UNIVERSITY OF CALIFORNIA

Los Angeles

# Nitrate Removal

# by Biochar-Amended Woodchip Biofilters

A thesis submitted in partial satisfaction of the

requirements for the degree Master of Science

in Civil Engineering

by

Alexander William Berger

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ABSTRACT OF THE THESIS

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Professor Sanjay K. Mohanty, Chair

Stormwater biofilters, particularly woodchip biofilters, have been used to remove nitrate from stormwater, but their performance is expected to decrease under extreme weather conditions such as prolonged drying and high rainfall intensity, which are expected to be more frequent during climate change. The objective of this study is to examine the effect of biochar amendment on nitrate removal by woodchip biofilters subjected to increasing antecedent drying conditions and rainfall intensity. The experiments were designed to test the following hypothesis: the addition of biochar would increase the resiliency of woodchip-amended biofilter by enhancing the physical, chemical, and biological processes that support the removal of nitrate.

Biochar-amended woodchip biofilters were packed with a homogeneous mixture of woodchips and biochar at 0, 5, 10, or 20% biochar volume in plastic columns (5.1 cm diameter, 61 cm height). Stormwater spiked with nitrate was injected through biofilters, and the effluent was collected by a raised outlet (30-cm submerged zone) to enhance denitrification. Antecedent drying duration was varied between 1 d to 8 d, and hydraulic residence time (HRT) was varied between 0 to 20 h to examine the effect of drying duration and high rainfall intensity on denitrification.

Results showed that biochar improved denitrification potential of woodchip biofilters. This improvement is attributed to changes in pore water chemistry, such as a decrease in dissolved oxygen (DO) concentration and an increase in dissolved organic carbon (DOC) trapped in pore water, and an increase in robust denitrifying biofilm supported on biochar particles, which has higher surface area than woodchips. Increase in antecedent drying duration had a net positive impact on denitrification, and the addition of biochar further increase nitrate removal during drying period. Antecedent drying periods helped replenish denitrification capacity of biofilters by increasing the dissolution of DOC and decreasing DO. Overall, the results suggest that addition of biochar could increase the resiliency of woodchip biofilters for denitrification during high intensity rainfall expected during climate change—the conditions at which the performance of woodchip biofilters typically deteriorates quickly.

The thesis of Alexander William Berger is approved.

Jennifer A. Jay

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University of California, Los Angeles

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Table of Contents

# List of Figures

# List of Tables

# List of Acronyms

| | |
|---|---|
| BMPs | Best management practices |
| °C | Degree(s) centigrade |
| C | Effluent concentration |
| $C_0$ | Influent concentration |
| $CH_3OH$ | Methanol |
| $C_3H_8O_3$ | Glycerin |
| d | day(s) |
| DO | Dissolved oxygen |
| DOC | Dissolved organic carbon |
| HPDE | High density polyethylene plastic |
| HRT | Hydraulic residence time |
| ID | Inner diameter |
| $KNO_3$ | Potassium nitrate |
| LID | Low-impact development |
| PVC | Polyvinyl chloride |
| $NH_4NO_3$ | Ammonium nitrate |
| $NO_3^-$ | Nitrate |
| q | flux |
| SUVA | Specific ultraviolet absorbance |
| $UV_{254}$ | Ultraviolet absorbance at 254 nanometers |

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## 1. Introduction

Nitrogen is an essential nutrient for plant growth, but excessive amounts of nitrogen application via fertilizer can lead to contamination of surface waters and groundwater and consequently cause environmental and human health problems. For instance, nitrate exposure can cause blue baby syndrome, a phenomenon whereby nitrate hijacks hemoglobin's ability to bind oxygen (Council 1995). Excess nitrogen in surface waters accelerates algal growth in a process termed eutrophication, which is the primary cause of oxygen depletion in lakes and streams. Algal growth has direct and indirect human health consequences, from algae containing neurotoxins to suffering fish populations and clogging water intake screens for wastewater treatment plants (Camargo and Alonso 2006). Eutrophication is expected to increase during climate change due to changes in land use that either increase application of fertilizer or provide limited buffer to absorb nitrogen, increase loading of nitrogen surface waters, and help rapid growth of algae in warmer temperatures (Whitehead et al. 2009). Thus, it is critical to develop strategies to increase removal of nitrate from surface waters and groundwater.

The main management strategy for nitrate reduction is source identification and treatment at the source. Agricultural activity and increased urbanization typically increase net nitrogen export (Silva et al. 2002). The primary source of nitrogen is fertilizer from agricultural lands and decayed biomass from urban environments (Kaushal et al. 2011, Silva et al. 2002). Fertilizers, such as inorganic nitrate salts (e.g. $NH_4NO_3$, $KNO_3$), readily dissolve in water and excess nitrogen leaches to surface waters and groundwater. Animal manures and atmospheric deposition also contribute to excess nitrate pollution (Puckett 1994). Dissolved nitrogen in water exists in three main forms: nitrate, ammonium or ammonia, and organic nitrogen. Among these, nitrate is harder to remove from water.

Nitrate removal by conventional wastewater treatment plants is impractical due to its origin from nonpoint sources. For removal of nitrate from non-point sources, infiltration based low-impact development (LID) is used (Fletcher et al. 2015). Among different types of LID, biofilter is particularly attractive because it has a small footprint and it requires filtration of stormwater, where controlling factors like filter media depth can be optimized based on contaminant loading rates. A biofilter is a depressed area with or without plants, which is typically designed by replacing a portion of native soil by sand and compost or other filter material that permits rapid infiltration of stormwater runoff. Biofilters with plants actively remove pollutants such as nutrients through the root systems. A biofilter is designed to restore hydrological functions (primarily infiltration) in impervious urban areas using natural materials (Dietz 2007), where nitrate is removed by biological processes mediated by plants and soil microorganisms. In soil, denitrifying bacteria, a class of heterotrophic anoxic and anaerobic bacteria, fix inorganic nitrate near the root zone (Cleveland et al. 1999). These microorganisms oxidize dissolved organic carbon to reduce nitrate (Inglett et al. 2005). The process is termed denitrification, where nitrate is transformed to nitrogen gas by a series of intermediate reactions (Ambus and Zechmeister-Boltenstern 2007). The redox half reaction for denitrification is provided below:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$$

Microorganisms respire nitrate when dissolved oxygen (DO) concentrations are low (Gómez et al. 2002). High DO of turbulent influent stormwater deactivates the enzymes involved in denitrification, which can be neutralized by low DO of pore water between drying durations (Gómez et al. 2002). Based on the equation above, for denitrification to be efficient, three conditions must be met: (1) dissolved oxygen concentration should be low (preferably below 3 mg/L), (2) sufficient amount of electron donors must be present, and (3) the conditions such as pH (proton concentration) should be favorable for microorganisms to strive. In stormwater treatment systems, woodchips provide the organic substrate or electron donors for denitrification (Christianson et al. 2017, Halaburka et al. 2017, Hoover et al. 2016). Under submerged conditions (Afrooz and Boehm 2017, Wang et al. 2018), dissolved organic carbon (DOC) including organic acids leach out of woodchips, which drive this biologically mediated process. Denitrifying bacteria in LID use organic carbon sources for growth and as an electron donor (Korom 1992). Because the biological process is slow (kinetically limited), nitrate should remain in the system for long enough time to be utilized by microorganism. Thus, hydraulic residence or retention time (HRT) plays a critical role in removal of nitrate. Typically, increases in HRT lead to increased denitrification (Abusallout and Hua 2017, Damaraju et al. 2015, Halaburka et al. 2017, Hassanpour et al. 2017, Hoover et al. 2016, Jiang et al. 2017).

To examine the potential of LID to remove nitrate from contaminated water, several laboratory and field studies have utilized different types of filter media (Table 1). Conventional materials in LID, such as sand and compost, have limited capacity to remove nitrate (Ulrich et al. 2017). Unlike wastewater treatment, where organics such as ethanol, glucose, acetate, and methanol can be added to improve denitrification (Gómez et al. 2000), stormwater treatment depends on the sustained leaching of DOC from natural or synthetic carbon materials such as woodchips and newspaper, to name a few (Kim et al. 2003). These organic materials in LID are important in supporting bacterial metabolism, providing surfaces for biofilm growth, and controlling dissolved oxygen (DO) concentrations. A submerged zone sustains leaching of DOC, and decomposition of organic matter drives down the oxygen concentration of the pore water during drying (time between precipitation events) (Schipper et al. 2010). For denitrification, typically woodchips are used (Lopez-Ponnada et al. 2017). Although woodchips and organic filter media satisfy the DOC requirement, the denitrification potential varies widely (Table 1) based on other conditions such as hydraulic retention time and presence of sufficient surface areas on filter media to support biofilm growth.

To increase denitrification potential of woodchip biofilters, biochar—a porous carbonaceous black carbon produced from waste biomass by pyrolysis—has been used recently in many studies (See review by Mohanty et al. 2018). These studies showed that biochar can improve denitrification, but the mechanisms by which biochar improves denitrification is not clear. Biochar can abiotically capture nitrate via ion exchange, similar to how activated carbon adsorb nitrate (Erickson et al. 2016). Biochar, with its network of pores, could decrease the hydraulic conductivity and increase HRT or contact time (Bock et al. 2018). Biochar, due to its higher surface area than woodchips, could also increase biofilm quantity. Furthermore, biochar could increase the water holding capacity of filter media (in the absence of submerged layer) and retain contaminated water within the pores for nitrate to be utilized by microorganisms during rainless period. Improving the understanding of the dominant mechanism for nitrate removal in biochar-amended biofilter can help optimize the biofilter design to increase the nitrate removal in adverse conditions where nitrate removal is expected to be low.

Biofilters are subjected to dynamic weather conditions in nature. Two types of weather conditions can change denitrification: high intensity rainfall and prolonged drying before a rainfall. Both conditions are highly relevant during climate change, yet their impacts on the resiliency of biofilter to remove nitrate from stormwater have not been tested systematically. Drying condition is relevant for changes in weather pattern during climate change, as some areas are expected to be drier while others may become wetter (Knapp et al. 2015). Only two studies have examined the effect of antecedent dry conditions on nitrate removal (Lynn et al. 2015, Wang et al. 2018). Both studies showed that antecedent dry conditions help increase dissolution of dissolved organic carbon from woodchips, and maintain a high rate removal rate, thereby depleting the concentration of nitrate in pore water. Consequently, the infiltration of stormwater after the drying period becomes diluted with low nitrate pore water. The impact of drying duration on biochar-amended woodchip biofilter has not been evaluated. It is expected that the addition of biochar would retain more water within the pores, and trap the DOC leached from woodchips during drying conditions (Mohanty et al. 2014). Thus, biochar may enhance the impact of drying duration on denitrification potential of woodchip biofilter. Although biofilters are designed to mitigate the impact of climate change, the processes by which LID can remove contaminants such as nitrate can be highly susceptible to weather conditions that are expected to change during climate change. Thus, it is critical to examine whether nitrate removal capacity of biofilter remains sustainable during different weather condition scenarios: antecedent drying duration and high intensity rainfall.

The goals of this study are to quantitatively compare the nitrate removal capacity of woodchip biofilters with and without biochar amendment, examine nitrate removal mechanism by biochar-amended biofilters, and evaluate their potentials to remove nitrate under two dynamic weather conditions: drying duration and high intensity rainfall. Isolating these parameters will help optimize biofilter design to make them more resilient during climate change. Furthermore, this study provides a guideline to assess the performance of biofilter systems subjected to variable conditions.

Table 1. Summary of literature review on studies that used wood chips or biochar to remove nitrate.

| Study Type | Experimental details† | Key results | References |
|---|---|---|---|
| Field | • 90% hardwood chips and 10% biochar by volume.<br>• 4 h residence time for a 4.6 cm (1.8 in) storm event<br>• Dimension of columns: 7.31 m × 5.49 m × 1.83 m<br>• Total Vol.: 73.4 $m^3$<br>• Input nitrate concentration: 25 mg/L $NO_3^-$-N | • Woodchip biofilters removed 21% to 95% nitrate<br>• Woodchip with biochar removed 32% to 100% nitrate<br>• Estimated N-removal costs range between $15 to $40 kg/yr which is comparable to many other agricultural BMPs | (DeBoe et al. 2017) |
| Field | • 7.6 cm (3 inch) woodchip mulch layer over a soil mixture (50% sand, 20% shredded hard wood mulch, & 30% sandy loam planting soil<br>• Inundation durations: 1.7-13.83 d<br>• Surface area of 0.02 ha (0.06 acres) and average depth 71 cm | • 56% decrease in total nitrogen removal across the entire treatment system<br>• Lower gene abundance for denitrifiers in deeper portions of the medium | (Chen et al. 2013) |
| Field | • Aged woodchips<br>• HRT: 2 d<br>• Site dimension: 13.7 m × 1.6 m × 1.2 m and 10.1 m × 0.9 m × 1.4 m<br>• $C_0$: 160 mg/L $NO_3^-$-N<br>• With or without carbon enrichment using $CH_3OH$ & $C_3H_8O_3$ | • Removal in unenriched biofilter was 15 mg/L $NO_3^-$-N/d, whereas removal in enriched biofilter was an order of magnitude greater: 155 mg/L $NO_3^-$-N/ d<br>• C-enrichment studies using $CH_3OH$ & $C_3H_8O_3$ showed that denitrification rates increased significantly with $CH_3OH$ | (Hartz et al. 2017) |
| Field | • Media: Woodchips with or without biochar (10% by volume)<br>• Area: Two 25-$m^3$ bioreactors | • Woodchip-only treatment more effective when $C_0$ < mg/L $NO_3^-$-N; biochar treatment more effective when $C_0$ > 5-10 mg/L $NO_3^-$-N<br>• Nitrate removal: 2-22 g N $m^{-3}$ $d^{-1}$ | (Bock et al. 2016) |

| Study Type | Experimental details[†] | Key results | References |
| --- | --- | --- | --- |
| Lab | • Woodchips: white oak chips and a hardwood chip mixture (yellow poplar, black cherry, red oak, and white oak);<br>• Woodchips & biochar<br>• Flow rate: 600 mL/min<br>• HRT: 2 d<br>• Column dimensions: 20 cm ID and 60 cm height (30 cm gravel drainage + 30 cm wood treatment)<br>• $C_0$: 12-61 mg/L $NO_3^-$-N | • All systems become the source of nitrate indicating nitrate removal is low.<br>• Total nitrogen mass removal efficiency: 51-67%, but removal of total Kjeldahl nitrogen compensated by the leaching of nitrate. | (Christianson et al. 2017) |
| Lab | • Weathered woodchips<br>• Flow rate: 2.6 and 5.4 mL/min<br>• HRT: 12 and 24 h<br>• Column dimension (I.D. x height), 13.5 cm x 50.8 cm & 15.2 x 41.2 cm<br>• Pore volume: 4.1 L<br>• Tested at two temperatures:10°C and 21.5°C | • Increasing HRT and temperature both significantly increased percent removal<br>• Removal at 10°C: 29% (12 h HRT) and 48% (24 h HRT); Removal at 21.5°C: 67% (12 h HRT) and 96% (24 h HRT) | (Hoover et al. 2016) |
| Field | • 6 bioretention cells: 3 woodchip cells (ash tree) and 3 woodchip & biochar (2-10% biochar (by vol.) cells<br>• HRT: 0.3-2.8 d<br>• Volume: 9.46-7.1 $m^3$<br>• $C_0$: 6.2 - 18.4 mg/L $NO_3^-$-N | • $NO_3^-$-N removal efficiency: 42%-68%<br>• HRT controls $NO_3^-$ removal in 2 of 3 bioreactors<br>• Increased removal above 16°C | (Hassanpour et al. 2017) |
| Lab | • Woodchips (California redwood, oak, and Douglas fir)<br>• Dimension (ID x height): 10 cm x 50 cm<br>• Flow rates (mL/min): 1.5, 3.8, & 8.4<br>• HRT: 0-35 h<br>• $C_0$: 2, 5, & 11 mg/L | • Nitrate removal: 2.53 ± 0.39 g-N/$m^3$-media-d<br>• HRT controls $NO_3^-$ removal rates | (Halaburka et al. 2017) |

| Study Type | Experimental details† | Key results | References |
|---|---|---|---|
| Field | • Media: Woodchips (maple)<br>• 4 field bioreactors with volume 10.1-33 $m^3$, which is designed to handle 20% of peak drainage flow<br>• Flow rate: 7.3 L/s<br>• HRT: 14.1 h<br>• $C_0$: 0.01-21.59 mg/L $NO_3^-$-N | • Removal efficiency: (99% of flow-weighted average) 6.84 g $NO_3^-$ -N/$m^3$-d)<br>• No apparent relationship between HRT & percentage removal of $NO_3^-$-N from influent water | (Husk et al. 2017) |
| Lab | • 5 media: Sand, sand & 20% compost (by volume), sand & 33% compost (by volume), sand with compost (20% by vol.) & biochar (33% by vol.), sand with compost (20% by vol.) & granulated activated carbon (12.5% by vol.)<br>• Column dimensions: ID 15.24 cm, height 50 cm (20 cm ponding zone, 10 cm planted layer, 10 cm sorbent-amended layer, 10 cm drainage layer)<br>• Pore Volume: 1.6 L<br>• $C_0$: 0.69 mg/L $NO_3^-$-N | • >68% $NO_3^-$ -N removal<br>• Biochar-amended biofilters demonstrated superior nitrate removal | (Ulrich et al. 2017) |
| Lab | • 3 media types: Hardwood chips, hardwood chips with stainless steel anode & graphite cathodes, hardwood chips with graphite anode & graphite cathodes<br>• Column dimensions: 15.2 cm ID and 50.8 cm height<br>• Pore volume: 4.9 L<br>• Current: 0, 100, and 500 mA.<br>• Flow rates (mL/min): 19.2 & 26.8<br>• HRT: 5.9-8.2 h<br>• $C_0$: 30 mg/L of $NO_3^-$ -N | • $NO_3^-$ removal efficiency increased with application of current (500 mA): control, 14.0 ± 6.5%; stainless steel anode, 24.0 ± 11.0%; graphite anode, 40.5 ± 19.5%<br>• $NO_3^-$ removal efficiencies improved using electrical stimulation at 500 mA, yet not at 100 mA<br>• No $NO_3^-$ removal in cold temperature study | (Law et al. 2018) |

| Study Type | Experimental details† | Key results | References |
|---|---|---|---|
| Lab | • Untreated woodchips<br>• Pore volume: 2.4 L<br>• $C_0$: 1.18 mmol/L $KNO_3$ | • Nitrate loading rate affects the microbial community in the woodchip biofilter and influences the removal processes. | (Grießmeier et al. 2017) |
| Lab | • Sand and biochar | • Saturation zone saw an avg. 25% improvement in $NO_3^-$ removal compared to unsaturated columns | (Afrooz and Boehm 2017) |
| Lab | • 4 columns with soil, sand, wood chips, and vermiculite in varying fractions<br>• Dimensions: 15 cm ID and 130 cm height<br>• Flow rate: 12 mL/min<br>• $C_0$: 8-9 mg/L | • Mean $NO_3^-$ removal rate: >80%<br>• Layered bioretention with mixed media can remove $NO_3^-$ as well as dissolved organic matter. | (Wan et al. 2017) |
| Lab | • Constructed wetland device filled with bark<br>• Flow rates (mL/min): 2.47, 2.06, 1.64, 0.83, & 0.41<br>• HRT: 18 h, 21.6 h, 26.9 h, 53.8 h, 107.5 h<br>• $C_0$: 27.05-28.54 mg/L | • Greatest $NO_3^-$ removal at highest HRT (107.5 h) | (Jiang et al. 2017) |
| Lab | • Horizontal flow reactor with hardwood chips<br>• Column dimensions: 17.8 ID and 50.8 cm height<br>• HRT: 4, 8, & 12 h<br>• $C_0$ (mg/L $NO_3^-$): 14.8 at 4 h HRT, 31 at 8 h HRT, and 52 at 12 h HRT | • $NO_3^-$ -N removal efficiency positively related with HRT<br>• Increase in volumetric loading rate & biomass concentration decreased $NO_3^-$-N removal efficiency<br>• $NO_3^-$ removal: >99% ($C_0$: 50 mg/L $NO_3^-$ ; HRT: 12 h) | (Damaraju et al. 2015) |
| Lab | • Two upflow column reactors with two media: Wood chips and steel byproducts<br>• HRT: 24 h (wood chips), and 9.5 h (steel byproducts)<br>• $C_0$: 20 mg N/L & 50 mg N/L | • Higher HRTs correspond to greater DOC releasing potential | (Abusallout and Hua 2017) |

| Study Type | Experimental details† | Key results | References |
|---|---|---|---|
| Lab | • Nine carbon media at two treatment temperatures:14 & 23.5 °C | • Carbon substrate and temperature affects nitrate removal rate more than hydraulic properties of media do.<br>• Except, maize cobs, nitrate removal increased with temperature for all other types of carbon media. | (Cameron and Schipper 2012) |
| Lab | • Media: 50 mm woodchip, 45 cm mixed soil, sand & newspaper (5% by vol.)<br>• One column without saturated zone, two columns with a saturation zone, and six columns with varying saturation zone depths (0-60 cm)<br>• Flow rates (L/h): 20 and 70<br>• HRT: 1 h<br>• Drying duration: 0-72 h (0-3 d)<br>• $C_0$: 2.5 mg/L | • Near complete $NO_3^-$ removal in saturation zone within 12 h<br>• $NO_3^-$ removal supported by low DO (<0.5 mg/L) and 3 d drying<br>• Deeper saturation zone corresponds to improved denitrification | (Wang et al. 2018) |
| Field | • Two field 25 $m^3$ woodchip bioreactors with 10% biochar (by volume) | • $NO_3^-$ removal efficiency: 9.5%<br>• Low removal efficiency due to periods of low HRT and low pH<br>• Nitrate removal increased with increasing influent concentration and temperature | (Bock et al. 2018) |

†HRT: hydraulic retention time; $C_0$: influent concentration of nitrate; I.D.: internal diameter; DO: dissolved oxygen; DOC: dissolved organic carbon; BMPs: best management practices

## 2. Materials and Methods

### 2.1. Stormwater collection

Stormwater was collected from Ballona Creek in Los Angeles, CA (34 0’36’’ N 118 23’29’’W) each week in three 20 L HPDE plastic carboys following USGS guidelines for collection of water samples (Wilde and Radtke 1998). Ballona Creek receives water from a 123 $mi^2$ urban area with 82% developed and 61% impervious surface and drains it into Santa Monica Bay (Gold et al. 2015). The creek banks are bordered by commercial, industrial and residential properties, contributing dry-weather irrigation runoff from homes and as well as runoff from industrial sites into the creek. Collected stormwater was characterized for pH, dissolved oxygen (DO), and turbidity, and then pretreated to remove large particulates. Large particulates were removed from stormwater by gravimetrically settling particles for 1 h without disturbance. The supernatant was stored in a refrigerator at 4 °C to minimize bacterial growth but brought to room temperature prior to use in experiments.

### 2.2. Biofilter media

Woodchips and biochar were used as biofilter media. Woodchips have been used for denitrification (Addy et al. 2016, Bock et al. 2016, Bruun et al. 2016, Damaraju et al. 2015, Hoover et al. 2016, Robertson 2010) because they provide dissolved organic carbon (DOC), an electron donor, for denitrification and a solid substrate for biofilm growth (Lopez-Ponnada et al. 2017). Pine woodchips without chemical treatment (Whittier Fertilizer Company, CA) were sieved (sieve # 20) to remove woodchips with size greater than 1.27 cm. These woodchips are commonly used as a top dressing in playground and landscaping applications.

A commercially available biochar (Biochar Supreme, Everson, WA) was selected for this study, because it has been studied for treatment of heavy metals and organic contaminants in stormwater and wastewater (Karunanayake et al. 2016, Karunanayake et al. 2017, Miles et al. 2016). The biochar was produced by high-temperature (900–1000 °C) gasification of softwood (Douglas fir). It has a high surface area (690-720$m^2/g$), low ash content (4%) and low moisture content (10%). Biochar was oven dried to remove moisture before packing. Woodchips and biochar were manually mixed in a plastic chamber to create uniform woodchip-biochar mixtures with 5, 10, and 20% biochar by volume.

### 2.3. Biofilter Design

To examine the effect of biochar concentration on denitrification potential of woodchip biofilter, woodchips without (control) and with biochar at 5%, 10%, or 20% by volume were packed in PVC columns (5 cm I.D. × 61cm length). Triplicate columns were used for each geomedia mixture (Figure 1). Gravel was first filled in bottom PVC fitting with a screen (plastic screen with 100 µm pore size) on the top. To pack the geomedia on top of the gravel layer, about 100 g of uniform media mixture was added incrementally at 5 cm height and compacted by tapping with a steel rod. The procedure was repeated until the total filter media depth was 45.7 cm. Gravel was added on the top of filter layer to prevent erosion of fine biochar particles by impact of influent droplets. To create a 30.5-cm submerged filter layer, the outlet was raised to a position 15.2 cm below the top surface of filter layer. All columns were wrapped with foil to prevent algal growth and fixed to a metal platform (Figure 1). To displace air from pores, the packed geomedia was first saturated from the bottom by feeding deionized (DI) water via gravity, and then the pore water was drained through a raised outlet to maintain the submerged layer. Stormwater samples were delivered to the top of the filter media from 20 L HPDE plastic carboys using a peristaltic pump (Cole-Parmer, Model No. 07528-30), and the effluent was collected at regular intervals through the raised outlet using 300 mL plastic amber bottles.

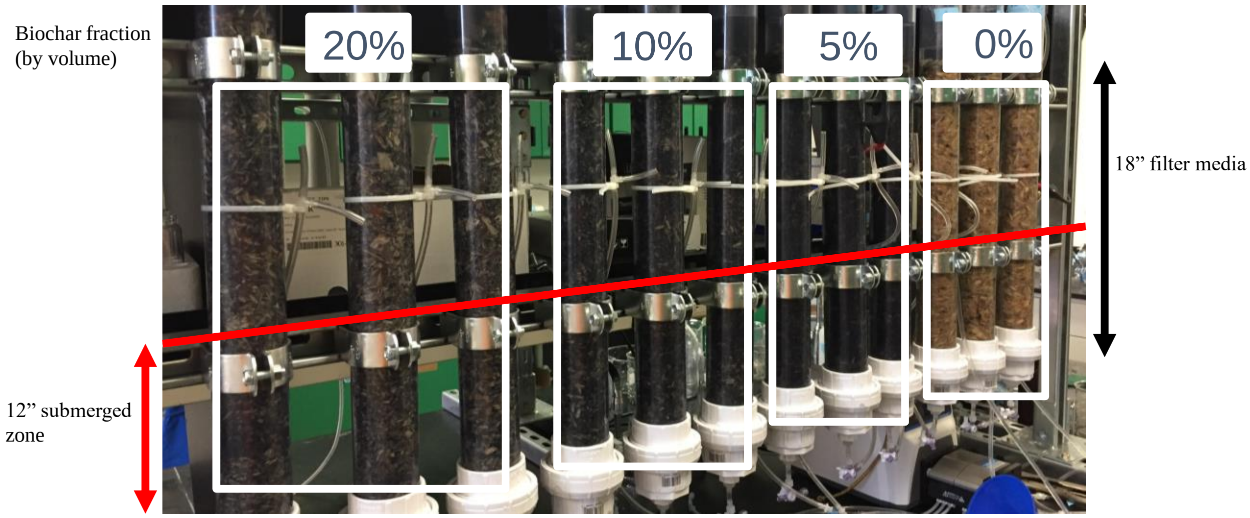


Figure 1. Column setup showing biochar fraction, filter media depth, and submerged zone. Triplicates columns (total 12 columns) were used for each mixture type.

### 2.4. Estimation of pore volume of columns by tracer study

Bromide tracer has been used to determine hydraulic characteristics of porous media (Levy and Chambers 1987). Tracer tests were performed to measure the pore volumes of woodchip columns packed with different fractions of biochar. To determine the changes in pore volume as a result of biochar addition, bromide contaminated stormwater was injected through the column. Potassium bromide (KBr) salt was added to pretreated stormwater to achieve an initial bromide concentration of 73.7 mg/L. After injection of bromide-free stormwater for 4 h to condition the flow rate, bromide-laden stormwater was applied at 5 mL/min (flux of 14.8 cm/h) for 4 h on the top of columns, followed by injection of bromide-free stormwater for additional 4 h. 5 mL effluent samples were collected at 20-min intervals, and bromide concentration were measured. The pore volume was estimated based on the volume of stormwater required to increase the effluent bromide concentration to 50% of the injected concentration.

### 2.5. Nitrate injection

Prior to injection of nitrate, the columns were conditioned with stormwater to grow biofilm and maintain denitrifying community. During conditioning phase, stormwater was applied on top of columns periodically (0 to 15 d) for two months.

About 18 mL of concentrated nitrate stock solution (20,000 mg/L) was spiked to 18 L of stormwater and mixed vigorously in a 20 L carboy for about one minute to achieve a targeted initial nitrate concentration around 20 mg/L. The initial concentration might be slightly higher than 20 mg/L based on background concentration of nitrate in stormwater. To determine the effect of rainfall duration on nitrate removal, stormwater with 24.7 mg/L nitrate was injected at 14.8 cm/h for 12 h following 4 days of antecedent drying. Time zero was denoted when the effluent started dripping into sample collection bottles, which occurred approximately 5 minutes after starting the pump. Effluents were collected at 1 h intervals, and selected samples (1, 2, 4, 6, 8, 10, and 12 h) were analyzed for nitrate and other water quality parameters including dissolved oxygen, pH, and UV absorbance.

In nature, rainfall events can differ by rainfall intensity and the rainless or drying period before a rainfall event. Increase in rainfall intensity can affect HRT — a measure of time stormwater remains in a biofilter before being collected or eluted — whereas antecedent drying period can affect water chemistry of pore water. Denitrification can be affected by both factors: drying (Subramaniam et al. 2016, Wei et al. 2017) and HRT (Halaburka et al. 2017, Hoover et al. 2016, Lynn et al. 2016, Nordstrom and Herbert 2017). Thus, experiments were designed to examine the effect of both parameters on denitrification in biochar-augmented biofilters. Stormwater was injected at a flow rate between 0.625 – 5 mL/min (flux: 1.85 – 29.62 cm/h) to achieve a desired HRT between 0 and 20 h, and the effluent was collected at regular intervals (~0.5 pore volume fraction).

To examine the effect of antecedent drying duration or rainless period on denitrification, stormwater with nitrate (20.8 ± 6.5 mg/L) was injected at a targeted flow rate of 5 mL/min (flux: 14.8 cm/h) for 4 h after a gap of 1, 2, 4, or 8 days. This gap simulated the drying conditions at room temperature (22 °) for different durations. To examine the effect of HRT on nitrate removal, ~1.2 L of stormwater containing nitrate (20.8 ± 6.5 mg/L) was injected through each column at a targeted flow rate of 0.625 mL/min to 10 mL/min (flux: 1.9 cm/ h to 29.6 cm/h) with corresponding targeted HRTs of 16.6 ± 0.5 to 1.04 ± 0.03 h.

### 2.6. Sample analysis

All column effluents and influents before and after spiking nitrate solution were collected in 300 mL amber HPDE bottles for a series of water quality analyses and nitrate concentration. Effluent samples were weighed to determine the volume of stormwater injected or collected, and immediately capped to prevent dissolved oxygen equilibration with ambient air. For all drying duration experiments, samples were collected once every hour for the 4-h long experiments.

Immediately after sample collection, column effluents were analyzed for pH (Fisher Scientific #9107BN), dissolved oxygen (Fisher Scientific 087010MD), and UV absorbance ($UV_{254}$) (PerkinElmer Lambda 365 UV-Visible Spectrophotometer). A portion of (~15 mL) of effluent was stored in a 15 mL centrifuge tube at 4 °C and later analyzed for nitrate. To estimate the quantity and quality of dissolved organic carbon (DOC) leached from woodchips, UV absorbance of effluents were measured. 1 mL of sample was poured from amber bottle directly into a quartz cuvette (10 mm path). Specific ultraviolet absorbance (SUVA) at 254 nm provides a measure of aromaticity of DOC molecules (Vesely et al. 2016). UV absorbance was used as a surrogate measurement for total organic carbon, assuming SUVA for DOC leached from woodchips remained constant during the experimental period (Abusallout and Hua 2017).

Nitrate concentrations were determined by ion chromatography using a Dionex Integrion HPIC (ThermoScientific) with 20 mM KOH as the eluent. Calibration standards were prepared at concentrations between 1 and 25 mg/L of nitrate, and nitrate concentrations in samples were measured at an elution time (10.3 min).

### 2.7. Data Analysis

Nitrate removal for each sample columns was calculated using the equation: $\left(1 - \frac{C}{C_0}\right) \times 100$, where $C$ is effluent concentration and $C_0$ is influent concentration. Removal was calculated for each column type at all intervals. Nitrate removal capacity can be exhausted with increases in injection volume of contaminated stormwater. The exhaustion rate was calculated based on the slope of linear fit of the data showing decrease in removal with increases in stormwater volume.

## 3. Results

### 3.1. Determination of pore volume from bromide tracer test

Relative bromide concentration in the effluents increased with increases in injection volume of bromide-laden stormwater in all columns and reached to nearly 100% after injection of 1312 ± 67.8 mL of stormwater (Figure 2). After switching the solution to bromide-free stormwater, bromide concentrations in the effluents decreased rapidly. The recovery of bromide in all columns was 97 ± 3.6%. Based on the volume of stormwater for effluent concentration to reach 50% of injected concentration, the pore volume (mL) of columns with 0%, 5%, 10% and 20% biochar (by volume) were estimated to be 649.1 ± 64.8, 623.4 ± 10.8, 616.0 ± 34.0, and 607.8 ± 23.2, respectively. The result indicates that the mean pore volume (without accounting for the variation between columns) decreased with increases in biochar fractions in the woodchips columns.

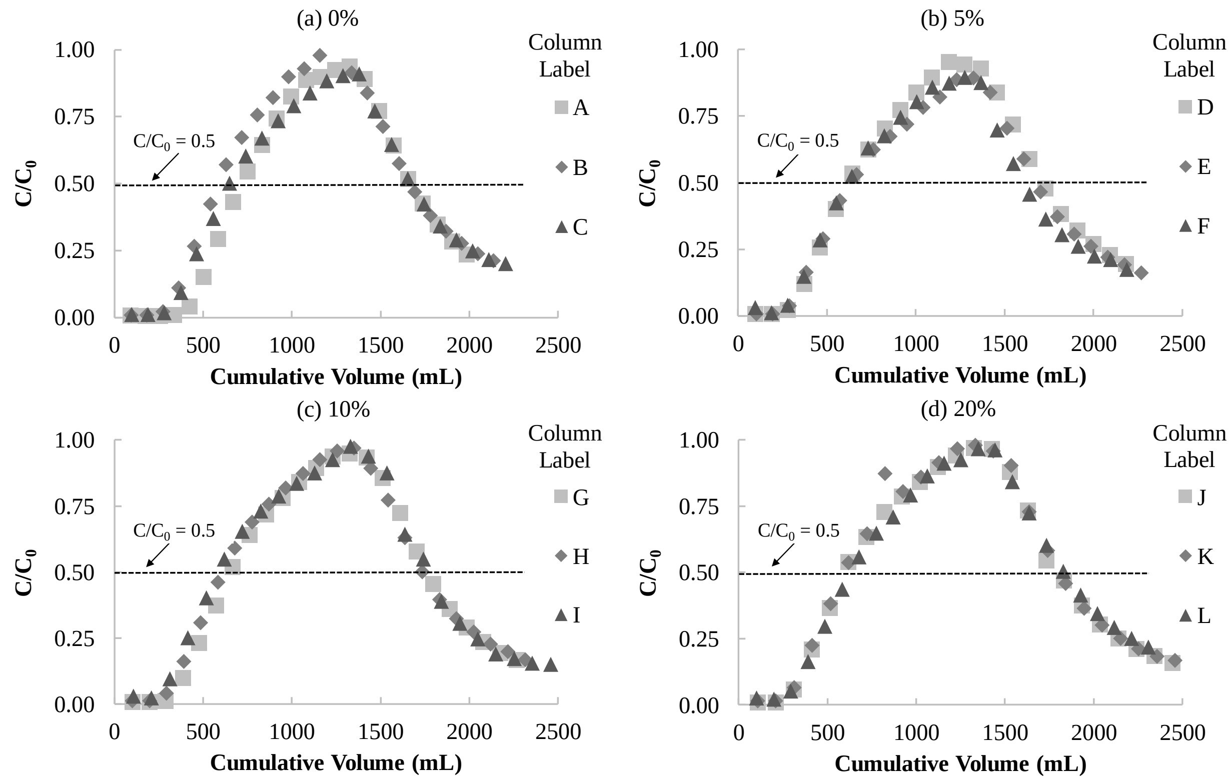


Figure 2. Relative concentration of bromide in the influent ($C/C_0$) as a function of cumulative volume for all columns. Bromide breakthrough curves are grouped according to triplicate woodchips columns with different biochar fractions: (a) 0%, (b) 5%, (c) 10%, and (d) 20% (by volume). Bromide input concentration was 73.7 mg/L, and stormwater application rate was 14.8 cm/h. Dashed horizontal line at $C/C_0 = 0.5$ intersect the rising breakthrough curve at points corresponding to cumulative volumes equal to one pore volume.

### 3.2. Effect of biochar fraction and stormwater injection volume on nitrate removal

Irrespective of biochar content in the woodchips biofilter, nitrate removal decreased with increases in volume of applied stormwater (Figure 3). After injection of roughly 0.5 PV of water, nitrate removal was still above 90% among all column types. However, the removal decreased to 25-60% as more stormwater, up to 5.5 PV, was injected. Nitrate removal varied between columns with different fractions of biochar. The average nitrate removal of biochar-amended columns was higher than the average removal by biochar-free columns (woodchips). However, a greater variation in nitrate removal was observed in biochar-amended columns compared with woodchip columns. Comparing the lowest mean nitrate removal by biofilter with and without biochar, it is estimated that biochar-amended columns can treat at least additional 1.3 pore volumes of stormwater compared with biochar-free woodchip biofilters to achieve the same treatment goal or effluent nitrate concentration.

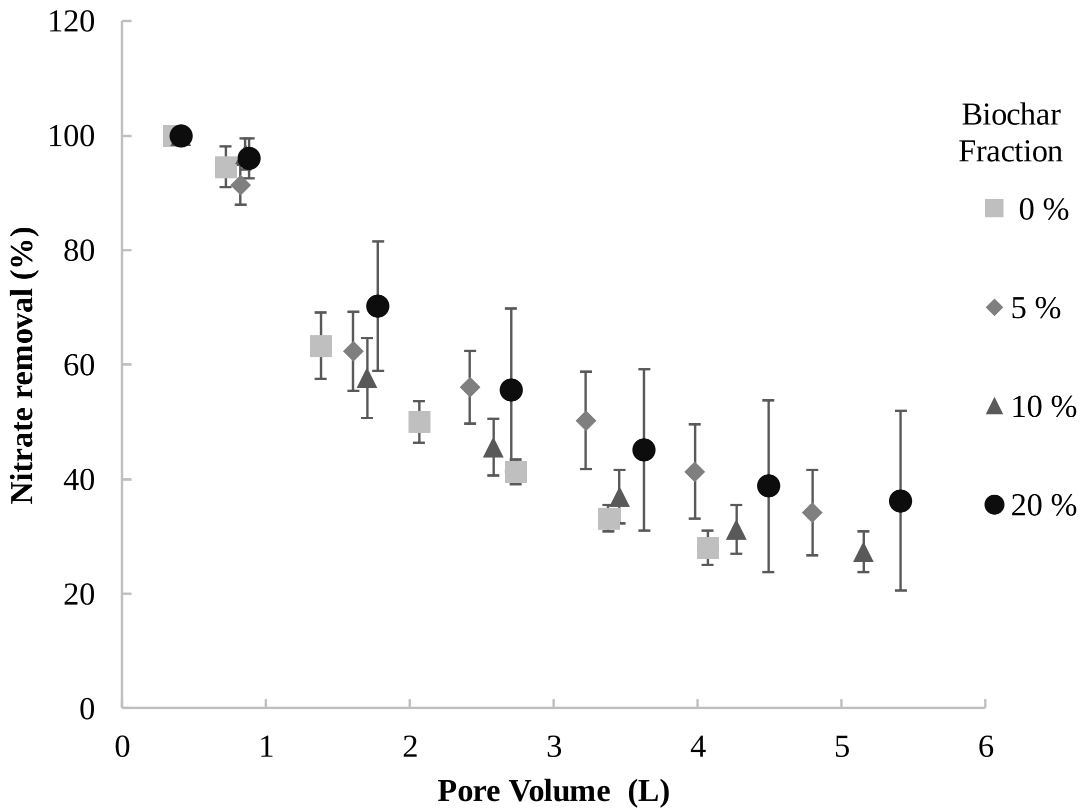


Figure 3. Effect of stormwater quantity or injected pore volume of nitrate-contaminated stormwater ([$NO_3^-$]: 24.76 mg/L) on nitrate removal. Removal percentages were averaged across same column types: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean in triplicate columns of each type.

### 3.3. Effect of rainfall intensity on nitrate removal

Nitrate removal decreased with increasing stormwater infiltration velocity or flux (Figure 4). Nitrate was completely removed (100%) in all columns at low infiltration velocity (below 3.7 cm/h). With increases in infiltration velocity, nitrate removal declined rapidly. Nitrate removal declined at a faster rate in experiment with higher flux. The addition of just 5% biochar by volume, however, improves nitrate removal rate by 8%. The slope of the linear trendline provides a quantitative estimate of exhaustion of nitrate removal capacity of biofilter with increases in injection volume of stormwater. At highest infiltration rate, 20% biochar columns have a nearly 10% improvement on exhaustion rate than woodchip-only columns.

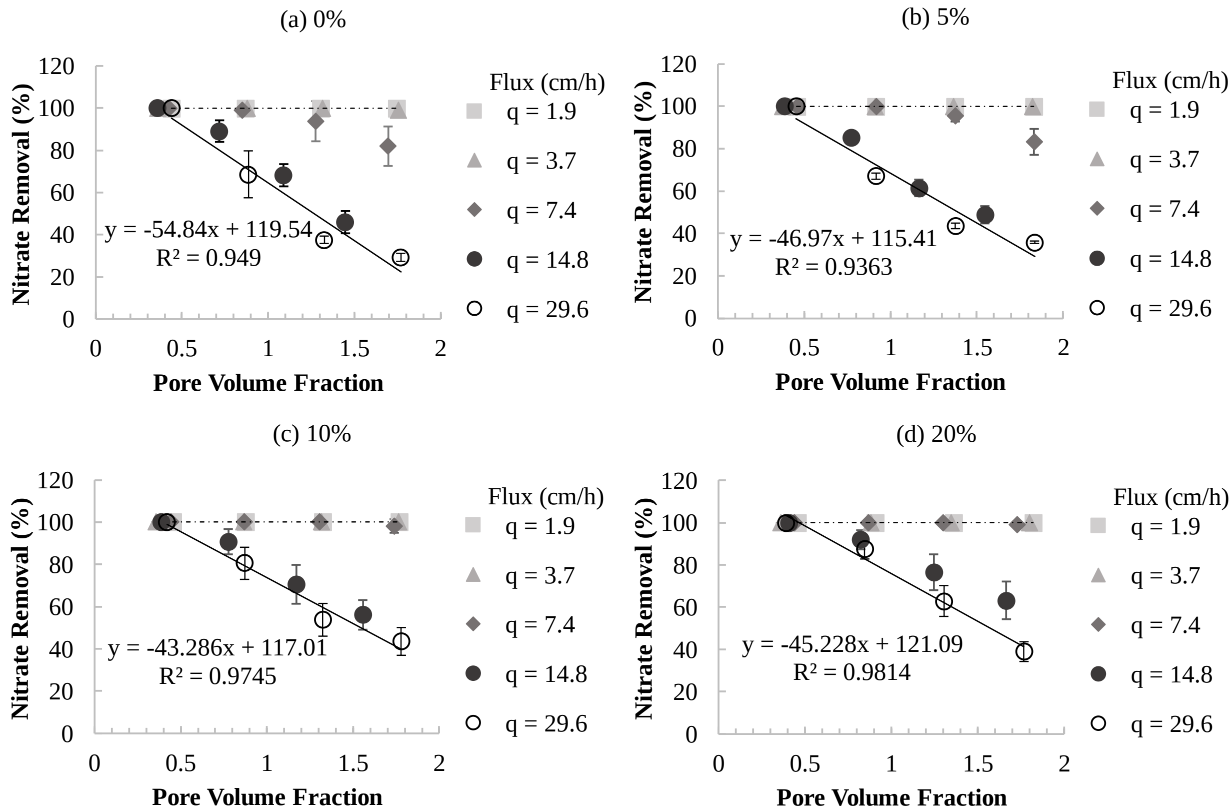


Figure 4. Effect of flux (1.9 cm/h, 3.7 cm/h, 7.4 cm/h 14.8 cm/h, and 29.6 cm/h) on nitrate removal in woodchip biofilter with different fractions of biochar: (a) 0%, (b) 5%, (c) 10%, and (d) 20% biochar by volume. Removal percentages were averaged across same types of columns: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean nitrate removal in triplicate columns of each type. Solid trendline refers to a flux of 29.6 cm/h and dashed trendline to a flux of q = 1.9 cm/h. Trendline equations for q = 1.9 cm/h not shown as nitrate was completely removed (100%) from all columns, regardless of biochar content.

Based on pore volume determined from the tracer study and stormwater application rate, HRT was estimated for all columns, and the average nitrate removal in each type of column during entire experiment was compared against HRT (Figure 5). Figure 5-a showed that nitrate removal increased with increasing HRT, but beyond a critical HRT, nitrate removal remained constant (100%). The critical HRT in this study was about 5 h. When HRT decreased to 5 h or less, nitrate removal in all columns decreased up to 58%, where the lowest removal was observed in woodchip columns at HRT 1.13 h. At lower HRT (< 5 h), nitrate removal was higher in biochar-augmented woodchips biofilter compared to woodchips only biofilter. At HRT of 10 h or higher, all columns removed 100% of nitrate.  For the same HRT, increases in biochar fraction increased nitrate removal (Figure 5-b). At HRT of 1.13 h, woodchips without biochar removed 58.90 ± 4.10% of injected nitrate; increasing biochar content to 20% increased nitrate removal to 81.90 ± 4.10%, which is a 23% increase compared to the control.

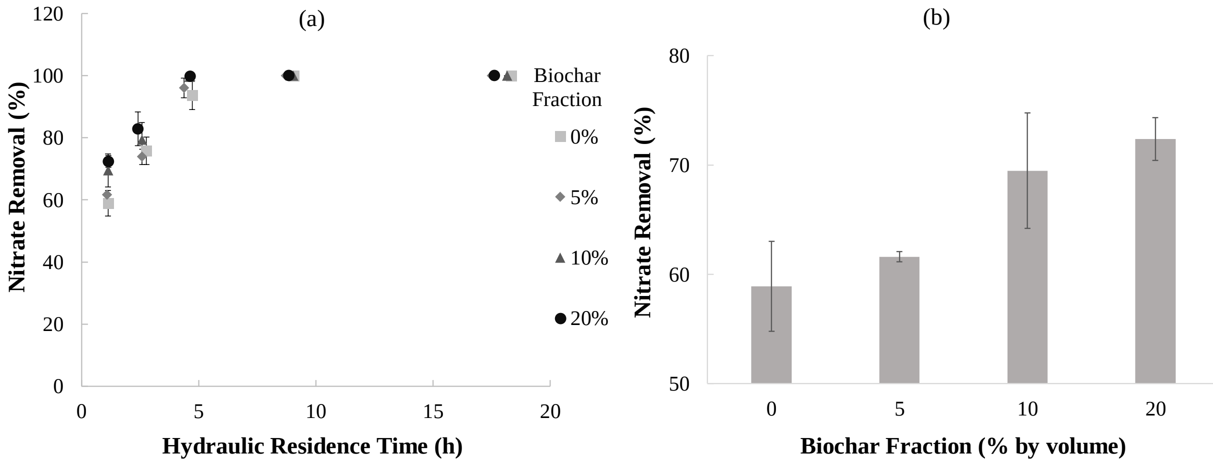


Figure 5. (a) Effect of HRT on nitrate removal (%) in columns with increasing biochar fractions by volume: 0%, 5%, 10%, and 20%; (b) Effect of biochar fraction (0%, 5%, 10%, and 20% by volume) when HRT is approximately 1 h. Removal percentages were averaged across same types of columns: 0%, 5%, 10%, and 20 % biochar. Y-axis range in (b) is from 50% to 80%.

To understand the mechanism of nitrate removal, pore water chemistry such as pH, DO, and UV absorbance (a surrogate measurement for DOC quantity and quality) were monitored during the experiment and reported in Figure 6. pH of effluents from all columns remained consistent at 7.5 ± 0.1, irrespective of HRTs or biochar fractions (Figure 6-a). In all columns, dissolved oxygen of influent stormwater decreased from 9.2 ± 0.4 mg/L (influent) to 3.3-4.9 mg/L (Figure 6-b) across all HRTs. At HRT of 1 h, DO was similar among all column types (4.6 ± 0.1 mg/L), whereas increases in HRT decreased the DO of pore water. At HRT near 5 h, only 20% biochar columns had dissolved oxygen concentrations below 4 mg/L. A further increase in HRT to 18 h did not decrease DO of pore water. DO was lower in biochar columns compared with woodchip only columns. Regardless of HRT, biochar-free woodchip columns reduced on average 51% of influent stormwater DO, while 20% biochar columns removed on average 58% of influent stormwater DO.

Increased UV absorbance (at 254 nm) was used as a surrogate measurement for DOC quantity in pore waters. At low HRT (~1 h), $UV_{254}$ absorbance of all samples from all types of columns were similar (mean: 0.67 $cm^{-1}$). As HRTs increased, only the control woodchip columns exhibited increases in $UV_{254}$ absorbance. At HRT near 5 h, higher biochar fraction columns (10 and 20% by volume) exhibited decreases in $UV_{254}$ absorbance. When HRT was nearly doubled from 9 to 18 h, $UV_{254}$ absorbance generally remained constant across all columns indicating DOC concentration depends on HRT up to a threshold value.

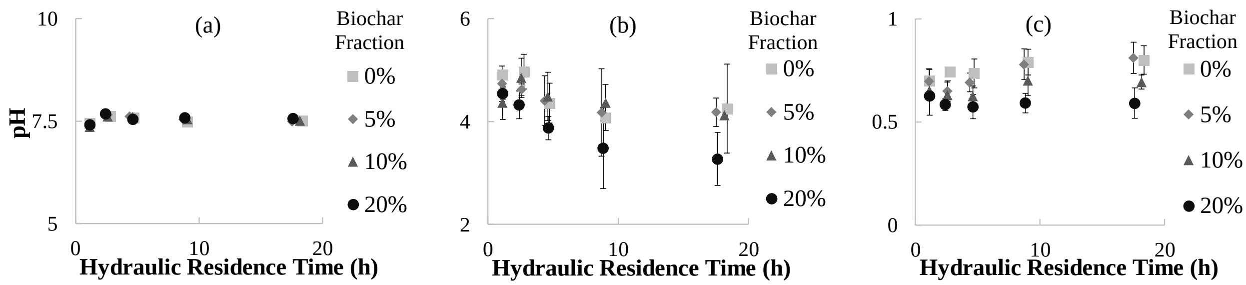


Figure 6. Effect of HRT (1.13 – 18.3 h) on water quality parameters: (a) pH, (b) dissolved oxygen (mg/L), and (c) $UV_{254}$ absorbance ($cm^{-1}$). Data is shown for five HRT experiments at the following targeted flux in cm/h: 1.9, 3.7, 7.4, 14.8, and 29.6. Parameter values were averaged across similar columns: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean parameter value in triplicate columns of each type.

### 3.4. Effect of drying duration on nitrate removal

Effluent nitrate concentration increased with increases in injected stormwater volumes. Thus, nitrate removal decreased with increases in injection volume (Figure 7). The decrease in removal was slower when the experiment was conducted after a longer drying duration. During stormwater injection, the removal fraction (%) decreased in all columns, but the rate of decrease in removal, or exhaustion rate, was a function of drying duration (indicated by the slope of the linear trendlines). Increase in drying duration decreased the exhaustion rate. For example, in woodchips only biofilter, with 1 day drying, nitrate removal decreased at a rate of 25% per injection of pore volume of applied stormwater. For 8 days drying, the nitrate removal capacity was exhausted at a rate of 13.4% per applied pore volume. The trend is similar for all other filters with different amount of biochar. This result suggests that increasing drying duration would decrease the exhaustion rate.

For clarity, the data in Figure 7 is replotted in Figure 8 to compare the decrease in nitrate removal between different types of columns (or fractions of biochar). For the same drying duration, removal capacity of biofilter was exhausted at a slower rate with increase in concentration of biochar. Increase in biochar fraction decreased the exhaustion rate. Trendlines for control woodchip columns (0% biochar) show a faster decline in nitrate removal than 20% biochar at all drying durations. For example, during the experiment after 1 day drying, the rate of nitrate removal in woodchip columns declined by 65% of its initial value with injection every pore volume of stormwater, whereas nitrate removal declined at smaller rate (43% per pore volume injection) in columns with 20% biochar. The trend is similar for all other drying durations. This result suggests that increasing biochar would decrease the exhaustion rate.

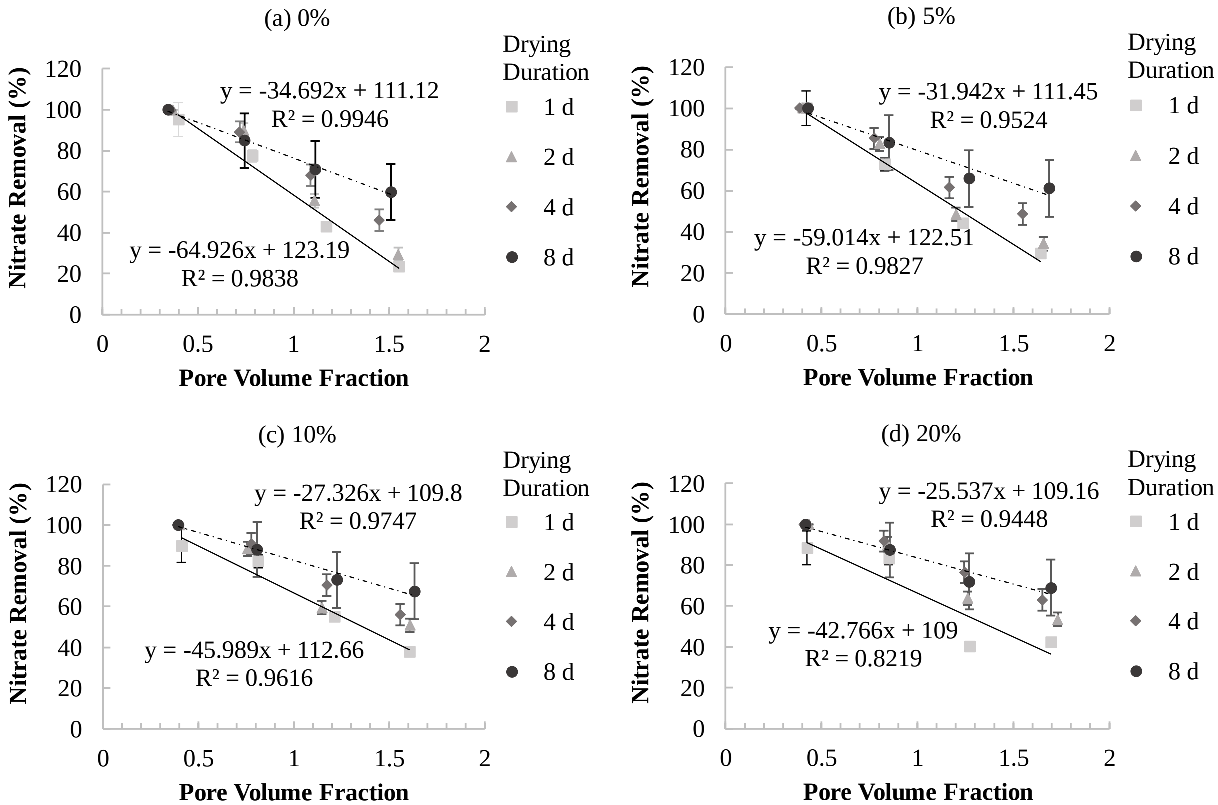


Figure 7. Effect of antecedent drying duration (1 d, 2 d, 4 d, and 8 d) on nitrate removal in woodchip biofilter with different fractions of biochar: (a) 0%, (b) 5%, (c) 10%, and (d) 20% biochar by volume. Removal percentages were averaged for columns of same configurations: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean nitrate removal in triplicate columns. Stormwater containing 20.8 ± 6.5 mg/L nitrate was injected at a flow rate of 5 mL/min (rainfall intensity of 14.8 cm/h) for a total duration of 4 h. Mean HRT among all drying duration experiments was 2.5 ± 0.3 h. Removal percentage is calculated using equation: $(1 - C/C_0) \times 100$, where $C$ is effluent concentration and $C_0$ is influent concentration. Solid linear trend line refers to 1 d drying and dashed linear trend line refers to 8 d drying.

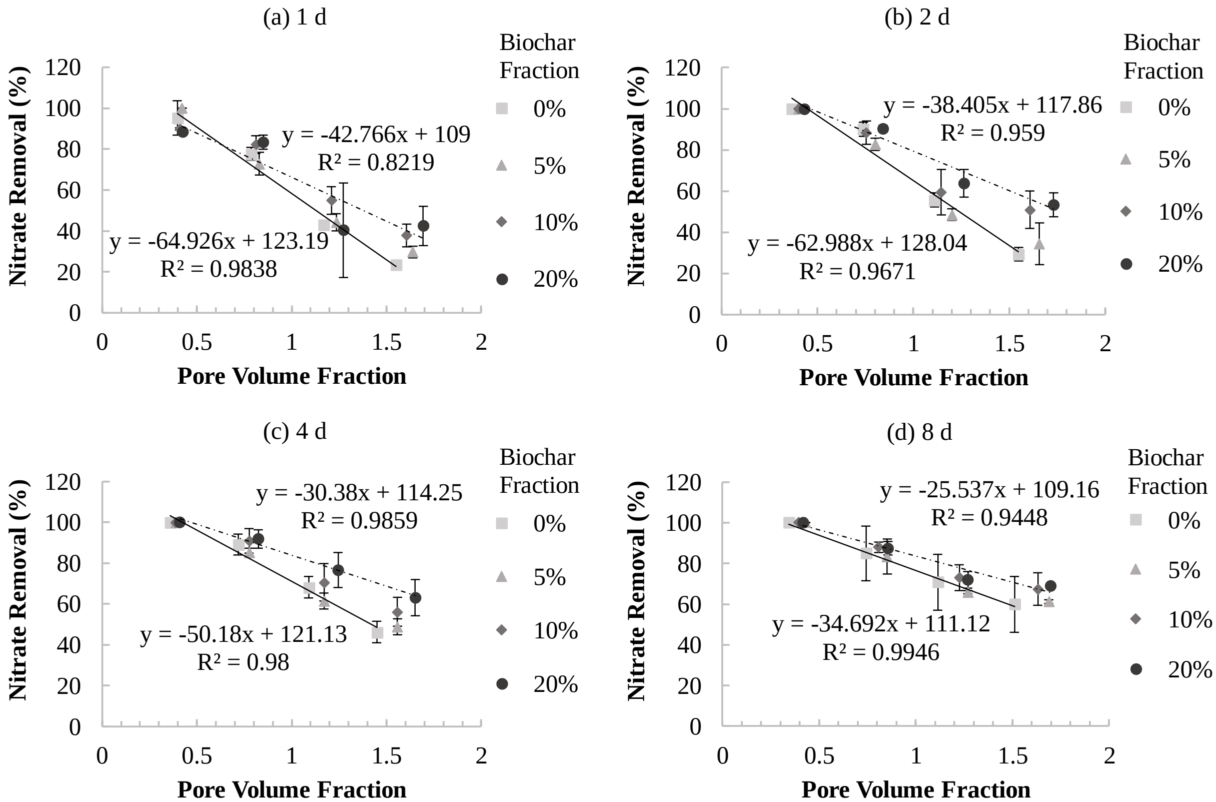


Figure 8. Effect of increasing biochar fraction by volume (0, 5, 10, and 20%) on nitrate removal (%) at different drying durations: (a) 1 d, (b) 2 d, (c) 4 d, and (d) 8 d. Data from Figure 7 is replotted here in terms of biochar fraction for clarity. Removal displayed as a function of injected pore volumes (as determined from bromide tracer test). Removal percentages are averaged across similar columns: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean nitrate removal in triplicate columns.

The results of drying duration experiments are summarized in Figure 9, which shows that increases in antecedent drying duration increased nitrate removal. Addition of biochar increased mean nitrate removal at longer drying durations (> 2 days); however, the increase in removal because of biochar addition was modest. After 1 day drying duration, control woodchip columns removed 59.9% of influent nitrate, while 20% biochar columns removed 63.7% of influent nitrate; this difference is most pronounced at 2 day drying duration (68.7% vs. 76.8%). Nitrate removal was maximized at 4 d drying duration. It appears that drying beyond 4 days had no further impact on nitrate removal.

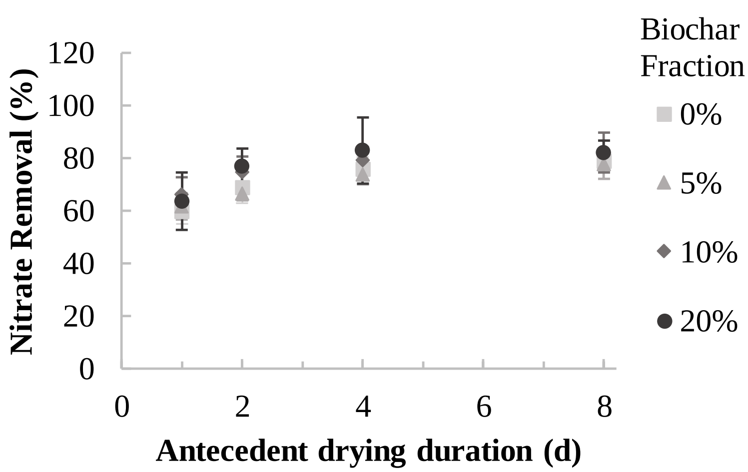


Figure 9. Effect of antecedent drying durations (1 d, 2 d, 4 d, and 8 d) on nitrate removal in woodchip biofilters with different fraction of biochar: 0%, 5%, 10%, and 20% biochar by volume. Removal percentages were averaged across columns of same type of geomedia mixture: 0%, 5%, 10%, and 20 % biochar. Error bars represent one standard deviation over mean removal in triplicate columns of each type.

Changes in pore water chemistry such as DO, pH, and DOC concentration during drying may provide clues to explain any changes in nitrate removal during a rainfall after drying or a period of no rainfall. Increase in drying duration increased the amount of DO removed from pore water. During 1 d of drying, less than 1 mg/L of DO was removed. When drying duration was increased to 4 and 8 days, most columns removed 2 mg/L of DO. Addition of biochar resulted in greater dissolved oxygen removal for 1, 2, and 4 d drying, but not for 8 d.

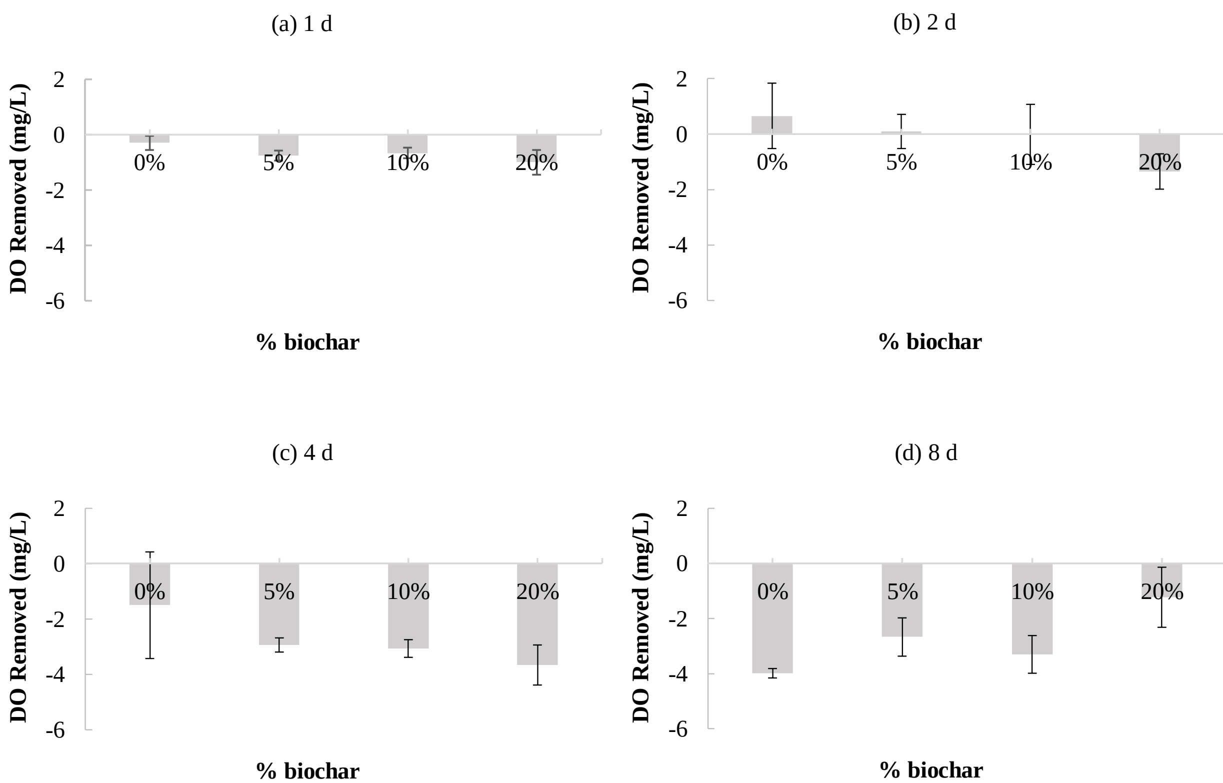


Figure 10. Effect of increasing biochar fraction by volume (0, 5, 10, and 20%) on dissolved oxygen removed in pore water during different drying periods: (a) 1 d, (b) 2 d, (c) 4 d, and (d) 8 d. DO removed during drying period was calculated based on the difference in DO of column effluents before and after drying. Error bars represent one standard deviation over mean DO removal in triplicate columns of each type.

Increasing drying duration increased $UV_{254}$ absorbance of effluents across all columns. Addition of biochar fraction did not affect UV absorbance of effluent, unless the drying duration was 8 days. In general, control woodchip columns had the highest $UV_{254}$ absorbance values.

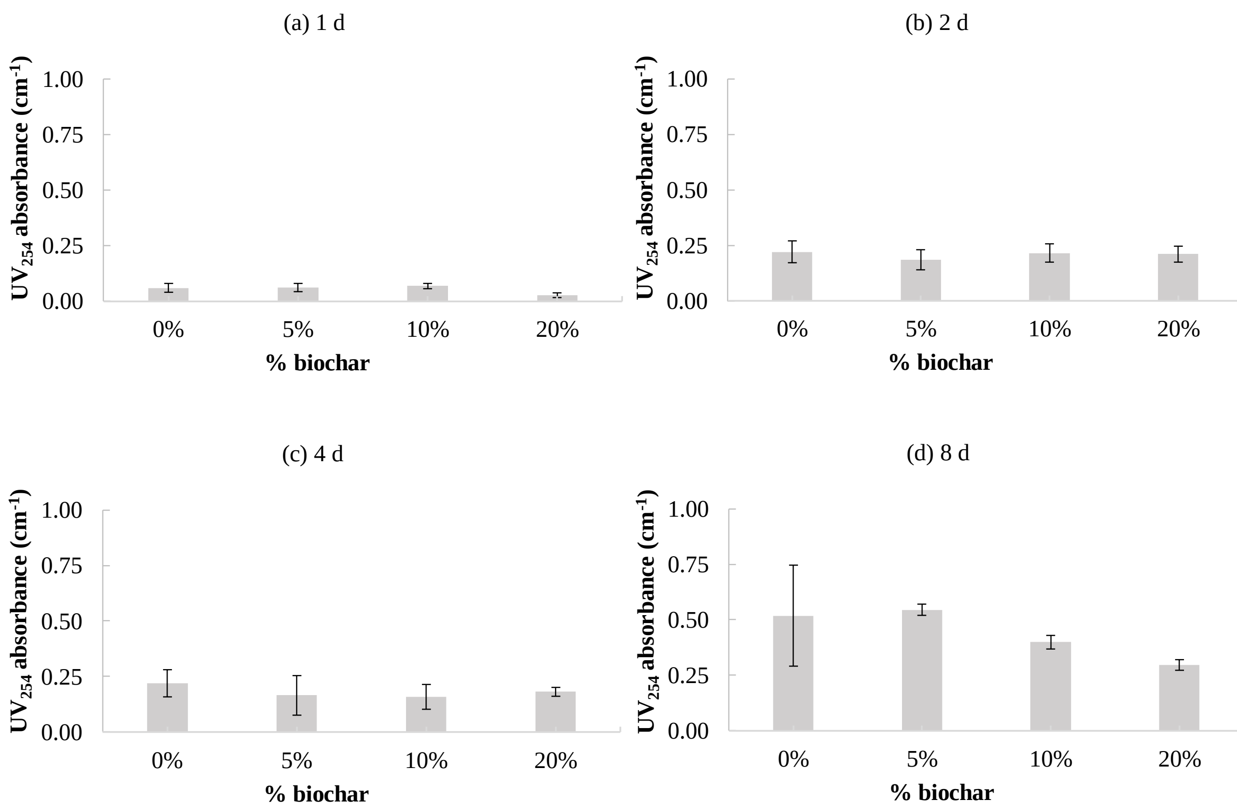


Figure 11. Effect of increasing biochar fraction by volume (0, 5, 10, and 20%) on UV absorbance at 254 nm of effluent collected in experiment after different drying durations: (a) 1 d, (b) 2 d, (c) 4 d, and (d) 8 d. The UV absorbance of samples before and after drying period was plotted against biochar fraction. Increase in UV absorbance at 254 nm is assumed to be because of DOC accumulation. Error bars represent one standard deviation over mean difference in UV absorbance of effluents before and after drying in triplicate columns of each type.

The pore water chemistry during injection of stormwater after certain duration of drying was plotted in Figure 13. The results indicate that drying had no effect on pH, but increase in drying periods decreased DO, and increased $UV_{254}$ absorbance of pore water during experiment.

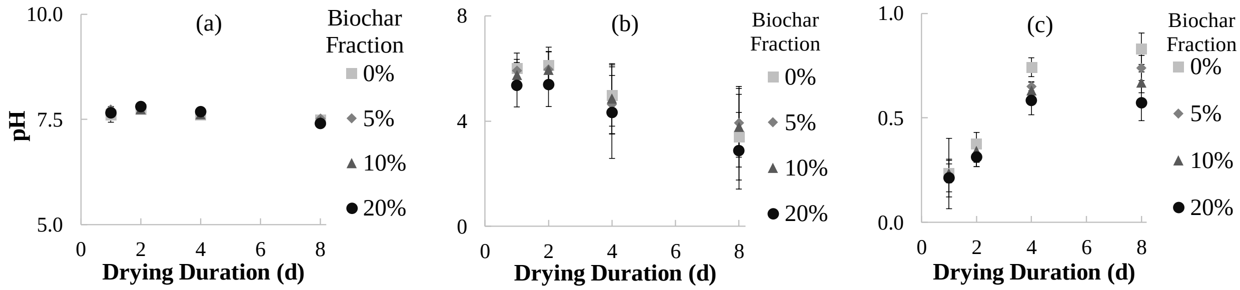


Figure 12. Effect of biochar fraction (0%, 5%, 10%, and 20%) on water quality parameters: (a) pH, (b) dissolved oxygen (mg/L), and (c) $UV_{254}$ absorbance ($cm^{-1}$) during infiltration at different drying durations (1 d, 2 d, 4 d, and 8 d). Parameter values are averaged across similar columns: Error bars represents one standard deviation over mean in triplicate columns of each type. In the graphs above, pH ranges from 5 to 10, dissolved oxygen concentration ranges from 2 to 6 mg/L, and $UV_{254}$ range from 0 to 1 $cm^{-1}$.

# 4. Discussion

## 4.1. Effect of injection pore volume on nitrate removal

Most biofilters are designed to treat precipitation or runoff of specific quantity. These design criteria such as pore volume, or cumulative pore spaces within a biofilter depend on nitrate loading rate, which depends on nitrate concentration in stormwater or stormwater volume. Pore volume estimations from bromide tracer test were used to understand the nitrate removal dynamics with respect to influent stormwater volume. Nitrate in influent stormwater was consumed by denitrifying bacteria in all columns, yet the amount of nitrate removed decreased with every pore volume of stormwater added. The removal was higher (nearly 100%) when the injection volume was less than 1 pore volume of biofilter, indicating high removal is a result of mixing of contaminated stormwater with less contaminated pore water in biofilter. Effluents during initial period contains nitrate concentrations in the pore water stored in submerged zone after antecedent dry periods (Wang et al. 2018). Effluent nitrate concentrations progressively increased due to mixing between low nitrate concentration pore water in submerged zone and high nitrate concentration influent stormwater. After injection of 4 pore volumes of stormwater, the nitrate removal appears to become steady around 30%. This result indicates that performance of biofilter where hydraulic residence time of stormwater is low (< 5 h) can be highly variable based on the volume of stormwater passed through the biofilter during a rainfall. Volume of stormwater runoff depends on rainfall intensity and catchment area that contributes to the runoff volume. Thus, biofilter size (or pore volume) should be designed accordingly based on the catchment area size and average precipitation data.

## 4.2. Effect of biochar fraction on nitrate removal

Addition of biochar to biofilters improved their nitrate removal capacity. Biochar-amended woodchip biofilters treat more stormwater than that treated by woodchip-only biofilters to achieve the same effluent concentration. This is despite the fact that mean pore volumes of biochar-amended columns were slightly smaller than pore volume of woodchip biofilters (as measured based on bromide breakthrough). Biochar could occupy the void spaces between woodchips and can decrease the porosity, similar to how it was observed in a recent study (Trifunovic et al. 2018). Thus, even though relatively more pore volumes of stormwater was injected through biochar columns compared with woodchip columns, the effluent concentration of nitrate in biochar columns was smaller than the effluent concentration of nitrate in woodchip columns. This result indicates that biochar can increase the nitrate removal capacity of woodchip biofilters. This result is similar to the results observed in other studies where biochar was used along with woodchips (Bock et al. 2015, Bock et al. 2016, Bock et al. 2018, DeBoe et al. 2017, Hassanpour et al. 2017, Ulrich et al. 2017).

Biochar can remove nitrate by either altering hydraulic properties of filter media such as woodchips or by affecting growth of bacteria that are known to assimilate nutrients. The efficiency of denitrification depends on hydraulic residence time (Nordstrom and Herbert 2017). Because the rate of biological transformation of nitrate decreases with a decrease in hydraulic retention time or storage volume, it is critical to add geomedia that can increase residence time and retain nitrate in pore water. In this study, biochar addition decreased pore volume, but increase nitrate removal, indicating pore volume changes by biochar addition could not explain the observed increase in nitrate removal. In contrast to woodchips, biochar has internal pores where nitrate can be trapped for release during rainless period. These internal pores could increase the storage volume where nitrate can be trapped and utilized by microorganisms. Furthermore, addition of biochar could increase denitrifying community due to increased attachment of bacteria on biochar, which has larger surface area than woodchips. Biochar could also change the pore water chemistry that favors denitrifying communities. In this study, DO concentration in biochar-amended columns was consistently smaller than woodchip columns, which supports the idea that biochar can help denitrifying community to strive. Furthermore, biochar could retain high concentration of DOC on its surface and within its pores and increase the kinetics of denitrification that highly depend on concentration of dissolved organic carbon (Hartz et al. 2017). In this study, the UV absorbance of effluent from biochar columns was smaller than the UV absorbance of effluents from woodchip columns, which indicates that more DOC was retained and utilized in biochar-augmented columns.  Thus, biochar should be added to woodchip biofilters to improve denitrification.

### 4.3. Effect of stormwater infiltration velocity on nitrate removal

Infiltration velocity of stormwater in a biofilter depends on the hydraulic loading rate of stormwater, which increases with an increase in rainfall intensity or catchment area. Increase in infiltration velocity decreases hydraulic residence time, which is a metric describing the amount of time a given solute (e.g. nitrate) remains within the reactor volume or pore volume. Results from this study show that an increase in HRT increased overall nitrate removal capacity of biofilters. The result is in accordance with other studies that used woodchips for denitrification (Lynn et al. 2016). In this study, a HRT above 5 h is sufficient to remove nearly 100% of applied nitrate.

The addition of biochar increased nitrate removal. The result is similar to that observed in other studies (Bock et al. 2016, Bock et al. 2018, DeBoe et al. 2017). Biochar can impede percolation of infiltrating stormwater and improve nitrate removal (Bock et al. 2015). The effect of biochar is more apparent at lower HRT (< 5 h). For example, at fast flux (29.6 cm/h), corresponding to HRT of 1 h among all columns, only biochar-fraction columns could sustain nitrate removal above 60%. At lowest flux (1.9 cm/h), biochar addition did not provide any additional benefits because nitrate was completely removed (100%) in all columns. At highest flux (29.6 cm/h), 20% biochar removes roughly 10% more nitrate than woodchip biofilters for every pore volume of stormwater added. Thus, biochar helps improve nitrate removal in one of the worst-case conditions: low HRT. This is relevant to one climate change extreme. Because of global warming, the frequency of high-intensity rainfall is expected to increase, thereby decreasing the potential nitrate removal capacity of traditional biofilters. Thus, biochar addition could alleviate this issue.

A relative high removal of nitrate by biochar-amended columns compared with woodchip columns can be attributed to an increase in storage volume and changes in water chemistry that favors denitrification. Biochar, with its network of micropores, could slow the velocity of infiltrating stormwater, increasing interaction between biofilm and nitrate. Biochar addition did not change the pH of pore water in woodchip biofilters, indicating pH did not explain the observed increase in nitrate removal by biochar-amended columns. On the other hand, DO and UV absorbance was lower in pore water from biochar-amended columns compared with pore water from woodchip columns, indicating that biochar is efficient at removing DO and trapping DOC in columns for bacterial utilization. Both conditions could explain why nitrate removal is relatively higher in biochar-amended columns.

### 4.4. Drying duration effect

Drying duration is analogous to intermittent precipitation or runoff conditions a field biofilter experiences. With climate change, the frequency of prolonged drying is expected to increase. Thus, it is important to understand how drying duration may influence denitrification. Increasing antecedent drying duration from 1 to 8 days improved nitrate removal, indicating that the drying duration is beneficial for nitrate removal. This result is similar to results observed in other studies (Lynn et al. 2015, Wang et al. 2018). The current study confirmed that antecedent drying conditions help increase concentration of pore water DOC from woodchips. Addition of biochar retained DOC leached from woodchips during drying conditions and removed nitrogen trapped inside the pores. Thus, biochar further increases the positive impact of drying duration on denitrification potential of woodchip biofilters.

Water quality parameters (pH, DO, and $UV_{254}$) during injection provide insight into pore water changes as it mixes with influent stormwater. These water quality parameters can be compared with nitrate removal at different sampling volumes, or pore volumes. For drying duration experiments, collected Ballona Creek water was basic with pH at $8.4 \pm 0.5$. All effluent samples had a pH of $7.6 \pm 0.2$, demonstrating that woodchip bioreactors, with and without biochar amendment, have the capacity to decrease pH of stormwater. Organic acids leached from submerged woodchip media provide hydrogen ions to decrease pH from basic to neutral conditions. Since nitrate removal changed, regardless of pH, it was assumed that pH had little effect on denitrification during drying duration. On the other hand, DO concentration decreased and UV absorbance of pore water increased during drying, indicating that these two parameters could help explain the effect of drying on denitrification. Increase in UV absorbance of pore water after drying suggests that an increase in drying duration caused more DOC to leach into pore water. DOC supports microbial metabolism, accelerating the growth of bacterial communities, and provides electron donors for denitrification. Increases in DOC concentration decreased the DO concentration of the pore water, permitting denitrifying community to seek out alternative electron acceptors such as nitrate for metabolic needs. The addition of biochar absorbs leached DOC during infiltration in its expansive micropore network. This is most evident at longest drying duration (8 d) and is reflected with lower DO concentrations in the highest biochar content columns (20%).

During drying, biochemical changes in pore water allow favorable water quality conditions to develop for denitrifying bacteria to consume nitrate. Denitrification is kinetically slow, needing a carbon source, neutral pH, and low DO to proceed. Stormwater has usually high concentration of dissolved oxygen, and without submerged zone, capacity for nitrate removal is minimal. A submerged zone that has sufficient drying time to drive changes in pore water and can offset conditions that impede denitrification (e.g. high DO). As stormwater is stored in filter media pore volume over greater lengths of time, oxygen is used for bacterial respiration until it is exhausted. Denitrifying bacteria thus seek alternative electron acceptors, like nitrate, when dissolved oxygen levels are low. This can only occur during a drying time sufficient enough for anoxic conditions to advance.

## 5. Conclusion

Nitrate removal capacity of woodchip biofilters amended with different fractions (by volume) of biochar was compared by applying contaminated stormwater at different flow rates and after different durations of drying at room temperature (22 °C). Higher infiltration velocity and longer drying duration is expected to provide mechanistic understanding of how nitrate removal may vary during different climate change scenarios where extreme rainfall events (high intensity rainfall) and prolonged drying are expected to be more frequent. The conclusions of this study are following:

- Increases in injected volume of stormwater decreased nitrate removal, due to exhaustion of removal capacity of biofilters.
- Addition of biochar to woodchip biofilters can improve nitrate removal capacity and make them more resilient during adverse conditions.
- Increases in rainfall intensity decreased hydraulic residence time, which consequently decreased nitrate removal.
- Addition of biochar could alleviate the impact of high intensity rainfall. If the hydraulic retention time is more than 5 h, then addition of biochar may not be necessary as woodchip biofilter is sufficient to achieve high removal capacity. Thus, biochar addition can help improve the nitrate removal in worst case conditions (low HRT).
- At high intensity rainfall, a decrease in nitrate removal is attributed to a decrease in contact time of nitrate with biofilm, increase in DO, and decrease in DOC of pore water.

- Increase in antecedent drying duration increased nitrate removal in biofilters irrespective of amount of biochar fraction.
- Longer drying duration helped deplete DO of pore water and increase the concentration of DOC in pore water; both conditions favor nitrate removal.

There are a few limitations of this current study. The drying duration or rainless period did not drain the water from columns or decreased moisture content of filter layer due to raised outlet design. The biofilters that do not have the raised outlet can become dry during prolong drying, and it can affect removal of contaminants including nitrate. Nevertheless, raised outlet is recommended for denitrification, and further study should examine the effect of extended drying (over more than few months) to examine their impact on moisture content in the submerged layer and its impact on denitrifying community. Another limitation of current study is fixed nitrate concentration. Nitrate concentration used in this study is about 20 mg/L, whereas the concentration can vary in nature. Previous studies showed that nitrate removal can vary as function of nitrate concentration in stormwater (Bock et al. 2018). Thus, nitrate removal estimated in this study may underestimate or overestimate the actual removal rate in field based on whether concentration of nitrate is higher or lower than the concentration used in this study. The column was conditioned for 2 months prior to the experiment. Thus, nitrate removal may differ if conditioning phase was longer. Finally, the biofilter in this study did not have any plants—a major sink for dissolved nitrate. Thus, nitrate removal may be much higher in field conditions where plants are present.

## 6. Appendices

List of peer-reviewed journal articles from the work:

1. Mohanty, S.K., Valenca, R., Berger, A.W., Yu, I.K.M., Xiong, X., Saunders, T.M. and Tsang, D.C.W. (2018) Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. Science of The Total Environment 625, 1644-1658.
2. Berger, A.W., Valenca, R., Ravi, S., Mohanty, S.K et al. (2018). Nitrate removal by biochar-amended woodchip biofilters: Effect of biochar fractions, antecedent drying conditions, and stormwater infiltration velocity. Water Research. (*In Preparation.*)

Conference abstract:

Berger, A. W., Valenca, R., and Mohanty, S.K (2018) Resiliency of biochar-amended woodchips-biofilter to remove nitrate from urban stormwater during climate change. 256th ACS National Meeting in Boston, MA, August 19-23, 2018. (*accepted*).

## 7. References

Abusallout, I. and Hua, G.H. (2017) Characterization of dissolved organic carbon leached from a woodchip bioreactor. Chemosphere 183, 36-43.

Addy, K., Gold, A.J., Christianson, L.E., David, M.B., Schipper, L.A. and Ratigan, N.A. (2016) Denitrifying Bioreactors for Nitrate Removal: A Meta-Analysis. Journal of Environmental Quality 45(3), 873-881.

Afrooz, A.R.M.N. and Boehm, A.B. (2017) Effects of submerged zone, media aging, and antecedent dry period on the performance of biochar-amended biofilters in removing fecal indicators and nutrients from natural stormwater. Ecological Engineering 102, 320-330.

Ambus, P. and Zechmeister-Boltenstern, S. (2007) Biology of the Nitrogen Cycle. Ferguson, S.J. and Newton, W.E. (eds), pp. 343-358, Elsevier, Amsterdam.

Bock, E., Smith, N., Rogers, M., Coleman, B., Reiter, M., Benham, B. and Easton, Z.M. (2015) Enhanced Nitrate and Phosphate Removal in a Denitrifying Bioreactor with Biochar. Journal of Environmental Quality 44(2), 605-613.

Bock, E.M., Coleman, B. and Easton, Z.M. (2016) Effect of Biochar on Nitrate Removal in a Pilot-Scale Denitrifying Bioreactor. Journal of Environmental Quality 45(3), 762-771.

Bock, E.M., Coleman, B.S. and Easton, Z.M. (2018) Performance of an under-loaded denitrifying bioreactor with biochar amendment. Journal of Environmental Management 217, 447-455.

Bruun, J., Hoffmann, C.C. and Kjaergaard, C. (2016) Nitrogen Removal in Permeable Woodchip Filters Affected by Hydraulic Loading Rate and Woodchip Ratio. Journal of Environmental Quality 45(5), 1688-1695.

Camargo, J.A. and Alonso, Á. (2006) Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environment international 32(6), 831-849.

Cameron, S.G. and Schipper, L.A. (2012) Hydraulic properties, hydraulic efficiency and nitrate removal of organic carbon media for use in denitrification beds. Ecological Engineering 41, 1-7.

Chen, X., Peltier, E., Sturm, B.S. and Young, C.B. (2013) Nitrogen removal and nitrifying and denitrifying bacteria quantification in a stormwater bioretention system. Water Res 47(4), 1691-1700.

Christianson, L., DeVallance, D., Faulkner, J. and Basden, T. (2017) Scientifically advanced woody media for improved water quality from livestock woodchip heavy-use areas. Frontiers of Environmental Science & Engineering 11(3), 2.

Cleveland, C.C., Townsend, A.R., Schimel, D.S., Fisher, H., Howarth, R.W., Hedin, L.O., Perakis, S.S., Latty, E.F., Von Fischer, J.C. and Elseroad, A. (1999) Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems. Global biogeochemical cycles 13(2), 623-645.

Council, N.R. (1995) Nitrate and nitrite in drinking water, National Academies Press.

Damaraju, S., Singh, U.K., Sreekanth, D. and Bhandari, A. (2015) Denitrification in biofilm configured horizontal flow woodchip bioreactor: effect of hydraulic retention time and biomass growth. Ecohydrology & Hydrobiology 15(1), 39-48.

DeBoe, G., Bock, E., Stephenson, K. and Easton, Z. (2017) Nutrient biofilters in the Virginia Coastal Plain: Nitrogen removal, cost, and potential adoption pathways. Journal of Soil and Water Conservation 72(2), 139-149.

Dietz, M.E. (2007) Low impact development practices: A review of current research and recommendations for future directions. Water, air, and soil pollution 186(1-4), 351-363.

Erickson, A.J., Gulliver, J.S., Arnold, W.A., Brekke, C. and Bredal, M. (2016) Abiotic Capture of Stormwater Nitrates with Granular Activated Carbon. Environmental Engineering Science 33(5), 354-363.

Fletcher, T.D., Shuster, W., Hunt, W.F., Ashley, R., Butler, D., Arthur, S., Trowsdale, S., Barraud, S., Semadeni-Davies, A. and Bertrand-Krajewski, J.-L. (2015) SUDS, LID, BMPs, WSUD and more–The evolution and application of terminology surrounding urban drainage. Urban Water Journal 12(7), 525-542.

Gold, M., Hogue, T., Pincetl, S., Mika, K. and Radavich, K. (2015) Los Angeles Sustainable Water Project: Ballona Creek Watershed (Full Report).

Gómez, M., Hontoria, E. and González-López, J. (2002) Effect of dissolved oxygen concentration on nitrate removal from groundwater using a denitrifying submerged filter. Journal of Hazardous Materials 90(3), 267-278.

Gómez, M.A., González-López, J. and Hontoria-García, E. (2000) Influence of carbon source on nitrate removal of contaminated groundwater in a denitrifying submerged filter. Journal of Hazardous Materials 80(1), 69-80.

Grießmeier, V., Bremges, A., McHardy, A.C. and Gescher, J. (2017) Investigation of different nitrogen reduction routes and their key microbial players in wood chip-driven denitrification beds. Scientific Reports 7(1), 17028.

Halaburka, B.J., LeFevre, G.H. and Luthy, R.G. (2017) Evaluation of Mechanistic Models for Nitrate Removal in Woodchip Bioreactors. Environmental Science & Technology 51(9), 5156-5164.

Hartz, T., Smith, R., Cahn, M., Bottoms, T., Bustamante, S., Tourte, L., Johnson, K. and Coletti, L. (2017) Wood chip denitrification bioreactors can reduce nitrate in tile drainage. California Agriculture 71(1), 41-47.

Hassanpour, B., Giri, S., Pluer, W.T., Steenhuis, T.S. and Geohring, L.D. (2017) Seasonal performance of denitrifying bioreactors in the Northeastern United States: Field trials. Journal of Environmental Management 202, 242-253.

Hoover, N.L., Bhandari, A., Soupir, M.L. and Moorman, T.B. (2016) Woodchip Denitrification Bioreactors: Impact of Temperature and Hydraulic Retention Time on Nitrate Removal. Journal of Environmental Quality 45(3), 803-812.

Husk, B.R., Anderson, B.C., Whalen, J.K. and Sanchez, J.S. (2017) Reducing nitrogen contamination from agricultural subsurface drainage with denitrification bioreactors and controlled drainage. Biosystems Engineering 153, 52-62.

Inglett, P.W., Reddy, K.R. and Corstanje, R. (2005) Encyclopedia of Soils in the Environment, pp. 72-78, Elsevier, Oxford.

Jiang, Y.H., Li, Y., Zhang, Y. and Zhang, X.L. (2017) Effects of HRT on the efficiency of denitrification and carbon source release in constructed wetland filled with bark. Water Science and Technology 75(12), 2908-2915.

Karunanayake, A.G., Bombuwala Dewage, N., Todd, O.A., Essandoh, M., Anderson, R., Mlsna, T. and Mlsna, D. (2016) Salicylic Acid and 4-Nitroaniline Removal from Water Using Magnetic Biochar: An Environmental and Analytical Experiment for the Undergraduate Laboratory. Journal of Chemical Education 93(11), 1935-1938.

Karunanayake, A.G., Todd, O.A., Crowley, M.L., Ricchetti, L.B., Pittman, C.U., Anderson, R. and Mlsna, T.E. (2017) Rapid removal of salicylic acid, 4-nitroaniline, benzoic acid and phthalic acid from wastewater using magnetized fast pyrolysis biochar from waste Douglas fir. Chemical Engineering Journal 319, 75-88.

Kaushal, S.S., Groffman, P.M., Band, L.E., Elliott, E.M., Shields, C.A. and Kendall, C. (2011) Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environmental Science & Technology 45(19), 8225-8232.

Kim, H., Seagren, E.A. and Davis, A.P. (2003) Engineered bioretention for removal of nitrate from stormwater runoff. Water Environment Research 75(4), 355-367.

Knapp, A.K., Hoover, D.L., Wilcox, K.R., Avolio, M.L., Koerner, S.E., La Pierre, K.J., Loik, M.E., Luo, Y., Sala, O.E. and Smith, M.D. (2015) Characterizing differences in precipitation regimes of extreme wet and dry years: implications for climate change experiments. Global change biology 21(7), 2624-2633.

Korom, S.F. (1992) Natural denitrification in the saturated zone: a review. Water resources research 28(6), 1657-1668.

Law, J., Soupir, M.L., Raman, D.R., Moorman, T. and Ong, S.K. (2018) Electrical stimulation for enhanced denitrification in woodchip bioreactors: Opportunities and challenges. Ecological Engineering 110, 38-47.

Levy, B. and Chambers, R. (1987) Bromide as a conservative tracer for soil-water studies. Hydrological Processes 1(4), 385-389.

Lopez-Ponnada, E.V., Lynn, T.J., Peterson, M., Ergas, S.J. and Mihelcic, J.R. (2017) Application of denitrifying wood chip bioreactors for management of residential non-point sources of nitrogen. Journal of Biological Engineering 11.

Lynn, T.J., Ergas, S.J. and Nachabe, M.H. (2016) Effect of Hydrodynamic Dispersion in Denitrifying Wood-Chip Stormwater Biofilters. Journal of Sustainable Water in the Built Environment 2(4).

Lynn, T.J., Yeh, D.H. and Ergas, S.J. (2015) Performance of Denitrifying Stormwater Biofilters Under Intermittent Conditions. Environmental Engineering Science 32(9), 796-805.

Miles, T.R., Rasmussen, E.M. and Gray, M. (2016) Agricultural and Environmental Applications of Biochar: Advances and Barriers. Guo, M., He, Z. and Uchimiya, S.M. (eds), pp. 341-376, Soil Science Society of America, Inc., Madison, WI.

Mohanty, S.K., Cantrell, K.B., Nelson, K.L. and Boehm, A.B. (2014) Efficacy of biochar to remove *Escherichia coli* from stormwater under steady and intermittent flow. Water Research 61, 288-296.

Mohanty, S.K., Valenca, R., Berger, A.W., Yu, I.K.M., Xiong, X., Saunders, T.M. and Tsang, D.C.W. (2018) Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. Science of the Total Environment 625, 1644-1658.

Nordstrom, A. and Herbert, R.B. (2017) Denitrification in a low-temperature bioreactor system at two different hydraulic residence times: laboratory column studies. Environmental Technology 38(11), 1362-1375.

Puckett, L.J. (1994) Nonpoint and point sources of nitrogen in major watersheds of the United States, US Geological Survey.

Robertson, W.D. (2010) Nitrate removal rates in woodchip media of varying age. Ecological Engineering 36(11), 1581-1587.

Schipper, L.A., Robertson, W.D., Gold, A.J., Jaynes, D.B. and Cameron, S.C. (2010) Denitrifying bioreactors—an approach for reducing nitrate loads to receiving waters. Ecological Engineering 36(11), 1532-1543.

Silva, S., Ging, P., Lee, R., Ebbert, J., Tesoriero, A. and Inkpen, E. (2002) Forensic applications of nitrogen and oxygen isotopes in tracing nitrate sources in urban environments. Environmental Forensics 3(2), 125-130.

Subramaniam, D., Mather, P., Russell, S. and Rajapakse, J. (2016) Dynamics of Nitrate-Nitrogen Removal in Experimental Stormwater Biofilters under Intermittent Wetting and Drying. Journal of Environmental Engineering 142(3).

Trifunovic, B., Gonzales, H.B., Ravi, S., Sharratt, B.S. and Mohanty, S.K. (2018) Dynamic effects of biochar concentration and particle size on hydraulic properties of sand. Land Degradation & Development.

Ulrich, B.A., Loehnert, M. and Higgins, C.P. (2017) Improved contaminant removal in vegetated stormwater biofilters amended with biochar. Environmental Science-Water Research & Technology 3(4), 726-734.

Vesely, W.C., Callahan, T.J. and Vulava, V.M. (2016) Using Dissolved Organic Carbon Concentration and Character Data to Assess Land Use Change Effects on Coastal Waters.

Wan, Z., Li, T. and Shi, Z. (2017) A layered bioretention system for inhibiting nitrate and organic matters leaching. Ecological Engineering 107, 233-238.

Wang, C., Wang, F., Qin, H., Zeng, X., Li, X. and Yu, S.-L. (2018) Effect of Saturated Zone on Nitrogen Removal Processes in Stormwater Bioretention Systems. Water 10(2), 162.

Wei, D.B., Singh, R.P., Liu, J.W. and Fu, D.F. (2017) Effect of alternate dry-wet patterns on the performance of bioretention units for nitrogen removal. Desalination and Water Treatment 59, 295-303.

Whitehead, P., Wilby, R., Battarbee, R., Kernan, M. and Wade, A.J. (2009) A review of the potential impacts of climate change on surface water quality. Hydrological Sciences Journal 54(1), 101-123.

Wilde, F.D. and Radtke, D.B. (1998) Handbooks for Water-resources Investigations: National field manual for the collection of water-quality data. Field measurements, US Department of the Interior, US Geological Survey.