ASSESSMENT OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) FILTRATION METHODS FOR USE IN RURAL COMMUNITIES

by

BAILEY WILLIAMS

(Under the Direction of Gary Hawkins)

ABSTRACT

Treated wastewater effluent containing PFAS can be applied using a land application system (LAS) and may contaminate local lands or surface waters. There is minimal information about the efficacy of buffer zone soils surrounding land application systems to remove or retain PFAS. Therefore, research was conducted in a buffer zone plot study to compare influent and effluent concentrations of six PFAS chemicals (PFOS, PFOA, PFNA, PFBS, PFHxS, and 6:2 FTS) after passing through buffer zone plots. To mitigate PFAS concentrations in precipitation induced runoff from a LAS, a second study was conducted to assess percent removal of six PFAS after passing through a bioretention media mix column containing mixtures of Tifton loamy sand soil and pine sawdust.

Overall, concentrations of PFAS in the effluent were reduced after passing through buffer zone soils and bioretention media mixes. Results suggest that long-chain PFAS had higher removal rates than short-chain PFAS.

INDEX WORDS: Per- and polyfluoroalkyl substances, land application system, bioretention media mixes

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INTRODUCTION

The production of per- and polyfluoroalkyl substances (PFAS) also known as “forever chemicals” leads to the conundrum of PFAS removal from the environment. PFAS remediation is difficult and expensive because these chemicals are widespread and do not break down easily due to their resistance to heat, water, and corrosion. PFAS make their way into public water sources through manufacturing processes, wastewater treatment operations, and firefighting foams (Gaines, 2022; Prevedouros, et al., 2006). Municipal and industrial wastes containing PFAS are treated by public wastewater treatment facilities that do not have technology effective in filtering out or treating PFAS (Tavasoli, et al., 2021; Liu, et al., 2022; Belkouteb, et al., 2020). Land application of municipal biosolids and wastewater treatment facility effluent has been used as a soil amendment or as a tertiary treatment of wastewater in rural areas and can contain PFAS (Kim, et al., 2022). Buffer zones surrounding land application systems are required between the application area and adjacent water bodies (GEPD, 2019), but the effectiveness of their ability to retard or remove PFAS has not been studied extensively.

This two-part project compared influent and effluent concentrations of PFAS after passing through land-application system buffer zones and quantifies the amount of PFAS removal from water flowing through bioretention media mixes composed of Tifton Loamy Sand soil and sawdust. The PFAS used in these studies contained a mixture of six PFAS chemicals commonly found in wastewater treatment facility effluent and biosolids (Desgens-Martin, et al., 2023; Kim, et al., 2022; Letcher, et al. 2020; Thompson, et al., 2022). The PFAS used in this study were perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorobutane sulfonic acid

(PFBS), Perfluorohexane sulfonic acid (PFHxS), perfluorononanoic acid (PFNA), and 6:2 fluorotelomer sulfonate (6:2 FTS). The objective of this project was to assess naturally occurring and low-technology filtration methods that could be used in rural communities for removing PFAS in precipitation induced runoff and subsurface flow from land application systems.

CHAPTER 1

LITERATURE REVIEW

Per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds also known as "forever chemicals" that do not break down easily (Moyer, 2021). PFAS were originally produced in the late 1930s by the chemical company DuPont who discovered polytetrafluoroethylene (PTFE) while trying to manufacture new fluorinated refrigerants (Ebnesajjad, 2017). The reaction of tetrafluoroethylene (TFE) with hydrochloric acid (HCl) inside gas cylinders produced PTFE, or its brand name Teflon, which is resistant to heat, water, and corrosion (Ebnesajjad, 2017). The production of PTFE sparked the age of PFAS production, and thousands of PFAS have now been produced.

The ubiquity of PFAS in the environment can be attributed to manufacturing processes, wastewater treatment operations, and aqueous film forming foams (AFFF) (Gaines, 2022; Prevedouros, et al., 2006; Voulgaropoulos, 2022). Thousands of PFAS have been manufactured over the past 70 years for a wide range of uses in the industrial and governmental sectors as a water repellant, fire suppressant, and in materials such as nonstick cookware, carpets, clothing, cleaning solutions, and other similar uses (Gaines, 2022; Prevedouros, et al., 2006; USEPA, 2023c). The manufacturing of these products can create PFAS-laden waste. Industrial waste effluent, home waste effluent, and some city stormwater are treated by wastewater treatment plants (WWTPs) that may not have the technology to filter and remove PFAS (Link, et al., 2023; Voulgaropoulos, 2022). Biosolids, liquid effluent, and sewage sludge created by WWTPs may be recycled using a land application system (LAS). Additionally, PFAS make their way into the environment through the application of aqueous film forming foams (AFFF) as fire suppressants by military bases and firefighters during training exercises or when putting out active fires (Gaines, 2022). The PFAS in AFFF can make their way into groundwater and surface water surrounding sprayed sites causing non-point source pollution (Backe, et al., 2013; Prevedouros, et al., 2006). Exact formulations of AFFF are proprietary and specific to each producer, but testing has proved at least ten different PFAS in seven military certified AFFF compounds (Place & Field, 2012). PFAS mobility in the environment has been exacerbated by municipal, industrial, and governmental practices which has caused public apprehension. Information about PFAS toxicity and environmental impact is becoming more available from state and national entities (GEPD, 2023b; USEPA, 2023b).

The Environmental Protection Agency (EPA) proposed acceptable Maximum Contaminant Levels (MCLs) and Health Based Water Concentrations (HBWCs) in drinking water for six PFAS in the summer of 2023 to address and mitigate the risks associated with PFAS contamination (USEPA, 2023c). The MCLs for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are 4.0 parts per trillion and will require public water systems to monitor PFAS levels, notify the public of PFAS levels, and remediate if they exceed these MCLs (USEPA, 2023c). The other four PFAS under this rule, perfluorononanoic acid (PFNA), Perfluorohexane sulfonic acid (PFHxS), perfluorobutane sulfonic acid (PFBS), and HFPO-DA (GenX), will adhere to HBWCs that determine the level below which no health effects are estimated (USEPA, 2023c). This new rule will affect wastewater treatment due to levels of PFAS higher than proposed limits found in wastewater treatment facilities (Pan, et al., 2016; Wang, et al., 2022). The removal processes of PFAS can be lengthy, costly, and hard to scale-up to the wastewater treatment level (Ghaznavi, et al., 2023; Drenning, et al., 2023). Many public wastewater treatment plants do not have the technology to effectively reduce or remove PFAS to these new EPA MCLs and HBWC levels (Fredriksson, et al., 2022; Huset, et al., 2008; Voulgaropoulos, 2022; Link, et al., 2023; Pan, et al., 2016; Mojiri, et al., 2023). As a result, PFAS continue to be a significant pollutant in our source water systems requiring more research and effective solutions to prevent further contamination.

Physiochemical Properties of PFAS

PFAS physiochemical properties are unique to each compound but have common characteristics that make their treatment and removal challenging (Drenning, et al., 2023). PFAS with a chain length of seven or more carbon-fluorine (C-F) bonds are called long-chain PFAS; short-chain PFAS have six or less C-F bonds (CLU-IN, 2023; ITRC, 2022b). The high electronegativity of carbon-fluorine bonds in PFAS makes them the strongest bonds in organic chemistry requiring a high activation energy for breakage (Zhang, et al., 2021b). High electronegativity causes the polar bond to exhibit partial negative charges towards fluorine resulting in PFAS with carboxylic or sulfonic acid groups, also called functional groups, to be acidic (ITRC, 2022a; Leung, et al., 2023). The functional groups may also behave differently; sulfonate functional groups are more hydrophobic than carboxylate functional groups possibly due to their larger size (Higgins & Luthy, 2006). PFAS are amphiphilic because of their hydrophilic heads and hydrophobic tails leading to their surfactant nature (Lei, et al., 2023; ITRC, 2022a). This phenomenon causes PFAS to accumulate at air-water interfaces which can impact PFAS adsorption onto surfaces like soil (Buckley, et al., 2023; Yuan, et al., 2023; Luft, et al., 2022). The chain length also affects adsorption or desorption; shorter chains partition to water and longer chains partition to the soil solid phase because increasing chain length increases lipophilicity (Huang, et al., 2023; Seo, et al., 2019; Gagliano, et al., 2020). PFAS can exist as nonionic, anionic, cationic, or zwitterionic molecules depending on the chain-length and functional group (ITRC, 2022a; Backe, et al., 2013; Lei, et al., 2023). However, PFAS typically exist as anionic in wastewater (ITRC, 2022a; Backe, et al., 2013; Lei, et al., 2023).

PFAS behavior and adsorption rates are dependent on the temperature and pH of the system they are present in along with their ionic state (ATSDR, 2021; Frazar, et al., 2022; Hamid, et al., 2018; Higgins & Luthy, 2006). Within a soil system, the movement and retention rates of PFAS are influenced by the clay content of the soil because of PFAS attraction to mineral surfaces (Abou-Khalil, et al., 2023; Sima & Jaffé, 2021; Gagliano, et al., 2020). The charge and chain-length of the PFAS will determine how attracted a PFAS chemical is to a negatively charged clay particle (Abou-Khalil, et al., 2023; Sima & Jaffé, 2021; Gagliano, et al., 2020). Sorption capacity of PFAS can also be impacted by increasing the pH of the system (Abou-Khalil, et al., 2023; Sima & Jaffé, 2021; Higgins & Luthy, 2006). When PFAS are anionic, an environment with a higher pH will cause less absorption possibly due to positively charged calcium ions interacting with negatively charged media (Tülp, et al,, 2009; Higgins & Luthy, 2006). However, soil pH and clay content have less impact on PFAS adsorption and bioavailability compared to dissolved organic matter (DOM), total organic carbon (TOC), or soil organic matter (SOM) (Wen, et al., 2015; Wellmitz, et al., 2023; Sima & Jaffé, 2021). Carbon based materials have non-polar functional groups that facilitate sorption of hydrophobic PFAS with ease, but organic matter can compete with PFAS for adsorption sites onto clay particles present in soil (Qi, et al., 2022; Wen, et al., 2015; Sima & Jaffé, 2021; Bolan, et al., 2021).

To determine how a chemical will react in the environment, the acid dissociation constant (pK_a), organic carbon partition coefficient ($\log K_{oc}$), and octanol-water partition coefficient ($\log K_{ow}$) can be used. The acid dissociation constant (pK_a) is a measure of how strong an acid is in a solution and how it will dissociate in water (ACD Labs, 2023). The acid dissociation constant scale ranges from -10 to 50 (dimensionless) where a smaller pK_a value represents a stronger acid and greater dissociation in a solution at any pH (Concawe, 2016; ATSDR, 2021). PFAS with lower pK_a values tend to be anionic in wastewater whereas PFAS with higher pK_a values tend to have a neutral charge (Lei, et al., 2023). The organic carbon partition coefficient (log K_{oc}) is a measure of the ability of a water-based substance to adsorb to organic carbon; it ranges from -1 – 10 (dimensionless) where a higher log K_{oc} of a substance is correlated to higher adsorption to organic carbon (Dalahmeh, et al., 2018). For example, phenol has a log K_{oc} of 1.32 and Dichlorodiphenyltrichloroethane (DDT) has a log K_{oc} of 5.63 because DDT has a high affinity for organic carbon (OECD, 2001). Log K_{oc} is directly affected by the fraction of organic carbon (f_{oc}) in the soil and increases as a function of PFAS chain length (Connell, et al., 1997; Liu & Lee, 2007; Brusseau, 2023). The octanol-water partition coefficient (log K_{ow}) indicates how a chemical will partition to soil or living organisms and is inversely related to water solubility (Connell, et al., 1997; OECD, 2022). Log K_{ow} values generally have the same range as log K_{oc} values; substances with high K_{ow} tend to adsorb to organic material and accumulate in biota but have difficulty dissociating in water (Connell, et al., 1997; Dalahmeh, et al., 2018). Measuring log K_{ow} for PFAS is difficult because PFAS tend to separate into multiple layers in an octanol-water mixture due to PFAS functional groups or charge, and calculated values may not accurately predict PFAS sorption (Brooke, et al., 2004; OECD, 2002; Prevedouros, et al., 2006; Concawe, 2016). A compilation of physiochemical characteristics for the PFAS used in this study are listed in Table 1.1.

Perfluorooctane sulfonate (PFOS)

Perfluorooctane sulfonate, also called perfluorooctanesulfonic acid (PFOS), is comprised of a carbon chain with eight carbon-fluorine bonds and a sulfonic acid functional group attached (Table 1.1) (ATSDR, 2021). PFOS occurs in its potassium salt form most frequently but has 89

Table 1.1 PFAS Physiochemical Characteristics

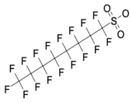
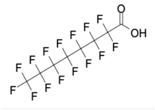
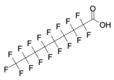
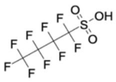
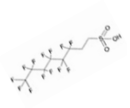
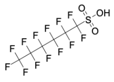
Characteristic	**Information**					
Chemical name	Perfluorooctanesulfonic acid (PFOS)	Perfluorooctanoic acid (PFOA)	Perfluoronona-noic acid (PFNA)	Perfluorobutane sulfonic acid (PFBS)	6:2 Fluorotelomer sulfonate (6:2 FTS)	Perfluorohexane-sulphonic acid (PFHxS)
Chemical Abstracts Service (CAS) number	1763-21-1	335-67-1	375-95-1	375-73-5	27619-97-2	355-46-4
Chemical formula	$C_8HF_{17}O_3S$	$C_8HF_{15}O_2$	$C_9HF_{17}O_2$	$C_4HF_9O_3S$	$C_8H_5F_{13}O_3S$	$C_6HF_{13}O_3S$
Chemical structure						
Water solubility	910 mg/L at 25 °C in pure water [6] 519 mg/L at 20±0.5°C in pure water [7] 680 mg/L at 24-25°C in pure water [7] 370 mg/L in freshwater [8] 25 mg/L in filtered sea water [8]	3300 mg/L at 25 °C in pure water [6]	9500 mg/L at 20-25°C in water [9]	510 mg/L in water (temperature unspecified) [12]	1300 mg/L at 20-25°C in water [9]	
Organic carbon partition coefficient (Log K_{oc})	2.57 ± 0.13 [5]	2.11 [5]	2.50 ± 0.12 [5]	1.0 [9]		1.78 [9]
Octanol-water partition coefficient (Log K_{ow})	6.3 [9] 4.13 [6]	5.3 [9] 6.3 [6]	5.92 [9]	3.9 [9]	4.44 [9]	5.17 [9]
pKa (calculated)	-3.27 [2]	-0.5 [10]	-0.21 [11]	-3.31 [11]	1.31 [9]	0.14 [11]
Half-Life	In Humans: 3.3-27 years [1] Atmospheric: 114 days [4] Water: > 41 years (at 25 °C) [4]	In Humans: 2.1-10.1 years [1] Atmospheric: 90 days [4] Water: > 92 years (at 25 °C) [4]	In Humans: 2.5-4.3 years [1]	In Humans: 665 hours [1]		In Humans: 4.7-35 years [1]

Table footnote. [1] (ATSDR, 2021), [2] (Brooke, et al., 2004) [3] (USEPA, 2017), [4] (USEPA, 2014), [5] (Higgins & Luthy, 2006), [6] (Inoue, et al., 2012) [7] (3M Company, 2003) [8] (OECD, 2002) [9] (Wang, et al., 2011) [10] (Goss, 2008) [11] (National Center for Biotechnology Information, 2023) [12] (Rahman, et al., 2014) possible isomers (Rayne, et al., 2008). The precursor to PFOS, perfluorooctanesulfonyl fluoride (POSF), is formed in an electrochemical fluorination (ECF) cell where an electric current passes through a mixture of octanesulfonyl fluoride and hydrofluoric acid and the carbon-hydrogen bonds are substituted with carbon-fluorine bonds (OECD, 2002). Then, base-catalyzed hydrolysis of POSF produces PFOS and other byproducts called "PFOS equivalents" (Benskin, et al., 2010; Lindstrom, et al., 2011). PFOS was originally the main component in Scotchgard, a stain and water repellant produced by the 3M company but has since been phased out of production beginning in the early 2000s (Lindstrom, et al., 2011).

The physiochemical characteristics of PFOS reflect the recalcitrant nature of the C-F bond in all PFAS. The solubility of PFOS in water is dependent on the temperature and quality of the water; PFOS has higher solubility in pure water with no organic material than freshwater or seawater and has increasing solubility with increasing water temperature (OECD, 2002). The log K_{oc} of PFOS is measured at 2.57 meaning PFOS is attracted to organic carbon (Higgins & Luthy, 2006). The log K_{ow} for PFOS is measured to be 6.3 by Wang, et al. (2011) and calculated to be 4.13 by Inoue, et al. (2012). Increasing log K_{oc} and log K_{ow} correlate to an increased half-life hence the extended half-life of PFOS in humans at 3.3-27 years, in the atmosphere at 114 days, and more than 41 years in water because PFAS will attach to organic particles and not break down (ATSDR, 2021; USEPA, 2014; Connell, et al., 1997). The pKa of PFOS is calculated to be -3.27 and demonstrates that PFOS is a strong acid that readily gives up protons to dissociate into its anionic form in the environment (Brooke, et al., 2004; Concawe, 2016). Many PFAS physiochemical characteristics follow similar trends to PFOS.

Perfluorooctanoic acid (PFOA)

Perfluorooctanoic acid (PFOA) consists of eight carbon-fluorine bonds and is a fully fluorinated organic acid with a carboxylate functional group attached (Table 1.1) (ITRC, 2022b; USEPA, 2002). The 3M Company was the largest producer of PFOA in 1999 and used either Simons electrochemical fluorination process or telomerization to manufacture PFOA (USEPA, 2002). The electrochemical fluorination cell produces perfluorooctanoyl fluoride (PFOF) which is acidified and eventually produces PFOA (USEPA, 2002). PFOA salts are produced when the free acid is base neutralized (USEPA, 2002). Most studies concerning PFOA use the ammonium salt form for toxicology reports because its production leads to the anionic form found in the environment, but its free acid form has more physiochemical data available (USEPA, 2002; ITRC, 2022b). PFOA and PFOS have been called "legacy" PFAS because they are still prevalent in the environment even though they are not used in manufacturing anymore (Dickman & Aga, 2022).

PFOA physiochemical characteristics are comparable to PFOS, but differences can be attributed to variable testing conditions and methods of calculation. The water solubility of PFOA is 3300 mg/L at 25 °C in pure water with no organic material (Inoue, et al., 2012). PFOA log K_{oc} is 2.11 (Higgins & Luthy, 2006). The log K_{ow} is measured to be 5.3 by Wang, et al. (2011) and calculated to be 6.3 by Inoue, et al. (2012). The pK_a is calculated to be -0.5 which makes PFOA a strong acid (Goss, 2008). The half-life is estimated to be between 2.1 and 10.1 years in humans by ATSDR (2021), 90 days in the atmosphere, and greater than 92 years in water by USEPA (2014).

Perfluorononanoic acid (PFNA)

Perfluorononanoic acid (PFNA) is a long-chain PFAS consisting of nine carbon-fluorine bonds making it a perfluorinated carboxylic acid (Table 1.1) (Wishart, et al., 2015). The majority of PFNA produced is in an ammonium salt form that dissociates in water to less harmful compounds but can be present in a persistent anionic form in drinking water at pH range 6.5-8.5 (Rayne & Forest, 2010; Goss, 2008). The phase out of long-chain PFAS have caused PFOS concentrations in the environment to decrease and PFOA concentrations to remain unchanged in people living in the United States, whereas PFNA concentrations were increasing from 1999-2008 in both (Kato, et al., 2011). This phase out is part of a voluntary stewardship program between the USEPA and PFAS manufacturing companies, although not all companies in the U.S. participate in this program (Lindstrom, et al., 2011; Gleason, et al., 2015). PFNA levels could have been increasing during 1999-2008 because an estimated 60% of PFNA produced between 1975 and 2004 was released into the environment globally during manufacturing and processing of fluoropolymers (Prevedouros, et al., 2006; Gleason, et al., 2015; Hamid, et al., 2018). Conversely, when exposure to PFNA ceased, concentrations of PFNA decreased in humans over a three-year period because the half-life of PFNA is reported to be 2.5-4.3 years in humans (Yu, et al., 2021; ATSDR, 2021). Although the majority of manufacturing could be overseas now, long-range transportation of PFNA occurs by the ocean's current and through atmospheric deposition, and humans could be inadvertently exposed (Lau, et al., 2007; Butt, et al., 2010).

PFNA's physiochemical characteristics are most similar to PFOA, but its water solubility value was calculated much higher at 9500 mg/L in 20-25 °C water (Wang, et al., 2011). The log K_{oc} is 2.5 (Higgins & Luthy, 2006). The log K_{ow} is measured to be 5.92 (Wang, et al., 2011). The pK_a is calculated to be -0.21 (National Center for Biotechnology Information, 2023). The half-life is estimated to be between 2.5 and 4.3 years in humans (ATSDR, 2021).

6:2 fluorotelomer sulfonate (6:2 FTS)

6:2 fluorotelomer sulfonate (6:2 FTS) is a polyfluorinated compound composed of six carbon-fluorine bonds and two non-fluorinated carbon atoms (Table 1.1) (NASF, 2019). It is an ingredient in AFFF with uses in the chromium plating industry; it has been introduced as an alternative to PFOS but has shown deleterious effects in humans and animals (Duan, et al., 2023; Gomis, et al., 2018; Yang, et al., 2023). However, 6:2 FTS has been found to be eliminated from the body faster than PFOS and is not considered to have bioaccumulative properties (Chang, et al., 2012; Arnot & Gobas, 2006). Though less likely to accumulate in the human body, short chain PFAS such as 6:2 FTS have higher persistence in the environment in anaerobic conditions than aerobic conditions where they will break down easier (NASF, 2019; Kim, et al., 2022; Zhang, et al., 2016).

The physiochemical properties of 6:2 FTS compared to other PFAS are not well-documented, and the limited information available consists mostly of calculated values rather than observed data. The values available are pKa and K_{ow} which were calculated to be 1.31 and 4.44, respectively (Wang, et al., 2011). A pKa of 1.31 indicates a relatively lower tendency to release its protons compared to PFOS, and a log K_{ow} value of 4.44 indicates a greater potential for bioaccumulation (Wang, et al., 2011; Sangster, 1997). Its water solubility is documented to be 1300 mg/L in 20-25 °C water (Wang, et al., 2011).

Perfluorobutane sulfonic acid (PFBS)

Perfluorobutane sulfonic acid (PFBS) is a short-chain PFAS consisting of four carbon-fluorine bonds and has been introduced as a replacement for PFOS (Table 1.1) (Xue, et al., 2022; ITRC, 2022b; Cai, et al., 2012). Short-chain PFAS are thought to be a safer alternative to long-chain PFAS with less bioaccumulation thus the recent shift towards short-chain production (Otero-Sabio, et al., 2022; Hamid, et al., 2018). However, other studies suggest that short-chain PFAS are as persistent and bioaccumulative as long-chain PFAS (Gomis, et al., 2018; Wilkinson, et al., 2017). Due to the increase in short-chain PFAS production, short-chain PFAS are found in higher concentrations than long-chain PFAS in the environment (Fuertes, et al., 2017; Li, et al., 2012). The toxicity of PFBS to humans is less well-known, and current studies evaluating its toxicity have evaluated the effects on algae, bottlenose dolphins, and lettuce germination rates (Xue, et al., 2022; Li, et al., 2023; Otero-Sabio, et al., 2022; ATSDR, 2021). As of 2019, there were three times as many studies on long-chain PFAS than short-chain ones indicating that more research needs to be conducted before there are definitive conclusions on PFBS toxicity, bioaccumulation, and environmental fate as well as other short-chain PFAS (Ateia, et al., 2019; ATSDR, 2021).

Compared to PFOS, the half-life of PFBS is much shorter at 665 hours in humans, but other physiochemical characteristics were almost identical to PFOS making it an ideal replacement for industrial needs (ATSDR, 2021). The water solubility was measured to be 1300 mg/L in water (Rahman, et al., 2014). The log K_{oc} is calculated to be 1.0 (Wang, et al., 2011). The log K_{ow} is calculated to be 3.9 (Wang, et al., 2011). The pK_a is calculated to be -3.31 (National Center for Biotechnology Information, 2023).

Perfluorohexane sulfonic acid (PFHxS)

Perfluorohexane sulfonic acid (PFHxS) is a short chain perfluorinated sulfonic acid with six C-F bonds and has a SO_3^- (sulfonate) functional group like PFOS and PFBS (ECHA, 2020). PFHxS has also been used as an alternative to PFOS and is found alongside PFOS in the metal-plating industry (ECHA, 2020; Haley & Aldrich, 2017; Wee & Aris, 2023). The United Nation Environment Programme suggests that because of its physiochemical similarities to PFOS, PFHxS will have similar toxicity to humans (UNEP, 2017). The physiochemical characteristic of PFHxS suggest that it could be worse than its long-chain counterparts; the mean estimated half-life of PFHxS in humans was 5.3 years which was higher than PFOS at 3.4 years and PFOA at 2.7 years in the same study (Li, et al., 2018). The pKa value of PFHxS is 0.14, indicating that has a lower tendency to lose protons and dissociate which could be attributed to its longer half-life (National Center for Biotechnology Information, 2023). A literature search did not yield data regarding PFHxS solubility in water, however Ateia, et al. (2019) explained that short-chain PFAS generally have high solubility in water. The log K_{oc} is calculated to be 1.78 (Wang, et al., 2011). The log K_{ow} is calculated to be 5.17 (Wang, et al., 2011). The pK_a is calculated to be 0.14 (National Center for Biotechnology Information, 2023).

Land Application Systems

A land application system (LAS) is a type of final disposal water treatment system that applies liquid effluent, biosolids, or sewage sludge directly on nonpublic contact sites such as agricultural lands and forests or public contact sites such as parks, plant nurseries, and golf courses to amend soil and fertilize the land (USEPA, 2023a). The EPA (1994) defines sewage sludge as, "a solid, semi-solid, or liquid residue generated during the treatment of domestic sewage in a treatment works," and biosolids as "a primarily organic solid product produced by wastewater treatment processes that can be beneficially recycled". Public wastewater treatment systems generate biosolids and sewage sludge that have some degree of pretreatment to prevent odors and bacteria which can then be land applied using a LAS (USEPA, 2023a; Popoola, et al., 2023). As of 2019, 51% of biosolids were land applied because they are nutrient dense and can serve as economical replacements for commercial fertilizers and soil amendments, but land application loading rates have to be closely monitored (USEPA, 1994; USEPA, 2023a; USEPA, 2021a). Heavy metals, pathogens, and nutrients are monitored through soil and groundwater sampling annually, and land application must cease if annual pollutant loading rates exceed concentration limits (GEPD, 2019; USEPA, 1994). Though PFAS have been detected in soil samples following land application, MCLs are not enforced and do not require monitoring as of the date of this thesis (Johnson, 2022; Sepulvado, et al., 2011; Chu & Letcher, 2017).

Georgia Environmental Protection Division (GEPD) and Georgia Department of Agriculture (GDA) do not exclude any soil type from land application; agronomic loading rates of sewage sludge (on a dry weight basis) are determined based on the soil series present within the land application site so as not to exceed pollutant ceiling concentrations or raises in soil pH (GEPD, 2019; GDA, 2023). The sludge or biosolids must also be incorporated into the soil within six hours of application (GDA, 2023). In addition to agronomic loading rates, best management practices and physical limitations such as buffer zones, setbacks from water sources, and slope limitations are enforced on land application sites to prevent water contamination (GEPD, 2019; USEPA, 1994). A 50-foot-wide vegetative buffer strip is required along all streams and drainage ditches near a land application system to catch any potential storm-induced runoff (GEPD, 2019). Where land application occurs, the slope should not exceed 10%, but the surrounding buffer zone has no such requirements (GEPD, 2019). According to the Georgia EPD, there should be no runoff of land applied material because the amount of effluent applied should not exceed soil retention rates (GEPD, 2006). Buffer zones may not catch all pollutants from land application because pollutants have been found downstream of LAS activity (USDA NRCS, 2012; Chen, et al., 2021). These pollutants were transported across the buffer zone during precipitation events thus the need for immobilization of PFAS by additional adsorbents or physical barriers. Several studies have assessed pollutant loads in LAS runoff though none have evaluated the reduction of PFAS concentrations after passing through the soil profile of a land application system buffer zone (Hall, et al., 2020; Gray, et al., 2017; Clarke, et al., 2017; Caniglia, et al., 2022).

Mitigation of PFAS in Soils and Runoff

Remediation of PFAS contaminated lands can happen *in situ* or *ex situ* where contaminated material is taken elsewhere for destruction or regeneration of spent material (Quinnan, et al., 2022; Bolan, et al., 2021). Common *in situ* remediation methods for PFAS-contaminated soils are soil flushing and adsorption (Ross, et al., 2018; Popoola, et al., 2023; Bolan, et al., 2021). Soil flushing occurs when the contaminated area is injected with a flushing solution that mobilizes the PFAS; the solution is captured on a media, physically removed, and treated off site (Bolan, et al., 2021; Grimison, et al., 2023). Adsorption can occur when PFAS come into contact with adsorbents and are bounded to the material (Bolan, et al., 2021). The mechanisms involved in PFAS adsorption include electrostatic attraction, hydrophobic interaction, anion exchange, and ligand exchange (Lei, et al., 2023). Figures 1.1 and 1.2 illustrate PFAS adsorption mechanisms. Both *in situ* and *ex situ* methods may have cost, energy, time limitations, or further environmental concerns due to the relative difficulty of PFAS removal (Bolan, et al., 2021; Lu, et al., 2019; Ross, et al., 2018).

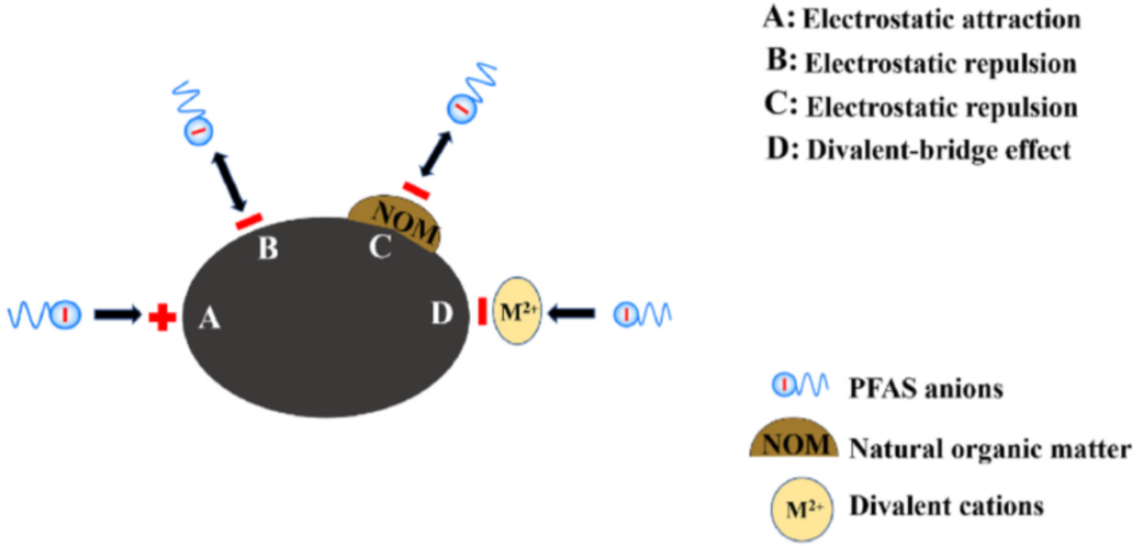


Figure 1.1 Electrostatic attraction and repulsion and the divalent-bridge effect in PFAS adsorption. Black oval represents a soil particle. Reprinted from "A review of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities" by Lei, et al., 2023, *Environmental Pollution*, *321*, p.8.

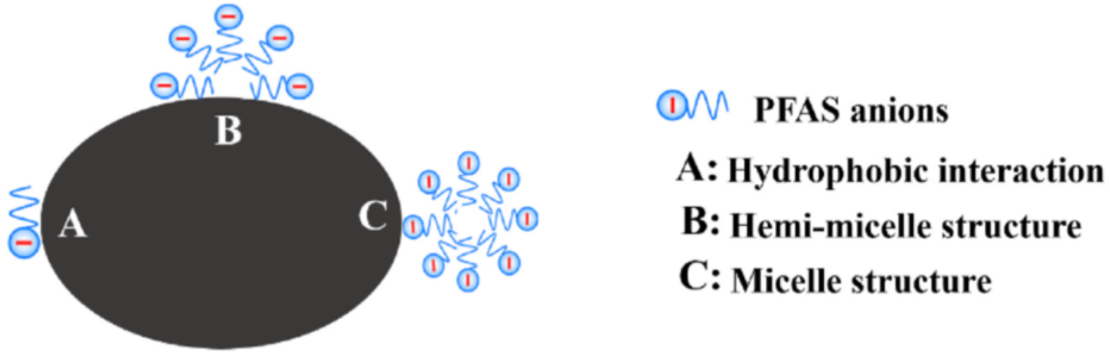


Figure 1.2 Hydrophobic aggregation of PFAS onto adsorbent. Black oval represents a soil particle. Reprinted from "A review of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities" by Lei, et al., 2023, *Environmental Pollution*, *321*, p.8.

In areas where repeated application of PFAS laden material occurs, *in situ* treatment methods are more applicable for PFAS remediation (Bolan, et al., 2021; Kabiri, et al., 2021). In land application areas, PFAS have been found in groundwater 17 m below ground surface and in soil 18 m below ground surface (Johnson, 2022). PFAS mobility in soil would make *ex situ* remediation unaffordable due to high transportation costs of heavy soil in addition to replacing contaminated soils (Mahinroosta & Senevirathna, 2020; Ross, et al., 2018). Though not an *in situ* treatment method, buffer zone soils and plants may impede runoff or subsurface flow from a land application site. Buffer zones surrounding land application systems have naturally occurring adsorbents in the soil including clay, sediments, and minerals (Lei, et al., 2023; Bolan, et al., 2021; Kabiri, et al., 2021). When PFAS become immobilized by adsorption, they are less likely to leach and contaminate local water sources (Bolan, et al., 2021; Kabiri, et al., 2021).

Bioretention Basins as Means to Manage PFAS Runoff

To mitigate PFAS in runoff surrounding land application systems, runoff or shallow subsurface flow could be diverted to a bioretention basin at the edge of field. Bioretention basins have shown promising results in filtering out contaminants such as pesticides, artificial wastewater, and highway runoff (Zhang, et al., 2014; Janzen, et al., 2009; McIntyre, et al., 2015). To effectively filter contaminants, bioretention basins must have adequate storage capacity, proper design, and efficient drainage which will depend on flow rate, soil type, and size of drainage area (Wang, et al., 2019; USEPA, 2021b). A standard bioretention basin design usually consists of a filter media, transition layer, and a drainage layer (Hunt, et al., 2015). Improper design will limit the efficacy of a bioretention basin. Basins that collect runoff from large drainage areas can become encumbered by sediment, but a system of consecutive basins can be developed to prevent sediment overload with adequate storage capacity (USEPA, 2021b). There are no soil limitations, but additional design components such as underdrains may be added if soils have low infiltration rates (USEPA, 2021b).

To maximize effectiveness, bioretention media mixes can be optimized to filter and target specific contaminants by incorporating adsorbents into them (Hsieh & Davis, 2005). A common adsorbent used to treat PFAS is activated carbon (AC) because of its high surface area due to pores within its structure (Marsh & Rodriguez-Reinoso, 2006; USEPA, 2021c; Riegel, et al., 2023). Granular activated carbon (GAC) can be incorporated into soil mixtures to enhance sorption capacity for a low-cost solution to immobilize PFAS (Riegel, et al., 2023). There are many types of GACs and the removal efficiency of PFAS will depend on the GAC used; in one assessment of PFAS removal efficiencies with different GAC types, a lignite-based GAC removed the highest amount of PFOA but the lowest amount of perfluorobutanoic acid (PFBA) (Riegel, et al., 2023). Competition for adsorption sites on GAC can occur between short and long-chain PFAS and inorganic or organic salts; electrostatic and hydrophobic interactions will determine what adsorbs first (Zhang, et al., 2023; Lei, et al., 2023). Carbon based adsorbents must be replenished or regenerated because their filtration efficiency diminishes over time, and desorption of PFAS may occur (Lei, et al., 2023; Kabiri, et al., 2021).

The selection of plant species in bioretention basins can also improve filtration capacity (Gobelius, et al., 2017; Bolan, et al., 2021; Hunt, et al., 2015). Many studies have assessed various plants in their ability to uptake PFAS; all reported some amount of PFAS uptake (Gobelius, et al., 2017; Dalahmeh, et al., 2018; Zhang, et al., 2021b). Trees have shown the highest uptake rates, but grasses such as bermuda and tall fescue will accumulate PFAS as well (Gobelius, et al., 2017; Yoo, et al., 2011). Plant diversity and placement is crucial for the success of a bioretention basin (Hunt, et al., 2015). Plants with higher drought tolerance can be placed further from the inlet while plants nearest to the inlet may be inudated with water at times and need to be water tolerant (Hunt, et al., 2015). Although maintenance is typically low for bioretention basins, vegetation may need to be pruned or mowed and invasive species removed (Hunt, et al., 2015). Plants can be utilized in bioretention basins for higher removal rates of PFAS in addition to adsorbents added in media mixes.

PFAS mitigation technologies can be unaffordable for local governments to implement in wastewater treatment facilities because of expensive chemicals or machineary needed to break down PFAS. Biosolids produced from wastewater treatment facilities may have concentrated PFAS in them due to influx of manufacturing waste containing PFAS. Land application of wastewater effluent or biosolids may introduce PFAS into adjacent water sources, and affordable solutions for PFAS filtration need to be assessed to protect rural communities. The following chapters contain two studies: one examimes the efficacy of buffer zones surrounding land application sites in their ability to filter PFAS through Tifton loamy sand soil, and the second study examines the efficacy of bioretenion basin media mixes containing Tifton loamy sand soil and pine sawdust in their ability to filter PFAS. These studies are essential in evaluating low-technology methods to filter PFAS and protect rural communities from potiential water contamination from land application systems.

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CHAPTER 2

EFFICIENY OF BUFFER ZONES SURROUNDING LAND APPLICATION SYSTEMS TO FILTER PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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ABSTRACT

In some rural areas, treated effluent from wastewater treatment plants is irrigated on the land surface (e.g., a land application system) as the final disposal, but this material can contain hazardous chemicals such as per- and polyfluoroalkyl substances (PFAS). Buffer zones typically surround land application systems to prevent any potential runoff or subsurface flow from reaching local water sources, but their efficacy to remove or retain PFAS has not been studied. Therefore, the objective of this study was to compare concentrations of PFAS in influent and effluent after passing through buffer zone soils in a plot study with various plot lengths of 30 60 or 90 cm. Results indicate significant reductions of PFOS and PFNA after passing through buffer zone soils, whereas PFOA, PFBS, PFHxS, and 6:2 FTS effluent concentrations were both significant and not significantly different from influent concentrations based on plot lengths. Effluent concentrations of all PFAS were significantly lower than influent concentrations on PFAS solution application days.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds also known as “forever chemicals” that do not break down easily (Moyer, 2021). The ubiquity of PFAS in the environment can be attributed to manufacturing processes and wastewater treatment operations (Gaines, 2022; Prevedouros, et al., 2006). Thousands of PFAS have been manufactured over the past 70 years for a wide range of uses in the industrial, commercial, and governmental sectors as a water repellant, fire suppressant, and in materials such as nonstick cookware, carpets, clothing, cleaning solutions, and other similar uses (Gaines, 2022; Prevedouros, et al., 2006; USEPA, 2023c). The manufacturing process of these products can create PFAS-laden wastewater. Industrial waste effluent, home waste effluent, and city stormwater are treated by wastewater treatment plants (WWTPs). However, most wastewater treatment operations do not effectively filter or treat PFAS to proposed levels recommended by the Environmental Protection Agency (EPA) (Fredriksson, et al., 2022; Huset, et al., 2008; Voulgaropoulos, 2022; Link, et al,, 2023; Pan, et al., 2016; Mojiri, et al., 2023). The EPA proposed acceptable Maximum Contaminant Levels (MCLs) and Health Based Water Concentrations (HBWCs) in drinking water for six PFAS in the summer of 2023 to address and mitigate the risks associated with PFAS contamination (USEPA, 2023c). The MCLs for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are 4.0 parts per trillion and will require public water systems to monitor PFAS levels, notify the public of PFAS levels, and remediate if they exceed these MCLs (USEPA, 2023c). The other four PFAS under this rule, perfluorononanoic acid (PFNA), Perfluorohexane sulfonic acid (PFHxS), perfluorobutane sulfonic acid (PFBS), and HFPO-DA (GenX), will adhere to HBWCs that determine the level below which no health effects are estimated (USEPA, 2023c). Thus, biosolids and sewage sludge created by WWTPs may have levels of PFAS that exceed these limits (Fredriksson, et al., 2022; Huset, et al., 2008; Voulgaropoulos, 2022; Popoola, et al., 2023).

Public wastewater treatment systems generate biosolids and sewage sludge that have some degree of pretreatment to prevent odors and bacteria which can then be land applied using a land application system (LAS) (USEPA, 2023a; Popoola, et al., 2023). A LAS is a type of final disposal water treatment system that applies treated liquid effluent, biosolids, or sewage sludge directly on nonpublic contact sites such as agricultural lands and forests or public contact sites such as parks, plant nurseries, and golf courses to amend soil and fertilize the land (USEPA, 2023a). As of 2019, 51% of biosolids were land applied because they are nutrient dense and can serve as economical replacements for commercial fertilizers and soil amendments, but land application loading rates have to be closely monitored (USEPA, 1994; USEPA, 2023a; USEPA, 2021a). Heavy metals, pathogens, and nutrients are monitored through soil and groundwater sampling annually, and land application must cease if annual pollutant loading rates exceed regulated concentration limits (GEPD, 2019; USEPA, 1994). Although PFAS have been found in biosolids and sewage sludge that is land applied, PFAS are not currently a regulated or monitored chemical. PFAS in soils surrounding LASs are found in higher concentrations following land application compared to background levels (Johnson, 2022; Sepulvado, et al., 2011; Chu & Letcher, 2017). Land application systems that apply treated sewage sludge or biosolids may be a significant source of PFAS contamination in the environment in areas where WWTPs cannot effectively remove or treat PFAS.

Georgia Environmental Protection Division (GEPD) and Georgia Department of Agriculture (GDA) do not exclude any soil type from land application; Agronomic loading rates of sewage sludge (on a dry weight basis) are determined based on soil series present within the land application site so as not to exceed pollutant ceiling concentrations or raises in soil pH (GEPD, 2019; GDA, 2023). The sludge or biosolids must also be incorporated into the soil within six hours of application (GDA, 2023). In addition to agronomic loading rates, best management practices and physical limitations such as buffer zones, setbacks from water sources, and slope limitations are enforced on land application sites to prevent water contamination (GEPD, 2019; USEPA, 1994). Where land application occurs, the slope should not exceed 10%, but the surrounding buffer zone has no such requirements (GEPD, 2019). A 50-foot-wide vegetative buffer strip is required along all streams and drainage ditches near the land application system to catch any potential storm-induced runoff (GEPD, 2019). According to the Georgia EPD, there should be no runoff of land applied material because the amount of effluent applied should not exceed soil retention rates (GEPD, 2006). Buffer zones may not be catching all pollutants from land application because pollutants have been found downstream of LAS activity (USDA NRCS, 2012; Chen, et al., 2021). These pollutants were transported across the buffer zone during precipitation events, thus the need for immobilization of PFAS by additional adsorbents or physical barriers. Several studies have assessed pollutant loads in LAS runoff though none have evaluated the reduction of PFAS concentrations after passing through the soil profile of a land application system buffer zone (Hall, et al., 2020; Gray, et al., 2017; Clarke, et al., 2017; Caniglia, et al., 2022). The objective of this study was to evalutate the efficacy of buffer zones soils surrounding land application systems in their ability to filter PFAS. We achieved this by comparing influent concentrations of a PFAS solution to effluent concentrations after passing through buffer zone soil plots.

Materials and Methods

This experiment was conducted from July to October 2023 in Oconee County Georgia at J. Phil Campbell farm inside a greenhouse with open ends (33.8758° N, -83.4222° W). The plots were placed inside the greenhouse to shield them from precipitation events. Buffer zone plots containing Tifton loamy sand (Fine-loamy, kaolinitic, thermic Plinthic Kandiudults) and Bermuda grass sod grown in Tifton soil were constructed, and a PFAS solution or "clean" municipal water was drip irrigated on the plots to simulate land application system runoff or shallow subsurface flow passing through a buffer zone. The Tifton soil was collected from Tifton vegetable park on University of Georgia property in Tifton, Georgia, and the Bermuda sod was grown in Tifton, GA.

PFAS mixture used in experiment

The PFAS used in this study were Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA), Perfluorobutane sulfonic acid (PFBS), Perfluorohexane sulfonic acid PFHxS, Perfluorononanoic acid (PFNA), and 6:2 Fluorotelomer sulfonate (6:2 FTS) because they were commonly found in wastewater treatment facility effluent and biosolids in the following concentrations: 1.7 μg/L PFOS, 6.3 μg/L PFOA, 8.0 μg/L PFBS, 7.2 μg/L PFHxS, 0.8 μg/L PFNA, and 0.8 μg/L 6:2 FTS (Desgens-Martin, et al., 2023; Kim, et al., 2022; Letcher, et al. 2020; Thompson, et al., 2022). The pure chemical compounds were purchased from Sigma-Aldrich. All other materials were purchased from Home Depot unless stated otherwise.

Buffer Zone Plot Description

There were twelve buffer zone plots used in this study. The internal plot dimensions were 30 cm by 30 cm, 30 cm by 60 cm, and 30 cm by 90 cm with three replicates of each and three additional 30 cm by 30 cm control plots. The plots were constructed using 5.08 cm by 15.24 cm (2” by 6”) lumber for the sides, plywood for the bottom, lined with plastic, and sealed with caulk to prevent water leaks. A 1.9 cm (¾”) Schedule 40 PVC pipe drilled with holes on either side was inserted into the bottom of the plots to allow for subsurface drainage, and 2.54 cm of gravel was filled to the top of the PVC pipe. The subsurface drainage pipe emptied into 8-liter buckets. Tifton soil was added on top of the gravel and packed to achieve a bulk density of 1.6 g/cm^3. The amount of Tifton soil added was calculated by multiplying the bulk density and the volume of the plot minus the gravel height (2.54 cm) and 2.54 cm below the top of the plots which came to be six cm of soil added in each plot. Bermuda sod grown in Tifton soil was cut slightly bigger than the inner dimensions of the plot and packed into the plots tightly so there were no gaps. The front view of a plot can be seen in Figure 2.1, and a cross section plot schematic can be seen in Figure 2.2.

The plots were placed inside the greenhouse on a bench with a 12% slope, and drip irrigation was fitted to the top of the plots (Figure 2.3). A piece of Sch. 40 PVC pipe with holes drilled in the bottom was attached to each plot 2.54 cm above the sod. The pipe was the width of the plot. Drip emitters that emitted 2.27 liters/hour (0.6 gallons/hour) were fitted into the PVC pipes. One drip emitter was installed per 30 cm of plot length. The 30 cm length plots had one drip emitter, the 60 cm length plots had two, and the 90 cm length plots had three drip emitters. The number of drip emitters per plot was determined by the volume of water each plot needed to achieve 2.54 cm of irrigation per application. A single drip tube connected all the plots, but ball valves were placed on both ends and between the control plots and the PFAS plots to prevent the PFAS solution from entering on to the control plots. The purpose of the control plots was to assess whether or not PFAS were present in the soil or any of the materials used in the experiment.

Buffer Zone Irrigation

The plots received 5.08 cm of irrigation per week simulating two precipitation events with "clean" water and a land application spray event containing the PFAS solution (only on the treatment plots). The "clean" water supply was municipal water supplying the J. Phil Campbell Research and education center. "Clean" in this study meant water free of PFAS. Municipal water was pumped from a 190-liter tank using a Dayton Self-Priming ½ horsepower pump with an irrigation pressure regulator and was attached to the drip emitter tube connecting all plots. Samples of this water source were taken throughout the study to test for PFAS concentrations in the water. A separate 130-liter tank contained the PFAS solution and was filled with 94.6 liters of water every two weeks with the municipal water, and 9.5 mL of the PFAS solution was added and mixed to achieve the wastewater treatment concentrations. Samples of the PFAS influent were taken so the concentrations of PFAS in the effluent could be compared to influent concentrations.

On Mondays and Fridays, the plots received 31 minutes and 15 seconds of "clean" water, which was sourced from the municipal tap and accounted for 2.54 cm of irrigation total for both days. On Wednesdays, the plots received 1 hour 2 minutes and 30 seconds of a PFAS solution which accounted for the other 2.54 cm. The runoff and subsurface flow were collected in 8-liter buckets, and 500 mL samples were taken from each bucket for analysis if available. The samples were refrigerated at 4 degrees Celsius until analysis.

Sample Analysis

Water samples were analyzed by Dr. Matthew Henderson's lab from the Region 4 Environmental Protection Agency. Liquid chromatography was performed using an Agilent 1290 infinity II interfaced to an Agilent 6495 Triple Quad (Agilent Technologies, Palo Alto, CA, USA). An Acquity UPLC BEH C18 (2.1 x 100mm) with a particle size of 1.7µm (Waters Corporation, Milford, MA, USA) was used and operated at ambient temperature. Injection volume was 10µL with mobile phase consisted of (A) water with 0.1% formic acid and (B) acetonitrile with 0.1% formic acid at a flow rate of 0.5mL/min. The gradient was as follows: 20% B for 0.5 min, then 20% to 30% B for 2 min, then 30% to 90% B for 16 min, hold at 90% B for 28.1 min, then returned to 20% B for 30 min and hold for 34 min. Mass spectrometer was set in negative electrospray ionization (ESI-) mode with capillary voltage set to 400mV. The source used nitrogen gas at a temp of 200°C and flow of 14L/min. The detector operated in dynamic multiple reaction monitoring mode with settings in Table 2.1.

Statistical Analysis

Data was analyzed in JMP Pro version 17.2. Normality of data was assessed for each PFAS chemical using the Shapiro-Wilks test. A one-way analysis of variance (ANOVA) with $\alpha = 0.05$ was used to compare the effect of plot length on the concentrations of PFAS found in the effluent. PFAS application days and clean water application days were analyzed separately for each PFAS due expected concentration differences of the effluent between the days. There were five clean water application days and three PFAS solution application days that were averaged. The null hypothesis was that plot length had no effect on the concentration of PFAS in the effluent. If the results of the one-way ANOVA revealed a Prob > F less than $\alpha = 0.05$, then the null hypothesis was rejected, and Tukey's honest significance test (HSD) test was used to make multiple comparisons between plot lengths for individual PFAS. Data was graphed in Excel version 16.77.1.

Results and Discussion

During the construction of the plots, assumptions were that the majority of the effluent collected would be runoff from the top of the plots. However, when we began to irrigate the plots there was little to no runoff, and the majority of effluent collected was from subsurface flow. Tifton soil is classified as a sandy loam soil, and the NRCS (2022) states that sandy and silty soils have a steady-state infiltration rate of 1 to 2 cm per hour while loamy soils have an infiltration rate of 0.5 cm to 1 cm per hour. Consequently, the majority of the effluent collected was from subsurface flow. The PVC pipe and gravel located in the bottom of the plots was supposed to catch any water that leached into the soil profile and was not captured as runoff. The shallow soil profile and slope of the plots caused the influent to pass through the soil, enter the gravel layer, and quickly exit as subsurface flow. As such, the length of the plots may have had little influence on the removal of PFAS as it passed over the soil surface because the high infiltration rate of the Tifton soil. Water infiltrated through the soil profile at a rate that equaled or exceeded the flow rate down the slope of the plots.

Despite the high infiltration rates of the soil, the one-way ANOVA revealed statistically significant differences in at least two plot lengths on clean water and PFAS application days in all six PFAS, except there were no significant differences between plot length on clean water application days in 6:2 FTS. Multiple comparisons were made using Tukey's honest significance test (HSD) with a 95% confidence interval.

PFOS concentrations in influent vs. effluent

On clean water application days (Figure 2.4), effluent concentrations in the 30, 60, and 90 cm plots were significantly higher than the control plots and influent concentrations of PFOS, but the 30, 60, and 90 cm plots were not significantly different. PFOS concentrations on clean water days is expected to come from desorption from PFAS application days. On PFAS solution application days (Figure 2.5), concentrations of PFOS in the influent were significantly higher than effluent concentrations in all of the plots. Effluent concentrations of PFOS in the 30 cm plot were significantly higher than the 60 cm and control plots but were not different than the 90 cm plots. Effluent concentrations in the 90 cm plot were significantly higher than the control plots but were not significantly different than the 60 cm plots.

PFOA concentrations in influent vs. effluent

On clean water application days (Figure 2.4), effluent concentrations in the 60 and 90 cm plots were significantly higher than the 30 cm plots, control plots, and influent concentrations of PFOA, but the 60 and 90 cm plots were not significantly different. Effluent concentrations in the 30 cm plots were significantly higher than the control plots and influent concentration. Effluent concentrations in the control plots were not significantly different than influent concentrations. On PFAS solution application days (Figure 2.5), concentrations of PFOS in the influent were significantly higher than effluent concentrations in the 60 and 90 cm plots but were not significantly higher than effluent concentrations in the 30 cm plots. Effluent concentrations in the 30, 60, and 90 cm plots were not significantly different but were significantly higher than the control plot concentrations.

PFNA concentrations in influent vs. effluent

On clean water application days (Figure 2.4), effluent concentrations in the 30, 60, and 90 cm plots were significantly higher than the control plots and influent concentrations of PFNA, but the 30, 60, and 90 cm plots were not significantly different. On PFAS solution application days (Figure 2.5), concentrations of PFNA in the influent were significantly higher than all of the plots. Effluent concentrations in the 30 and 90 cm plots were significantly higher than effluent concentrations in the 60 cm plots and the control plots, but the 30 and 90 cm plots were not significantly different. Effluent concentrations in the 60 and 90 cm plots were not significantly different.

PFBS concentrations in influent vs. effluent

On clean water application days (Figure 2.4), effluent concentrations in the 60 and 90 cm plots were significantly higher than the 30 cm plots, control plots, and influent concentrations of PFNA, but the 60 and 90 cm plots were not significantly different. PFBS concentrations were not significantly different in the 30 cm plots, control plots, and influent. On PFAS solution application days (Figure 2.5), concentrations of PFBS in the influent were significantly higher than effluent concentrations in the 90 cm plots and control plots but were not significantly different than the 30 and 60 cm plots. Effluent concentrations in the 30, 60, and 90 cm plots were not significantly different but were significantly higher than the effluent concentrations in the control plots.

PFHxS concentrations in influent vs. effluent

On clean water application days (Figure 2.4), effluent concentrations in the 60 and 90 cm plots were significantly higher than the 30 cm plots, control plots, and influent concentrations of PFHxS, but the 60 and 90 cm plots were not significantly different. Effluent concentrations in the 30 cm plots were significantly higher than the control plots and influent concentrations. PFHxS concentrations were not significantly different in the control plots and influent. On PFAS solution application days (Figure 2.5), concentrations of PFHxS in the influent were significantly higher than effluent concentrations in the 60 cm, 90 cm, and control plots but were not significantly different than effluent concentrations in the 30 cm plots. Effluent concentrations in the 30, 60, and 90 cm plots were not significantly different but were significantly higher than effluent concentrations in the control plots.

6:2 FTS concentrations in influent vs. effluent

On clean water application days (Figure 2.4) there were no significant differences of 6:2 FTS concentrations in any plot lengths. On PFAS solution application days (Figure 2.5), concentrations of 6:2 FTS in the influent were significantly higher than all plots. Effluent concentrations in the 30 cm plots were significantly higher than effluent concentrations in the 60 cm plots and control plots but were not significantly different than effluent concentrations in the 90 cm plots. Effluent concentrations in the 60 and 90 cm plots were not significantly different but were significantly higher than effluent concentrations in the control plots.

Discussion

In examining the one-way ANOVA results for each PFAS, we can conclude that buffer zone soils reduced concentrations of PFAS in precipitation induced runoff from land application systems in this plot configuration. PFOS and PFNA influent concentrations were significantly reduced after passing through buffer zone soils, whereas PFOA, PFBS, PFHxS, and 6:2 FTS effluent concentrations were sometimes not significantly different from influent concentrations. PFOS and PFNA concentrations may have been significantly reduced due to their long chain lengths and the sulfonate functional group on PFOS. PFOA, PFBS, PFHxS and 6:2 FTS concentrations may be less affected by buffer zone soils because they have less affinity for soil due to their shorter chain lengths or the carboxylate functional group on PFOA. This may also be caused by the soil type used in this study. The Tifton loamy sand soil may not have the greatest adsorption capacity for PFAS, thus less reduction of PFAS overall compared to a clay-rich soil (Lei, et al., 2023).

On clean water days, the 30 cm plots outperformed the 60 and 90 cm plots for removal of PFOA, PFBS, and PFHxS in the effluent. These results contradict our initial thoughts that a longer buffer length would remove PFAS more efficiently. However, the higher effluent concentrations could be due to the longer plot lengths receiving more PFAS solution to achieve the correct irrigation amount. On clean water days, desorption of the short-chain PFAS and PFOA from the soil profile may happen. The lack of significant differences in effluent concentrations between plots lengths in PFOS and PFNA could be because PFOS and PFNA will be removed more efficiently by the soil regardless of plot length. On PFAS solution application days, effluent concentrations of PFOS and PFNA in all plot lengths were significantly lower than influent concentrations. Effluent concentrations of PFOA, PFBS, PFHxS, and 6:2 FTS were significantly lower than influent concentrations in the 90 cm plots which contradicts findings on the clean water days.

PFOS and PFNA concentrations overall were much lower than the other PFAS in this study because they reflect average concentrations in wastewater treatment plant effluent and biosolids. However, the concentrations of PFOS and PFOA in the effluent of this study greatly exceed the EPA's recommended maximum contaminant levels of 4.0 parts per trillion. PFNA concentrations may or may not exceed the EPA's hazard index level for this chemical. Average PFOS and PFOA concentrations from all plots on clean water application days were 104.6 and 844.0 ng/L, respectively. Average PFOS and PFOA concentrations from all plots on PFAS solution application days were 338.9 and 3037.9 ng/L, respectively. PFAS concentrations may vary in wastewater treatment effluent over time, though. This study only offers insight into a short period in time of PFAS concentrations in land applied material and may not accurately reflect years of land application.

Though land application systems are not currently required to monitor PFAS concentrations in applied material, they may be required to in the near future. This study and others that have evaluated the occurrence of PFAS in land-applied wastewater treatment byproducts (Johnson, 2022; Sepulvado, et al., 2011), suggest that PFAS are mobile in the environment despite precautionary measures such as buffer zones. These studies also found similar results to our study regarding PFAS chain length; short-chain PFAS are consistently more mobile in the environment than long-chain PFAS.

Summary and Conclusions

The objective of this project was to assess land application system buffer zone soils in their ability to naturally remove or retain PFAS from precipitation induced runoff or shallow subsurface flow. This project found that buffer zone soils were able to retain and remove long-chain PFAS, like PFOS and PFNA, from effluent concentrations more efficiently than short-chain PFAS. PFOA, although a long-chain PFAS, did not follow similar trends to PFOS and PFNA. Effluent concentrations of the short-chain PFAS, like PFBS, and PFHxS, were not significantly different from the influent concentrations indicating the higher mobility of short-chain PFAS in the environment. On clean water days, the 60 and 90 cm plots had higher concentrations in the effluent that the 30 cm plots for PFOA, PFBS, and PFHxS indicating that desorption of these PFAS may occur. On PFAS application days, effluent concentrations of all PFAS in the 90 cm plots were consistently lower than influent concentrations.

Overall, even though PFAS may be found in lower concentrations in runoff and subsurface flow than in influent concentrations, they still may exceed proposed MCLs based on the plot configuration of this research. Based on these plot studies, additional barriers are needed to prevent contamination of lands and water bodies near land application systems, but further studies need to be conducted on larger plots or real land application systems.

Figure 2.1. Front view of buffer zone plot with drip irrigation pipe located above the plot and subsurface drainage pipe diverting water down and out of the plot. Aluminum flume was attached to plots to divert runoff to a collection bucket.

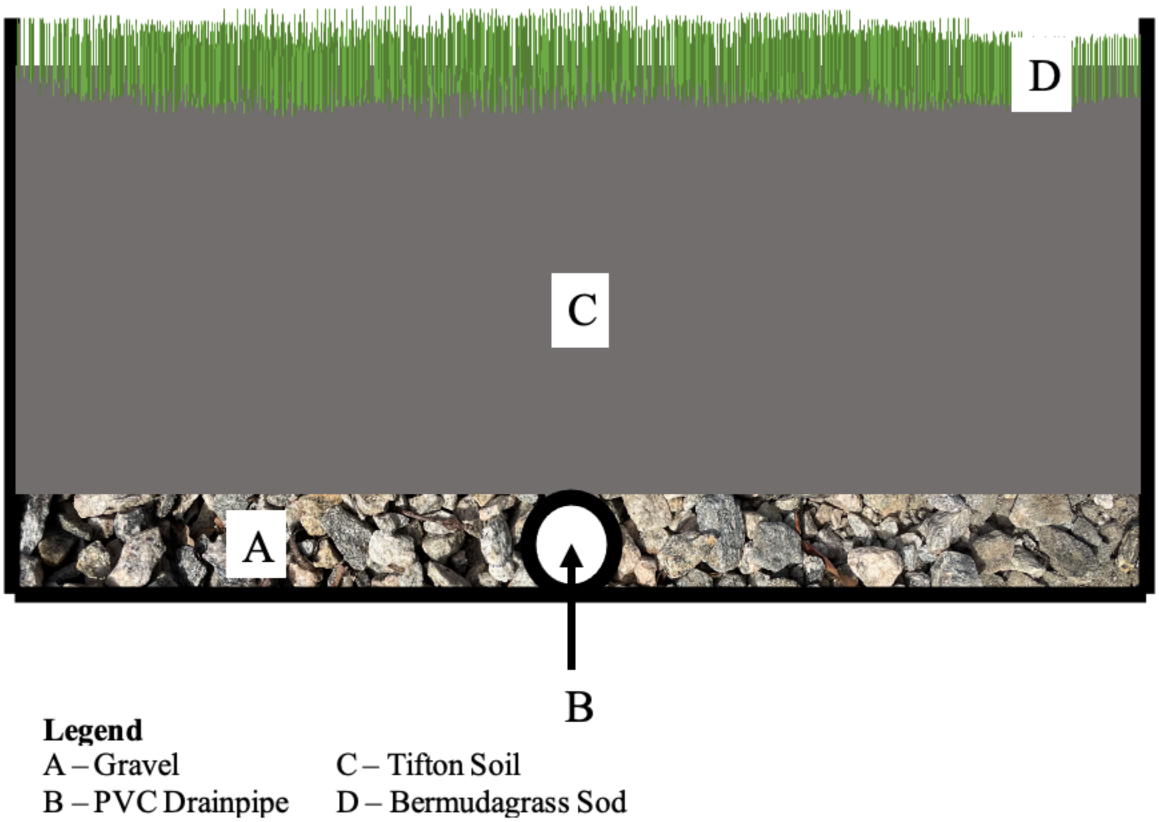

Figure 2.2. Front view cross section buffer zone plot schematic.

Figure 2.3. All buffer zone plots on bench in greenhouse. Runoff collection in topmost buckets, and subsurface drainage collected in bottommost buckets.

Table 2.1. Selected mass transitions for 6-2 FTS, PFBS, PFHxS, PFNA, PFOA, and PFOS. With internal standard M2-6-2FTS, M3PFBS, M3PFHxS, M8PFOA, M8PFOS, and M9PFNA.

Analyte	Precursor Ion	Product Ion	Ret Time (min)	Fragmentor	Collision energy (eV)
6-2FTS	427	81	6.41	380	42
6-2FTS	427	406.8	6.41	380	30
M2-6-2FTS	429	408.9	6.41	380	26
M2-6-2FTS	429	81	6.41	380	42
M3PFBS	302	98.9	4.45	380	30
M3PFBS	302	80.1	4.45	380	34
M3PFHxS	402	99	7.4	380	34
M3PFHxS	402	80.1	7.4	380	46
M8PFOA	421	376	7.4	380	6
M8PFOA	421	171.8	7.4	380	14
M8PFOS	507	99	10.62	380	50
M8PFOS	507	80.2	10.62	380	54
M9PFNA	472	426.9	8.9	380	6
M9PFNA	472	172	8.9	380	14
PFBS	299	99	4.45	380	38
PFBS	299	80.1	4.45	380	38
PFHxS	399	99	7.4	380	38
PFHxS	399	80	7.4	380	58
PFNA	463	418.9	8.9	380	8
PFNA	463	219	8.9	380	14
PFOA	413	368.8	7.4	380	2
PFOA	413	169	7.4	380	18
PFOS	499	98.9	10.62	380	46
PFOS	499	80.1	10.62	380	80

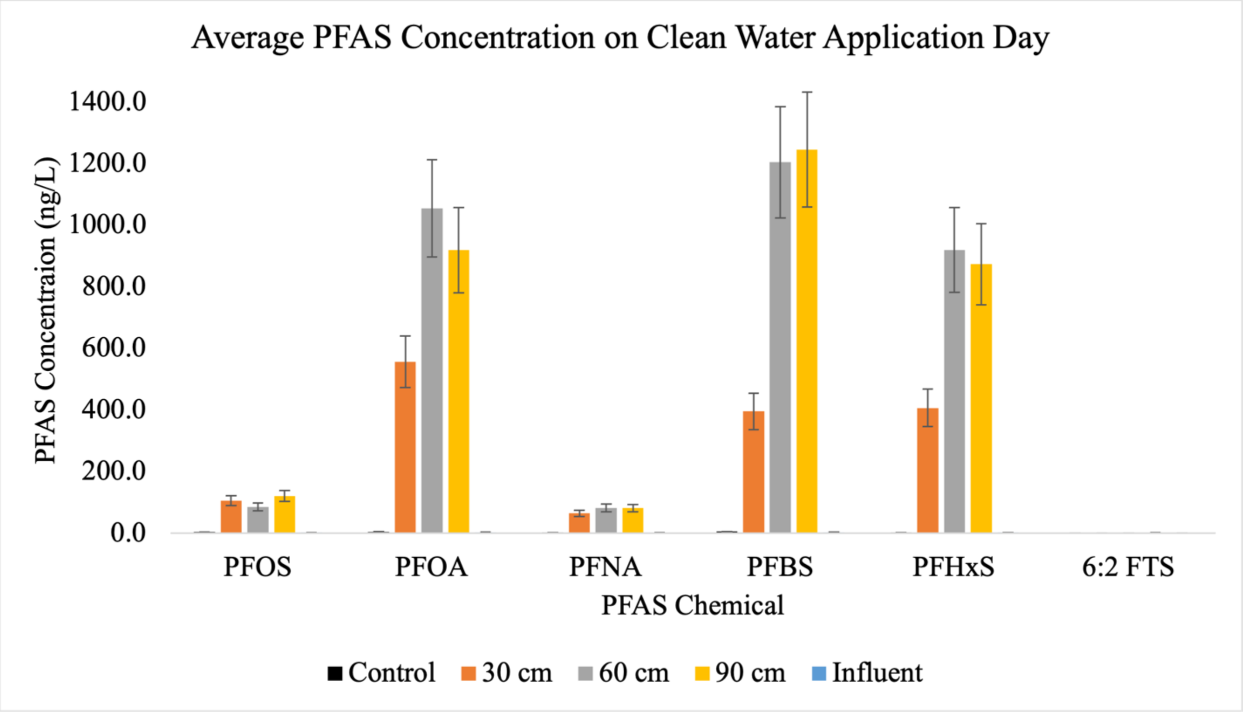

Figure 2.4. PFAS concentrations in the influent and effluent on clean water application days. Error bars represent standard error. Control, influent, and 6:2 FTS values are present but were all less than 6.0 ng/L.

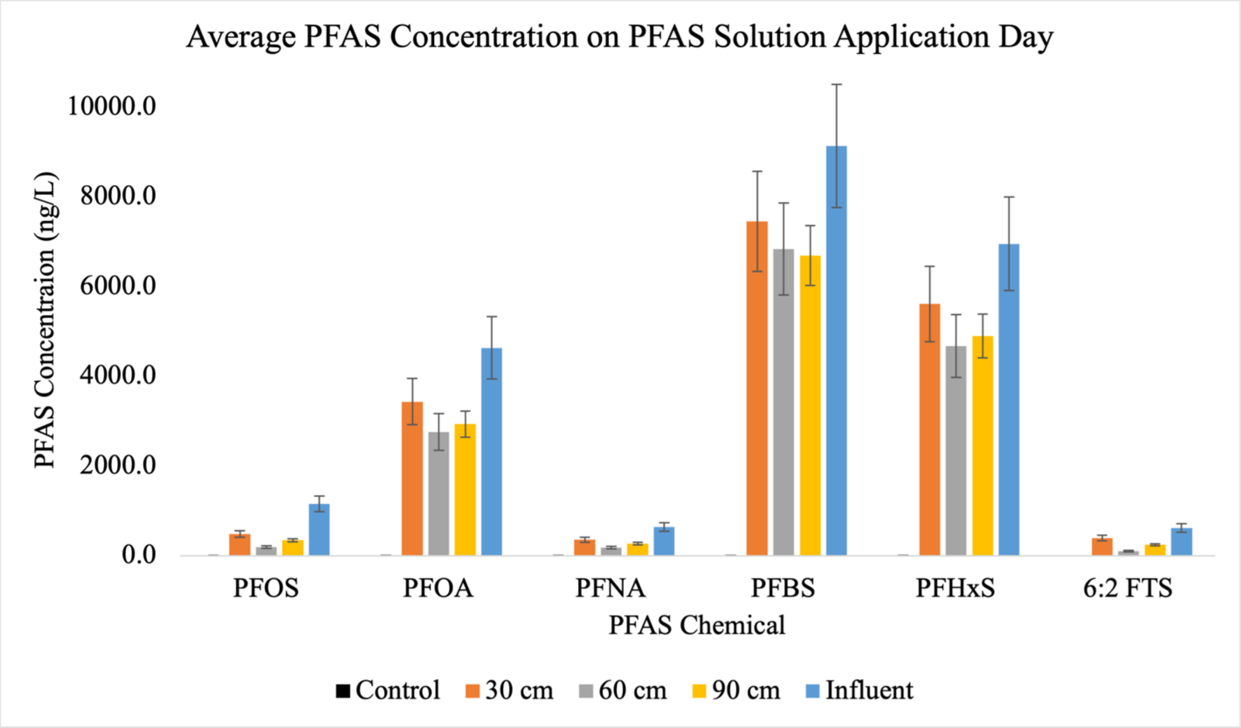

Figure 2.5. PFAS concentrations in the influent and effluent on PFAS solution application days. Error bars represent standard error. Control values are present but were all less than 6 ng/L.

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CHAPTER 3

EFFICIENCIES OF BIORETENTION MEDIA MIXES TO FILTER PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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ABSTRACT

Contamination of soil and water by per- and polyfluoroalkyl substances (PFAS) due to application of biosolids or treated effluent from wastewater treatment plants onto land application systems (LAS) can lead to public and environmental health concerns in rural communities. Stricter regulations on drinking water standards set by the EPA have lowered the amount of PFAS acceptable in drinking water to levels measured in the parts per billion range, thus any land application of wastewater containing a small amount of PFAS could result in these chemicals entering water sources through precipitation induced runoff or subsurface flow. The addition of a bioretention basin at the edge of field of a LAS could reduce PFAS concentrations using widely available materials such as soil and sawdust. This study assessed percent removal of six PFAS and used six bioretention media mixes consisting of Tifton loamy sand and pine sawdust. The mixes ranged from 100/0 Tifton soil/sawdust and decreased in 20 percent increments to 0/100 Tifton loamy sand/sawdust. Percent removal was highest in the 100/0 Tifton/sawdust mix for PFOS and PFNA. There were no significant differences of percent removal in any mix for PFHxS, PFBS, and 6:2 FTS. Based on results from this study, a bioretention media mix should be chosen based on the PFAS that need to be targeted for removal. Overall, results of this work can provide insight into PFAS reduction and removal methods for rural communities.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds also known as “forever chemicals” that do not break down easily (Moyer, 2021). The ubiquity of PFAS in the environment can be attributed to manufacturing processes and wastewater treatment operations (Gaines, 2022; Prevedouros, et al., 2006; Voulgaropoulos, 2022). Thousands of PFAS have been manufactured over the past 70 years for a wide range of uses in the industrial and governmental sectors as a water repellant, fire suppressant, and in materials such as nonstick cookware, carpets, clothing, cleaning solutions, and other similar uses (Gaines, 2022; Prevedouros, et al., 2006; USEPA, 2023c). The manufacturing process of these products can create PFAS-laden wastewater. Industrial waste effluent, home waste effluent, and some city stormwater are treated by wastewater treatment plants (WWTPs) that may not have the technology to filter and remove PFAS (Link, et al., 2023; Voulgaropoulos, 2022). Biosolids, liquid effluent, and sewage sludge created by WWTPs may be recycled using a land application system (LAS).

Land application systems receiving biosolids or treated wastewater effluent may be contributing to PFAS contamination of surrounding lands and water sources due to precipitation induced runoff. Although the Georgia Environmental Protection Division (GEPD) sets agronomic loading rates and requires buffer zones between sprayed areas and water sources, PFAS have been detected in soil and water samples down gradient of LASs (Johnson, 2022; Chu & Letcher, 2017; GEPD, 2019; Sepulvado, et al., 2011). Precipitation events may cause leaching and desorption of PFAS from the soil, but this is dependent on the PFAS present and characteristics of the soil.

PFAS behavior and adsorption rates are dependent on chain length, functional groups attached to the carbon-fluorine bonds, and their ionic state (ATSDR, 2021; Frazar, et al., 2022; Higgins & Luthy, 2006; Hamid, et al., 2018). Short chain PFAS, with six or less C-F bonds, generally partition to water while long chain PFAS, seven or greater C-F bonds, are preferential to soil and exhibit higher hydrophobicity (Huang, et al., 2023; Seo, et al., 2019; Link, et al., 2023). Carbon-fluorine bonds do not break down easily casuing PFAS to be environmentally persistant. Hydrophobicity of long-chain PFAS can vary based on PFAS functional groups. PFAS with a sulfonate funtional group such as perfluorooctane sulfonate (PFOS) are more hydrophobic due to the larger size of the sulfonate molecule, while PFAS with carboxlate functional groups such as perfluorooctanoic acid (PFOA) are slightly smaller and may partition to water easier (Ahmad, et al., 2023; Higgins & Luthy, 2006). PFAS can exist as nonionic, anionic, cationic, or zwitterionic molecules depending on the chain-length and functional group, though they typically exist as anionic in wastewater due to the molecular heads being surrounded by negative oxygen atoms (ITRC, 2022a; Backe, et al., 2013; Lei, et al., 2023). The acid dissociation constant (pK_a) is a measure of how strong an acid is in a solution and how it will dissociate in water; PFAS with lower pK_a values tend to be anionic in wastewater whereas PFAS with higher pK_a values tend to have a neutral charge (Lei, et al., 2023; ACD Labs, 2023).

Within a soil system, the movement and retention rates of PFAS are influenced by the clay content, organic content, and pH; sorption capacity of PFAS decreases with increasing pH of the system (Abou-Khalil, et al., 2023; Sima & Jaffé, 2021). The charge and chain-length of the PFAS will determine how attracted a PFAS chemical is to a negatively charged clay particle (Abou-Khalil, et al., 2023; Sima & Jaffé, 2021; Gagliano, et al., 2020). However, soil pH and clay content have less impact on PFAS adsorption and bioavailability compared to dissolved organic matter (DOM), total organic carbon (TOC), or soil organic matter (SOM) (Wen, et al., 2015; Wellmitz, et al., 2023; Sima & Jaffé, 2021). Carbon based materials have non-polar functional groups that facilitate sorption of hydrophobic PFAS with ease, but organic matter can compete with PFAS for adsorption sites onto clay particles present in soil (Qi, et al., 2022; Wen, et al., 2015; Sima & Jaffé, 2021; Bolan, et al., 2021).

The mechanisms involved in PFAS adsorption include electrostatic attraction, hydrophobic interaction, and anion exchange, (Lei, et al., 2023). Electrostatic attraction or repulsion is influenced by the charge of the functional group on the PFAS and the charge of the adsorbent. When the solution pH is low, adsorbents are positively charged, PFAS are anionic, and there is an increase in electrostatic attraction (Lei, et al., 2023). Whereas negatively charged adsorbents may cause electrostatic repulsion of PFAS. Hydrophobic interaction occurs when non-polar molecules repel polar molecules (Chandler, 2005). PFAS with long-chains are more hydrophobic than short-chain PFAS which explains their tendency to attach onto other hydrophobic surfaces (Lei, et al., 2023). Hydrophobic interaction can overcome electrostatic repulsion because the hydrophobicity of some PFAS can be higher than their charge repulsion (Lei, et al., 2023; Leung, et al., 2023). Anion exchange occurs when an adsorbent such as an anion exchange resin can easily release OH^- or Cl^- and a PFAS anion will replace it by ion-exchange (Lei, et al., 2023).

To mitigate PFAS in runoff surrounding land application systems, runoff or subsurface flow could be diverted to a bioretention basin at the edge of field. Bioretention basins have shown promising results in filtering out contaminants such as pesticides, artificial wastewater, and highway runoff (Zhang, et al., 2014; Janzen, et al., 2009; McIntyre, et al., 2015). To effectively filter contaminants, bioretention basins must have adequate storage capacity, proper design, and efficient drainage which will depend on flow rate, soil type, and size of drainage area (Wang, et al., 2019; USEPA, 2021b). Bioretention media mixes can be optimized to filter and target specific contaminants. This can be accomplished using widely available materials such as soil and sawdust that are low-cost and environmentally friendly. This study aimed to assess percent removal of PFAS in bioretention basin media mixes using Tifton loamy sand soil and pine sawdust for use in rural communities. The specific objective was to evaluate PFAS removal percentages by media mixes between 0 and 100 percent Tifton loamy sand soil and pine sawdust by running a PFAS solution through columns containing the media mixes.

Materials and Methods

This experiment was conducted in the Spring of 2023 in Oconee County Georgia at J. Phil Campbell Sr. Research and Education Center at the JPC Hydraulics Lab (33.8758° N, -83.4222° W). Stainless steel columns were used to hold bioretention media mixes consisting of Tifton loamy sand (Fine-loamy, kaolinitic, thermic Plinthic Kandiudults) and pine sawdust from a local sawmill. A PFAS solution was run through the columns containing the media mixes, and the effluent was collected to assess percent removal of each PFAS.

PFAS mixture used in experiment

The PFAS used in this study were Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA), Perfluorobutane sulfonic acid (PFBS), Perfluorohexane sulfonic acid (PFHxS), Perfluorononanoic acid (PFNA), and 6:2 Fluorotelomer sulfonate (6:2 FTS). The pure chemical compounds were purchased from Sigma-Aldrich, and a solution consisting of PFOS, PFOA, PFBS, PFHxS, PFNA, and 6:2 FTS was obtained from Dr. Jack Huang's lab at UGA Griffin Campus. The pure solution was mixed into 10 L of water to achieve the following concentrations: 1.7 μg/L PFOS, 6.3 μg/L PFOA, 8.0 μg/L PFBS, 7.2 μg/L PFHxS, 0.8 μg/L PFNA, and 0.8 μg/L 6:2 FTS because they were commonly found in wastewater treatment facility effluent and biosolids in these concentrations (Desgens-Martin, et al., 2023; Kim, et al., 2022; Letcher, et al. 2020; Thompson, et al., 2022).

Media mixes used in experiment

Tifton loamy sand (Fine-loamy, kaolinitic, thermic Plinthic Kandiudults) and pine sawdust were used in the bioretention media mixes. The Tifton soil was collected from Tifton vegetable park on University of Georgia property in Tifton, Georgia. The sawdust was obtained from a local sawmill in the Athens Georgia area. The media mixes were 100/0 Tifton soil/Sawdust, 80/20

Tifton soil/Sawdust, 60/40 Tifton soil/Sawdust, 40/60 Tifton soil/Sawdust, 20/80 Tifton soil/Sawdust, and 0/100 Tifton soil/Sawdust by volume of soil and sawdust (Figure 3.1). Samples of each media mix were analyzed for pH, cation exchange capacity (CEC), organic matter content (OM), and naturally occurring elements by University of Georgia College of Agriculture and Environmental Sciences Agricultural and Environmental Services Laboratories (AESL) in Athens, GA (Table 3.1). Samples of the soil and sawdust were also analyzed for particle size distribution using a W.S. Tyler RX-812 Coarse Sieve Shaker, and particle size distribution curves were generated for each material (Figure 3.2 and 3.3). The majority of the soil and sawdust had sand sized particles which are less ideal for adsorption due to a smaller surface area.

To determine the bulk density of soil and sawdust for larger scale mixing of media mix, a drop test was conducted to achieve equal compression of the materials in the columns. Soil or sawdust was filled to the brim of the column, weighed, and dropped three times from a height of ten cm onto a wooden board and weighed again. This was repeated ten times. The average weight of soil or sawdust was divided by the volume of soil in the column after compaction, and bulk density was calculated.

Stainless Steel Columns used in experiment

The stainless-steel columns used to hold the media mixes had a diameter of 5.7 cm and a height of 28 cm. The internal volume of the cylinder was 710 cm^3. The columns had a mesh bottom to allow for drainage, and a hook attached to the top. This type of stainless-steel column is typically used in bovine semen collection and storage.

The columns were hung from a rod, and a methanol rinsed plastic container was stationed underneath each column for effluent collection (Figure 3.4). A 500 mL sample of the PFAS solution was poured through each column by inverting a plastic container over the top of the column. The effluent was collected 24 hours later and stored in a refrigerator at 4 degrees Celsius until analysis.

Sample Analysis

The PFAS solution samples were analyzed using Ultra Performance Liquid Chromatography (UPLC) coupled with tandem mass spectrometry (UPLC-MS/MS) (Waters®, Milford, MA) by Yifei Wang, Ph.D. from Dr. Jack Huang's lab at the University of Georgia Griffin Campus. The UPLC was operated with methanol (A) and water (B) (5 mM ammonium acetate) as the mobile phases at a flow rate of 0.3 mL/min using a gradient condition listed in Table 3.2. Electrospray ionization (ESI) was operated in a negative mode with capillary voltage at 1.14 kV, cone voltage 60 V, source temperature at 350 °C and desolation temperature at 550 °C. The mass transitions and spectrometry conditions for Multiple Reaction Monitoring (MRM) monitoring are specified in Table 3.3. Quantification of each PFAS was based on the ratio between the analyte and the corresponding mass-labeled standard in Table 3.4.

Once the samples were analyzed, percent removal was calculated using equation (1)

$$100 - C_{out}/C_{in} * 100$$

where C_{out} is the concentration of PFAS in the effluent and C_{in} is the concentration of PFAS in the influent.

Statistical Analysis

Data was analyzed in JMP Pro version 17.2. Normality of data was assessed for each PFAS chemical using the Shapiro-Wilks test. A one-way analysis of variance (ANOVA) with $\alpha = 0.05$ was used to compare the average percent removal of PFAS in each media mixture. The null hypothesis was that all percent removal averages between media mixtures were the same. If the results of the one-way ANOVA revealed a Prob > F less than $\alpha = 0.05$, then the null hypothesis was rejected, and Tukey's honest significance test (HSD) test was used to make multiple comparisons between media mixtures for individual PFAS. Data was graphed in Excel version 16.77.1.

Results and Discussion

The one-way ANOVA revealed significant differences between percent removal of PFAS in the six media mixtures in PFOS, PFNA, and PFOA as shown by connecting letters in their respective figures (Figures 3.5, 3.6 & 3.7). Mixes with the same letter were not significantly different from each other. There were no significant differences of percent removal between media mixes in 6:2 FTS, PFBS, or PFHxS as shown in their respective figures (Figures 3.8, 3.9 & 3.10).

PFOS removal percentage in column study (Figure 3.5)

The average PFOS removal in the 100/0 Tifton/sawdust mixture was 95% which was significantly highest. The average PFOS removal in the 80/20 and 60/40 mixtures was 82% and 79%, respectively. The percent removal of PFOS in the 80/20 and 60/40 mixes was not significantly different from each other but was significantly lower than the 100/0 mix. The average precent removal of PFOS removal in the 40/60 mixture was 67% which was significantly lower than the 100/0, 80/20, and 60/40 mixes. The average PFOS removal in the 0/100 mixture was 47% which was significantly lower than 100/0, 80/20, 60/40, and 40/60. Lastly, the average PFOS removal in the 20/80 mixture was 33% which was significantly the lowest out of all the media mixes.

PFOS removal could have been the highest in the 100/0 mixture because of long-chain PFAS preference to adsorb to soil and their hydrophobicity. PFOS's sulfonate functional group is hydrophobic which would cause it to repel polar water molecules. PFOS tended to have higher percent removal in the mixes with higher soil content, although PFOS removal was the lowest in the 20/80 mixture but increased in the 0/100 mixture. The downward trend of sorption from the 100/0 to the 20/80 mixtures may be explained by the electrostatic interactions between the sawdust and the soil. The sawdust had higher levels of calcium and magnesium which may be attracted to negatively charged soil particles and inhibit PFOS sorption on to the soil. This would also explain the increased removal in the 0/100 mixture because there was no soil to interfere with sorption. The PFOS could attach to cations in the sawdust which has exhibited elevated anion exchange capacity and could possibly increase PFAS sorption (Zhang, et al., 2021a).

PFOA removal percentage in column study (Figure 3.6)

The average PFOA removal in the 100/0, 80/20, 60/40, 40/60, and 0/100 was 29%, 20%, 22%, 20% and 34%, respectively. There were no significant differences between these mixes. The 20/80 mix had an average percent removal of 8% which was significantly lower than the 100/0 and 0/100 mixes. There were no significant differences between the 60/40, 80/20, 40/60, and 20/80 mixes. Even though PFOA is a long-chain PFAS, it exhibited less preference than PFOS or PFNA, both long-chain PFAS, to adsorb to the media mixes. This could be due to the carboxylate functional group which is not as hydrophobic as the sulfonate group on PFOS. Also, the media mixes may not have been acidic enough to facilitate PFOA adsorption onto the mixes because PFOA will adsorb better in lower pHs (Sahara, et al., 2023).

PFNA removal percentage in column study (Figure 3.7)

The average PFNA removal in the 100/0 mix was 87% which was significantly the highest out of all the mixes. The average PFNA removal in the 80/20 and 60/40 mixes was 64% and 59% respectively. The percent removal in the 80/20 and 60/40 mixes was not significantly different but was significantly lower than the 100/0 mix. The average PFNA removal in the 40/60 was 49% which was not significantly different from the 60/40 mix but was significantly lower than the 80/20 and 100/0 mixes. The average PFNA removal in the 0/100 mix was 44% which was not significantly different from the 40/60 mix but was significantly lower than the 60/40, 80/20 and 100/0 mixes. The average PFNA removal in the 20/80 mix was 22% which was significantly lowest out of all the mixes. Although PFNA has the carboxylate functional group like PFOA, it also has an additional carbon-fluorine bond giving it a chain length of nine whereas PFOA only has a chain length of eight. This could account for PFNA's preference to adsorb to the media mixes with higher soil concentrations more effectively than PFOA.

6:2 FTS removal percentage in column study (Figure 3.8)

6:2 FTS removal in all mixes was not significantly different. The average percent removal of 6:2 FTS in the mixes from 100/0 to 0/100 was 28%, 37%, 25%, 13%, 8%, and 31% respectively. 6:2 FTS only has 6 carbon-fluorine bonds, and the short chain-length of 6:2 FTS could account for higher concentrations in the captured effluent. The mixes did have some adsorption capacity for 6:2 FTS but overall, 6:2 FTS tended to stay suspended in the solution.

PFBS removal percentage in column study (Figure 3.9)

PFBS removal in all mixtures was not significantly different. The average percent removal of PFBS in the mixtures from 100/0 to 0/100 was 4%, 7%, 10%, 6%, 17%, and 37% respectively. PFBS is a short-chain PFAS, so it did not prefer to adsorb to the media mixes more than it preferred to stay in solution.

PFHxS removal percentage in column study (Figure 3.10)

PFHxS removal in all mixtures was not significantly different. The average percent removal of PFHxS in the mixtures from 100/0 to 0/100 was 17%, 22%, 24%, 22%, 13%, and 38% respectively. PFHxS is a short-chain PFAS, so it did not prefer to adsorb to the media mixes more than it preferred to stay in solution.

Overall, bioretention media mixes do exhibit some capacity for removal of PFAS from precipitation induced runoff. The chain length of the PFAS directly affected the removal rates of PFAS by the media mixes. PFOS and PFNA had removal rates of 95% and 87% in the 100/0 Tifton/sawdust mix, respectively. The media mix used in a bioretention basin can be determined based on the PFAS that needs to be targeted. For example, a media mix with higher soil content may need to be used for removal of the long-chain PFAS. The short-chain PFAS were removed by the media mixes but at much lower rates than the long-chain PFAS. This result may indicate the need for additional adsorbents or use of a different soil type in the media mixes.

Summary and Conclusions

The purpose of this study was to assess percent removal of PFAS in bioretention media mixes containing Tifton soil and pine sawdust. The results indicate that bioretention media mixes containing Tifton soil and pine sawdust may partially reduce PFAS concentrations in precipitation induced runoff from land application systems. Percent removal of PFAS was specific to the type of PFAS and media mix used.

This study was completed alongside another student assessing North Georgia clay soil and pine sawdust media mixes. The results of that study are being worked on for publication at the time of writing this thesis. Future studies assessing bioretention media mixes used for PFAS filtration need to be assessed in the field with full-scale bioretention basins. Due to minimal research using bioretention media mixes for PFAS filtration, land application system operators may use this research to determine a bioretention media mix that may be used to filter PFAS in an edge of field bioretention basin.

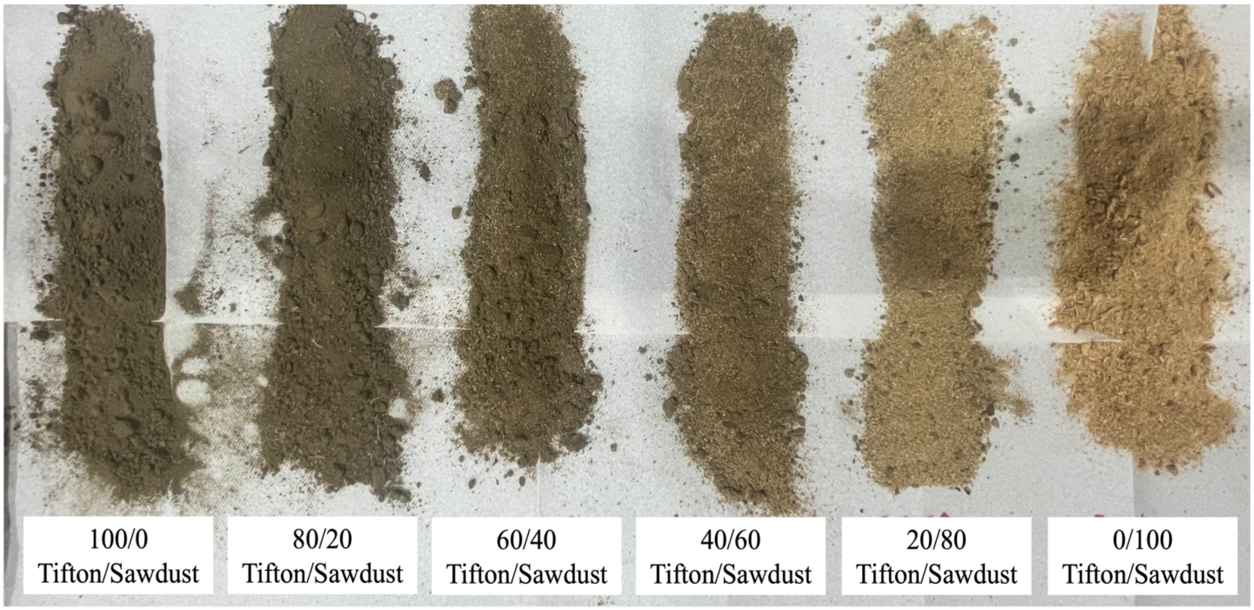

Figure 3.1. Tifton soil and sawdust bioretention media mixtures with 20% decreases of Tifton soil from left to right.

Table 3.1. Soil test results for the media mixes.

Media Mix	**100/0**	**80/20**	**60/40**	**40/60**	**20/80**	**0/100**
LBC 1 (ppm $CaCO_3$/pH)	144	155	183	269	458	703
pH_{CaCl2}	5.69	5.63	4.97	4.75	4.55	4.28
Equivalent water pH	6.29	6.23	5.57	5.35	5.15	4.88
Base Saturation (%)	85.79	84.36	70.52	61.33	47.98	44.73
CEC (meq/100g)	3.401	3.749	4.691	6.657	9.448	15.64
% Organic Matter	0.92	3.09	5.76	9.47	25.31	86.48
Ca (Calcium) (kg/ha)	1118	1199	1217	1434	1502	1977
Cd (Cadmium) (kg/ha)	0.1926	0.1872	0.1853	0.1701	0.1577	0.0758
Cr (Chromium) (kg/ha)	0.20	0.20	0.22	0.21	0.15	0.0758
Cu (Copper) (kg/ha)	2.447	2.450	2.668	3.038	2.967	2.560
Fe (Iron) (kg/ha)	47.95	52.80	54.99	79.35	58.53	26.30
K (Potassium) (kg/ha)	80.4	105.6	106.2	160.4	209.5	560.5
Mg (Magnesium) (kg/ha)	79.2	86.4	110.6	157.3	207.7	425.1
Mn (Manganese) (kg/ha)	23.2	32.1	40.1	55.8	73.4	130.5
Mo (Molybdenum) (kg/ha)	0.0096	0.0110	0.0204	0.0375	0.0336	0.0758
Na (Sodium) (kg/ha)	19.76	24.01	30.41	60.30	88.75	187.18
Ni (Nickel) (kg/ha)	0.1877	0.1706	0.1947	0.2952	0.2349	0.1439
P (Phosphorus) (kg/ha)	40.05	38.97	42.53	50.05	46.67	43.63
Pb (Lead) (kg/ha)	26.33	27.84	29.23	29.30	23.26	2.85
Zn (Zinc) (kg/ha)	25.59	25.65	25.58	26.24	26.69	24.37

Table Footnote. LBC denotes Lime Buffer Capacity. CEC denotes Cation Exchange Capacity.

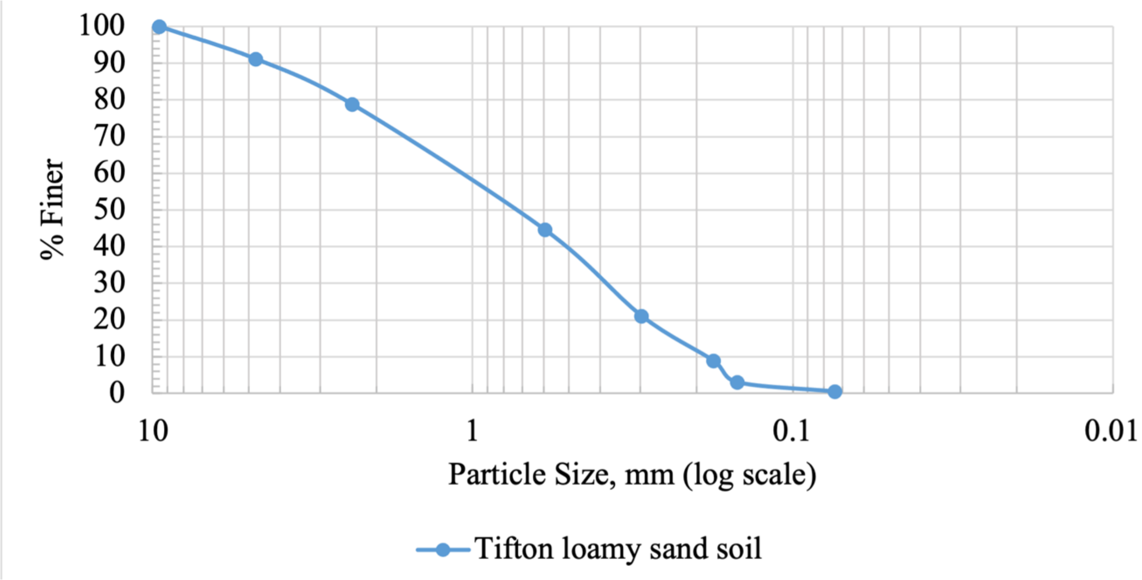

Figure 3.2. Tifton soil particle distribution curve. Particles between 6 x 10^{-5} and 3.9 x 10^{-3} mm are clay sized, between 3.9 x 10^{-3} and 6.25 x 10^{-2} mm are silt sized, between 6.25 x 10^{-2} and 2.0 mm are sand sized, and >2.0 mm is gravel sized.

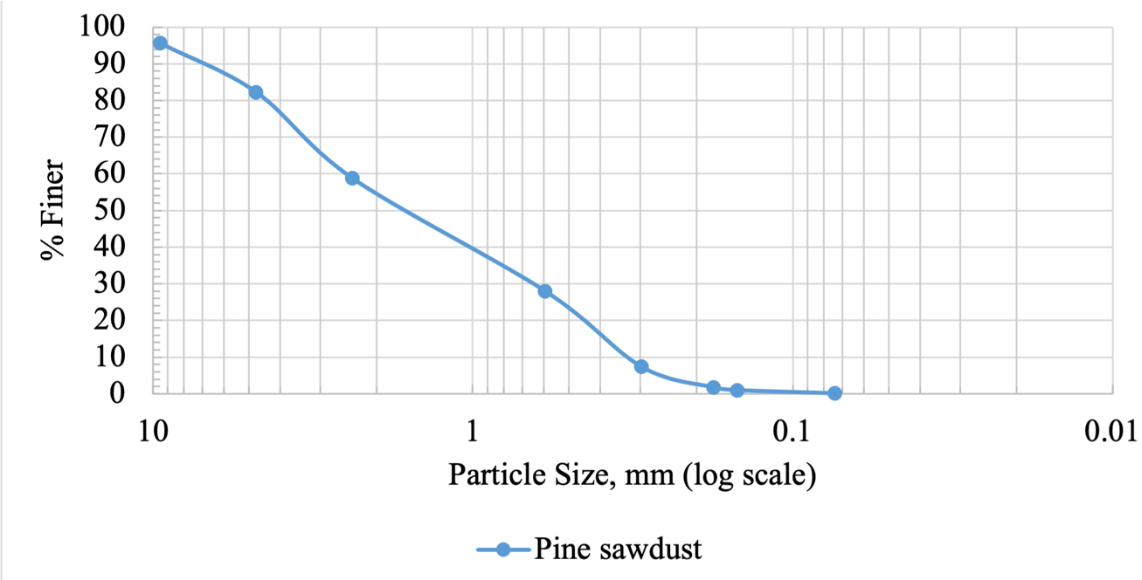

Figure 3.3. Pine sawdust particle distribution curve. Particles between 6 x 10^{-5} and 3.9 x 10^{-3} mm are clay sized, between 3.9 x 10^{-3} and 6.25 x 10^{-2} mm are silt sized, between 6.25 x 10^{-2} and 2.0 mm are sand sized, and >2.0 mm is gravel sized.

Figure 3.4. Bailey Williams flushing yellow dyed PFAS mixture through stainless steel columns with effluent collection bottles below.

Table 3.2. Analyte-specific mass spectrometer parameters and limit of quantitation (LoQ) for PFASs.

PFAS	Parent (m/z)	Daughter (m/z)	Dwell (s)	Cone Voltage (V)	Collision Voltage (V)	LoQ (µg/L)
PFBA	213	169	0.005	15	10	4.1
PF_4OPeA (PFMPA)	228.88	84.89	0.005	18	10	3
PFPeA	263	219	0.005	15	9	2.5
PF_5PHxA (PFMBA)	278.88	84.89	0.005	20	12	1.6
HFPO-DA (GenX)	285	169	0.005	12	8	3.7
3,6-OPFHpA	294.94	200.9	0.005	12	6	3.2
PFBS	298.9	80.1	0.005	56	26	1.6
PFHxA	313	269	0.005	14	10	3.8
PFEESA	315	135	0.005	44	20	1.1
4:2PTS	326.86	306.86	0.005	42	22	3.6
PFPeS	349	80.1	0.005	45	25	2.3
PFHpA	363	319	0.005	15	7	1.9
NaDONA	377	251	0.005	14	12	2.9
PFHxS	399	80	0.005	52	30	3.7
PFOA	412.86	368.8	0.005	14	10	2.4
6:2FTS	427	407	0.005	47	22	4.4
PFHpS	449	80.2	0.005	60	35	2.6
PFNA	463	418.9	0.005	20	10	1.3
FOSA	498	77.9	0.005	40	30	1.3
PFOS	498.78	80	0.005	60	35	1.6
PFDA	513	468.9	0.005	20	10	1.7
8:2FTS	527	506.8	0.005	53	28	2.7
9Cl-PF3ONS	531	351	0.005	55	25	1.9
PFNS	549	80.2	0.005	65	45	4.8
PFUdA	563	518.9	0.005	18	10	1.8
N-MeFOSAA	570	418.9	0.005	30	20	1.7
N-EtFOSAA	584	418.8	0.005	30	20	2.1
PFDS	599	80.2	0.005	70	50	2.7
PFDoA	613	568.9	0.005	22	10	2.4
11Cl-PF3OUdS	631	451	0.005	60	30	1.6
PFTrDA	663	618.9	0.005	22	15	2.6
PFTeDA	713	668.9	0.005	15	14	5.4

Table 3.3. The flow rate and the gradient condition of UPLC program.

Time (min)	Flow (mL/min)	%A	%B	Curve
Initial	0.3	95	5	Initial
0.5	0.3	95	5	6
1.5	0.3	60	40	6
10	0.3	20	80	6
11	0.3	5	95	6
11.1	0.3	95	5	6
13	0.3	95	5	6

Table 3.4. PFAS and the corresponding mass-labeled standard.

PFAS	**Mass-Labeled Standard**
PFBA	$^{13}C_4$-PFBA
PFPeA	$^{13}C_5$-PFPeA
PFHxA	$^{13}C_5$-PFHxA
PFHpA	$^{13}C_4$-PFHpA
PFOA	$^{13}C_8$-PFOA
PFNA	$^{13}C_9$-PFNA
PFDA	$^{13}C_6$-PFDA
PFUnA	$^{13}C_7$-PFUnA
PFDoA	$^{13}C_2$-PFDoA
PFTrDA	$^{13}C_2$-PFTeDA
PFTeDA	$^{13}C_2$-PFTeDA
PFBS	$^{13}C_3$-PFBS
PFPeS	$^{13}C_3$-PFHxS
PFHxS	$^{13}C_3$-PFHxS
PFHpS	$^{13}C_8$-PFOS
PFOS	$^{13}C_8$-PFOS
PFNS	$^{13}C_8$-PFOS
PFDS	$^{13}C_8$-PFOS
FOSA	$^{13}C_8$-FOSA
8:2FtS	$^{13}C_2$-4:2 FTS
6:2FtS	$^{13}C_2$-6:2 FTS
4:2FtS	$^{13}C_2$-8:2 FTS
N-EtFOSAA	d5-NEtFOSAA
N-MeFOSAA	d3-NMeFOSAA
HFPO-DA (GenX)	$^{13}C_3$-HFPO-DA
PFMPA	$^{13}C_4$-PFBA
PFMBA	$^{13}C_5$-PFPeA
ANODA	$^{13}C_4$-PFHpA
NFDHA	$^{13}C_5$-PFHxA
PFEESA	$^{13}C_3$-PFBS
11Cl-PF3OUdS	$^{13}C_8$-PFOS
9Cl-PF3ONS	$^{13}C_8$-PFOS

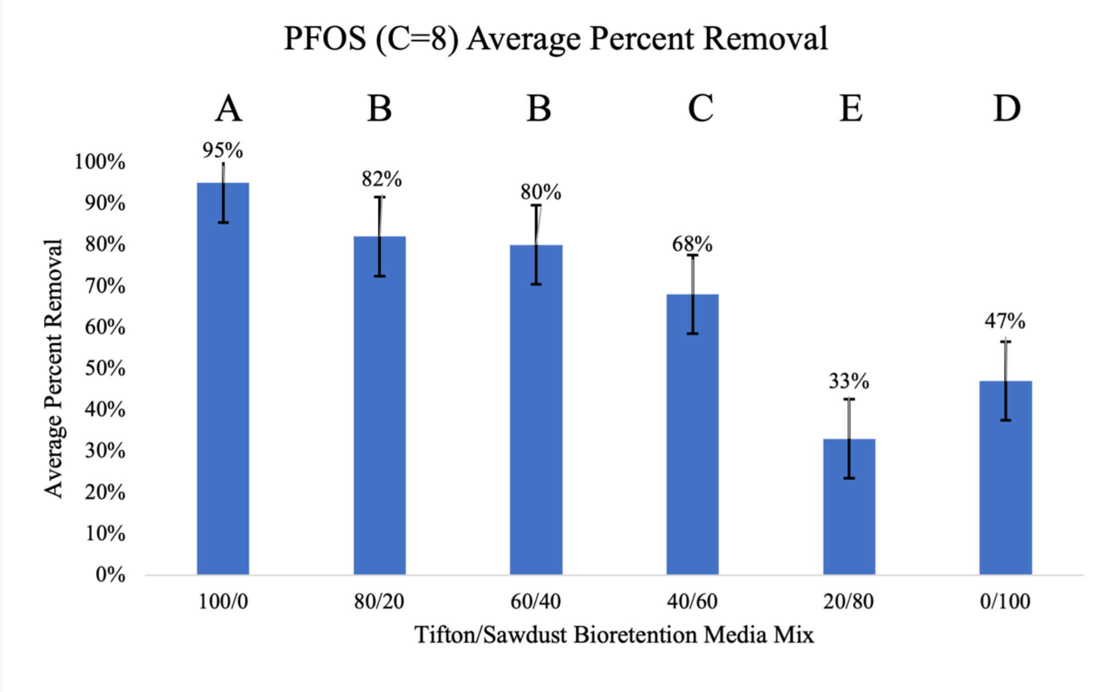

Figure 3.5. Average percent removal of PFOS in the six media mixes with connecting letters report.

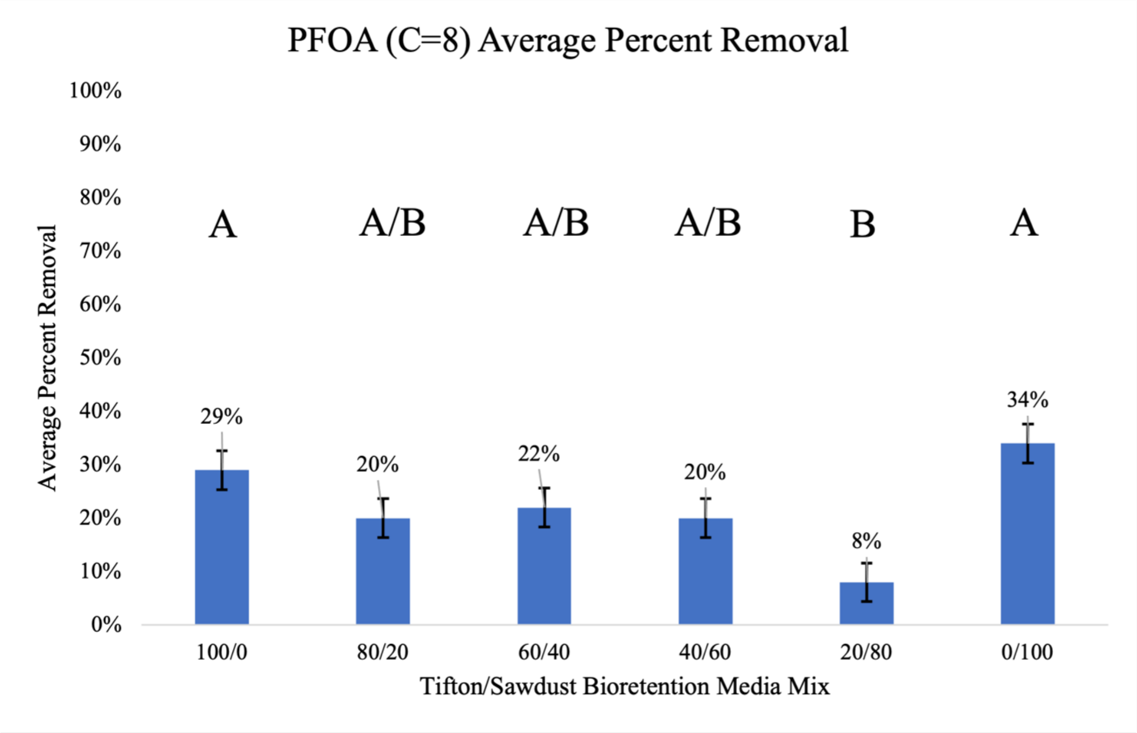

Figure 3.6. Average percent removal of PFOA in the six media mixes with connecting letters report.

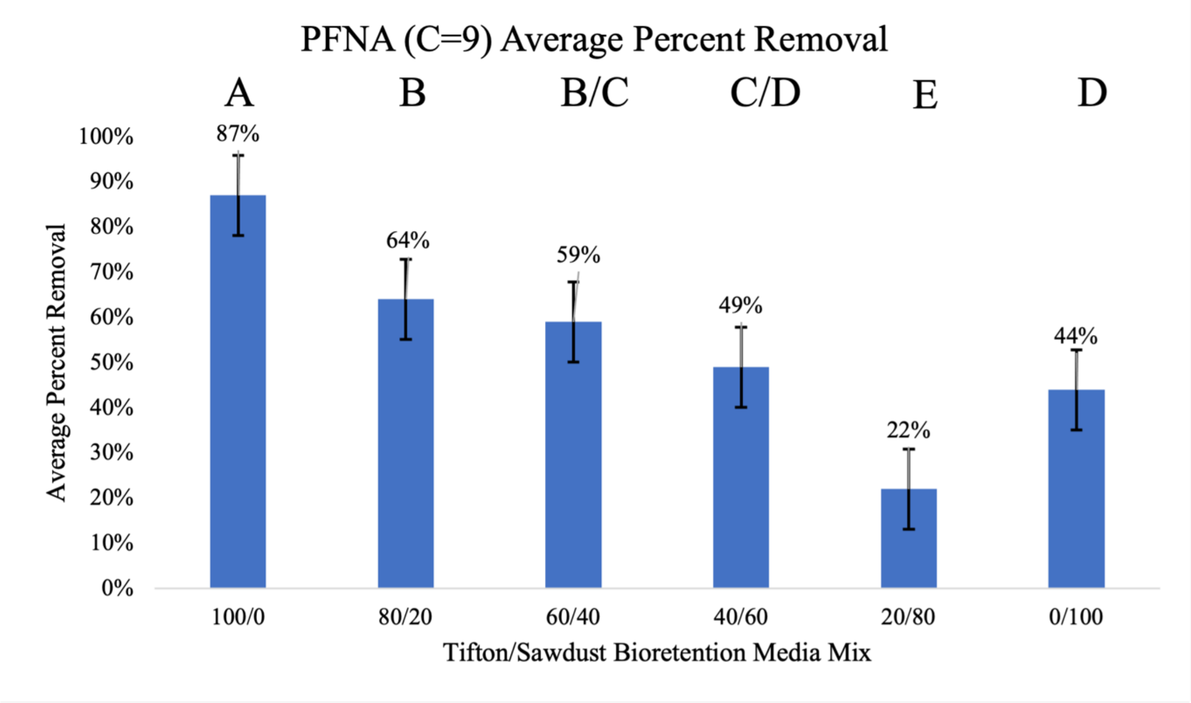

Figure 3.7. Average percent removal of PFNA in the six media mixes.

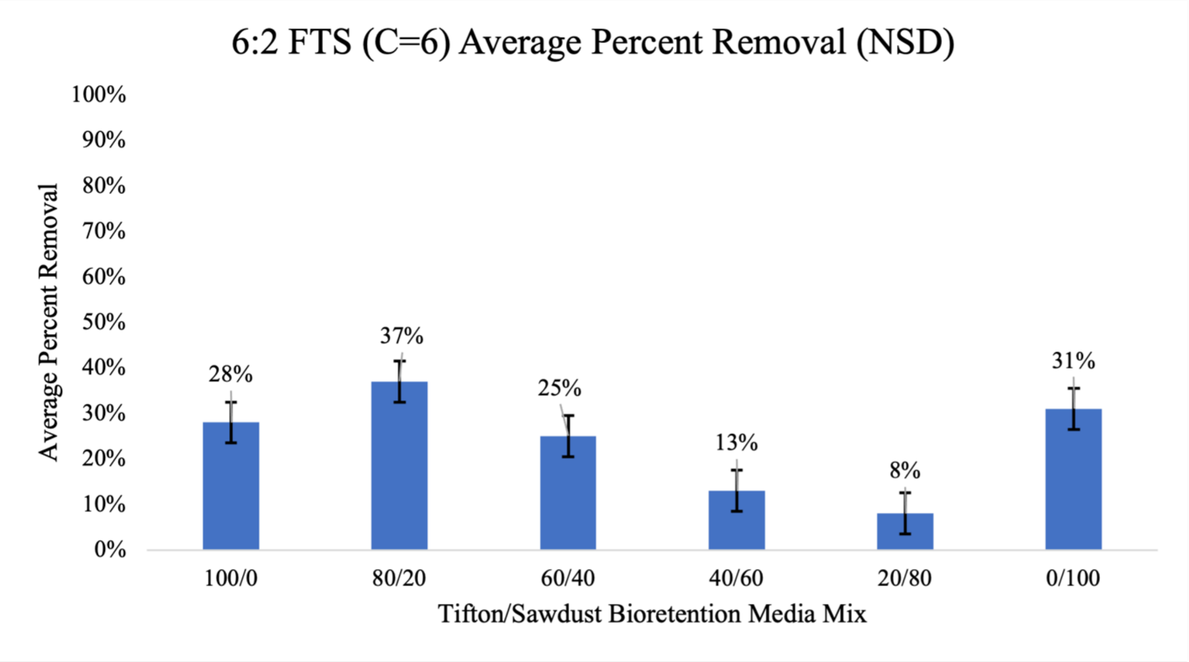

Figure 3.8. Average percent removal of 6:2 FTS in the six media mixes.

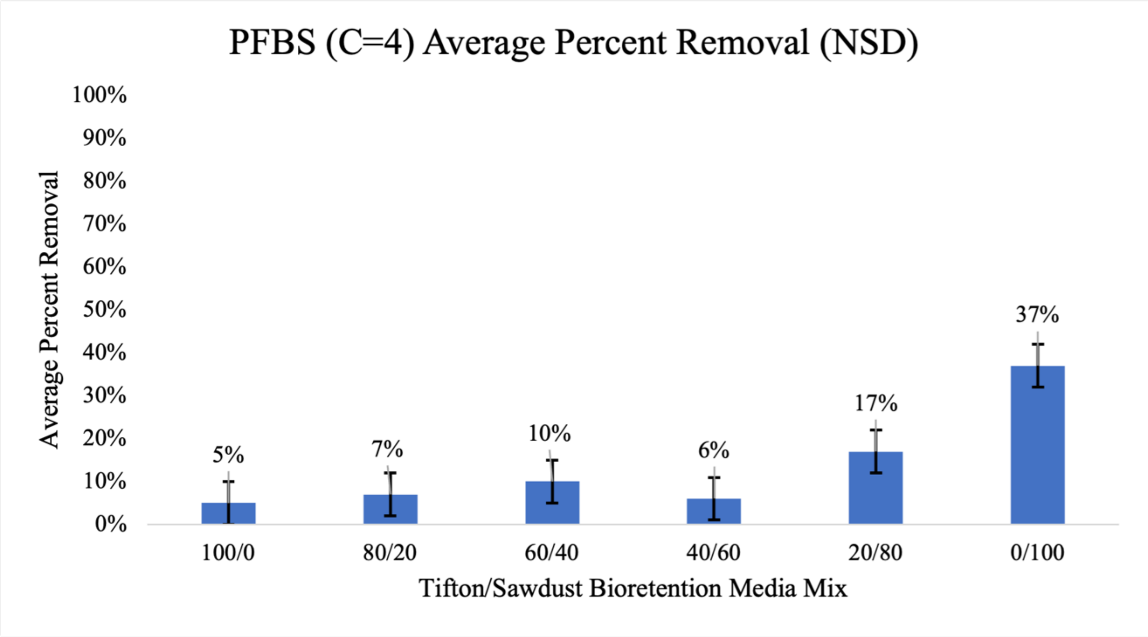

Figure 3.9. Average percent removal of PFBS in the six media mixes.

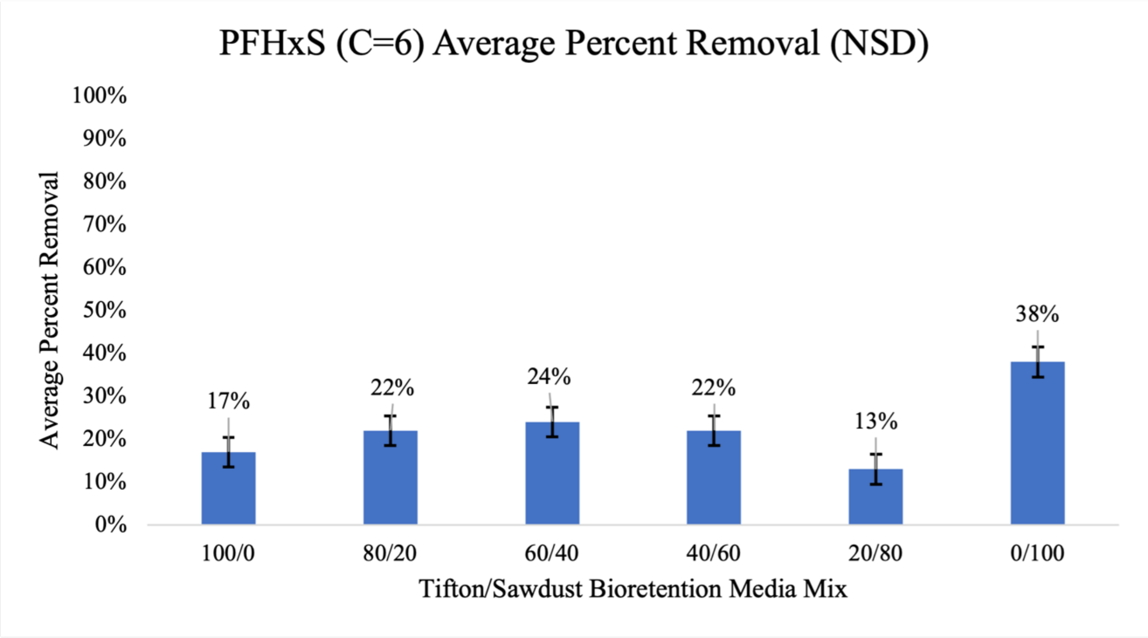

Figure 3.10. Average percent removal of PFHxS in the six media mixes.

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CHAPTER 4

OVERALL CONCLUSIONS

Overall, rural communities must be protected from land application system precipitation induced runoff and subsurface flow containing PFAS with methods that are affordable and effective. Two studies were conducted to assess the removal of six PFAS commonly found in wastewater from land application system runoff or subsurface flow after 1) passing through buffer zone soil plots containing Tifton soil and Bermudagrass sod, and 2) after passing through bioretention media mix columns containing Tifton soil and pine sawdust.

In chapter 2, the efficiency of land application system buffer zone soils to remove or retain six PFAS were assessed by constructing 30, 60, or 90 cm (length) by 30 cm (width) plots containing Tifton soil and Bermudagrass sod and irrigating with a PFAS solution. The effluent concentrations of PFAS were compared with the influent concentrations. Results showed that concentrations of PFOS and PFNA decreased after passing through the buffer zone because the buffer materials retained the chemicals through adsorption. Concentrations of PFOA, PFBS, PFHxS, and 6:2 FTS were less affected after passing though buffer zone soils possibly due to chain length and functional group present in the PFAS. Due to a shallow soil profile and high infiltration rates of Tifton soil, the length of the buffer zone plots had little impact on the removal of PFAS in our plot configuration.

In chapter 3, the efficiencies of bioretention media mixes to remove six PFAS were assessed by filling stainless steel columns with six mixtures of Tifton soil and pine sawdust ranging from 100/0 Tifton soil/sawdust to 0/100 Tifton soil/ sawdust with 20% decreases in Tifton soil.

Percent removal was calculated, and results revealed significant differences between media mixes in the long-chain PFAS: PFOS, PFNA, and PFOA. There were no significant differences between media mixes in the short-chain PFAS: 6:2 FTS, PFBS, or PFHxS. The use of a bioretention media mix to remove or retain PFAS may be selected based on the chain length of the PFAS. Longer-chain PFAS prefer media mixes with higher soil content while short-chain PFAS did not prefer one media mix over another but rather preferred to stay in solution.