganisms may coexist within one filter by being distributed separately along the depth of the filter or within anaerobic microenvironments within the biofilm. Aerobic heterotrophs have a higher specific growth rate than nitrifying autotrophs by almost a factor of 10 (Rittmann and Snoeyink 1984). Provided with enough organic substrate at the top of the filter, more than 100 mg COD/L for this wastewater filtration study, aerobic heterotrophs will outcompete nitrifying autotrophs (Fdz-Polanco et al. 2000). Increasing substrate loading reduces nitrification activity from near complete ammonia oxidation to approximately 10% (Wijeyekoon et al. 2004). As filter depth increases, organic carbon and DO decrease, selecting for a different microbial community of primarily slow-growing Gram-positive and anaerobic bacteria (Moll et al. 1999). These conditions are preferable for nitrifying microorganisms to proliferate in the lower layers of the filter (Madoni et al. 2001). With this combination of microorganisms, conditions may allow for simultaneous NOM and contaminant removal to occur within the filter.

A diverse microbial community creates opportunity for cooperative degradation. There is often a consortium of microorganisms responsible for contaminant degradation rather than a single microorganism. Cooperative metabolism generally occurs as associated metabolism or complementation of metabolic deficiencies (Dejonghe et al. 2003). Associated metabolism occurs when members of the consortia cross-feed on metabolites from the degradation pathways of other consortia members (Dejonghe et al. 2003). In this case, at least one member of the consortium is capable of initiating degradation of the target compound in isolation (Hoefel et al. 2006). This mechanism has been demonstrated with consortia isolated from agricultural soil and sediment capable of degrading the herbicide atrazine (De Souza et al. 1998; Smith, Alvey, and Crowley 2005; Satsuma 2009). Complementation of metabolic deficiencies occurs when there is a dependence between members of the consortium to provide essential growth factors or nutrients (Dejonghe et al. 2003). An example of this type of cooperative metabolism has been demonstrated with geosmin at nanogram-per-liter concentrations. In batch tests, three microorganisms

isolated from a sand biofilter were required to fully metabolize at least 95% of geosmin, while pure cultures or any combination of two strains showed no degradation (Hoefel et al. 2006). Unfortunately, experiments using this consortium to inoculate sand filters were less successful, only achieving 75% geosmin removal for a 15 minute contact time with no significant difference between inoculated and non-inoculated filters (McDowall et al. 2009). These interactions are important to consider, as an imbalance in the microbial community may explain low contaminant removal. Utilizing consortia inoculations to degrade targeted compounds may become more effective with future research.

In addition, there are interactions between different trophic levels that take place in the context of a biofilm that affect the microbial community. Ciliated protozoa grazing on heterotrophic microorganisms can reduce competitive pressure enough to allow nitrifying microorganisms a chance to grow within the filter (Madoni et al. 2001). Biofilms grazed by the snail *Potamopyrgus antipodarum* show decreased biomass and increased extracellular polymeric substance (EPS) production, which has been previously shown to be a defense mechanism against grazing (Barranguet et al. 2005; Matz, Deines, and Jurgens 2002). Predatory pressure are highly species specific, as the snail *Potamopyrgus antipodarum* may reduce competition allowing for filamentous bacteria to proliferate, while they can be severely predated by the protozoa *Chilodonella cucullulus* (Barranguet et al. 2005; Scholz and Martin 1997). Trophic and predatory interactions are vital to monitor, as the ecological equilibrium may be disturbed resulting in substantial losses of biomass.

The period between filter operation startup and the achievement of steady state removal by the microbial community is generally regarded as the acclimation period. This parameter is an important measurement of performance progress for a biological filter, as well as a critical design parameter. The biomass usually displays a typical sigmoidal growth curve during start up, with a characteristic lag time followed by a period of high growth eventually reaching steady state (Xiang et al. 2013; Servais, Billen, and Bouillot 1994). This pattern reflects a transition from physical limitations to biofilm growth to biological limitations. Potential causes for the lag time include time for biomass to increase, time for

enzyme production, preferential degradation of other organic compounds, or acclimation time to inhibiting compounds (Ho, Sawade, and Newcombe 2012). Once a filter is acclimated, the performance of the filter is expected to be relatively consistent. For this reason, it is desirable to achieve acclimation quickly. Various nutrients and water quality metrics of the water source can drastically impact the ability of the microbial community to acclimate and metabolize the target contaminants, as well as the physical parameters of the filter and the compound of interest.

These types of biological interactions are crucial to consider, since they could have a profound effect on the health and removal capacity of the microbial community. Within the biofilter, the microbial community is a complex ecosystem, but it may be optimized to increase removal for particular groups of compounds.

REMOVAL PERFORMANCE OF SELECT TRACE ORGANIC CONTAMIANT GROUPS

Many trace organic contaminants are resistant to conventional drinking water treatment, i..e., coagulation/flocculation/ sedimentation/filtration/chlorine disnfection. Prescription and non-prescription drugs and their metabolites, fragrance compounds, flame retardants and plasticizers, and cosmetic compounds have been found in finished drinking water (Stackelberg et al. 2004). Due to this resistance to conventional drinking water treatment, many studies have examined the removal of these trace organic contaminants through biofiltration. Trace organic contaminants are typically grouped according to their source and function. In some cases, their removal behavior can also be described using these classifications and this is explored in the following sections.

Pharmaceutical and Personal Care Products

Pharmaceutical and personal care products cover a wide range of contaminants that typically enter drinking water treatment facilities through sources impacted by wastewater effluent. Three main sources of pharmaceuticals in drinking water are human medical use (including discharge from hospitals, private households, and improper disposal), veterinary medical use, and pharmaceuticals manufacturing (Buttiglieri and Knepper 2008). Seasonal personal care products, such as DEET, result in annual concentration variations in water sources (Buttiglieri and Knepper 2008). Some pharmaceutical compounds can directly impact the biomass in a biofilter. Erythromycin, a common antibiotic, has been shown to negatively impact removal of other compounds (Zearley and Summers 2012).

Biofiltration removal mechanisms vary widely within this broad category, as do the expected removals, due to differences in chemical structures, filter operation, and treatment process (Onesios, Yu, and Bouwer 2009). For example, carbamazepine is considered recalcitrant while ibuprofen is generally highly removed (Hallé, Huck, and Peldszus 2015; Rattier et al. 2014; Zearley and Summers 2012). Other pharmaceuticals exhibit strong sorption properties to sediments and organic matter, such as estrogen hormones (Diaz-Cruz and Barceló 2008). This characteristic is important in distinguishing how compounds are removed in biological filters. For strongly sorbing compounds, it is difficult to differentiate between removal by sorption and removal by microbial activity, particularly in GAC filters. This study is solely interested in biological removal, so sorption will be carefully considered as it may interfere with attempts to measure biological removal alone.

Pesticides, Flame Retardants, and Plasticizers

Pesticides in drinking water sources can be traced to both agricultural and urban sources based on concentration profiles correlated with weather and other events (Wittmer et al. 2010). Pesticide concentrations in water vary during the year because most pesticides are used on a seasonal basis. Diazinon, diuron, atrazine, simazine, and malathion are a few of the most common and environmentally significant pesticides detected in wastewater treatment effluents (Köck-Schulmeyer et al. 2013). Polar herbicides, such as mecoprop, are less likely to adsorb to activated sludge and may therefore be found in wastewater impacted source waters and biofilter influents (Buttiglieri and Knepper 2008). Different conditions lead to varying levels of removal for pesticides. Chlorinated pesticides, such as DDT, are more effectively biodegraded in environmental soil samples under anaerobic conditions than aerobic conditions

(Guenzi and Beard 1968) and may be better removed by biofilters with low influent DO or high enough EBCTs so that DO is depleted in the lower part of the biofilter. However, aerobic processes are associated with high removals of phenoxy pesticides (Diaz-Cruz and Barceló 2008). Metabolites from pesticide biodegradation can also be problematic. Phenoxy pesticides degrade to chlorophenol compounds under aerobic conditions, but both compounds are carcinogenic (Diaz-Cruz and Barceló 2008; Dich et al. 1997). Cyanazine, a metabolite of triazine pesticides, competitively inhibits the degradation of atrazine, one of its parent compounds (Gebendinger and Radosevich 1999), presenting another obstacle to removal.

Despite these difficulties, some pesticides show promise of potential biodegradation in filters. Mecoprop can be removed to nearly 100% in laboratory activated sludge systems, however input concentrations are relatively high compared to drinking water applications (1 mg/L versus 15 ng/L) and acclimation time is 35 days (Diaz-Cruz and Barceló 2008; Nitschke et al. 1999). 2,4-D can also reach greater than 99% removal in sequencing batch reactors, but only after a 4 month acclimation period (Mangat and Elefsiniotis 1999). Although these studies show potential biodegradability of pesticides, the required acclimation times are prohibitively long for application in biofilters, especially for a seasonal contaminant.

Flame retardants are commonly used in fabrics, household items, electrical equipment, upholstered furniture, building materials, and packing materials to prevent them from easily catching and spreading fire. Due to an increase in concern for consumer safety, flame retardant production and application increased in the 1960s and 1970s (Agency for Toxic Substances and Disease Registry 2012). Many flame retardants are also plasticizers, such as phosphate ester compounds (Agency for Toxic Substances and Disease Registry 2012). Plasticizers are added to materials to increase their fluidity. They are especially common in polyvinyl chlorine (PVC) plastics, which are commonly used in household plumbing. Conventional wastewater treatment is ineffective at removing these compounds, so they are frequently detected in the environment. Agricultural runoff or deposition from snow and rain transport these compounds to drinking water sources. Based on the organic carbon-water partitioning coefficient

(K_{oc}), phosphate ester compounds are poorly soluble in water and tend to sorb strongly to soil (Boethling and Cooper 1985). Flame retardants are generally recalcitrant because they are designed to resist oxidation through burning. Therefore, many oxidation treatment processes, such as ozonation, are not very effective. Nonhalogenated phosphate ester compounds are more easily biodegraded than halogenated phosphate ester compounds are more easily biodegraded than halogenated phosphate ester compounds (Agency for Toxic Substances and Disease Registry 2012). However, there has been some success with degrading halogenated phosphate ester compounds using hydroxyl radicals generated by ultraviolet light or ozone (Watts and Linden 2009). Tris(2-carboxyethyl)phosphine was consistently removed below detection limit following ozonation and biologically active GAC filtration at the pilot-scale with a 30 minute EBCT (Sundaram and Emerick 2010). However, most flame retardants and plasticizers are notoriously recalcitrant. Opportunity for improving biofiltration performance exists in refining pretreatment strategies and finding synergies between oxidation and biological degradation.

EFFECTS OF OPERATIONAL PARAMETERS

Many parameters may affect the biofilter, but some are within the boundaries of engineering control. This section gives an overview of two parameters that can be manipulated or chosen in order to optimize biofiltration.

Empty Bed Contact Time

The EBCT is a measure of the amount of time that the water is in contact with the media. EBCT depends on the volume of the media (V) and the rate of flow through the media (Q) or the ratio of the bed length (L) to the filter velocity (v), as shown in Equation (1):

$$EBCT = \frac{L}{v} = \frac{V}{Q}$$
(1)

Most EBCTs in drinking water filters range from 2 to 30 minutes, although some can be as high as 60 minutes or longer, such as for slow sand filtration. The ideal EBCT would balance the capital costs of filter media while maximizing contaminant removal. A lower EBCT achieving high removal would balance both goals.

The reaction rate describing contaminant degradation at low concentrations in biological filters is described as by a pseudo-first order reaction equation:

$$r = \frac{dC}{dt} = -kC$$
(2)

where r is the reaction rate in ngL⁻¹min⁻¹, C is the contaminant concentration in the influent in ng/L, t is the time in minutes, and k is the pseudo-first order rate constant in in minutes⁻¹. Integrating this rate equation over the depth or total EBCT of the filter results in the following integrated rate equation describing the resulting contaminant concentration for a certain EBCT:

$$C_{EBCT} = C_{Inf} * e^{-k*EBCT}$$
(3)

When the EBCT is equal to the full depth of the filter, the integrated rate equation may be substituted and rearranged:

$$\frac{C_{\text{eff}}}{C_{\text{inf}}} = e^{-k^* \text{EBCT}}$$
(4)

This relationship relates the fraction of contaminant in the effluent $\left(\frac{C_{eff}}{C_{inf}}\right)$ to the rate constant and the EBCT by an exponential decay relationship. The rate constant is indicative of how rapidly the contaminant decays to negligible amounts remaining at low EBCTs. A contaminant with a higher rate constant will be more effectively removed at lower EBCTs than a contaminant with a higher rate constant.

Media Type

Both inert media (typically sand and anthracite) and adsorptive media (such as GAC) are commonly used in biofilters. With the high sorption capacity of GAC media, it is often difficult to determine whether contaminant removal is due to biological activity or adsorption to the media. The operational age of the media, among other metrics such as the type and concentration of other organic compounds in the influent, can be used to judge the amount of removal occurring due to biological activity versus adsorption. The longer a GAC media has been in operation in a filter, the more contaminants that have adsorbed to the media surface and less adsorption sites are available. The media may be colonized and acclimate to the substrate as run time increases. As the GAC becomes exhausted of adsorption sites, biological processes take over as the primary removal mechanism for biodegradable compounds as illustrated in Figure 2.1. One measure of operational age of the media is the throughput (in bed volumes) that have passed through the filter, which is the ratio of the total filter run time to the EBCT. The effect of increasing operational time on the fraction of contaminant remaining for the GAC and inert media types is shown in Figure 2.1.

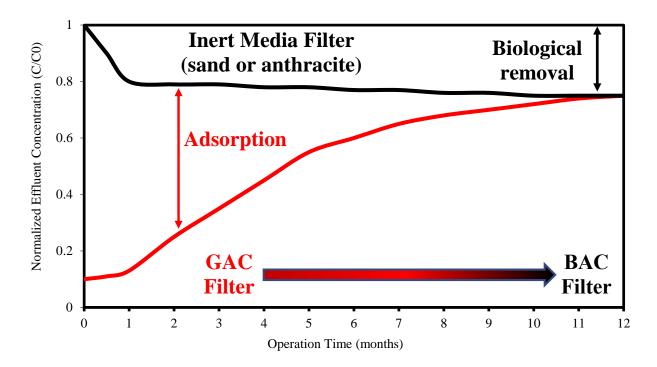


Figure 2.1: The effect of operation time on effluent concentration from a GAC biofilter

As operation time increases, GAC media and removal by adsorption transitions to BAC (biological activated carbon) media and biological degradation of contaminants. Adsorption is the dominant removal mechanism during the initial period of GAC filter start up. This results in much higher removals for the highly sorptive GAC media than the inert media. As the filter continues to operate, the sorption sites on the GAC media are exhausted, so removal decreases as biological removal becomes the dominant removal mechanism. Meanwhile, the inert media is colonized and the microbial community increases removal. The operational time required for biological activity to effect removal varies based on the compound targeted and operating conditions, such as temperature and primary substrate. There is also a period of time where acclimation to the specific compound occurs. This acclimation time may take a few weeks to a few months (Zearley and Summers 2012). Due to these inherently different interactions with contaminants, GAC and inert media types will be considered separately in this study.

CHAPTER 3 META-ANALYSIS OF OPERATIONAL PARAMETERS AND CONTAMINANT REMOVAL

INTRODUCTION

One goal of this study is to consolidate the information presented in the literature so that it is more accessible and the data can be evaluated for trends and relationships. This will be accomplished by first compiling extensive information from published literature on removal performance and operational parameters that may affect contaminant removal. This compiled data was analyzed for trends in the effects of operational parameters on contaminant removal. In addition, contaminants were separated into groups that characterize typical removal for the contaminant.

METHODS

Empty bed contact time and media type were identified as fundamental biofiltration criteria and were therefore used as parameters to refine the data set.

There is a wide variety of filter media types that may be used for biofiltration. Each media type varies in size, internal porosity, sorption capacity, and density, among other attributes. These are important to consider in a biofiltration context because a parameter such as porosity may affect colonization and biomass density. More porous media with high internal surface areas, such as GAC, can support more biomass than less porous media such as sand and anthracite (Wang, Summers, and Miltner 1995; Wang et al. 2007). Sorption capacity is an important parameter used to describe the affinity of chemical compounds to sorb to the media surface. Contaminant removal by sorption can interfere with assessment of biological removal. The data were therefore separated into Inert Media (anthracite and sand with low sorption capacity), GAC Media (high sorption capacity), and Other Media (plastic media, expanded clay, ceramic, etc.). The Other Media data set is small, so it was removed from consideration, leaving anthracite, sand, and GAC media.

EBCT is important because it is strongly correlated to removal by sorption and biotreatment. Data from filters with very short EBCTs and very long EBCTs that are not reflective of practical operational conditions are not helpful for making generalizations about compound removal. Data with EBCTs less than two minutes or greater than 30 minutes were removed from the data set, leaving EBCTs between two minutes and 30 minutes. In addition, when gathering data from multiple sources, it can be difficult to find an even distribution of experimental EBCTs for one compound. To address this, EBCTs were grouped into the following categories: 2 to < 5 minutes, 5 to < 10 minutes, 10 to < 20 minutes, and 20 to 30 minutes.

These refinements of the data set reduced the original data library (1,400 data points, 200 compounds, 100 sources) down to a select data set of 850 data points, 150 compounds, and 55 sources for quantitative analysis. MIB and geosmin are two widely studied taste and odor compounds that were selected for analysis due to high amounts of available data. MIB and geosmin have 106 and 78 removal data points, respectively. There are not as much removal data available for other compounds. There were 116 compounds with data sets of 2 to 29 removal data points and 65 compounds with data sets consisting of one removal data point. After separating the data by media type and the EBCT groups mentioned above, there were not enough data in each category to draw statistically significant conclusions. Therefore, the data for MIB and geosmin were used to analyze the effects of EBCT and media type.

Data analysis was performed with MVPstats (Petrovich 2012; Version 20120906) and Microsoft Excel (Microsoft Office 365 ProPlus 2016; Version 16.0.6001.1078). Data sets under each EBCT group for each compound were first analyzed for normality using the Anderson-Darling test, the Shaprio-Wilk test, the Lin-Mudholkar test, Skewness, and Kurtosis (D'agostino, Belanger, and D'Agostino Jr 1990; Shaprio, Wilk, and Chen 1968; Stephens 1974; L. S. Nelson 1998; Lin and Mudholkar 1980). If the data set failed any one of these tests, it was considered non-normal and any analysis performed comparing that data with another data set used a nonparametric test. All of the data sets proved to be non-normal. Therefore, the Kruskal-Wallis Oneway ANOVA was used to test for equality of means among multiple

data sets. If this test came back positive, Wilcoxon-Mann-Whitney test was used to test for equality of means for all data combinations until all significant differences were identified. Data sets were considered significantly different for p < 0.05.

RESULTS AND DISCUSSION

Geosmin and MIB

Due to the high level of variability in the data gathered from the literature review, box-andwhisker plots were used to create figures. Figure 3.1 shows the effect of EBCT and media type on geosmin removal. The median removals for inert media (n = 78) for each EBCT group are 14% for 2 to < 5 minutes, 31% for 5 to < 10 minutes, and 69% for 10 to < 20 minutes. No data were available for geosmin removal by inert media with EBCTs between 20 and 30 minutes. The median removals for GAC media for each EBCT group are 52% for 2 to < 5 minutes, 99% for 5 to < 10 minutes, 95% for 10 to < 20 minutes, and 97% for 20 to 30 minutes. The number of removal data points included and statistical relationships are shown above each media type within each EBCT group.

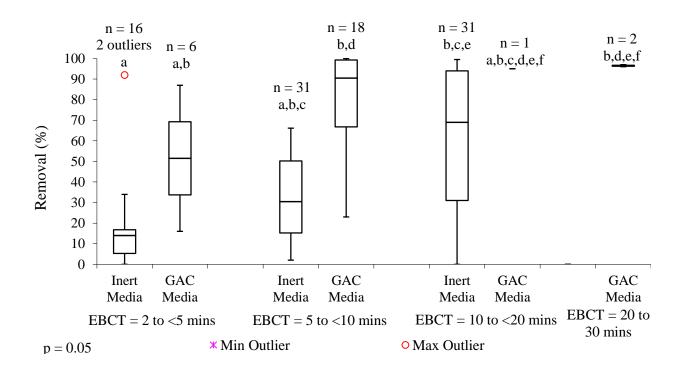


Figure 3.1: Geosmin removal performance by EBCT and media type

Statistical analysis for inert media reveals that the only significant difference is between the removal for 2 to < 5 minute EBCTs and the removal for 10 to < 20 minute EBCTs. The removal that occurs for EBCTs between 5 and < 10 minutes is not statistically different from the higher removal for EBCTs between 10 and < 20 minutes. The lack of significant difference for results across the range of EBCTs would suggest that other operational parameters, such as temperature and acclimation time, can impact removal. EBCTs between 5 and < 10 minutes can be recommended for operation due to the lack of significant difference between 10 and < 20 minutes. Increasing the EBCTs between 5 and < 10 minutes and for EBCTs between 10 and < 20 minutes. Increasing the EBCT does not lead to significantly more removal. This approach maximizes contaminant removal while minimizing the capital costs of the filter. Therefore, recommending an EBCT between 5 and < 10 minutes would be a justifiable approach for inert media, although these results must be confirmed for each target compound at the specific treatment site. MIB removal shows similar statistical results for inert media (Figure 3.2, n = 64).

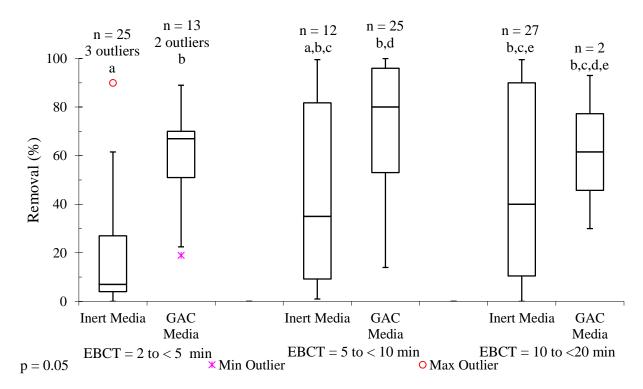


Figure 3.2: MIB removal performance by EBCT and media type

This range of results could also be narrowed down by simultaneously considering EBCT alongside another variable that impacts removal. In order to increase precision, a multivariate analysis was attempted with EBCT and temperature as the independent variables and removal as the dependent variable. However, there was insufficient temperature data for a single compound and media type to perform this analysis.

Figure 3.1 also shows the effect of EBCT on geosmin removal for GAC media (n = 27). Statistical analysis for GAC media reveals that there are no significant differences for any of the EBCT groups. This would imply that EBCT does not have an effect on contaminant removal with GAC media. The lack of data for the 2 to < 5, 10 to < 20, and 20 to < 30 minute EBCT groups makes statistical analysis for these groups less reliable. The variability is also high for the data in the 2 to < 5 and 5 to < 10minute EBCT groups. Analysis for MIB removal with GAC media yielded similar statistical results with little data for EBCTs above 10 minutes (Figure 3.2, n = 40). However, the consistently high removal values suggest that there is another mechanism contributing to removal other than biodegradation. MIB and geosmin both adsorb well to GAC media (Yang, Yuan, and Weng 2010; Summers et al. 2013). For EBCTs below 10 minutes, biodegradation would contribute less to overall removal than at higher EBCTs, so the impact of additional adsorption would more strongly skew the results at lower EBCTs than higher EBCTs. At higher EBCTs, biodegradation may already be maximized, so sorption may not contribute much additional removal. The number of bed volumes treated is not represented in Figure 3.1 or Figure 3.2. Analysis was attempted with data restricted to various levels of bed volumes. Even at the most lenient limitation of at least 60,000 bed volumes, there was insufficient data to make statistical conclusions. Adsorption of MIB and geosmin in addition to biodegradation may be increasing the removal above what is expected at lower contact times and obscuring the effect of EBCT for GAC media.

Figure 3.1 and Figure 3.2 also show a direct comparison between removal with inert and GAC media for different EBCT groups for geosmin and MIB, respectively. For EBCTs between 10 and 20

minutes, there is no significant difference between GAC and inert media, as shown in Figure 3.1 and Figure 3.2. This is likely due to increased biodegradation at higher EBCTs overshadowing the effect of media type or adsorption, as was described for the EBCT analysis.

GAC media removes significantly more MIB for EBCTs between 2 to < 5 minutes and 5 to < 10 minutes. However, removal with GAC media may be elevated due to residual adsorption after the media has been acclimated. The combination of residual adsorption on biological GAC (BAC) has been shown to be more effective at DOC removal than fresh GAC alone (Xing et al. 2008). Bed volumes were also unrestricted for this analysis to maintain larger sample sizes, allowing for the possibility of residual adsorption to affect the removal results. The effect of GAC throughput measured in bed volumes on MIB removal based on literature review data is shown in Figure 3.3. For adsorption alone, the model of Summers et al. 2013 for influent TOC of 1 to 3 mg/L would predict a 50% MIB breakthrough between 30,000 and 60,000 bed volumes which is representative of the data shown in Figure 3.3. Again, the variability in performance may be due to other study-specific factors. The data is also broken down by the contributing study to highlight studies that may be biased toward higher or lower removals. There are some studies that tend toward high removal (Persson et al. 2007) and some that have lower removal (Elhadi, Huck, and Slawson 2006), suggesting that a factor other than compound, media type, filter operation time, or EBCT differs among these studies and impacts removal.

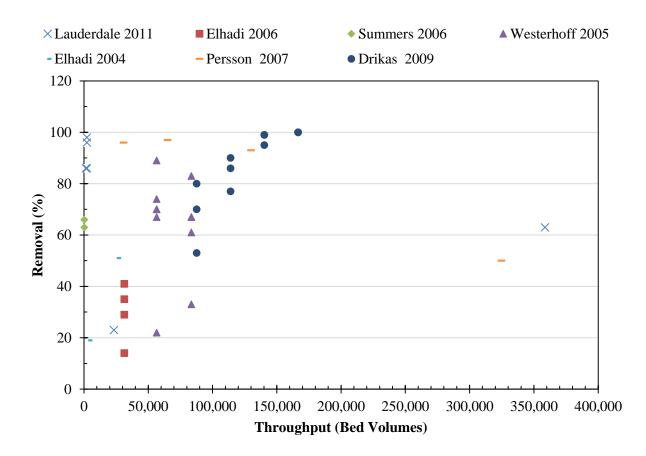


Figure 3.3: The effect of throughput on GAC media removal of MIB, shown by study

This media type analysis supports the assertions that adsorption impacts the analysis of EBCT on contaminant removal. For GAC media, adsorption may make an important contribution at low EBCTs, while biodegradation and EBCT are the dominant mechanism and parameter at higher EBCTs.

Pseudo-first order modeling was applied to the literature review data. Figure 3.4 and Figure 3.5 show pseudo-first order modeling applied to Figure 3.1 and Figure 3.2. These rate constants were approximated from exponential decay trend lines fitted to median percent remaining data plotted as EBCT versus percent remaining with the y-intercept set to 100% at an EBCT of 0 minutes. The resulting rate constants are 0.071/min for geosmin and 0.028/min for MIB. The associated R² values are 0.9 for geosmin and 0.7 for MIB. Westerhoff, Summers, and Chowdhury, 2005 found very similar rate constants, 0.079/min for geosmin and 0.036/min for MIB.

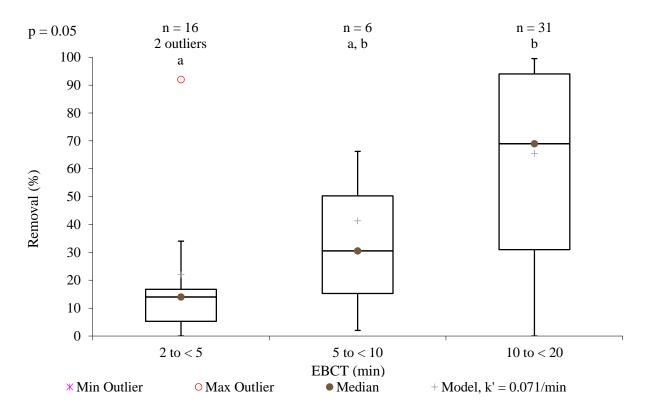


Figure 3.4: Geosmin removal performance by inert media for grouped empty bed contact times with pseudo-first order model

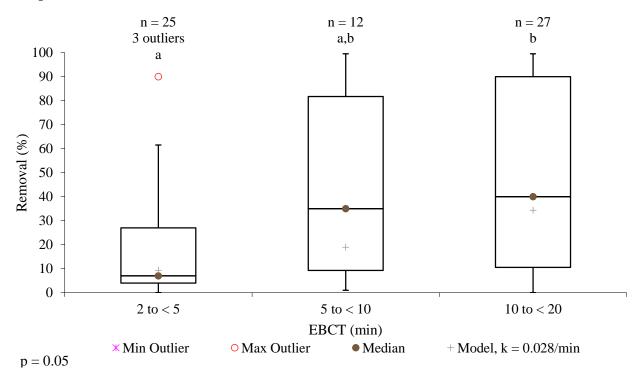


Figure 3.5: MIB removal performance by inert media for grouped empty bed contact times with pseudo-first order model

The modeled removals for each EBCT group fit relatively well, with almost all modeled removals within the interquartile range except for the 2 to < 5 minute EBCT group for geosmin, which has an exceptionally small upper quartile. Almost all of the modeled percent removals fall within 10 percentage points of the median percent removals. The greatest differences (+11 and -16 percentage points for geosmin and MIB, respectively) fall in the 5 to < 10 minute EBCT group.

Other Contaminants

After the refinements of the data set created by the literature review, removal data was analyzed for each compound. This was achieved by using the median of certain parameters of interest, such as removal percentage. These median removals fell into four groups (0 - 15%, > 15 - 50%, > 50 - 85%, and >85%) previously described by Zearley and Summers 2012. A sample of 32 compounds are shown in Table 3.1 organized by removal level, with the number of data points associated with that compound for inert media (n). A more extensive table featuring more compounds, information for both inert and GAC media, removal, EBCT, temperature, and references from the literature review is included in Appendix A. There were very few compounds that fell into the high removal category for inert media, so all of the compounds in that category are included in the table below. For the other three categories, compounds are featured below because they were later measured as part of the experimental verification or because they are commonly studied compounds with high data availability.

High		Ν	Low				
>85%	>85% n		>50-85% n >15-50% n		n	0-15%	n
Benzo[a]pyrene	1	Acetaminophen	5	Caffeine	7	Atenolol	3
DDT	1	Aldicarb	2	DEET	25	Carbamazepine	16
Fluoxetine	1	Chlorobenzene	6	Erythromycin	5	Meprobamate	2
Formaldehyde	7	Clofibric Acid	3	Diclofenac	4	Primidone	2
Ibuprofen	11	Dimethoate	2	Gemfibrozil	4	Sucralose	1
Molinate	2	Naproxen	26	Geosmin	53	Sulfamethoxazole	7
p-Toluenesulfonic Acid	18	Phenol	13	MIB	65	TCEP	2
Saxitoxin C2	1	Triclosan	4	Trimethoprim	5	Trichloromethane	14

Table 3.1: Median removal groups with inert media for selected compounds

This analysis may be used to verify or predict removal in a broad sense and may contribute to the development of indicator compounds that can be used as proxies to imply removal of a larger group of compounds. These expected removals were compared against the experimental data presented in Chapter 4.

CONCLUSIONS

Analysis of literature review data reveals that the only statistically different EBCT groups for inert media are 2 to < 5 minutes and 10 to < 20 minutes for geosmin and MIB. Removals for EBCTs between 5 and < 10 minutes were not statistically different from those between 2 and < 5 minutes and 10 to < 20 minutes. EBCTs at 5 minutes or above are recommended to ensure the most complete removal. The range of EBCTs between 5 and < 10 minutes could be explored during pilot testing to further narrow down the ideal operational EBCT for each site. For GAC removal results, there were no statistical differences between any of the EBCT groups for geosmin and MIB. There were very little data for statistical analysis in some of the groups, especially those with EBCT greater than 10 minutes. In addition, the consistently high removals achieved with GAC media implied another mechanism contributing to removal, likely adsorption. GAC media achieved significantly higher MIB removal than the inert media for the 2 to < 5 and 5 to < 10 EBCT groups. However, for the 10 to < 20 minute group, there was no significant difference between media types, suggesting that EBCT is the dominant parameter for determining removal performance at high EBCTs. Table 3.2 summarizes the results from the EBCT and media type analysis in Figure 3.1 and Figure 3.2. MIB and geosmin data for inert media filters was also modeled using pseudo-first order kinetics. The resulting rate constants are 0.071/min for geosmin and 0.028/min for MIB with associated R² values of 0.9 for geosmin and 0.7 for MIB.

		Median Removal for EBCT Ranges							
Contaminant	Media Type	2 to < 5 minutes	5 to < 10 minutes	10 to < 20 minutes	20 to 30 minutes				
Geosmin	Inert	14%	31%	69%					
	GAC	52%	91%	95%	97%				
MIB	Inert	7%	35%	40%					
	GAC	67%	80%	93%	97%				

Table 3.2: Summary of median removals for MIB and geosmin from literature review data

150 contaminants were also grouped into four categories (0 - 15%), > 15 - 50%, > 50 - 85%, and >85%) according to median removal with inert media as determined from the literature review data shown in Table 3.1. The >85% removal category had the fewest compounds of the four removal categories. These predicted removal groups were compared against experimental data in the Removal Groups section in Chapter 4.

CHAPTER 4 TRACE ORGANIC CONTAMINANT REMOVAL IN BENCH-AND PILOT-SCALE BIOFILTERS

INTRODUCTION

The goal of this study was to experimentally assess the removal of trace organic contaminants in tertiary-filtered wastewater for bench- and pilot-scale filters. Comparable results from bench- and pilot-scale filters would imply that bench-scale experimentation could be used in lieu of or to inform the design of more expensive pilot-scale experimentation. Bench-scale experimentation is less expensive and easier to maintain. This study investigated an approach of initially recirculating tertiary-filtered wastewater through bench-scale columns to facilitate filter colonization, followed by a single pass flow-through mode to assess performance. This approach is advantageous because it could be conducted remotely from the water source, such as in a controlled laboratory.

MATERIALS AND METHODS

All experimental filter runs took place at the Clark County Water Reclamation Facility (CCWRF) in Las Vegas, Nevada between December 2015 and May 2016. The average plant flow rate at is 32.5 million gallons per day (MGD). The CCRWF utilizes an advanced wastewater treatment process including primary treatment (bar screen, ferric chloride coagulant, grit removal, anion polymer, primary clarification), secondary treatment, tertiary treatment, and ultraviolet disinfection. Secondary treatment is comprised of a modified Johannesburg process for biological nitrogen and phosphorus removal. Tertiary treatment is dual media (anthracite/sand) filtration. Figure 4.1 is a schematic of the CCWRF treatment process. The bench- and pilot-scale filters were fed tertiary-filtered wastewater, while the full-scale filter treats effluent from the secondary clarifier.

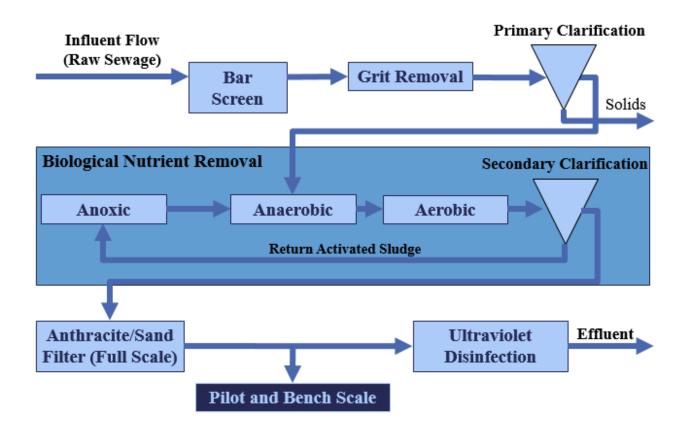


Figure 4.1: Basic schematic of treatment process at Clark County Water Reclamation Facility in Las Vegas, Nevada

Full-Scale Filter

There are 16 full-scale dual media filters at CCWRF that are 4.5 feet deep, with 3.5 feet of anthracite over 1 foot of sand and 1 foot of support gravel. The EBCT varies between 7 and 14 minutes with a maximum loading rate of 5 gpm/ft². The effective size of the anthracite media when it was new was 1.62 millimeters and the specific gravity was 1.65. The effective size of the sand media when it was new was 0.89 millimeters and the specific gravity was 2.65. This media has been in use for at least 10 years. Each filter is 60 feet long and 20 feet wide for a length to width ratio of 3 to 1 and an area of 1,200 square feet. The average design filter run time is 24 hours for an average of one backwash per day. Combined influent and combined effluent water quality samples were collected on February 23, 2016. Figure 4.2 is a photo of the full-scale filters as seen from the roof of the filter building.



Figure 4.2: Full-scale filters at Clark County Water Reclamation Facility

Pilot-Scale Filter

The pilot-scale filters are contained by six 15-foot-tall, 6-inch diameter PVC columns on a skid built by Intuitech. One of these columns was filled with 4 feet of anthracite and 1 foot of sand. This results in an EBCT of 10 minutes and a hydraulic loading rate (HLR) of 3.75 gpm/ft² for a filter surface area of approximately 0.2 square feet. The anthracite media has been running at CCWRF for approximately 1.5 years. The effective size of the fresh anthracite media as reported by the manufacturer was 1.35 to 1.45 millimeters with a uniformity coefficient of less than 1.40. The flow rate into the filter is 0.75 gpm. Backwashing occurred once per week. Samples from the influent to the pilot skid and effluent of the anthracite filter were collected on a monthly basis. Data from February 10, 2016 to May 10, 2016 are included in this report. Figure 4.3 is a photo of the pilot filter skid.



Figure 4.3: Pilot-scale filter column

The pilot-scale anthracite filter treated effluent wastewater from the full-scale filter. Table 4.1 shows the typical water quality parameters of the influent to the pilot filter. Parameters reported as less than an average value had one or more samples below the reporting limit. DOC and pH information is included with trace organic contaminant parameters in Table 4.6.

Parameter	Units	Average	Standard Deviation	Count of Data Points
Turbidity	NTU	0.5	0.02	4
Alkalinity, CO3	mg/L	< 1	1	4
Alkalinity, HCO3	mg/L	140	9	4
Alkalinity, OH	mg/L	< 1	1	4
Alkalinity, Total	mg/L	140	9	4
Ammonia as Nitrogen	mg/L	< 0.1	0.1	4
Nitrate as Nitrogen	mg/L	12	1	3
Nitrite as Nitrogen	mg/L	< 0.05	0.05	3
Total Dissolved Nitrogen	mg/L	12	1	2
UV 254	/cm	0.1	0.005	4
UV 280	/cm	0.1	0.004	4
o-Phosphate as P	mg/L	0.04	0.01	4
Calcium	mg/L	99	4	4
Magnesium	mg/L	38	2	4
Potassium	mg/L	18	2	4
Sodium	mg/L	181	7	4
N-Nitrosodiethylamine	ng/L	< 5	0	4
N-Nitrosodimethylamine	ng/L	< 3	0	4
N-Nitrosodi-n-butylamine	ng/L	< 8	3	4
N-Nitrosodiphenylamine	ng/L	< 8	3	4
N-Nitrosomethylethylamine	ng/L	< 3	0	4
N-Nitrosomorpholine	ng/L	12	1	4
N-Nitroso-n-propylamine	ng/L	< 10	0	4
N-Nitrosopiperidine	ng/L	< 20	0	4
N-Nitrosopyrrolidine	ng/L	< 20	0	4
Bromodichloromethane	mg/L	< 0.001	0	4
Bromoform	mg/L	< 0.001	0	4
Chlorodibromomethane	mg/L	< 0.001	0	4
Chloroform	mg/L	0.001	0	4
Total Trihalomethanes (TTHM)	mg/L	0.001	0	4
Bromoacetic Acid	mg/L	< 0.001	0	4
Chloroacetic Acid	mg/L	< 0.002	0	4
Dibromoacetic Acid	mg/L	< 0.001	0	4
Dichloroacetic Acid	mg/L	< 0.001	0	4
Trichloroacetic Acid	mg/L	< 0.001	0	4
Total Regulated Haloacetic Acids (HAA5)	mg/L	< 0.001	0.001	4

 Table 4.1: Typical water quality and nutrients in the influent to the pilot filter

Parameter	Units	Average	Standard Deviation	Count of Data Points
Aluminum	mg/L	0.1	0.01	4
Antimony	mg/L	< 0.001	0	4
Arsenic	mg/L	0.001	0.0001	4
Barium	mg/L	0.05	0.004	4
Beryllium	mg/L	< 0.0004	0	4
Cadmium	mg/L	< 0.001	0	4
Chromium	mg/L	< 0.003	0	4
Copper	mg/L	< 0.01	0	4
Iron	mg/L	0.1	0.02	4
Lead	mg/L	< 0.001	0	4
Manganese	mg/L	0.1	0.2	4
Molybdenum	mg/L	0.01	0.001	4
Nickel	mg/L	< 0.01	0	4
Selenium	mg/L	0.002	0.0004	4
Silver	mg/L	< 0.01	0	4
Thallium	mg/L	< 0.0002	0	4
Vanadium	mg/L	< 0.01	0	4
Zinc	mg/L	0.03	0.003	4

Bench-Scale Filter

Three bench-scale filters also treated tertiary-filtered wastewater after passing through the fullscale filter. The water quality parameters shown in Table 4.1 can also be applied to the bench-scale filters because both received the same influent. The bench-scale filters consisted of three glass chromatography columns (Ace Glass #5820) filled with anthracite media. The columns are 5 centimeters in diameter and 45 centimeters, 60 centimeters, and 120 centimeters in length with nylon threaded adapters on both ends. Plastic tubing (Tygon E-3603, 1/4 in ID, 3/8 in OD, Saint-Gobain Performance Plastics) was used to connect the columns to the water source and waste. The same anthracite media that had previously treated CCWRF tertiary-filtered wastewater for over 1.5 years that was used in the pilot filter was also in the bench-scale filters to allow for faster acclimation time and consistency across scales. A short layer (less than 3 centimeters) of glass beads on top of a mesh screen was used to support the anthracite media. The three media heights within the glass columns were 25 centimeters, 50 centimeters, and 100 centimeters. From December 2015 to January 2016, the flow rate was set at 0.08 gpm (304 mL/min) for three peristaltic pumps leading to each filter for EBCTs of 2, 3, and 6 minutes and an HLR of 3.67 gpm/ft². In February 2016, the flow rate was changed to 0.03 gpm (101 mL/min) to each filter for EBCTs of 5, 10, and 20 minutes and an HLR of 1.38 gpm/ft². The filters were set up as a recirculating batch system with a 13.2 gallon (50 liter) feed reservoir of tertiary-filtered wastewater that was changed three times per week. The reservoir fed all three filters with tertiary-filtered wastewater. The filter effluents were then routed back to the feed reservoir, resulting in a batch process. Each week, one batch of tertiary-filtered wastewater was run for five days, then replaced with fresh tertiary-filtered wastewater and run for two days. Before collecting filter influent and effluent, a fresh batch of tertiary-filtered wastewater was collected and filters were switched into flow through mode with treated water going to waste. Twenty bed volumes were allowed to pass through each filter before samples were taken. The filters were allowed to run in flow through mode between sampling campaigns. Once a week, shortly after sampling, the filter media was manually fluidized without rinsing. After sampling each week, tubing was also massaged and rinsed with tap water at >0.2 gal/minute (>1000 mL/minute). The rinse water was routed through air release valves and not allowed to enter the filters. This was done to remove and discourage bacterial growth on the tubing. Columns and tubing were also covered in piping insulation to block out light and discourage phototrophic growth. Figure 4.4 is a picture of the bench-scale columns without the insulation.

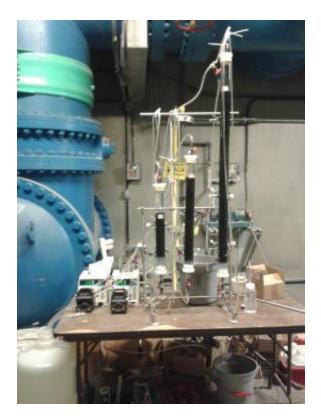


Figure 4.4: Three bench-scale filter columns run in parallel

Analytical Methods

17 trace organic compounds that represent a variety of usage classes, chemical structures, and partitioning behavior were selected for experimental analysis. The compounds and select properties are shown in Table 4.2. Values for molecular weight, $log(K_{oc})$, and $log(K_{ow})$ (where noted), were estimated using the KOWWIN and PCKOCWIN programs of the EPI Suite from the U.S. EPA and Syracuse Research Corp. Values with an asterisk are pH dependent.

Compound	Molecular Weight (g/mol)	log(K _{oc})	log(K _{ow})	Usage Class		
Acetaminophen	151.17	1.65	0.46 ¹	Analgesic ² , NSAID ³		
Atenolol	266.34	1.83	0.16 ¹	Beta-Blocker ^{1,3}		
Caffeine	194.19	1.00	0.07^{-1}	Psychoactive Compound ² , Stimulant ³		
Carbamazepine	236.28	3.12	2.30 ¹	Psychoactive Compound ² , Anticonvulsant ³ , Antiepileptic ¹		
DEET	191.28	2.05	2.26 4	Pesticide ² , Insect Repellant ^{3,5}		
Fluoxetine	ioxetine 309.33		1.95 ¹	Psychoactive Compound ² , Antidepressant ¹		
Gemfibrozil	250.34	2.64*	4.77 ⁴	Heart Medication ² , Lipid Regulator ¹		
Ibuprofen	206.29	2.63*	3.50 ¹	Analgesic ²		
Meprobamate	218.25	2.27	0.98 4	Psychoactive Compound ² , Anticonvulsant ³		
Naproxen	230.27	2.52*	3.18 ¹	Analgesic ²		
Primidone	218.26	2.14	0.73 4	Anticonvulsant ³ , Antiepileptic ^{1,5}		
Sucralose	397.64	1.00	-1.00 ⁴	Food Additive ⁵		
Sulfamethoxazole	253.28	2.41	0.89 ¹	Antimicrobial ² , Antibiotic ^{1,3}		
TCEP	250.19	2.83*	0.02 4	Flame Retardant ^{2,3}		
Triclosan	289.55	4.37	4.53 ¹	Antimicrobial ² , Antiseptic ¹		
Trimethoprim	290.32	2.87	0.91 ¹	Antimicrobial ² , Antiseptic ¹		

 Table 4.2: Experimental trace organic compounds and select properties

- 1. Rosal, R. et al. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. Water Res. 44, 578–588 (2010).
- Snyder, S. A., Wert, E. C., Lei, H. D., Westerhoff, P. & Yoon, Y. Removal of EDCs and pharmaceuticals in drinking and reuse treatment processes. Am. Water Work. Assoc. Res. Found. Rep. 331 (2007).
- Teerlink, J., Martínez-Hernández, V., Higgins, C. P. & Drewes, J. E. Removal of trace organic chemicals in onsite wastewater soil treatment units: A laboratory experiment. Water Res. 46, 5174– 5184 (2012).
- 4. United States Environmental Protection Agency. Estimation Programs Interface Suite. (2012). at http://www.epa.gov/oppt/exposure/pubs/episuite.htm>
- Hollender, J. & Zimmermann, S. Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. Environ. Sci. Technol. 43, 7862–7869 (2009).

The trace organic compounds in this study were measured through solid phase extraction, liquid

chromatography/tandem mass spectrometry with isotope dilution, and analytical protocols based on

previously published methods (Vanderford and Snyder 2006). Tandem mass spectrometry of the analytes

and their isotopic surrogates was performed using an API 4000 triple-quadruple mass spectrometer.

Method reporting limits for each compound are included in Table 4.6. DOC analysis was carried out according to Standard Method 5310B. Samples were collected for DOC analysis each week, immediately acidified using 2-N-hydrochloric acid to pH less than 2, and filtered through GE Whatman glass microfilber filters (1.5 µm) which had been rinsed twice with ultrapure water. DOC was measured using a Shimadzu TOC-L CPH total organic carbon analyzer.

pH, DO, and temperature were measured on a weekly basis at the influent and effluent of the pilot column. pH was measured using an Accumet AP115 portable pH meter (Fisher Scientific, catalog no. 13-636-AP115). DO and temperature were measured using a SensION+ DO6 DL portable DO meter (Hach, product no. LPV4500DL.97.02) with a sensION+ 5130 portable polarographic DO probe (Hach, product no. LZW5130.97.0002). A 50 mL glass beaker was used to collect water samples for probe analysis. The probe remained submerged in the sample for at least 30 seconds before recording the stabilized reading.

Media samples were collected with sterile sample bottles for ATP measurement before commencing bench scale experimentation (December 3, 2015) and after bench scale experimentation concluded (March 1, 2016 – April 27, 2016). ATP levels on the solid filter media were measured using a Deposit and Surface Analysis test kit (Luminultra, DSA-100).

RESULTS AND DISCUSSION

Bench- and Pilot-Scale Water Quality

Average pH levels through the pilot-scale anthracite column are shown in Table 4.3. The pH remains relatively consistent through the filter. The values in Table 4.3 were averaged from seven sampling events between February 11, 2016 and April 20, 2016.

	Minimum pH	Average pH	Maximum pH	Standard Deviation	Sample Size
Influent	6.7	6.9	7.1	0.1	7
Effluent	6.3	6.7	6.9	0.2	7

Table 4.3: Influent and effluent pH for pilot-scale filter

A summary of DO measurements for the bench- and pilot-scale filters is shown in Table 4.4. The DO values for the bench-scale filters were averaged from three sampling events, while values for the influent and effluent to the pilot-scale column were averaged from five and thirteen sampling events, respectively. The effluent DO concentrations indicate the filters are aerobic and the decrease in DO in the effluent suggests the presence of biological activity.

Scale	Sample Location	Minimum DO (mg/L)	Average DO (mg/L)	Maximum DO (mg/L)	Standard Deviation	Sample Size
	Influent	1.3	2.1	2.6	0.7	3
	Filter 1 Effluent (EBCT = 2, 5 min)	1.2	1.4	1.6	0.2	3
Bench	Filter 2 Effluent (EBCT = 3, 10 min)	0.8	1.2	1.9	0.6	3
	Filter 3 Effluent (EBCT = 6, 20 min)	0.8	1.2	1.7	0.5	3
Pilot	Influent	0.14	1.02	2.01	0.67	5
(EBCT = 10 min)	Effluent	0.01	0.57	2.08	0.58	13

 Table 4.4: DO for bench- and pilot-scale filters

Temperature measurements for the water influent to the bench and pilot filters during the experimental period are shown in Figure 4.5. Samples for the bench- and pilot-scale were collected within the same time period (December 15, 2016 – May 10, 2016), so temperature is not likely a factor in comparing the removal performance between system scales.

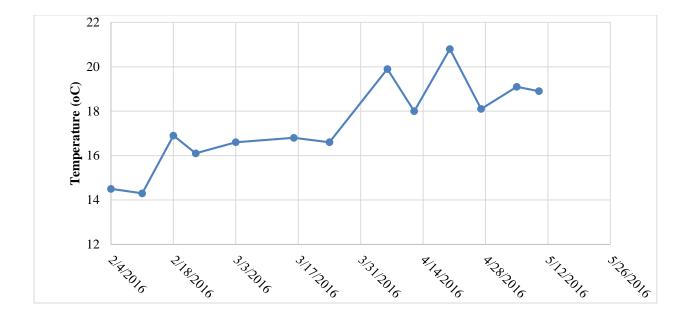


Figure 4.5: Water temperature influent to the bench- and pilot-scale filters

Influent and effluent DOC concentratios are shown in Table 4.6. The removal of DOC was modeled as a pseudo-first order reaction for both the bench- and pilot-scale filters and removal was observed to increase with increasing EBCT. Results are consistent with removal of the biodegradable fraction of the DOC and removal seen in other biofilter studies (Rattier et al. 2014). It is interesting to note that the DOC removal (16% - 22%) in the full-scale tertiary filter may have reduced the available fraction of biodegradable DOC that would otherwise be available as primary substrate for the microbial community in the pilot- and bench-scale filters. It has been shown that the low BDOC levels found in tertiary effluent are insufficient to support some heterotrophic bacteria (Shoji, Ochi, and Ozaki 2008).

Scale	Sample Location	Minimum DOC (mg/L)	Average DOC (mg/L)	Maximum DOC (mg/L)	Standard Deviation	Sample Size
	Influent	5.4	6.2	7.4	0.7	39
	Filter 1 Effluent (EBCT = 2 min)	5.2	5.4	5.5	0.1	5
	Filter 2 Effluent (EBCT = 3 min)	5.1	5.4	5.5	0.2	5
	Filter 3 Effluent (EBCT = 6 min)	5.1	5.3	5.4	0.1	6
Bench	Filter 1 Effluent (EBCT = 5 min)	4.9	5.6	6.2	0.4	8
	Filter 2 Effluent (EBCT = 10 min)	4.7	5.5	6.4	0.6	8
	Filter 3 Effluent (EBCT = 20 min)	5.0	5.6	6.0	0.4	7
	Influent	4.9	5.3	6.2	0.4	
Pilot	Effluent (EBCT = 10 min)	4.0	5.0	5.9	0.4	23

Table 4.5: DOC for bench- and pilot-scale filters

Influent Concentrations of Trace Organic Contaminants

The ambient influent concentrations for the trace organic contaminants over the course of the pilot- and bench-scale studies are presented in Table 4.6. The abbreviations conc., for concentration, Std. Dev., for standard deviation, and Coeff. of Var., for coefficient of variance, are used in Table 4.6.

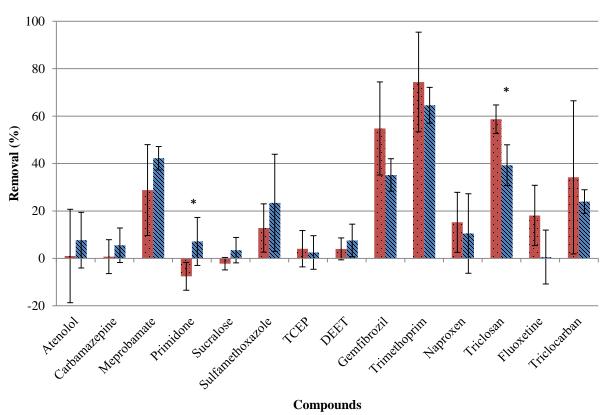
Compound	Minimum Conc. (ng/L)	Average Conc. (ng/L)	Median Conc. (ng/L)	Maximum Conc. (ng/L)	Std. Dev.	Coeff. of Var.	Reporting Limit (ng/L)	Number of Samples Collected	Number of Samples above Detection Limit
Acetaminophen		< 5 (all samp	les below d	letection limit)			5	15	0
Atenolol	< 20	< 26	< 25	36	5	0.17	1	15	11
Caffeine		< 5 (all samp	les below d	letection limit)			5	15	0
Carbamazepine	110	136	130	170	17	0.12	0.5	15	15
DEET	64	127	130	210	40	0.32	1	15	15
Fluoxetine	15	29	29	41	7	0.23	0.5	15	15
Gemfibrozil	1	2	2	9	2	0.90	0.25	15	15
Ibuprofen	< 1.0	< 2.0	< 2.0	2.4	0.5	0.23	1	15	3
Meprobamate	190	225	230	250	17	0.08	0.25	15	15
Naproxen	9	12	11	18	3	0.23	0.5	15	15
Primidone	120	136	130	190	18	0.14	0.5	15	15
Sucralose	35000	43933	42000	53000	5175	0.12	25	15	15
Sulfamethoxazole	810	1093	1100	1400	181	0.17	0.25	15	15
ТСЕР	200	237	230	340	35	0.15	10	15	15
Triclocarban	4	11	12	16	4	0.38	2	15	15
Triclosan	9	22	21	40	9	0.40	1	15	15
Trimethoprim	12	35	33	75	19	0.55	0.25	15	15

Table 4.6: Influent concentrations for experimental compounds during bench- and pilot-scale studies (12/14/15 – 5/10/16)

Acetaminophen and caffeine were below their detection limits for all the samples collected during the study period, so they were not considered for further analysis. The overall variability is relatively low, with an average coefficient of variance of 0.3. Consistency of influent concentration is beneficial for experimental study and data analysis. These experimental concentrations are comparable to two other studies in the United States and one in Greece of trace organic contaminants in wastewater effluent (E. D. Nelson et al. 2011; Batt, Kostich, and Lazorchak 2008; Botitsi, Frosyni, and Tsipi 2007). Consistent influent concentrations were observed, which is preferable for the experimental design. Highly variable influent concentrations could affect filter performance and acclimation to specific trace compounds (Zearley and Summers 2015; Hallé, Huck, and Peldszus 2015).

Bench- and Pilot-Scale Performance

Figure 4.6 shows the average percent removal of 14 measured trace organic contaminants for the pilot- and 10 minute EBCT bench-scale filters. Analysis of the bench-scale removal data was restricted to the filter with an EBCT of 10 minutes to be consistent with the pilot-scale filter. Error bars are one standard deviation above and below the average. Averages are calculated from four data points from the bench- and pilot-scale filters. Data marked with asterisks above indicates a statistically significant difference (p = 0.05) between the removal achieved by the bench- and pilot-scale filters.





Bench n = 4 Pilot Scale n = 4

Figure 4.6: Average removals of experimental trace organic contaminants for bench- and pilot-scale filters

Interestingly, for all but two of the compounds shown in Figure 4.6, there is no significant statistical difference between the average removal achieved at the bench- and pilot-scales (shown in red with dots and blue with stripes, respectively). This indicates very good agreement in terms of removal performance between the bench- and pilot-scale filters. Of the two compounds with significant removal differences, there appears to be some consensus that primidone is very poorly removed with both filters and average removal values are within one standard deviation, although they are statistically significantly different. Primidone is generally poorly removed in sand biofilters (0%), even in cases with much lower experimental HLRs (0.0002 to 0.002 gpm/ft²) (Teerlink et al. 2012). However, there appears to be more separation in average removal values between the bench- (59%) and pilot-scale (39%) for triclosan.

Published results for triclosan removal with biofilters range from levels similar to the pilot-scale (37%, Snyder et al. 2007) to much higher than the bench-scale (90%, Zearley and Summers 2012). With a relatively large log(K_{ow}) (Rosal et al. 2010; Ying, Yu, and Kookana 2007), triclosan tends to partition into soil from the aqueous phase. This would suggest that the high removals are most likely due to adsorption. Up to 70% biodegradation of triclosan has been documented in batch experiments, but utilize initial concontrations (0.5 - 2 mg/L) much larger than in most trace organic contaminant studies (Roh et al. 2009). If the higher removal seen at the bench-scale is due to adsorption, this would contradict the assertion that the anthracite media used in the filters was truly exhausted after 1.5 years of operation on the same source water. Furthermore, the same media was used at both the bench- and pilot-scale, so the media at both scales should have the same level of adsorption exhaustion. Removal disparity would not be due to a difference in adsorption capacity between the two filters at different scales, but the adsorption may be occurring on another surface, such as the biomass and EPS.

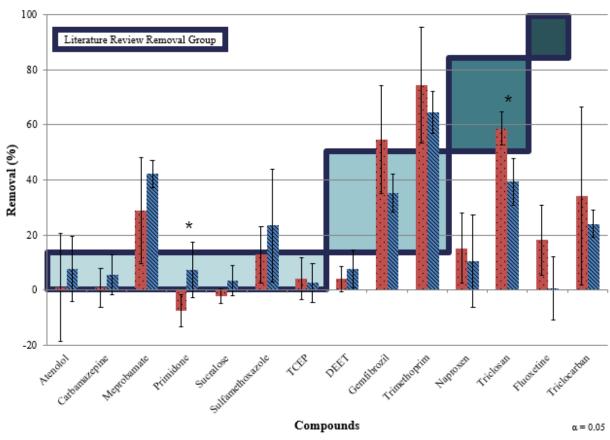
Even with the significant differences between the bench- and pilot-scale for primidone and triclosan, the other 15 compounds included in this experiment showed similar removal. The primidone results overlap by one standard deviation and the triclosan results agree with others found in literature. The experimental results presented here demonstrate that a bench-scale biofilter can produce similar removal results and potentially serve as an alternative to pilot-scale testing.

Removal Groups

The experimental data can be used to test the predicted removal groups as determined in the Results and Discussion section in Chapter 3. Figure 4.7 shows the experimental data from Figure 4.6 with the addition of removal groups based on the literature review in the Results and Discussion section in Chapter 3. The removal groups are represented by shaded blue boxes that outline the upper and lower limit of the removal group. Triclocarban was not discovered in the literature review, so there is no

48

predicted removal group shown on Figure 4.7. Inclusion of these removal groups allows for analysis of literature results and a broader comparison of experimental removal performance to literature results.



Error Bars = ± 1 Standard Deviation Bench n = 4
Pilot Scale n = 4

Figure 4.7: Comparison of predicted removal with inert media based on literature review and experimental removal of trace organic compounds

Based on the literature review, half of the experimental compounds measured in this study fell into the 0% to 15% removal group. Based on the experimental results, most of these compounds were indeed removed in the 0% to 15% range. Low removal of atenolol, carbamazepine, primidone, sulfamethoxazole, and TCEP in bench- and pilot-scale biofilters or soil is well-documented (Rattier et al. 2014; Teerlink et al. 2012; Snyder et al. 2007; Zearley and Summers 2012). Sucralose is not only recalcitrant to biological treatment, but also several chemical oxidation processes such that it has been considered as an indicator of wastewater contaminantion of surface waters (McKie, Andrews, and Andrews 2016; Oppenheimer et al. 2011; Lee, Howe, and Thomson 2012). Meprobamate was removed to a higher degree at both the bench- and pilot-scale than suggested by the literature review removal group. A similar pilot-scale study conducted with anthracite media filtering drinking water with spiked contaminants at Southern Nevada Water Authority (SNWA) resulted in much lower meprobamate removal (Snyder et al. 2007). This study had much lower influent DOC than the pilot-scale filter described here (2.52 versus 5.96 mg/L), although this does not indicate the biodegradable fraction of the DOC which contributes to biomass growth and maintenance.

DEET, Gemfibrozil, and Trimethoprim fell into the 15% to 50% removal category. Gemfibrozil was the only compound in this category to fall within this range. Gemfibrozil has been shown to be removed within the 15% to 50% range (Rattier et al. 2014), as well as achieving both lower (Dowdell 2012; Snyder et al. 2007) and higher (McKie, Andrews, and Andrews 2016; Zearley and Summers 2012) removal levels. Gemfibrozil likely fell into this removal category due to this wide range of reported removals. DEET removal was very low in this experiment, well below the removal range of 15% to 50%. Similar levels of removal have been documented (8%, Snyder et al. 2007), but higher removal levels (85% to 100%) are more commonly reported (Hallé, Huck, and Peldszus 2015; Rattier et al. 2014). Experimental trimethoprim removals for this study were all above 50% with the exception of one sample, matching the high removal results seen by Zearley and Summers 2012, although many other studies place trimethoprim removal between 15% to 40% (Dowdell 2012; Reungoat et al. 2011).

Experimental removal for naproxen and fluoxetine during this study was much less than results found during the literature review. Naproxen is generally reported to be well-removed (60% to 99%) in published literature (Hallé, Huck, and Peldszus 2015; Zearley and Summers 2012; Matamoros et al. 2007; Rattier et al. 2014), so it fell under the 50% to 85% removal group. However, low naproxen removal levels consistent with this study (3% to 29%) have also been shown (McKie, Andrews, and Andrews 2016; Dowdell 2012; Snyder et al. 2007). Fluoxetine was placed in the highest removal category based on

one data point (97%, Snyder et al. 2007), but other studies have found lower removal levels (30%, Vasskog et al. 2006) more similar to the experimental results presented here.

Most of the compound removals measured in this study fell into the removal groups created from the literature review. Many compounds that are commonly not removed in biofiltration literature were similarly not removed in this study (atenolol, carbamazepine, primidone, sucralose, sufamethoxazole, TCEP). Moderate removal of gemfibrozil was achieved, falling into the 15% to 50% removal category as predicted in the literature review. Meprobamate and trimethoprim were more highly removed than expected, while DEET, naproxen, and fluoxetine were not as highly removed as their literature review removal category suggested. Although many of the compounds fell within their expected removal groups, for those that did not, removal groups may be adjusted to better reflect the experimental results of this study. Changing the removal group boundaries to 25 - 50% and 0 - 25% was explored, matching those established by Rattier et al., 2014 rather than Zearley and Summers, 2012. This did not noticeably change the fit of the experimental data shown in Figure 4.7 to the revised removal groups.

Figure 4.8 and Figure 4.9 show how removal changes with EBCT for trimethoprim and meprobamate, respectively. For both compounds, removal generally increases with EBCT (Zearley and Summers 2012). Consistent removals were observed at EBCT > 10 minutes.

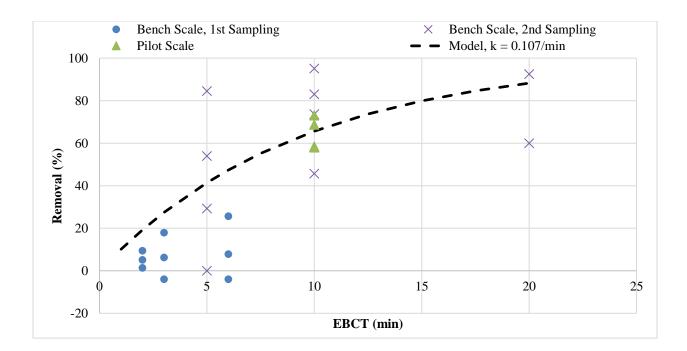
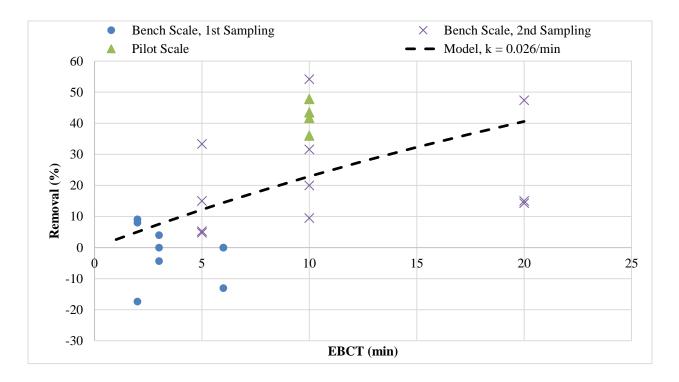
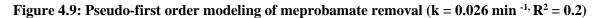


Figure 4.8: Pseudo-first order modeling of trimethoprim removal ($k = 0.107 \text{ min}^{-1}$, $R^2 = 0.4$)





These results were modeled as described in Chapter 3 using the pseudo-first order equation resulting in rate constants of 0.107/min for trimethoprim and 0.026/min for meprobamate. Quality of trend line fit was measured using R^2 , resulting in 0.4 for trimethoprim and 0.2 for meprobamate. These low R^2 values are due to high scatter in the data. Trend lines for all other contaminants had R^2 values that were less than .0.2, so only trimethoprim and meprobamate are shown. Modeling contaminant removal allows for the possibility of removal prediction based on EBCT and comparison of rate constants to other published literature. Zearley and Summers, 2012 reported a rate constant of 0.25/min for trimethoprim.

CONCLUSIONS

This study experimentally assessed the removal of trace organic contaminants in tertiary-filtered wastewater effluent at bench- and pilot-scales. Influent water quality was relatively consistent, which facilitates removal comparisons where the effluent concentrations can be normalized by a consistent influent value throughout the study. Water quality parameters provide evidence of biological activity in the filters. DO levels were low overall, but decreased through each filter. DOC was also removed by an average of 10% through the columns, indicating microbial activity. There was no significant difference between trace organic compound removal at the bench- and pilot-scale for all compounds except primidone and triclosan (Figure 4.6). Primidone is generally poorly removed and experimental removals overlapped within one standard deviation. Literature review on triclosan reveals removals that range from 37% to 90%, encompassing the removal achieved in this study. Most experimental results agreed with other published studies, especially the poorly removed compounds atenolol, carbamazepine, primidone, sucralose, sulfamethoxazole, and TCEP (Figure 4.7). Based on comparisons to literature, meprobamate and trimethoprim had higher removals than expected, while DEET, naproxen, and fluoxetine had lower removal than expected. These differences suggest site-specific conditions that contribute to the ability of a biofilter to remove a specific compound. Removal of some compounds showed a dependency on EBCT, especially trimethoprim and meprobamate (Figure 4.8, Figure 4.9).

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These results imply that a bench-scale filter can be a good supplement to literature review results to estimate pilot-scale removal performance. The pilot- and bench-scale filters used the same media and were fed the same tertiary treated wastewater during the same experimental period, while the literature review groups were created from large amounts of data representing a wide range of conditions. With these limitations of the literature review and predicted categories in mind, the bench-scale filter should be a more precise indicator of pilot-scale removal. These positive results support the idea of scaleability between biofilters. Similar experiments with different water qualities at other sites could reinforce the relationship between the bench- and pilot-scale biofilters.

CHAPTER 5 CONCLUSIONS AND OPPORTUNITIES FOR FUTURE WORK

From a large data library of 1,400 data points, 200 compounds, 100 sources, refinements by media type (GAC, sand, anthracite) and EBCT (> 2 minutes and < 30 minutes) narrowed down the database to 850 data points, 150 compounds, and 55 sources for quantitative analysis. MIB and geosmin were the most well-studied, so these compounds were used for analysis. Analysis of the data reveals that inert media showed a trend of increasing removal with EBCT while GAC media did not show significant differences in removal with increasing EBCT (Figure 3.1, Figure 3.2). While EBCTs above 10 minutes are recommended for inert media to ensure complete removal, the range of EBCTs between 10 and 20 minutes could be explored during bench- or pilot-scale testing to further narrow down the ideal operational EBCT for each site. The consistently high removals achieved with GAC media implied another mechanism contributing to removal, likely long term adsorption. An analysis by media type (Figure 3.2) type showed that GAC media achieved significantly higher removal than the inert media for EBCTs less than 10 minutes. Pseudo-first order analysis was applied to the data for MIB and geosmin resulting in rate constants of 0.071/min for geosmin and 0.028/min for MIB with R² values of 0.9 for geosmin and 0.7 for MIB. Based on the literature review data, contaminants were also grouped into four groups (0 - 15%) > 15 - 50%, > 50 - 85%, and > 85%) according to median removal. This literature review analysis revealed removal trends associated with media type and EBCT that informed the experimental portion of this work.

Consistent influent water quality and concentrations of trace organic compounds led to robust experimental results. Comparing removal data for 14 compounds from three bench-scale filters and one pilot-scale filters, only two compounds (primidone, triclosan) had significantly different levels of removal. This indicates that the bench-scale filter is a cost effective and easy to manage indicator of pilotscale removal performance. Given the similar performance by the bench- and pilot-scale filters, data from both sources was combined for pseudo-first order modeling, which resulted in low R² values as measures of model fit (Figure 4.8, Figure 4.9). The experimental results were also compared to the removal groups created from literature review data in Chapter 3. Experimental removal for most compounds fit the literature review groups, especially the poorly removed compounds (atenolol, carmabazepine, primidone, sucralose, sulfamethoxazole, TCEP). However, some experimental removals were higher than expected (meprobamate, trimethoprim) and some were lower than expected (DEET, naproxen, fluoxetine), indicating a need for further site-specific studies at other locations.

The boundaries of the removal groups may be explored further in order to better predict compound removals. Future work toward adjustment of the predicted removal groups may include refining the process of creating the predicted indicator groups, narrowing the scope of the data included for higher specificity, creating more flexible boundary cutoffs, and reducing the variability of the removal data. In addition, attempts to correlate chemical structure with microbial communities and removal capability could lead to more specific categories to characterize trace organic contaminants. The results presented in this study mostly point toward verification of the results of the literature review analysis and the reasonable consideration of the bench batch recirculation as a replication of pilot-scale removal performance.

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Contoninent	Media	F	Removal (%	(0)	1	EBCT (min	ı)	Ten	nperature	(°C)	I	Bed Volum	es		Ref.
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Kei.
1,2-dichlorobenzene	Inert	72	63	83	4	4	4							6	[1]
1,4-dichlorobenzene	Inert	71	61	79	4	4	4							6	[1]
1,7-Dimethylxanthine	Inert	0	0	0	20	20	20		12	22				1	[2]
	GAC	94	45	99	21	20	30				12653	106	25200	2	[3]
17β-Estradiol	Inert	5	5	5	11	11	11							1	[3]
2,3,4-Trichlorophenol	Inert	1	1	1	4	4	4							3	[1]
2,4,6-Trichlorophenol	Inert	1	1	1	4	4	4							3	[1]
2,4-Dichlorophenol	Inert	28	23	30	4	4	4							3	[1]
2,4-Dichlorophenoxyacetic	GAC	70	70	70	18	18	18				7305	7305	7305	1	[4]
Acid	Inert	73	68	77	12	8	16	20	20	20				2	[5]
2,6-Dichlorophenol	Inert	24	21	28	4	4	4							3	[1]
4-Nonylphenol	Inert	0	0	0	20	20	20		12	22				1	[2]
4-tert-Octylphenol	Inert	0	0	0	20	20	20		12	22				1	[2]
	GAC	89	82	95	10	2	18				7305	7305	7305	2	[4], [6]
Acetaminophen	Inert	59	0	80	8	2	20	20	20	23				5	[2], [5]– [7]
Acetochlor	Inert	13	8	17	11	8	16	20	20	20				2	[5]
Albuterol	Inert	0	0	0	20	20	20		12	22				1	[2]
Aldicarb	Inert	61	49	72	12	8	15	20	20	20				2	[5]
Amoxicillin	Inert	0	0	0	20	20	20		12	22				1	[2]
	GAC	97	97	97	2	2	2							1	[8]
Androstenedione	Inert	41	41	41	2	2	2							1	[8]
	GAC	98	75	98	18	9	30		23	29	35064	7305	472390	3	[4], [9]
Atenolol	Inert	0	0	44.5	8	7	20	23	23	23				3	[2], [7], [10]
Atorvastatin	GAC	100	100	100	30	30	30				35064	35064	35064	1	[9]

APPENDIX A: Literature Review Table

	Media	F	Removal (%	(o)	I	EBCT (min	l)	Ten	nperature	(°C)	I	Bed Volume	s		D.f
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
	GAC	48	-20	83	8	2	30	26	26	26	33205	1527	143234	6	[8], [9], [11], [12]
Atrazine	Inert	0	0	15	15	2	30	20	20	23				9	[2], [5]– [7], [10], [13]
Atrazine-Desethyl	Inert	8	8	8	7	7	7		10.3	22				1	[10]
Atrazine-Hydroxy	Inert	15	15	15	7	7	7		10.3	22				1	[10]
Dango[a]nymana	GAC	89	89	89	2	2	2							1	[6]
Benzo[a]pyrene	Inert	89	89	89	2	2	2							1	[6]
Benzophenone	GAC	51	51	51	30	30	30				35064	35064	35064	1	[9]
Benzotriazole	Inert	19	19	19	7	7	7		10.3	22				1	[10]
Bezafibrate	Inert	40	40	40	7	7	7		10.3	22				1	[10]
BHA	GAC	99	99	99	30	30	30				35064	35064	35064	1	[9]
Disphanal A	GAC	7	7	7	30	30	30				35064	35064	35064	1	[9]
Bisphenol A	Inert	64	64	64	8	8	8	20	20	20				1	[5]
Bromacil	Inert	0	0	0	20	20	20		12	22				1	[2]
Bromochloroacetic Acid	GAC	0	0	0	18	18	18				85225	85225	85225	1	[14]
Bromodichloromethane	GAC	46	0	75	2	2	18				57600	28800	85225	3	[14], [15]
Bromophenol	Inert	0	0	0	15	15	15	14	11	18				2	[16]
Bupropion	Inert	-5	-5	-5	6	6	6							1	[17]
Butalbital	Inert	0	0	0	20	20	20		12	22				1	[2]
Coffeine	GAC	84	38	189	14	2	30	26	23	29	7305	106	472390	6	[3], [4], [6], [9], [12]
Caffeine	Inert	40	0	80	8	2	20	20	20	23				7	[2], [3], [5]–[7], [17]
Carbadox	Inert	0	0	0	20	20	20		12	22				1	[2]
Carbamazepine	GAC	90	40	100	7	2	30	26	26	26	18296	1527	35064	3	[6], [9], [12]

Contraction of	Media	R	emoval (%	()	I	EBCT (min	l)	Ten	nperature	(°C)	F	Bed Volume	es		Def
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
Carbamazepine	Inert	0	0	20	8	2	20	12	20	23				10	[2], [5]– [7], [17], [18]
Carbaryl	Inert	10	3	17	12	8	16	20	20	20				2	[5]
Chlorobenzene	Inert	75	51	77	4	4	4							6	[1]
Chlorpyrifos	Inert	73	63	83	12	8	16	20	20	20				2	[5]
Cimetidine	Inert	0	0	0	20	20	20		12	22				1	[2]
Citalanana	GAC	91	85	97	14	9	18		23	29	239848	7305	472390	2	[4]
Citalopram	Inert	4	0	9	7	6	8	23	23	23				2	[7], [17]
Clarithromycin	Inert	50	50	50	7	7	7		10	22				1	[10]
Clofibric Acid	Inert	52	35	66	8	7	16	20	20	20				3	[5], [10]
Cotinine	Inert	23	0	39	16	8	20	20	20	20				3	[2], [5]
DACT	Inert	0	0	0	20	20	20		12	22				1	[2]
DDT	GAC	85	85	85	2	2	2							1	[6]
DDT	Inert	94	94	94	2	2	2							1	[6]
	GAC	87	80	93	16	2	30				35064	35064	35064	2	[6], [9]
DEET	Inert	45	0	100	5	2	20	13	1	23				11	[2], [6], [7], [17], [19]
Deethylatrazine	GAC	0	-4	3	8	7	9	26	26	26	28259	23314	33205	2	[12]
Dehydronifedipine	Inert	0	0	0	20	20	20		12	22				1	[2]
Deisopropylatrazine	GAC	4	0	8	8	7	9	26	26	26	28259	23314	33205	2	[12]
Diatrizoate	Inert	13	13	13	7	7	7		10	22				1	[10]
D:	GAC	90	84	96	16	2	30				35064	35064	35064	2	[6], [9]
Diazepam	Inert	15	15	15	2	2	2							1	[6]
	GAC	90	90	90	18	18	18				7305	7305	7305	1	[4]
Diazinon	Inert	26	4	80	8	7	16	20	20	23				4	[5], [7], [10]
Dibromochloromethane	GAC	0	0	0	18	18	18				85225	85225	85225	1	[14]

a	Media	F	Removal (%	6)]	EBCT (mir	ı)	Ter	nperature	(°C)	I	Bed Volum	25		D
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
Dichloroacetic Acid	GAC	63	0	98	8	5	20	4	4	30	196584	65544	262176	8	[14], [20]
5110	GAC	87	75	100	16	2	30				35064	35064	35064	2	[6], [9]
Diclofenac	Inert	17	0	28	8	2	16	20	20	23				4	[5]–[7]
Dimethoate	Inert	78	75	81	12	8	16	20	20	20				2	[5]
	GAC	66	32	99	14	9	18		23	29	239848	7305	472390	2	[4]
Diuron	Inert	0.2	0	8	12	8	20	20	20	23				4	[2], [5], [7]
	GAC	90	80	97	18	9	18		23	29	85225	7305	472390	3	[4], [14]
Doxylamine	Inert	0	0	0	8	8	8	23	23	23				1	[7]
	GAC	67	55	78	10	2	18				7305	7305	7305	2	[4], [6]
Erythromycin	Inert	25	0	31	8	2	20	20	12	23				5	[2], [5]– [7]
Erythromycin z.T. mit Metabolit	Inert	74	74	74	7	7	7		10	22				1	[10]
	GAC	70	45	94	16	2	30				35064	35064	35064	2	[6], [9]
Estradiol	Inert	1	1	1	2	2	2							1	[6]
Estradiol Equivalent	GAC	98	98	98	30	30	30				35064	35064	35064	1	[9]
E-tri-1	GAC	92	92	92	2	2	2							1	[6]
Estriol	Inert	0.5	0.5	0.5	2	2	2							1	[6]
Estrone	GAC	90	84	95	16	2	30				35064	35064	35064	2	[6], [9]
Estione	Inert	0.6	0	96	15	2	15							3	[6], [13]
	GAC	91	91	91	2	2	2							1	[6]
Ethinyl Estradiol	Inert	17	1	41	12	2	16	20	22	25				4	[5], [6], [13]
	GAC	98	98	98	2	2	2							1	[6]
Fluorene	Inert	28	28	28	2	2	2							1	[6]
	GAC	99	99	100	16	2	30				35064	35064	35064	2	[6], [9]
Fluoxetine	Inert	97	97	97	2	2	2							1	[6]
Formaldahyda	GAC	84	68	92	10	5	20				576	288	1152	3	[21]
Formaldehyde	Inert	70	66	74	10	5	20							3	[21]
Furosemide	GAC	10	10	10	18	18	18				7305	7305	7305	1	[4]

	Media	F	Removal (%	6)	J	EBCT (min	ı)	Ter	nperature	(°C)	I	Bed Volum	es		Df
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
Furosemide	Inert	13	0	25	14	8	20	23	23	23				2	[2], [7]
Galaxolide	GAC	74	74	74	2	2	2							1	[6]
Galaxonde	Inert	12	4.21	19	4	2	6							2	[6], [17]
	GAC	95	74	100	9	2	30		23	29	253727	35064	472390	3	[4], [6], [9]
Gemfibrozil	Inert	42	0	94	8	2	20	20	20	23				5	[2], [6], [7], [22]
	GAC	92	16	100	5	4	30	15	8	26	87660	3600	324782	23	[12], [23]– [26]
Geosmin	Inert	38	0	100	13	3	17	20	6	22				53	[17], [25], [27]– [35]
<i>c</i> 1 1	GAC	78	58	93	10	5	20				576	288	1152	3	[21]
Glyoxal	Inert	65	45	74	10	5	20							3	[21]
	GAC	82	65	99	14	9	18		23	29	239848	7305	472390	2	[4]
Hydrochlorothiazide	Inert	0	0	0	8	8	8	23	23	23				1	[7]
The due of dome	GAC	92	92	92	2	2	2							1	[6]
Hydrocodone	Inert	14	14	14	2	2	2							1	[6]
Hydroxyatrazine	GAC	31	19	43	8	7	9	26	26	26	28259	23314	33205	2	[12]
	GAC	70	58	83	16	2	30				35064	35064	35064	2	[6], [9]
Ibuprofen	Inert	95	30	100	5	2	16	17	1	23				11	[5]–[7], [19]
Indomethacin	Inert	25	25	25	8	8	8	23	23	23				1	[7]
Iohexol	Inert	12	0	24	13	7	20		10	22				2	[2], [10]
Iomeprol	Inert	15	15	15	7	7	7		10	22				1	[10]
Iopamidol	Inert	7	7	7	7	7	7		10	22				1	[10]
	GAC	42	42	42	2	2	2							1	[6]
Iopromide	Inert	7	0	13	8	2	20	20	20	23				6	[2], [5]– [7], [10]
Ioxitalamic acid	Inert	34	34	34	7	7	7		10	22				1	[10]
Ketoprofen	Inert	25	0	50	14	8	20	23	23	23				2	[2], [7]
Ketorolac	Inert	0	0	0	20	20	20		12	22				1	[2]

Contract of	Media	R	Removal (%	6)	J	EBCT (min	ı)	Ter	nperature	(°C)	E	Bed Volume	es		Def
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
Lidocaine	Inert	0	0	0	20	20	20		12	22				1	[2]
Lincomycin	Inert	0	0	0	8	8	8	23	23	23				1	[7]
Lindane (y-BHC)	GAC	91	91	91	2	2	2							1	[6]
Lindane (γ -BHC)	Inert	7	7	7	2	2	2							1	[6]
Linuron	Inert	0	0	0	20	20	20		12	22				1	[2]
Malaoxon	Inert	33	16	49	12	8	16	20	20	20				2	[5]
Meclofenamic Acid	Inert	0	0	0	20	20	20		12	22				1	[2]
Mecoprop	Inert	31	15	46	7	7	8		10	22				2	[10], [36]
Meprobamate	GAC	20	11	81	7	2	30	26	26	26	28259	1527	35064	5	[6], [9], [12]
Weprobalilate	Inert	2	0	4	11	2	20		12	22				2	[2], [6]
Methomyl	Inert	9	5	12	12	8	16	20	20	20				2	[5]
	GAC	84	75	95	10	5	20				576	288	1152	3	[21]
Methyl glyoxal	Inert	84	70	89	10	5	20							3	[21]
	GAC	0	0	79	7	2	9	26	26	26	28259	23314	33205	3	[6], [12]
Metolachlor	Inert	4	-8	9	8	2	16	20	20	23				5	[5]–[7], [17]
	GAC	82	65	99	14	9	18		23	29	239848	7305	472390	2	[4]
Metoprolol	Inert	0	0	27	27	7	20		10	23				3	[2], [7], [10]
	GAC	70	14	100	5	2	30	20	8	30	64956	273	358609	41	[12], [23]– [26], [35], [37], [38]
MIB	Inert	25	0	100	7	2	17	21	6	25				65	[5], [17], [25], [27], [28], [30], [32]- [35], [38], [39]

	Media	F	Removal (%	6)	1	EBCT (mir	ı)	Ter	nperature	(°C)	I	Bed Volume	es		D 4
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
	GAC	70	50	100	15	15	15	25	25	25	3648	2976	20256	5	[40]
Microcystin-LA	Inert	50	0	100	15	15	15	25	25	25				2	[40]
Misse section LD	GAC	91	82	100	15	15	15	25	25	25	3648	2976	19968	5	[40]
Microcystin-LR	Inert	54	8	100	15	15	15	25	25	25				2	[40]
Molinate	Inert	91	85	97	12	8	16	20	20	20				2	[5]
Monochloroacetic Acid	GAC	84	39	100	5	5	20	4	4	30	262080	65544	262176	7	[20]
Musk Ketone	GAC	55	27	83	16	2	30				35064	35064	35064	2	[6], [9]
WIUSK Ketone	Inert	10	10	10	2	2	2							1	[6]
	GAC	91	82	100	16	2	30				35064	35064	35064	2	[6], [9]
Naproxen	Inert	81	0	100	5	2	20	17	1	23				12	[2], [5]– [7], [19]
N-Nitrosodiethylamine	Inert	33	33	33	7	7	7		10	22				1	[10]
N-Nitrosodimethylamine	Inert	7	3	52	15	7	15		10	25				3	[10], [13]
N-Nitrosodi-n-butylamine	Inert	14	14	14	7	7	7		10	22				1	[10]
N-Nitrosomorpholine	Inert	28	28	28	7	7	7		10	22				1	[10]
N-Nitrosopiperidine	Inert	20	20	20	7	7	7		10	22				1	[10]
o-chlorophenol	Inert	82	69	85	4	4	4							3	[1]
Octylphenol	GAC	25	25	25	30	30	30				35064	35064	35064	1	[9]
Oxolinic Acid	Inert	0	0	0	20	20	20		12	22				1	[2]
Oxybenzone	GAC	98	98	98	2	2	2							1	[6]
Oxybenzone	Inert	14	14	14	2	2	2							1	[6]
Dontovifulling	GAC	90	90	90	2	2	2							1	[6]
Pentoxifylline	Inert	13	13	13	2	2	2							1	[6]
Perindopril	GAC	11	0	22	14	9	18		23	29	239848	7305	472390	2	[4]
remdopin	Inert	0	0	0	8	8	8	23	23	23				1	[7]
Phenol	Inert	84	10	99	4	4	15	18	11	18				13	[1], [16]
Phonytoin	GAC	90	80	95	18	2	30				21185	7305	35064	3	[4], [6], [9]
Phenytoin	Inert	0	0	19	8	2	20	23	23	23				3	[2], [6], [7]

	Media	R	Removal (%	6)	I	EBCT (min	l)	Ter	nperature	(°C)	I	Bed Volume	es		Df
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
D: 11	GAC	92	92	92	30	30	30				35064	35064	35064	1	[9]
Primidone	Inert	11	0	22	13	7	20		10	22				2	[2], [10]
D (GAC	99	99	99	2	2	2							1	[6]
Progesterone	Inert	52	52	52	2	2	2							1	[6]
Prometon	Inert	1	0	3	12	8	16	20	20	20				2	[5]
Propranolol	Inert	0	0	0	8	8	8	23	23	23				1	[7]
p-Toluenesulfonic Acid	Inert	87	30	99	12	3	30							18	[41]
Dereither marin	GAC	8	0	15	14	9	18		23	29	278808	85225	472390	2	[4], [14]
Roxithromycin	Inert	25	25	25	8	8	8	23	23	23				1	[7]
C-1:1:- A-: 4	GAC	7	7	7	22	22	22				106	106	106	1	[3]
Salicylic Acid	Inert	25	25	25	11	11	11							1	[3]
Saxitoxin C1	Inert	48	0	95	15	15	15							2	[42]
Saxitoxin C2	Inert	95	95	95	15	15	15							1	[42]
Saxitoxin GTX2	Inert	-360	-360	-360	15	15	15							1	[42]
Saxitoxin GTX3	Inert	-230	-360	-100	15	15	15							2	[42]
Sertraline	GAC	89	88	90	14	9	18		0	0	239848	7305	472390	2	[4]
Cimerine	GAC	58	29	88	8	7	9	26	26	26	28259	23314	33205	2	[12]
Simazine	Inert	8	7	8	12	8	16	20	20	20				2	[5]
Sucralose	Inert	0	0	0	20	20	20		12	22				1	[2]
Sulfadiazine	Inert	0	0	0	14	8	20	23	23	23				2	[2], [7]
Sulfamethazine	Inert	0	0	0	20	20	20		12	22				1	[2]
	GAC	63	50	98	18	2	30				21185	7305	35064	3	[4], [6], [9]
Sulfamethoxazole	Inert	1	-42	5	8	2	20	10	23	23				7	[2], [5]– [7], [10], [17]
	GAC	45	10	80	16	2	30				35064	35064	35064	2	[6], [9]
TCEP	Inert	5	0	10	11	2	20		12	22				2	[2], [6]
TCPP	GAC	20	20	20	30	30	30				35064	35064	35064	1	[9]

	Media	R	emoval (%	(0)	I	EBCT (min	ı)	Ter	nperature	(°C)	E	Bed Volume	es		Df
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	n	Ref.
Terbutylazine	Inert	13	13	13	7	7	7		10	22				1	[10]
Tractoritorio	GAC	96	96	96	2	2	2							1	[6]
Testosterone	Inert	35	35	35	2	2	2							1	[6]
Tetrachloroethylene	Inert	9	9	9	6	6	6							1	[17]
Theobromine	Inert	0	0	0	20	20	20		12	22				1	[2]
Theophylline	Inert	0	0	0	20	20	20		12	22				1	[2]
Tramadol	GAC	99	90	99	18	9	18		0	0	85225	7305	472390	3	[4], [14]
Trainador	Inert	0	0	0	8	8	8	23	23	23				1	[7]
Tris(2-chloroethyl) phosphate	Inert	19	19	19	6	6	6							1	[17]
Tris(dichloroisopropyl) phosphate	Inert	-11	-11	-11	6	6	6							1	[17]
Tributyl Phosphate	Inert	16	10	24	8	6	16	20	20	20				3	[5], [17]
Trichloroacetic Acid	GAC	82	7	99	15	5	20	15	4	30	131040	65520	262176	18	[14], [20], [43], [44]
Trichloromethane	GAC	5	1	40	2	2	18				28800	11520	85225	5	[14], [15]
memoromethane	Inert	14	5	21	8	4	8							8	[15], [45]
Triclopyr	GAC	22	9	35	14	9	18		23	29	239848	7305	472390	2	[4]
	GAC	98	97	99	16	2	30				35064			2	[6], [9]
Triclosan	Inert	64	0	90	12	2	20	20	20	20				4	[2], [5], [6]
	GAC	97	94	100	16	2	30				35064			2	[6], [9]
Trimethoprim	Inert	25	0	92	8	2	20	20	20	23				5	[2], [5]– [7]
	GAC	79	79	79	22	22	22				106	106	106	1	[3]
Trovafloxacin Mesylate	Inert	15	15	15	11	11	11							1	[3]
Valsartan	Inert	25	25	25	8	8	8	23	23	23				1	[7]
	GAC	98	75	99	18	9	18		23	29	85225	7305	472390	3	[4], [14]
Venlafaxine	Inert	4.2	0	12	6	6	8	23	23	23				3	[7], [17]
Warfarin	Inert	39	0	68	16	8	20	20	20	20				3	[2], [5]

Contominant	Media	R	emoval (%	b)	1	EBCT (min	l)	Ten	operature	(°C)	В	ed Volume	es		Ref.
Contaminant	Туре	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	п	Kei.
β-cyclocitral	Inert	45	30	55	3	3	3	18	18	20				4	[35]

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Scale/Mode			Full-Scale, EB	C T = 7 - 10 min
Date Collected	Units	Reporting Limit	2/23/	2016
Location			Influent	Effluent
Acetaminophen	ng/L	5	< 100	< 5.0
Atenolol	ng/L	1	96	< 20
Caffeine	ng/L	5	< 100	< 100
Carbamazepine	ng/L	0.5	130	120
DEET	ng/L	1	210	120
Fluoxetine	ng/L	0.5	33	24
Gemfibrozil	ng/L	0.25	9.2	2.9
Ibuprofen	ng/L	1	4.0	< 20
Meprobamate	ng/L	0.25	470	210
Naproxen	ng/L	0.5	9.6	14
Primidone	ng/L	0.5	170	130
Sucralose	ng/L	25	47000	46000
Sulfamethoxazole	ng/L	0.25	1400	1200
ТСЕР	ng/L	10	210	200
Triclocarban	ng/L	2	13	7.6
Triclosan	ng/L	1	41	16
Trimethoprim	ng/L	0.25	210	29

APPENDIX B: Experimental Measurements of Trace Organic Compounds

Scale/Mode		D (:			Pilo	ot-Scale, E	BCT = 10	min		
Date Collected	Units	Reporting Limit	2/10/	2016	3/14/	2016	4/12/	2016	5/10/	2016
Location		Linnt	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Acetaminophen	ng/L	5	< 100	< 100	< 100	< 5.0	< 5.0	< 5.0	< 5	< 5
Atenolol	ng/L	1	26	28	21	< 20	36	30	24	20
Caffeine	ng/L	5	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Carbamazepine	ng/L	0.5	150	140	120	120	140	140	130	110
DEET	ng/L	1	150	150	130	120	120	100	170	160
Fluoxetine	ng/L	0.5	41	39	34	39	34	34	33	29
Gemfibrozil	ng/L	0.25	2.2	1.6	0.8	0.45	2.1	1.4	1.1	0.7
Ibuprofen	ng/L	1	< 1.0	< 1.0	< 1.0	< 1.0	20	< 20	< 1	< 1
Meprobamate	ng/L	0.25	250	160	230	130	240	140	230	120
Naproxen	ng/L	0.5	15	16	9.9	< 10	12	8.8	8.7	6.7
Primidone	ng/L	0.5	160	160	130	130	140	110	140	130
Sucralose	ng/L	25	53000	47000	40000	39000	43000	43000	42000	42000
Sulfamethoxazole	ng/L	0.25	1400	1400	950	830	1100	670	880	510
ТСЕР	ng/L	10	220	210	260	280	220	210	230	210
Triclocarban	ng/L	2	14	10	11	9.0	14	11	13	9.4
Triclosan	ng/L	1	25	17	40	26	31	19	33	16
Trimethoprim	ng/L	0.25	48	15	13	3.5	19	7.9	12	< 5

Scale/Mode				Small Pilot: Ba	tch Mode (High I	Flow)		
Date Collected	Units	Reporting Limit	12/14/2015					
Location	Cints	Influent		Effluent EBCT = 2 min	Effluent EBCT = 3 min	Effluent EBCT = 6 min		
Acetaminophen	ng/L	5	< 5.0	< 5.0	< 5.0	< 5.0		
Atenolol	ng/L	1	28	23	< 20	< 20		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	130	140	130	130		
DEET	ng/L	1	64	61	56	55		
Fluoxetine	ng/L	0.5	25	19	23	22		
Gemfibrozil	ng/L	0.25	2.0	1.5	0.56	0.51		
Ibuprofen	ng/L	1	1.5	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	220	200	220	220		
Naproxen	ng/L	0.5	13	7.8	5.6	7.5		
Primidone	ng/L	0.5	120	130	130	130		
Sucralose	ng/L	25	40000	41000	40000	44000		
Sulfamethoxazole	ng/L	0.25	940	1000	1000	1000		
ТСЕР	ng/L	10	240 230		220	230		
Triclocarban	ng/L	2	12 4		3.8	2.8		
Triclosan	ng/L	1	18 9.1		10	9.8		
Trimethoprim	ng/L	0.25	39	37	32	29		

Scale/Mode				Small Pilot: Ba	tch Mode (High I	Flow)		
Date Collected	Units	Reporting Limit	12/21/2015					
Location	Omts	Influent		Effluent EBCT = 2 min	Effluent EBCT = 3 min	Effluent EBCT = 6 min		
Acetaminophen	ng/L	5	< 5.0	< 5.0	< 5.0	< 5.0		
Atenolol	ng/L	1	24	20	23	< 20		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	120	120	120	120		
DEET	ng/L	1	89	89	93	94		
Fluoxetine	ng/L	0.5	30	25	27	29		
Gemfibrozil	ng/L	0.25	5.8	5.2	4.3	3.1		
Ibuprofen	ng/L	1	2.0	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	230	270	240	260		
Naproxen	ng/L	0.5	9.1	10	11	11		
Primidone	ng/L	0.5	120	120	110	140		
Sucralose	ng/L	25	40000	42000	39000	44000		
Sulfamethoxazole	ng/L	0.25	1200	1200	1100	1200		
ТСЕР	ng/L	10	230 230		230	220		
Triclocarban	ng/L	2	16 5.3		3.7	4.2		
Triclosan	ng/L	1	24 13		13	12		
Trimethoprim	ng/L	0.25	64	58	60	59		

Scale/Mode				Small Pilot: Ba	tch Mode (High l	Flow)		
Date Collected	Units	Reporting Limit	12/28/2015					
Location	Cints	Keporting Limit	Influent	Effluent EBCT = 2 min	Effluent EBCT = 3 min	Effluent EBCT = 6 min		
Acetaminophen	ng/L	5	< 5.0	< 5.0	< 5.0	< 5.0		
Atenolol	ng/L	1	26	24	30	24		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	130	130	130	130		
DEET	ng/L	1	76	78	77	77		
Fluoxetine	ng/L	0.5	33	30	26	28		
Gemfibrozil	ng/L	0.25	9.2	8.0	7.3	6.1		
Ibuprofen	ng/L	1	2.4	1.3	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	250	230	240	250		
Naproxen	ng/L	0.5	18	19	18	22		
Primidone	ng/L	0.5	130	130	130	130		
Sucralose	ng/L	25	35000	37000	38000	40000		
Sulfamethoxazole	ng/L	0.25	1100	1000	980	1000		
ТСЕР	ng/L	10	230 220		230	210		
Triclocarban	ng/L	2	16 6.2		4.5	4.4		
Triclosan	ng/L	1	30 15		14	16		
Trimethoprim	ng/L	0.25	75	74	78	78		

Scale/Mode			Sn	nall Pilot: Flow T	hrough Mode (H	igh Flow)		
Date Collected	Units	Reporting Limit	1/7/2016					
Location	Cints	Influent		Effluent EBCT = 2 min	Effluent EBCT = 3 min	Effluent EBCT = 6 min		
Acetaminophen	ng/L	5	< 5.0	< 5.0	< 5.0	< 5.0		
Atenolol	ng/L	1	25	22	25	21		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	130	120	130	130		
DEET	ng/L	1	72	76	70	75		
Fluoxetine	ng/L	0.5	25	29	31	30		
Gemfibrozil	ng/L	0.25	1.6	1.4	0.99	0.89		
Ibuprofen	ng/L	1	< 1.0	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	220	220	220	240		
Naproxen	ng/L	0.5	11	12	11	13		
Primidone	ng/L	0.5	130	150	160	150		
Sucralose	ng/L	25	41000	41000	42000	40000		
Sulfamethoxazole	ng/L	0.25	1000	980	970	1100		
ТСЕР	ng/L	10	260 260		250	270		
Triclocarban	ng/L	2	13 15		14	12		
Triclosan	ng/L	1	19 19		18	16		
Trimethoprim	ng/L	0.25	47	49	50	49		

Scale/Mode			Sn	nall Pilot: Flow T	hrough Mode (H	igh Flow)		
Date Collected	Units	Reporting Limit	1/19/2016					
Location	СШС	Influe		Effluent EBCT = 2 min	Effluent EBCT = 3 min	Effluent EBCT = 6 min		
Acetaminophen	ng/L	5	< 5.0	< 5.0	< 5.0	< 5.0		
Atenolol	ng/L	1	22	25	23	24		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	150	160	150	160		
DEET	ng/L	1	130	140	140	120		
Fluoxetine	ng/L	0.5	29	34	33	34		
Gemfibrozil	ng/L	0.25	3.2	2.9	2.1	1.7		
Ibuprofen	ng/L	1	< 1.0	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	220	250	240	240		
Naproxen	ng/L	0.5	11	11	11	12		
Primidone	ng/L	0.5	120	140	150	140		
Sucralose	ng/L	25	46000	46000	44000	45000		
Sulfamethoxazole	ng/L	0.25	990	1000	940	1100		
ТСЕР	ng/L	10	270 280		280	280		
Triclocarban	ng/L	2	13 16		14	13		
Triclosan	ng/L	1	30 26		26	22		
Trimethoprim	ng/L	0.25	46	41	38	37		

Scale/Mode			S	mall Pilot: Flow	Through Mode (L	ow Flow)		
Date Collected	Units	Reporting Limit	2/10/2016					
Location	Cints	Influent		Effluent EBCT = 5 min	Effluent EBCT = 10 min	Effluent EBCT = 20 min		
Acetaminophen	ng/L	5	< 100	< 100	< 100	< 100		
Atenolol	ng/L	1	25	20	< 20	< 20		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	150	140	140	140		
DEET	ng/L	1	150	140	150	140		
Fluoxetine	ng/L	0.5	36	37	34	36		
Gemfibrozil	ng/L	0.25	1.9	1.9	2.4	2.6		
Ibuprofen	ng/L	1	< 1.0	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	230	200	180	210		
Naproxen	ng/L	0.5	14	14	19	20		
Primidone	ng/L	0.5	190	170	170	160		
Sucralose	ng/L	25	42000	43000	53000	50000		
Sulfamethoxazole	ng/L	0.25	1300	1300	1200	1300		
ТСЕР	ng/L	10	220	210	210	200		
Triclocarban	ng/L	2	9.5 9.4		9.0	8.9		
Triclosan	ng/L	1	17 22		27	22		
Trimethoprim	ng/L	0.25	45	20	31	31		

Scale/Mode				Small Pilot: B	atch Mode (Low F	Flow)		
Date Collected	Units	Reporting Limit	2/17/2016					
Location	Cints	Influent		Effluent EBCT = 5 min	Effluent EBCT = 10 min	Effluent EBCT = 20 min		
Acetaminophen	ng/L	5	< 100	< 100	< 100	< 100		
Atenolol	ng/L	1	< 20	< 20	< 20	< 20		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	170	160	160	160		
DEET	ng/L	1	130	130	120	150		
Fluoxetine	ng/L	0.5	27	27	25	30		
Gemfibrozil	ng/L	0.25	1.0	0.58	0.46	1.0		
Ibuprofen	ng/L	1	< 1.0	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	240	160	110	160		
Naproxen	ng/L	0.5	9.8	10	8.4	16		
Primidone	ng/L	0.5	140	150	160	160		
Sucralose	ng/L	25	51000	49000	53000	55000		
Sulfamethoxazole	ng/L	0.25	1300	1100	1000	1100		
ТСЕР	ng/L	10	220	230	230	230		
Triclocarban	ng/L	2	4.7 5.3		5.3	6.8		
Triclosan	ng/L	1	15 7.9		6.5	8.8		
Trimethoprim	ng/L	0.25	33	5.1	1.6	4.8		

Scale/Mode				Small Pilot: B	atch Mode (Low F	Flow)		
Date Collected	Units	Reporting Limit	2/23/2016					
Location	emus	Keporting Ellint	Influent	Effluent EBCT = 5 min	Effluent EBCT = 10 min	Effluent EBCT = 20 min		
Acetaminophen	ng/L	5	< 100	< 100	< 100	< 100		
Atenolol	ng/L	1	< 20	< 20	< 20	< 20		
Caffeine	ng/L	5	< 100	< 100	< 100	< 100		
Carbamazepine	ng/L	0.5	130	130	130	120		
DEET	ng/L	1	120	110	110	100		
Fluoxetine	ng/L	0.5	24	22	22	20		
Gemfibrozil	ng/L	0.25	2.0	0.94	0.64	0.31		
Ibuprofen	ng/L	1	< 20	< 1.0	< 1.0	< 1.0		
Meprobamate	ng/L	0.25	190	180	130	100		
Naproxen	ng/L	0.5	13	12	10	8.4		
Primidone	ng/L	0.5	130	140	140	160		
Sucralose	ng/L	25	51000	55000	51000	48000		
Sulfamethoxazole	ng/L	0.25	1300	1300	1300	1000		
ТСЕР	ng/L	10	200	200	200	190		
Triclocarban	ng/L	2	4.0	4.3	2.4	3.2		
Triclosan	ng/L	1	9.1 5.2		3.4	4.2		
Trimethoprim	ng/L	0.25	20	9.2	3.4	1.5		

Scale/Mode				Small Pilot: B	atch Mode (Low F	Flow)		
Date Collected	Units	Reporting Limit	4/25/2016					
Location	Omts	Keporting Limit	Influent	Effluent EBCT = 5 min	Effluent EBCT = 10 min	Effluent EBCT = 20 min		
Acetaminophen	ng/L	5	<5	<5	<5	<5		
Atenolol	ng/L	1	33	33	<20	<20		
Caffeine	ng/L	5	<100	<100	<100	<100		
Carbamazepine	ng/L	0.5	110	130	120	110		
DEET	ng/L	1	210	220	210	200		
Fluoxetine	ng/L	0.5	22	15	17	17		
Gemfibrozil	ng/L	0.25	0.8	0.75	< 0.25	0.52		
Ibuprofen	ng/L	1	<20	<20	<20	<20		
Meprobamate	ng/L	0.25	210	200	190	180		
Naproxen	ng/L	0.5	9.3	9.2	6.9	8.8		
Primidone	ng/L	0.5	140	150	140	110		
Sucralose	ng/L	25	49000	49000	49000	50000		
Sulfamethoxazole	ng/L	0.25	930	950	840	720		
ТСЕР	ng/L	10	220	210	200	200		
Triclocarban	ng/L	2	7.9	3.1	3.2	3.4		
Triclosan	ng/L	1	21 5.8		7.5	7.3		
Trimethoprim	ng/L	0.25	19	19	<5	73		

Scale/Mode				Small Pilot: B	atch Mode (Low F	Flow)		
Date Collected	Units	Reporting Limit	5/4/2016					
Location	Omts	Influent		Effluent EBCT = 5 min	Effluent EBCT = 10 min	Effluent EBCT = 20 min		
Acetaminophen	ng/L	5	<5	<5	<5	<5		
Atenolol	ng/L	1	<20	<20	<20	<20		
Caffeine	ng/L	5	<100	<100	<100	<100		
Carbamazepine	ng/L	0.5	160	140	150	140		
DEET	ng/L	1	170	150	170	150		
Fluoxetine	ng/L	0.5	15	10	9.9	15		
Gemfibrozil	ng/L	0.25	0.8	0.63	0.56	0.43		
Ibuprofen	ng/L	1	<1	<1	<1	<1		
Meprobamate	ng/L	0.25	200	170	160	170		
Naproxen	ng/L	0.5	8.8	11	9	7.8		
Primidone	ng/L	0.5	120	140	130	140		
Sucralose	ng/L	25	40000	43000	42000	43000		
Sulfamethoxazole	ng/L	0.25	810	750	660	740		
ТСЕР	ng/L	10	340	300	300	210		
Triclocarban	ng/L	2	4.6 2.2		2.3	2.6		
Triclosan	ng/L	1	9 4.2		4.4	4.6		
Trimethoprim	ng/L	0.25	14	9.9	7.6	5.6		

Scale/Mode	Date Collected	Location	EBCT (min)	DOC Concentration (mg/L)
		Influent	0	7.3
Full Scale Filter	2/23/2016	minuent	0	7.7
T un Seale T nier	2/23/2010	Effluent	7 - 14	6.1
			/ = 14	6.0
	2/10/2016	Influent	0	5.9
	2/10/2010	Effluent	10	5.4
	2/17/2016	Influent	0	5.8
	2/17/2010	Effluent	10	5.3
	2/23/2016	Influent	0	5.9
	2/23/2010	Effluent	10	5.6
	3/3/2016	Influent	0	6.2
	5/5/2010	Effluent	10	5.9
	3/14/2016	Influent	0	5.8
	5/14/2010	Effluent	10	5.4
	2/24/2016	Influent	0	5.3
	3/24/2016	Effluent	10	5.0
	4/6/2016	Influent	0	5.3
	4/0/2010	4/6/2016 Effluent	10	5.2
	4/10/0016	Influent	0	5.6
	4/12/2016	(12/2016 Effluent 10	5.3	
	4/20/2016	Influent	0	5.3
	4/20/2016	Effluent	10	5.1
Pilot Scale	4/04/0016	Influent	0	5.4
	4/24/2016	Effluent	10	5.0
	5/4/0016	Influent	0	5.1
	5/4/2016	Effluent	10	4.9
	5/10/001 6	Influent	0	5.2
	5/10/2016	Effluent	10	4.8
	5/10/2016	Influent	0	5.4
	5/19/2016	Effluent	10	5.1
	E 10 E 1001 -	Influent	0	5.1
	5/25/2016	Effluent	10	4.8
		Influent	0	5.1
	6/1/2016	Effluent	10	4.8
		Influent	0	4.9
	6/8/2016	Effluent	10	4.8
		Influent	0	5.1
	6/20/2016	Effluent	10	4.9
		Influent	0	5.2
	6/23/2016	Effluent	10	5.0

APPENDIX C: Experimental Measurements of Dissolved Organic Carbon

Scale/Mode	Date Collected	Location	EBCT (min)	DOC Concentration (mg/L)
	C/20/201C	Influent	0	5.0
	6/29/2016	Effluent	10	4.8
	7/6/2016	Influent	0	5.0
	7/6/2016	Effluent	10	4.8
	7/13/2016	Influent	0	4.9
	//15/2010	Effluent	10	4.7
	7/25/2016	Influent	0	5.0
	//23/2010	Effluent	10	4.0
	8/1/2016	Influent	0	4.9
	0/1/2010	Effluent	10	4.2
		Influent	0	5.8
	12/14/2015		2	5.5
	12/14/2013	Effluent	3	5.1
			6	5.1
		Influent	0	5.2
Small Pilot: Batch Mode	12/21/2015		2	5.5
(High Flow)	12/21/2013	Effluent	3	5.4
			6	5.4
	12/28/2015	Influent	0	5.4
			2	5.9
		Effluent	3	5.7
			6	5.3
		Influent	0	9.5
	12/21/2015	Effluent	2	6.1
	12/31/2015		3	5.9
			6	5.8
		Influent	0	5.5
	1/7/2016		2	5.3
	1/7/2016	Effluent	3	5.3
			6	5.9
		Influent	0	5.7
Small Pilot: Flow Through	1/11/2016		2	5.5
Mode (High Flow)	1/11/2016	Effluent	3	5.4
			6	5.2
		I CI /	0	5.8
		Influent	0	5.6
			2	5.8
	1/10/2016		2	5.5
	1/19/2016	T COL	2	5.5
		Effluent	3	5.5
			-	5.4
			6	5.7
	1/21/2016	Influent	0	5.6

Scale/Mode	Date Collected	Location	EBCT (min)	DOC Concentration (mg/L)
Small Pilot: Flow Through Mode (High Flow)				5.4
		Effluent	2	5.8
				5.2
			3	5.6
				5.4
			6	5.4
				5.2
Small Pilot: Flow Through Mode (Low Flow)	2/10/2016	Influent	0	7.1
				7.3
		Effluent	5	6.2
				6.1
			10	6.4
				6.3
			20	5.9
				6.0
Small Pilot: Batch Mode (Low Flow)	2/17/2016	Influent	0	6.4
				6.4
		Effluent	5	5.7
				5.4
			10	5.4
				5.3
			20	5.8
				5.8
	2/23/2016	Influent	0	7.4
				6.2
		Effluent	5	5.6
				5.4
			10	5.6
				5.4
			20	5.4
				7.5
	4/25/2016	Influent	0	6.2
		Effluent	5	5.4
			10	5.1
			20	5.1
	5/4/2016	Influent	0	5.8
		Effluent	5	4.9
			10	4.7
			20	5.0