Sorption of PFAS on Natural and Engineered Materials for Waste Containment

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Master of Science

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By
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Abstract

Per- and polyfluorinated alkyl substances (PFAS) are widely used surfactant chemicals that present engineering challenges due to their persistence in the environment and toxicity concerns for human health. PFAS enters landfills through consumer waste and can be present in landfill leachates at concentrations orders of magnitude greater than drinking water standards. The review serves as a starting point to assess the efficacy of engineered barrier systems to contain PFAS in landfill leachate by critically reviewing existing knowledge of PFAS sorption onto earthen and polymeric materials used in landfill liner systems.

Sorption of PFAS occurs through a combination of hydrophobic interactions from the fluorinated carbon chain and electrostatic interactions from the PFAS functional group. Factors influencing PFAS sorption include organic matter concentration, solution pH, ionic strength, soil minerology, and PFAS structure. Sorption of long chain PFAS (i.e. greater than 7 carbons) is primarily controlled by hydrophobic partitioning into organic matter, whereas sorption of short chain PFAS is primarily dependent on electrostatic interactions with charged surfaces. Bentonite clay used in geosynthetic clay liners (GCLs) may not be effective at sorbing PFAS, but polymeric components such as geomembranes and geotextiles may provide significant sorption of PFAS. Certain cross-linked and cationic polymer additives may be used in bentonite polymer composite GCLs for enhanced PFAS sorption.

An experimental method was developed to quantify PFAS sorption to typical landfill liner components using sorption batch tests. The PFAS analysis method was developed using a Thermo Scientific Altis LC-MS/MS. Experiments were unable to be fully conducted, but the developed method should provide guidance for future research.
ACKNOWLEDGMENTS

Thank you to Dr. Craig Benson for mentoring and guiding me these past two years. I would like to especially thank you for your flexibility and support when my thesis suddenly had to look very different than we were originally intending. Thank you to my committee members, Dr. Lisa Colosi Peterson and Dr. Janet Herman, for your support not only during these final stages, but throughout my entire graduate career. My thanks to Derek Henderson for all of the time we spent in the lab learning how to break and then fix the LC-MS/MS in new ways. To my labmates, Nick Chen and Sarah Gustitus-Graham, thank you for all of your guidance in and out of the lab, and for inspiring me to be a better scientist.

To my friends and quaranfam, thank you for listening to my thesis rants and for providing much needed outdoor breaks. Thank you, Juliet, for making our house a home. Finally, thank you to my family. All of you.
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1. INTRODUCTION

Per- and polyfluorinated alkyl substances (PFAS) are a suite of synthetically manufactured compounds that are of increasing concern in the environment. PFAS are hydrophobic, lipophobic, and highly resistant to degradation due to their fluorinated alkyl chain, making them effective for use as surfactants and coatings (Rayne and Forest 2009; Buck et al. 2011; Xiao 2017). Since their introduction in the 1940s, PFAS have been used in a wide array of consumer and industrial products including water and oil resistant textiles, nonstick cookware, fire-fighting foams, and food packaging such as pizza boxes and fast food wrappers (Buck et al. 2011, Lindstrom et al. 2011, Trier et al. 2011, Lang et al. 2016, Schaider et al. 2017). The use of PFAS has been so extensive that the United States Environmental Protection Agency (USEPA) estimates most people within the US have been exposed to PFAS and have small amounts in their blood (USEPA 2019).

The properties that make PFAS useful in consumer and industrial products contribute to their accumulation and persistence in the environment. PFAS has been found in aquatic environments and organisms across the globe, including the arctic, at concentrations ranging from a few ng/L to thousands of ng/L (Butt et al. 2007, Rayne and Forest 2009, Zareitalabad et al. 2013, Hu et al. 2016). Dust in households, classrooms, and cars have been shown to contain PFAS (Shoeib et al. 2011, Winkens et al. 2018). Crop fields fertilized with biosolids containing PFAS can result in PFAS concentrations in crop yield and food supply (Sepulvado et al. 2011, Yoo et al. 2011). The persistence of PFAS poses potential human health effects, including reproductive and carcinogenic effects due to association of PFAS into internal organs and through endocrine disruption (ASTDR 2012). USEPA has set an advisory limit for PFAS of 70 ng/L in drinking water, and some states have imposed regulations for PFAS that require notification for drinking water concentrations as low as 6 ng/L (USEPA 2019; CalEPA 2019).

Consumer goods and non-hazardous industrial wastes containing PFAS are discarded in municipal solid waste (MSW) landfills. Concentrations of PFAS in MSW landfill leachate can range
from a few ng/L to hundreds of µg/L, several orders of magnitude higher than drinking water standards (Table 1). An estimated 600 kg/year of PFAS is released to landfill leachate in the US (Lang 2017).

Landfill liners are used to contain leachate and prevent hazardous compounds from entering the groundwater system (Kong et al. 2017). Conventional geosynthetic clay liners (GCLs) are typically made with swellable bentonite clay encased by a polymeric geotextile. Advances in liner technology have introduced the use of bentonite-polymer composites (BPC-GCL) to create a chemical-resistant and more impermeable barrier (Di Emidio et al. 2011, Di Emidio et al. 2015). MSW landfill liners systems typically consist of a GCL beneath a high-density polyethylene (HDPE) geomembrane (Fig. 1).

![Conventional landfill liner system components](image)

**Figure 1.** Conventional landfill liner system components. Each component may have a different affinity for PFAS sorption.

Understanding how PFAS interacts with each component in a liner system is necessary to assess the efficacy of liners to contain PFAS in leachate. Park et al. (2012) and Benson et al. (2015) have previously studied the efficacy of liner systems to contain volatile organic compounds
using sorption batch and column tests that indicate the amount of chemical association occurring between the liner system and VOCs. Sorption behavior of VOCs and hydrophobic organic compounds (HOCs) may provide insight into the effectiveness of liners to contain PFAS (Park et al. 2012; Benson et al. 2015).

The recalcitrance of PFAS and their ubiquity in society suggests that PFAS will be present in landfills and landfill leachate for the foreseeable future. This thesis critically assesses existing knowledge of PFAS sorption to earthen and polymeric materials that are representative of those found in landfill liner systems. Section 2 of this thesis provides a review of PFAS chemistry and the mechanisms by which sorption occurs. Section 3 provides a review of PFAS sorption on earthen materials that might be used in engineered barriers. Section 4 provides a review of PFAS sorption on polymeric materials currently used in engineered barriers. Section 5 provides a review of PFAS sorption onto polymeric sorbents that might be added to engineered barriers to enhance sorption. Section 6 describes a method to quantify sorption of PFAS on materials used in engineered barriers. A summary and conclusions are provided in Section 7.

2. PFAS CHEMISTRY

2.1 Physical Properties of PFAS

PFAS consist of alkyl chains where hydrogen has been replaced partially (polyfluorinated) or fully (perfluorinated) with fluorine through electrofluorination or telomerization (Lehlmer 2005, Buck et al. 2011). There are over 900 existing registered chemicals categorized as PFAS by USEPA (Table 1) (USEPA 2020). In aqueous solution, PFAS are amphiphilic, meaning they have both hydrophobic and hydrophilic moieties (Schwarzenbach et al. 2003, Zhang et al. 2019). A hydrophobic fluorinated carbon chain (tail) and hydrophilic functional group (head) give them their unique surfactant properties.
Table 1. PFAS classes and compounds commonly identified in literature.

<table>
<thead>
<tr>
<th>PFAS Class</th>
<th>PFAS</th>
<th>Full Compound Name</th>
<th>Carbon Chain Length (n)</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFBA</td>
<td>Perfluorobutanoic acid</td>
<td>4</td>
<td>C4HF7O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFPeA</td>
<td>Perfluoropentanoic acid</td>
<td>5</td>
<td>C5F9O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFHxA</td>
<td>Perfluorohexanoic acid</td>
<td>6</td>
<td>C6HF11O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFHpA</td>
<td>Perfluoroheptanoic acid</td>
<td>7</td>
<td>C7HF13O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFOA</td>
<td>Perfluorooctanoic acid</td>
<td>8</td>
<td>C8HF15O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFNA</td>
<td>Perfluorononanoic acid</td>
<td>9</td>
<td>C9HF17O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFUnA</td>
<td>Perfluoroundecanoic acid</td>
<td>11</td>
<td>C11F21O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFDA</td>
<td>Perfluorodecanoic acid</td>
<td>10</td>
<td>C10HF19O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFDoA</td>
<td>Perfluorododecanoic acid</td>
<td>12</td>
<td>C13HF23O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Carboxylic Acid</td>
<td>PFTeDA</td>
<td>Perfluorotetradecanoic acid</td>
<td>14</td>
<td>C13F27O2</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFBS</td>
<td>Perfluorobutane sulfonic acid</td>
<td>4</td>
<td>C4HF5SO3</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFPeS</td>
<td>Perfluoropentane sulfonic acid</td>
<td>5</td>
<td>C5HF13SO3</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFHxS</td>
<td>Perfluorohexane sulfonic acid</td>
<td>6</td>
<td>C6HF13SO3</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFHpS</td>
<td>Perfluoroheptane sulfonic acid</td>
<td>7</td>
<td>C7HF13SO3</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFOS</td>
<td>Perfluoroctane sulfonic acid</td>
<td>8</td>
<td>C8HF17SO3</td>
</tr>
<tr>
<td>Perfluorooalkyl Sulfonic Acid</td>
<td>PFDS</td>
<td>Perfluorodecane sulfonic acid</td>
<td>10</td>
<td>C10HF19SO3</td>
</tr>
<tr>
<td>Fluorotelomer Sulfonic Acid</td>
<td>6:2FTSA</td>
<td>6:2 fluorotelomer sulfonate</td>
<td>6</td>
<td>C6F16C2H4SO3H</td>
</tr>
<tr>
<td>Fluorotelomer Sulfonic Acid</td>
<td>8:2FTSA</td>
<td>8:2 fluorotelomer sulfonate</td>
<td>8</td>
<td>C8F17CH2CH2SO3H</td>
</tr>
<tr>
<td>Perfluoroalkane sulfonamido</td>
<td>N-EtFOSAA</td>
<td>2-(N-ethylperfluoroctanesulfonamido)</td>
<td>8</td>
<td>C12H8F17NO4S</td>
</tr>
<tr>
<td>Perfluoroalkane sulfonamido</td>
<td>N-MeFOSAA</td>
<td>N-Methylperfluoroctane sulfonamido</td>
<td>8</td>
<td>C11H6F17NO4S</td>
</tr>
</tbody>
</table>

PFAS species are distinguished by carbon chain length and/or functional group, both of which affect chemical behavior. Species with 8 or more carbons are referred to as long chain PFAS, whereas those with fewer than 8 carbons are referred to as short chain PFAS. Perfluorinated PFAS chemical families include perfluoro carboxylic acids (PFCAs), perfluorooalkyl sulfonic acids (PFSAs), and perfluoroalkane sulfonamides (Buck et al. 2011). Fluorotelomers, perfluoroalkane sulfonamido derivatives, and semi-fluorinated n-alkanes are examples of polyfluorinated compounds that can be precursors or byproducts of PFAS. Figure 2 shows
structures of several PFAS classes. PFCAs and PFSAs are the most directly used in commercial products and can also be formed through the degradation of other PFAS such as fluorotelomers and perfluoro sulfonamides (Rayne and Forest 2009).

Figure 2. Structures of PFAS chemical families. Carbon chain length (n) can vary from 4 to 14 (from Lindstrom et al. 2011).

The distribution and concentration of PFAS compounds in MSW leachate can differ greatly between landfills, but some similarities are notable. Allred et al. (2014) analyzed the occurrence of 70 PFAS compounds in 7 U.S. MSW landfill leachates and reported a total PFAS concentration ranging 3200 to 160,000 ng/L (8.6 – 550 nM). PFCAs constituted the largest percentage of the total PFAS concentration, ranging from 20 to 88% of the PFAS makeup, whereas PFSAs made
up only 2.5 – 8.5 %. Greater than 97% of the PFCAs that were detected had between 4 carbons (PFBA) and 8 carbons (PFOA). Studies from Busch et al. (2010), Huset et al. (2011), Bensken et al. (2012), Li et al. (2012), and Fuertes et al. (2017) confirm the dominance of short-chain PFCAs in MSW landfill leachate, regardless of location and total PFAS concentration (Table 2).

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>PFAS Studied</th>
<th>Leachates Analyzed</th>
<th>Landfill/Leachate Characteristics</th>
<th>Sum of PFAS (ng/L)</th>
<th>PFCA (%)</th>
<th>PFSA (%)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Busch et al. (2010)</td>
<td>Germany</td>
<td>43</td>
<td>22</td>
<td>Treated MSW Leachate</td>
<td>3.97-8060</td>
<td>19-98</td>
<td>0.4-61</td>
<td>PFBS and PFBA accounted for approx. 50% of total PFAS</td>
</tr>
<tr>
<td>Huset et al. (2011)</td>
<td>U.S.</td>
<td>24</td>
<td>6</td>
<td>MSW and Non-MSW Leachate</td>
<td>3079-8446</td>
<td>39-71</td>
<td>13-26</td>
<td>Short chain PFAS more abundant than long chain</td>
</tr>
<tr>
<td>Benskin et al. (2012)</td>
<td>N. America</td>
<td>24</td>
<td>10</td>
<td>Untreated MSW Leachate</td>
<td>3800-36000</td>
<td>15-56</td>
<td>12-21</td>
<td>Monitored the same landfill over 5 months</td>
</tr>
<tr>
<td>Li et al. (2012)</td>
<td>Canada</td>
<td>13</td>
<td>28</td>
<td>Untreated Landfill Leachate</td>
<td>27-21300</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Short chain PFCAs accounted for 73% of total PFAS</td>
</tr>
<tr>
<td>Allred et al. (2014)</td>
<td>U.S.</td>
<td>70</td>
<td>7</td>
<td>Untreated MSW Leachate</td>
<td>3200-160000</td>
<td>20-88</td>
<td>2.5-8.5</td>
<td>Short chain PFAS more abundant than long chain</td>
</tr>
<tr>
<td>Fuertes et al. (2017)</td>
<td>Spain</td>
<td>16</td>
<td>6</td>
<td>Treated and Untreated MSW Leachate</td>
<td>639.2-1378.9</td>
<td>58-100</td>
<td>0-42</td>
<td>Analyzed for only PFCAs and PFSA. 8 of 16 analytes detected in leachates.</td>
</tr>
</tbody>
</table>

### 2.2. PHYSICAL PROPERTIES OF PFAS

The persistence of PFAS is due in part to the unique properties of fluorine and the C-F bond. Fluorine is the most electronegative element in the periodic table, ranked highest on the Pauling scale (Table 3) (Pauling 1932). The electronegative strength of fluorine results in a highly polar bond between carbon and fluorine (Biffinger et al. 2004, O’Hagan 2008). The C-F bond is both strong (Bond Dissociation Energy = 485 kJ/mol) and short (0.138 nm) due to the strong polar association with carbon (Table 3). Opposing C-F dipoles along a fully fluorinated carbon chain
neutralize each other and result in an overall nonpolar compound (Kirsch 2004, Rayne and Forest 2009).

**Table 3.** Characteristics of carbon-halogen (C-X) bonds (from Kirsch 2004).

<table>
<thead>
<tr>
<th>X</th>
<th>H</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Length, C-X (nm)</td>
<td>0.109</td>
<td>0.138</td>
<td>0.177</td>
<td>0.194</td>
</tr>
<tr>
<td>Dissociation Energy, C-X (kJ mol⁻¹)</td>
<td>410</td>
<td>485</td>
<td>323</td>
<td>269</td>
</tr>
<tr>
<td>Electronegativity, X (Pauling Scale)</td>
<td>2.20</td>
<td>3.98</td>
<td>3.16</td>
<td>2.96</td>
</tr>
<tr>
<td>Dipole moment, μ, C-X (C m)</td>
<td>1.33E-30</td>
<td>4.70E-30</td>
<td>4.87E-30</td>
<td>4.60E-30</td>
</tr>
<tr>
<td>Atom Polarizability (C m² V⁻¹)</td>
<td>5.97E-9</td>
<td>5.01E-9</td>
<td>1.96E-8</td>
<td>2.74E-8</td>
</tr>
</tbody>
</table>

Fluorine also has a lower polarizability than hydrogen due to size and electronegativity (Table 3). Low polarizability indicates a dense electron cloud that is not as susceptible to dispersion that would result in an uneven charge distribution of an atom (Schwarzenbach et al. 2003). Fluorine atoms along the C-F chain therefore have high steric repulsion that forces the atoms far from each other so as not to distort or disperse the electron cloud (Kirsch 2004). The steric repulsion between fluorine atoms causes PFAS to have a more rigid structure than hydrocarbons (Biffinger et al. 2004, Kirsch 2004). Densely packed fluorinated carbon chains have a shielding effect as a result of this low polarizability that reduces the tendency to participate in nonpolar intermolecular interactions such as Van der Waals forces or hydrogen bonding (Du et al. 2014, Wei et al. 2019). The combination of these fluorine properties yields a compound that resists chemical breakdown under natural settings due to the energy needed to break the C-F bond and the resistance to external molecular interaction with the fluorinated tail.

PFAS are mobile in aquatic systems due to the dissociation of the acidic functional group in water. PFSAs are expected to have an acid dissociation constant (pKa) < 1 (Lampic and Parnis 2020). The pKa of PFCAs are typically > PFSAs, although measured and estimated pKa for PFCAs vary (-0.5 to 4.2) (Table 4) (Goss 2008, Buck et al. 2011, Lampic and Parnis 2020). Low pKa indicates that PFAS will be present as an anion in most natural waters (pKa<pH). The pH of
MSW leachate changes over time as degradation takes place, from as low as 4 early in landfill life to as high as 9 later in life (Kjelsden et al. 2010). PFAS are therefore expected to be primarily anionic in MSW leachate, with the potential exception of PFCAs in the very acidic phase of a landfill.

Table 4. Relevant chemical properties of PFAS and HOCs of interest in leachate containment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>log K\textsubscript{ow}</th>
<th>pKa</th>
<th>Solubility in Water at 25° C (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>4.81\textsuperscript{a}</td>
<td>-0.5 - 4.2\textsuperscript{a}</td>
<td>9500\textsuperscript{b}</td>
</tr>
<tr>
<td>PFOS</td>
<td>4.49\textsuperscript{a}</td>
<td>&lt;1\textsuperscript{a}</td>
<td>680\textsuperscript{d}</td>
</tr>
<tr>
<td>PFBA</td>
<td>2.31\textsuperscript{a}</td>
<td>1.07\textsuperscript{a}</td>
<td>214000\textsuperscript{a}</td>
</tr>
<tr>
<td>PFBS</td>
<td>1.82\textsuperscript{a}</td>
<td>-3.31\textsuperscript{a}</td>
<td>344\textsuperscript{a}</td>
</tr>
<tr>
<td>PFHxA</td>
<td>3.48\textsuperscript{a}</td>
<td>-0.16\textsuperscript{a}</td>
<td>15700\textsuperscript{b}</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.13\textsuperscript{c}</td>
<td>-</td>
<td>1790\textsuperscript{d}</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.73\textsuperscript{c}</td>
<td>-</td>
<td>526\textsuperscript{d}</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>1.25\textsuperscript{c}</td>
<td>-</td>
<td>13000\textsuperscript{d}</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>1.46\textsuperscript{d}</td>
<td>-</td>
<td>8800\textsuperscript{d}</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.73\textsuperscript{c}</td>
<td>-</td>
<td>1160\textsuperscript{d}</td>
</tr>
<tr>
<td>1,2-dichloroethylene</td>
<td>2.07\textsuperscript{c}</td>
<td>-</td>
<td>4520\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Gagliano et al. (2020), \textsuperscript{b} ASTDR (2015), \textsuperscript{c} EPA 1996 \textsuperscript{d} National Center for Biotechnology Information. PubChem Database. https://pubchem.ncbi.nlm.nih.gov.

Octanol-water coefficients (K\textsubscript{ow}) provide insight into the hydrophobicity of PFAS in comparison to other organic pollutants common in landfill leachate (Table 4). Hydrophobicity increases with lipophilicity as more of the compound associates with octanol rather than water, resulting in higher K\textsubscript{ow}. Elzerman and Coates (1987) classify hydrophobic organic compounds (HOCs) as nonpolar compounds with logK\textsubscript{ow} > 2 and low solubility in water (<100 mg/L), indicating a strong preference to separate from the aqueous phase. The solubility reported in Table 4 is for the protonated PFAS species, and therefore indicates the readiness of PFAS to deprotonate into its anionic form. HOC sorption is typically controlled by hydrophobic partitioning into organic matter and described by an organic carbon partition coefficient (K\textsubscript{oc}), which is defined as:

\begin{equation}
K_{\text{oc}} = K_d / f_{oc}
\end{equation}
where $K_d$ is the solid-liquid partition coefficient and $f_{oc}$ is the organic carbon fraction (Langmuir 1997). Partitioning into organic matter is related to the hydrophobicity of the compound. Consequently, $K_{OC}$ is often estimated from $K_{ow}$ (Briggs 1981, Edil et al. 1995, Doucette 2003). The same cannot be said for PFAS due their combination of both hydrophobic and lipophobic properties. Unlike many HOCs, PFAS have low solubility in both water and octanol due to their lower surface tension, which makes $K_{ow}$ difficult to determine experimentally and a poor indicator of behavior in solution (Du et al. 2014).

### 2.3. PFAS Sorption Mechanisms

The amphiphilic nature of PFAS makes predicting sorption behavior complex. PFAS sorption occurs predominantly through electrostatic interaction with the hydrophilic functional group or hydrophobic interactions with the fluorinated tail (Higgins and Luthy 2006, Johnson et al. 2007, Xiao et al. 2012, Du et al. 2014). The $f_{oc}$, sorbent surface charge, solution pH, cation concentration, and PFAS structure have been shown to affect PFAS sorption (Higgins and Luthy 2006, Jeon et al. 2011, Schuricht et al. 2017, Campos Pereira et al. 2018, Zhang et al. 2019). Understanding the relative importance of these factors on sorption is an evolving area of knowledge, and is discussed in subsequent sections.

Electrostatic attraction is expected between the anionic head of PFAS and sorbents with a positive surface charge. Natural soils typically have a net negative charge, and thus are expected to repel PFAS (Langmuir 1997). Increased concentrations of positively charged elements in mineral surfaces, such as metal oxides, can provide sites for potential electrostatic attraction of PFAS (Fig. 3a) (Higgins and Luthy 2006, Johnson et al. 2007). Adsorption of cations in aqueous solution can decrease the negative surface charge and reduce intermolecular repulsion of anionic functional groups, allowing for more electrostatic attraction of PFAS (Tang et al. 2010, Xiao et al. 2011, Du et al. 2014). Adsorbed divalent cations have been shown to provide
bridges between PFAS compounds and negatively charged mineral surfaces (Fig. 3b) (You et al. 2010, Wang and Shih 2011, Du et al. 2014.)

![Diagram of metal oxides in soil providing positively charged surface sites that can attract anionic PFAS.](image1)

**Figure 3.** a. Metal oxides in soil provides positively charged surface sites that can attract anionic PFAS. b. Divalent cations provide a bridge for anionic PFAS to associate to negatively charged surfaces.

Hydrophobic interaction occurs between the fluorinated PFAS tail and hydrophobic sorbents due to the preferential separation of hydrophobic compounds from water (Fig. 4) (Edil et al. 1995, Chandler 2005). Hydrophobic natural organic matter (NOM) provides a partitioning surface for PFAS and other hydrophobic compounds (Delle Site 2001, Kleindam et al. 2002, Higgins and Luthy 2006). The hydrophobic association into organic matter can overcome electrostatic repulsion of PFAS functional groups by negatively charged surfaces (Higgins and Luthy 2006, Rayne and Forest 2009, Zhou et al. 2009, Ahrens et al. 2011, Deng et al. 2012, Milinovic et al. 2015). The affinity for hydrophobic interaction is seemingly in contrast with the lipophobic nature of PFAS. PFAS molecules may have greater hydrophobicity than lipophobicity, explaining their preference for partitioning into hydrophobic surfaces relative to remaining in an aqueous phase (Biffinger et al. 2004, Zhou et al. 2010, Du et al. 2014).
HOCs that are affected by van der Waals forces can adsorb to solids through hydrogen bonding (Yoon et al. 2004, Zhao et al. 2020). PFAS tails are not inclined to form hydrogen bonds due to the low polarizability of the C-F bond limiting intermolecular interaction from van der Waals forces (Du et al. 2014, Wei et al. 2020). There is disagreement in the literature regarding whether PFAS can form hydrogen bonds as a way to separate from solution. The oxygen in the PFAS functional group has been reported to accept hydrogen bonds from hydroxyl moieties on metal oxides and fiber membranes and increase sorption (Gao and Chorover 2012, Xu et al. 2013, Lu et al. 2016). In contrast, increased hydroxyl and carboxyl groups on soil solids decreased PFAS sorption to carbon nanotubes (Zhang et al. 2009, Deng et al. 2012). Sorption of PFAS onto soil surfaces is dominated by hydrophobic and electrostatic interaction, and hydrogen bonding is reported to be limited in most cases (Higgins and Luthy 2006, Gagliano et al. 2020, Wei et al. 2020).

PFAS sorption has been modeled using Langmuir and Freundlich isotherm equations with varying degrees of linearity (Higgins and Luthy 2006, Milinovic et al. 2015, Wang et al. 2015). The Langmuir isotherm models is:

Figure 4. Hydrophobic interaction occurs between the fluorinated tail of PFAS and hydrophobic organic matter.
\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \]  

(2)

where \( q_e \) is the equilibrium sorption capacity of the sorbent in mass of sorbate per mass sorbent, \( C_e \) is the equilibrium concentration of sorbate in solution in mass per volume, \( q_m \) is the maximum sorption capacity of the sorbent in mass of sorbate per mass of sorbent, and \( K_L \) is the Langmuir constant in volume per mass. The Freundlich model is:

\[ q_e = K_F C_e^n \]  

(3)

where \( q_e \) is the equilibrium sorption capacity of the sorbent in mass of sorbate per mass of sorbent, \( C_e \) is the equilibrium concentration of sorbate in solution in mass per volume, \( K_F \) is the Freundlich constant in mass per area times mass per volume, and \( n \) is the degree of linearity between 0 and 1. When the Freundlich model is fit to linear data, \( n = 1 \) and \( K_F = K_d \).

3. SORPTION TO EARTHEN MATERIALS

3.1. Intro

PFAS sorption to earthen materials is dependent on the composition of the soil solid, the solution chemistry, and the PFAS species present (Fig. 5). This section will discuss the environmental factors influencing PFAS sorption on soil solids.

\[ \text{Figure 5. The compound specific and environmental factors that influence PFAS behavior should all be considered when assessing PFAS sorption.} \]
3.2. Soil Organic Matter

The presence of hydrophobic organic matter in soil has a strong influence on PFAS sorption (Higgins and Luthy 2006, You et al. 2010, Zhou et al. 2010, Jeon et al. 2011, Mejia-Avendaño et al. 2020). As the organic carbon fraction ($f_{oc}$) increases, greater opportunity exists for partitioning of hydrophobic moieties to the soil (Edil et al. 1995, Kleineidam et al. 2002, Higgins and Luthy 2006). Higgins and Luthy (2006) conducted sorption batch tests using eight anionic PFAS compounds on five freshwater sediments from riverine and lacustrine sites to assess the relative impacts of sediment parameters on PFAS sorption. The sediments had $f_{oc}$ ranging from 0.0056 to 0.0966 and iron oxide content ranging from 116 to 1025 µmol/g. Initial PFAS concentrations ranged from 1 to 200 nM (approximately $5.0 \times 10^{-7}$ to $1.0 \times 10^{-4}$ mg/L). To directly compare sorption of the different PFAS compounds onto the six sediments, $K_d$ was evaluated at an equilibrium aqueous concentration of 5 nM. A strong relationship was found between $K_d$ and $f_{oc}$ for all eight PFAS compounds ($R^2 > 0.92$), indicating that sorption primarily occurred through partitioning into organic carbon (Higgins and Luthy 2006). Higgins and Luthy (2006) conclude that organic carbon fraction is the driving influence on PFAS sorption, and factors such as iron oxide content in the sediment may play a secondary role in sorption through influencing electrostatic behavior.

Ahrens et al. (2010) studied sorption of PFOA, PFOS, and PFOSA onto 3 different natural sediments: a sandy river sediment ($f_{oc} = 0.0003$), and two muddy river sediments ($f_{oc} = 0.016$ and $0.0047$). Batch tests were conducted at initial concentrations ranging from 1.4 to 142 ng/L. A statistically significant correlation was found between log $K_d$ and $f_{oc}$ for PFOS and PFOSA ($p < 0.0001$), indicating that association into organic matter was the driving force of sorption. The lowest sorption capacity was obtained for the sandy river sediment, which had the lowest organic carbon content (Ahrens et al. 2010).
Zhou et al. (2010) investigated sorption of PFOS onto an organoclay made from sodium montmorillonite (NaMt) that was coated with an organic cation surfactant (hexadecyltrimethylammonium bromide, HDTMAB, molecular weight = 364.45 g/mol). Coated clay was created by shaking 10 g NaMt with four concentration levels of HDTMAB (2.12 – 26.5 mmol) for 2 hours. Sodium on the montmorillonite was replaced with the cationic surfactant through cation exchange. Free bromide was washed off using Milli-Q water, leaving only organoclay. The $f_{oc}$ for the organoclays ranged from 0.06 to 0.75 and were interpreted using the following method:

$$f_{oc} = \frac{n \text{ mmol HDTMAB}}{10 \text{ g NaMt}} \times \frac{1}{(364.45 - 79.9) \text{ g mol HDTMA}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}}$$

where $n$ is the concentration level of HDTMAB given by Zhou et al. (2010) and molecular weight is adjusted for the loss of attached bromide ions. Batch tests were conducted for the organoclays and uncoated NaMt, with PFOS concentrations ranging 50 to 500 mg/L. The organoclay with the greatest $f_{oc}$ had a sorption capacity of 344.8 mg PFOS/g clay, which was almost twice the sorption capacity of the uncoated clay (181.9 mg PFOS/g clay). PFOS sorption increased with increasing organic carbon fraction and decreasing pH, indicating a combination of hydrophobic and electrostatic sorption mechanisms. Zhou et al. (2010) conclude that hydrophobic partitioning into organic matter is primarily responsible for sorption of PFOS to organo-montmorillonite, and pH has a secondary impact through electrostatic interaction between PFOS and organoclay.

PFAS sorption to soil may be inhibited at low $f_{oc}$ when soil organic matter is present in low quantities (Jeon et al. 2011, Zhang et al. 2014). Jeon et al. (2011) investigated sorption of PFOA and PFOS to kaolinite and montmorillonite clays coated with an organic mixture of humic acid, tannic acid, and natural river organic matter to achieve $f_{oc}$ ranging from 0.0017 to 0.0077. The clay coating method was similar to that described by Zhou et al. (2010). Batch tests were conducted for $10^{-4}$ mg/L of PFOA and PFOS with organo-coated and uncoated clays. A linear
relationship was found between $K_d$ and $f_{oc}$ for both PFOA and PFOS, indicating a relationship between sorption and organic matter content. Uncoated kaolinite and montmorillonite clays had greater $K_d$ than organo-coated clays (greater PFAS sorption to uncoated clays). Given the strong association of PFAS to hydrophobic organic matter, uncoated clays were expected to have a lower sorption capacity than organo-coated clays. Jeon et al (2011) indicate that there is competition between hydrophobic dissolved organic matter (DOM) and PFAS for sorption sites on the coated clays.

Zhang et al. (2014) investigated PFOS sorption onto coated and uncoated kaolinite and montmorillonite. Organo-coated clays ($f_{oc} < 0.001$) were generated through mixing with a humic acid solution over two weeks. Batch tests were conducted to compare the sorption capacities of 1.0 mg/L PFOS to the coated and uncoated clays. Uncoated montmorillonite had a sorption capacity of 77.6 µg/g and uncoated kaolinite had a sorption capacity of 54.5 µg/g. Sorption capacities of organo-coated clays were at least 19% lower than for uncoated clays. The organo-coated kaolinite had a sorption capacity of 62.2 µg/g and organo-coated montmorillonite had a sorption capacity of 40.7 µg/g. Zhang et al. (2014) suggest that PFOS sorption on the coated clays was hindered by an increase in electrostatic repulsion from the negatively charged humic acid and competition between PFOS and humic acid for mineral sorption sites. At the low level of carbon content in the study, there was not a sufficient layer organic matter to allow for hydrophobic partitioning of PFOS, so electrostatic interactions dominated sorption.

### 3.3. Mineral Composition

In the absence of sufficient organic matter for hydrophobic interaction, or for short-chain PFAS compounds less inclined to hydrophobic interaction, other factors can control PFAS sorption onto solid surfaces. Wei et al (2017) studied the sorption of PFOS onto six agricultural soils with $f_{oc}$ ranging 0.0087 to 0.0277, $\text{Fe}_2\text{O}_3$ concentration ranging 8.44 to 80.66 g/kg, and $\text{Al}_2\text{O}_3$ ranging 0.69 to 17.75 g/kg. Batch tests were conducted with PFOS at initial concentrations
ranging 10⁻⁵ to 10⁻³ mg/L. Equilibrium sorption data were fit with the Freundlich model (Eq. 3) and $K_F$ compared with the soil properties to determine if significant factors affecting sorption could be found. A significant positive correlation ($p < 0.05$) was found between $K_F$ and organic content, $\text{Al}_2\text{O}_3$ content, and $\text{Fe}_2\text{O}_3$ content. Metal oxides provide a positively charged surface site for electrostatic attraction of anionic PFAS. The trends in Wei et al (2017) suggest that increased presence of metal oxides in soil increases PFAS sorption.

The point of zero charge ($\text{pH}_{\text{pzc}}$), or isoelectric point, is the pH at which the mineral surface has a net surface charge of zero (no surface charge to be neutralized by ions in solution) (Sposito 2008). At $\text{pH} = \text{pH}_{\text{pzc}}$, the amount of positive and negative charges at the mineral surface are equal, resulting in a surface with a net neutral charge (Bakatula et al. 2018). In aqueous solutions where $\text{pH} < \text{pH}_{\text{pzc}}$, the mineral surface will have a net positive charge due to a surplus of hydrogen protons associating with the surface. Conversely, the mineral surface will have a net negative charge when $\text{pH} > \text{pH}_{\text{pzc}}$ from greater hydroxyl concentrations. Thus, the pH$_{\text{pzc}}$ of a mineral is an indicator of whether the surface will attract or repel anions such as PFAS (Johnson et al. 2007, Zhou et al. 2010, Hellsing et al. 2016).

Johnson et al. (2007) investigated PFOS sorption on Ottawa sand, iron oxide-coated quartz sand, goethite, and kaolinite. The iron oxide coating consisted of alumina, silica, and goethite nanoparticles. Batch tests were conducted with PFOS at initial concentrations ranging 0.12 to 8.9 mg/L. Ottawa sand and kaolinite were expected to have a net negative surface charge based on their pH$_{\text{pzc}}$, whereas goethite and iron-oxide coated sand were expected to have a net positive charge. PFOS was expected to preferentially sorb to goethite and high iron sand. However, PFOS sorbed per unit mineral surface area (molecules PFOS per nm²) was highest for Ottawa standard sand, followed by the iron-coated sand, kaolinite and goethite (Fig. 6). PFOS had a stronger affinity for the Ottawa and quartz sand particles than for clay or pure goethite. Johnson et al. (2007) suggest that PFOS preferentially sorbs to quartz surface in Ottawa and iron-
oxide coated sands, and therefore PFOS sorption was limited by iron-oxide occupying quartz surface sites. Goethite has a positively charged surface, which would indicate attraction of PFOS molecules and greater sorption to the solid. Electrostatic attraction between the PFOS functional group and goethite surface may not be strong enough to hold the molecule to the limited surface area of the goethite nanoparticles.

Zhang et al. (2014) conducted batch tests with PFOS (1.0 mg/L) onto kaolinite and montmorillonite with solutions having pH = 5 – 7. The pH_{pzc} was 3.2 for kaolinite and 2.0 for montmorillonite. Surface area normalized sorption of PFOS on kaolinite (7.3 x 10^{-3} molecules PFOS per nm^2) was more than 10 times greater than on montmorillonite (0.7 x10^{-3} molecules PFOS per nm^2) (Fig. 6). Both mineral surfaces had a net negative charge and were expected to repel anionic PFOS molecules. Electrostatic repulsion of PFOS may have been greater for montmorillonite because the difference between pH and pH_{pzc} was greater for montmorillonite. As pH increases above pH_{pzc}, the net charge of the surface becomes more negative, and more negative charge could result in greater repulsion of PFOS (Zhang et al. 2014). Jeon et al. (2011) similarly found that the surface area normalized sorption on kaolinite was 10 times greater than for montmorillonite, supporting the conclusion that montmorillonite clay will have less affinity for PFAS sorption than kaolinite clay (Fig. 6).

Hellsing et al. (2016) studied sorption of PFOA, PFNA, PFHxA, and PFOS onto silica and alumina using neutron reflection experiments, which allow for molecular-scale observations of sorption. Silica (pH_{pzc} = 2) and alumina (pH_{pzc} = 6) were chosen as minerals that are abundant in soils. At the pH range of the study (pH = 1.4 – 6.1), silica was expected to have a net negative charge and alumina was expected to have a net positive charge. The highest sorption capacity was reported for alumina and PFNA at 7.47 molecules PFNA per nm^2. Electrostatic attraction of anionic PFAS functional groups to positively charged alumina surface was responsible for
sorption. No measurable sorption of PFAS occurred on silica, which Hellsing et al. (2016) attribute to electrostatic repulsion between the negatively charged silica surface and anionic molecules.

_Bentonite clay used in GCLs consists mainly of montmorillonite, which Figure 5 indicates will not effectively sorb PFAS. Li et al. (2015) conducted batch tests with 10 µg/L PFAS and sodium bentonite barrier mixtures and report no removal of PFAS by bentonite. Negatively charged bentonite was reported to electrostatically repulse anionic PFAS, prohibiting sorption. Li et al. (2015) also report that PFAS did not negatively impact the hydraulic conductivity of the bentonite mixture, which is an important consideration in liner systems that are designed to be impermeable. Bentonite GCLs may not be an effective choice for the specific containment of PFAS given its low affinity for PFAS sorption._

**3.4. Solution pH**

Sorption of anionic organic compounds to soil typically increases with decreased solution pH due to the increase in positive surface charge of soil from addition of protons (Schwarzenbach
et al. 2003, Campos Pereira et al. 2019). Increased H⁺ concentration increases the net positive surface charge of organic matter and soils through adsorption of protons to negatively charged surface sites. As pH decreases, fewer negatively charged sites exist on mineral and organic surfaces, reducing repulsion of anionic compounds and permitting increased sorption of PFAS.

Solution pH can affect hydrophobic partitioning of PFAS on soil solids. Campos Pereira et al. (2018) assessed the impact of solution pH and cation composition on PFAS sorption to soil with f₀c = 0.45. Batch tests were carried out at four different cation concentrations (10 mM Na⁺, 3.0 mM Ca²⁺, 5.0 mM Ca²⁺, and 2.0 mM Al³⁺) at four pHs (pH = 3, 4, 5, 6). The initial PFAS concentration was held constant at 5 x 10⁻⁹ mg/L of each compound. There was a statistically significant (p < 0.05) inverse relationship between pH and Kₒc for 10 of the PFAS compounds, indicating greater hydrophobic partitioning of PFAS at lower pH. Log Kₒc decreased 0.32 log units (on average) with each unit increase in pH for pH between 3 and 6. Similarly, Higgins and Luthy (2006) report an average 0.37 log unit decrease in Kₐ with each unit increase in solution pH for PFAS sorption to organic rich soil (f₀c = 0.0434) over a pH range of 5.7 to 7.5. At lower pH, organic matter has less negative charge due to the adsorption of hydrogen protons, which allows PFAS to more easily overcome any electrostatic repulsion from sorbent surface and partition into the organic matter.

In the absence of organic matter, pH can affect the net surface charge of soil solid and influence electrostatic attraction of PFAS to the surface. Tang et al. (2010) studied the effect of pH on PFOS sorption to positively charged goethite (no organic content) by conducting batch tests at an initial PFOS concentration of 0.2 mg/L with pH ranging from 3 to 9. Sorption capacity of goethite decreased from 6.2 µg PFOS /g at pH 3 to below detection at pH 9, indicating a strong impact of pH on PFOS sorption. Tang et al. (2010) attribute greater sorption at lower pH to an increase in net surface charge form the association of protons that in turn increased electrostatic attraction of PFOS.
3.5. Ionic Strength

Increased cation concentration in solution can increase PFAS sorption to negatively charged surfaces by cations associating with the solid surface, reducing net negative surface charge or by cation bridging for anionic PFAS functional groups (Fig. 4) (Du et al. 2014). However, increased anion concentration at higher ionic strength can result in competition for positively charged sorption sites, reducing PFAS sorption (Du et al. 2014, Ateia et al. 2019). Higgins and Luthy (2006) report a 0.36 increase in log $K_d$ per increase in log $Ca^{2+}$ molarity, but no increase in $K_d$ with increasing $Na^+$ molarity. This suggests that divalent cation bridging had a stronger impact on the electrostatic interaction of PFAS than moderate reductions in net negative surface charge from association of monovalent cations. Xiao et al (2011) report increased $K_d$ for PFAS on kaolinite with increased $Na^+$ concentration and attribute the trend to decreased negative charge on the mineral surface. Higgins and Luthy (2006) used soils containing organic matter, which led to the conclusion that hydrophobic partitioning was the predominant mechanism for PFAS sorption, and the effect of cation concentration was considered a secondary influence. The kaolinite studied by Xiao et al. (2011) had no organic fraction, which implies that electrostatic interaction was the dominant sorption mechanism for PFAS and the influence of ionic strength is more apparent.

Greater ionic strength in solution can reduce the zeta potential of a mineral surface by compressing the bound water layer surrounding a solid particle, reducing the strength and reach of electrostatic forces (Langmuir 1997). For mineral surfaces that have a net positive charge ($pH_{pzc}>pH$), increased cation concentration can decrease PFAS sorption. Wang and Shih (2011) investigated the influence of $Ca^{2+}$, $K^+$, $Mg^{2+}$, and $Na^+$ concentration on the sorption of PFOS and PFOA to alumina ($pH_{pzc} = 8.5$). At $pH = 4.3$, PFOS and PFOA sorption decreased with increasing concentration of all four cations. Alumina has a net positive surface charge at $pH = 4.3$, and should promote electrostatic attraction of anionic PFAS. Wang and Shih (2011) attribute the decrease in
sorption with increasing ionic strength to a reduction in zeta potential from compression of the bound water layer. The attraction of anionic PFAS is weaker as a result, reducing sorption. This is the opposite of the effect seen by Xiao et al. (2011), where increased Na\(^+\) concentration reduced the zeta potential of negatively charged kaolinite, weakening electrostatic repulsion of PFAS and increasing sorption.

3.6. Dissolved Organic Matter

Dissolved organic matter (DOM) (also referred to as Dissolved Organic Carbon, DOC) is mobile organic matter with high molecular-weight such as humic or fulvic acid. DOM typically is negatively charged and participates in hydrophobic and electrostatic interactions (Delle Site 2001). Presence of DOM can decrease HOC sorption to soil solids by competing for sorption sites or by associating to the HOCs in solution and keeping them mobile (Hasset and Anderson 1981). DOM can also increase HOC sorption through hydrophobic partitioning onto DOM bound to the surface of the soil solid (Flores-Céspedes et al. 2006). Du et al. (2014) suggest that the effect of DOM on PFAS sorption is closely tied to the initial DOM concentration in solution. At DOM concentrations < 40 mg/L, DOM and PFAS compete for mineral sorption sites, resulting in decreased PFAS sorption (Pan et al. 2009, Zhou et al. 2011, Yu et al. 2012, Deng et al. 2015, Wang et al. 2015). Additionally, at low DOM concentrations, the amount of sorbed DOM may be insufficient for PFAS partitioning (Section 3.2) (Zhou et al. 2011).

Effluent from a waste water treatment plant (WWTP) with a DOM concentration of 7.3 mg/L was shown to reduce PFAS sorption onto powdered activated carbon (PAC), a common sorbent for HOCs (Foo and Hameed 2009, Yu et al. 2012). Yu et al. (2012) conducted sorption batch tests with PFOA and PFOS and found that \( K_F \) was reduced by 87.1\% for PFOS and 88.4\% for PFOA when DOM from the effluent was introduced to the sorbate solution. Competition for sorption sites between PFAS and DOM inhibited of PFAS sorption, which supports the conclusion
of Du et al. (2014). Yu et al. (2012) also attribute the reduction in sorption to increased electrostatic repulsion of anionic PFAS from DOM sorbed to the soil surface.

Wang et al. (2015) studied the effect of humic acid on sorption of PFOS and PFBS on two forms of positively charged boehmite. PFOS and PFBS sorption on boehmite pre-soaked in 10 mg/L humic acid was compared to PFOS and PFBS sorption on unmodified boehmite. Batch tests were conducted using initial aqueous concentrations of humic acid ranging from 2 to 50 mg/L. At initial humic acid concentration < 30 mg/L, low concentrations of humic acid sorbed to the mineral surface were insufficient to promote hydrophobic partitioning of PFAS and PFAS sorption was thus limited to available sorption sites. Pre-soaked boehmite had a sorption capacity 20% less than unmodified boehmite for PFOS (0.877 to 0.174 µg/m) and 13% less for PFBS (0.649 to 0.0834 µg/m) due to the competition for sorption sites. Greater concentrations of humic acid (50 mg/L) associated to the mineral surface provided hydrophobic partitioning sites for PFOS, increasing sorption capacity. Wang et al. (2015) suggest that short-chain PFBS did not partition into the humic acid due to having lower hydrophobicity. Sorption of PFBS would therefore be limited to available positively charged surface sites, and are outcompeted at higher concentrations of humic acid. Wang et al. (2015) conclude that low concentrations of humic acid in solution can hinder PFAS sorption through competition for sorption sites.

Solution pH can further influence the effect of DOM on PFAS sorption. Uwayezu et al. (2019) conducted batch tests to investigate PFOS sorption to goethite (pH_{pzc} = 7.5 – 9.5) with and without the addition of 20 mg/L humic acid over a pH range of 2 to 11. The log K_d for PFOS sorption to goethite increased from 1.51 to 1.96 in the presence of humic acid when pH was between 5.5 and 7.5. At pH > 7.5, sorption of PFOS to goethite decreased with additional humic acid. In acidic conditions, goethite has a net positive surface charge (pH < pH_{pzc}) and can support electrostatic attraction of humic acid and PFAS. Sorbed humic acid can also provide hydrophobic partitioning sites for PFOS, increasing the sorption capacity (Uwayezu et al. 2019). As pH
surpasses the $pH_{pzc}$ of goethite, the net surface charge becomes negative, resulting in electrostatic repulsion of PFOS and reducing sorption. Additionally, humic acid deprotonates into anions at higher pH ($pH > pKa$), and will also be repelled by the negatively charged goethite. Sorption of PFOS is therefore reduced due to electrostatic repulsion and the reduction of organic partitioning sites from sorbed humic acid.

### 3.7. PFAS Structure and Speciation

The impact that environmental factors such as organic matter and surface charge have on sorption varies between PFAS compounds. Functional group and carbon chain length can affect PFAS sorption capacity and sensitivity to changes in soil and solution parameters. Short chain PFAS are less hydrophobic and their sorption is predominantly influenced by electrostatic forces from the functional group. Low hydrophobicity also indicates that short chain PFAS do not as readily partition out of aqueous solution into organic matter (Du et al. 2014, Campos Pereira et al. 2018, Gagliano et al. 2020). In contrast, very long chain PFAS ($n > 10$) may more easily aggregate in solution through hydrophobic association and remain mobile as a larger micelle (Campos Pereira et al. 2018). Long chain PFAS ($n = 8 \text{ – } 10$) typically outcompete short chain PFAS for sorption sites due to their greater hydrophobicity (Du et al. 2014, Maimaiti et al. 2018).

PFSAs have a greater potential for hydrophobic partitioning than PFCAs of equal carbon chain length (Fig. 6) (Higgins and Luthy 2006, Ahrens et al. 2011, Labadie and Chevreuil 2011, Campos Pereira et al. 2018). Higgins and Luthy (2006) attribute the preference of PFSAs to slightly greater hydrophobicity from the larger sulfonate moiety compared to the carboxyl of PFCAs. In addition, PFCAs have one fewer $\text{CF}_2$ moiety due to the terminal carbon being part of the carboxyl group (i.e. PFOS has eight fluorinated carbons, PFOA has seven). The hydrophobicity of PFAS stems from the $\text{CF}_2$ moieties, and additional $\text{CF}_2$ groups increase the hydrophobicity of PFAS compounds (Higgins and Luthy 2006, Rayne and Forest 2009, Milinovic
et al. 2015). Therefore, PFCAs have less potential to participate in hydrophobic partitioning than PFSAs with equivalent carbons (Ahrens et al. 2011, Campos Pereira et al. 2018).

![Experimental $K_{oc}$ for PFSAs and PFCAs as a function of carbon chain length. Error bars denote the range of reported log $K_{oc}$ from literature. See Appendix A for source data.](image)

The $K_{oc}$ of PFCAs is more sensitive to carbon chain length than the $K_{oc}$ of PFSAs (Fig. 7). PFAS partitioning into organic matter is related to the hydrophobicity of the compound, which increases with fluorinated carbon chain length (i.e. $K_{oc}$ increases with hydrophobicity). Sorption of short chain PFAS is more dominated by electrostatic behavior from the functional group due to lower hydrophobicity. PFSAs show a weaker sensitivity to carbon chain length, indicating that hydrophobicity is not the only factor influencing PFSA partitioning into organic matter. Electrostatic effects from the anionic functional group may offset the impact of increased hydrophobicity. In contrast, PFCA sorption may not be as influenced by electrostatic interactions from the functional group, and therefore $K_{oc}$ has a greater increase per additional carbon.

There are fluorotelomers and PFCA/PFSA precursors that have pKa at environmentally relevant pH (5.5 – 8.5), and their speciation in aqueous solution determines their charge state.
and electrostatic behavior, which influences sorption. Zwitterionic compounds have can be present in solution with both a negatively charged and positively charged functional group, behaving as a cation or anion depending on pH (Xiao 2017). Mejia-Avendaño et al. (2020) studied sorption of nine PFAS compounds onto five soils ranging from sandy loam to clay with $f_{oc} = 0.017$ – 0.073. Batch tests were conducted with three synthesized zwitterionic perfluoroalkyl sulfonamides and fluorotelomers (perfluorooctane sulfonamido betaine, perfluorooctane amidoalkyl betaine, 6:2 fluorotelomer sulfonamidoalkyl betaine) and one cationic PFAS (perfluorooctane amidoalkyl ammonium salt, PFOAAmS) (Fig 8). Sorption was compared to batch test results for five common anionic PFAS (PFOA, FPDA, PFOS, 6:2 FTSA, 8:2 FTSA).

![SPARC Speciation Plot](image)

**Figure 8.** Speciation of zwitterionic PFAS compound PFOAB contains both positively charged groups and negatively charged groups at different pH. Speciation estimated using SPARC (SPARC Performs Automated Reasoning in Chemistry) software (from Mejia-Avendaño et al 2020).

The greatest sorption was reported for PFOAAmS, with log$K_d$ an order of magnitude higher than PFOA (Mejia-Avendaño et al. 2020). Stronger sorption was attributed to electrostatic attraction between the cationic functional group and negatively charged organic matter and soil surfaces. Additionally, sorption of zwitterionic PFAS depended on the solution pH and was maximized at pH ranges that favored cationic functional groups. Mejia-Avendaño et al (2020)
conclude that the sorption for zwitterionic compounds is strongly affected by pH due of the effect of pH on the speciation and charge state of the molecule.

4. PFAS SORPTION TO POLYMERIC MATERIALS

4.1 PFAS Sorption on Existing Polymeric Barrier Materials

PFAS sorption on geomembranes and geotextiles used in engineered barriers has not been explicitly studied, but there is research concerning PFAS sorption on the polymers commonly used to manufacture these barrier materials. Lath et al. (2019) conducted sorption experiments to determine potential PFOA loss to lab materials during bench scale experiments. PFOA loss was quantified for five polymeric syringe filters (polypropylene, polyethersulphone, polytetrafluoroethylene, polyvinylidene fluoride, nylon) and three polymeric test tubes (polycarbonate, polypropylene, polystyrene) at an initial concentration of 10 µg/L. The use of syringe filters reduced PFOA concentration by 24 to 78.8%, with the most uptake seen for nylon. The least reduction in PFOA was seen for polyvinylidene fluoride (24%) and polypropylene (27.7%). Lath et al. (2019) suggest that because polyvinylidene fluoride is a fluoropolymer, it may have biased the results by releasing fluoropolymer into solution. Polypropylene test tubes reduced PFOA concentration by 32 to 45% after 7 days of contact. Polystyrene and polycarbonate showed less uptake, reducing PFOA concentration by 22 to 35%. Lath et al. (2019) conclude that all polymeric lab materials should be considered as potential losses to experimental samples, specifically nylon and polypropylene.

PFAS sorption to microplastics (MPs) can provide further insight into the affinity of barrier polymers to contain PFAS. Ateia et al. (2020) studied the sorption of PFOA and PFOS on seven polymers that are present in waters as microplastics (polyethylene, polypropylene, polyethylene terephthalate, polystyrene, acrylonitrile butadiene styrene, poly(methyl methacrylate), polylactic acid, nylon). Sorption batch tests were conducted with PFOA and PFOAS at initial concentrations
of 50 µg/L and polymer materials ground to < 500 µm diameter. Greater uptake seen for PFOS than PFOA, which is consistent with previous work discussing the hydrophobic partitioning behavior of PFSAs and PFCAs (Section 3.7). Nylon sorbed the greatest amount of both PFOA and PFOS, removing 60% of PFOA and 90% of PFOS, which is consistent with the results from Lath et al. (2019). Polylactic acid removed > 90% of PFOS but did not show strong affinity for PFOA (< 30% uptake). Polystyrene and polypropylene removed 20 – 30% of PFOA and PFOS, which was the lowest uptake observed. Polyethylene removed 25 – 35% of PFOA and 40 – 60% of PFOS. Ateia et al. (2020) suggest that nylon has a stronger affinity for PFAS uptake due to the presence of polar N-H bonds in the polymer chain that may facilitate hydrogen bonding with PFAS.

4.2. Polymer Amendments to Engineered Barriers for Enhanced PFAS Sorption

Many studies report more rapid uptake and higher sorption capacities of PFAS using polymeric adsorbents relative to traditional mineral adsorbents such as granulated activated carbon (GAC) (Du et al. 2014, Gagliano et al. 2020). Anion exchange resins, cationic quaternary polymers, and various cross-linked polymers have been used to sorb PFAS at environmentally relevant concentrations (Fig. 9). Recent landfill liner technology has introduced the use of polymer amended clays to manufacture a chemically resistant and durable liner (Di Emidio et al. 2011, Scalia et al. 2011, Razakamanantsoa et al. 2016). Landfill liners amended with polymers used for PFAS sorption may be an effective way to contain PFAS in leachate. Polymer structure characteristics that influence PFAS sorption onto polymeric surfaces include the rigidity, functional groups, and degree of cross-linking.

Anion exchange resins are electrostatically charged polymer matrices with specific affinity for attracting anionic compounds (Holl 2000). Anion exchange resins can be modified for a specific pollutant of interest, making them a versatile and customizable sorbent for the removal of trace organics (Anderson and Maier 1979, Croué et al. 1999, Karcher et al. 2002). Zaggia et al.
Schuricht et al. (2017) studied PFOS sorption on seven mesoporous anion exchange resins, two porous polymer adsorbents and one gel-type anion exchange resin in comparison to sorption onto GAC and powdered activated carbon (PAC). Batch experiments were conducted at
initial PFOS concentrations ranging from 1 to 1000 mg/L. PFOS sorption was greatest to mesoporous anion exchange resins, which Schuricht et al. (2017) attribute to greater internal surface area and available cation functional groups. Mesoporous resins demonstrated a sorption capacity of at least 1900 mg PFOS/g, whereas the gel-type resin had a sorption capacity of 314.9 mg PFOS/g. PFOS sorbed to mesoporous anion exchange resins through ion exchange, and could then formed hydrophobic aggregates with other PFOS molecules, consistent with the mechanism reported by Zaggia et al (2014). The gel-type resin had limited pore space, restricting the diffusion of PFOS into the inner layers of the resin and reducing sorption. PFOS sorption decreased when the polymer functional group had longer alkyl chains, which contrasts the findings of Zaggia et al. (2014). Schuricht et al. (2017) suggest that polymers with a dense concentration of functional groups that have longer alkyl chains restrict access to sorption sites within the resin pore space. While Zaggia et al. (2014) reports that polymers with longer alkyl chains have increased hydrophobicity and therefore increased PFAS attraction, there may be a critical point where the length and density of polymer alkyl chains begins limit PFAS sorption.

Cross-linked polymers have large surface area and customizable surface chemistry, making them useful for removing pharmaceuticals, aromatic hydrocarbons, and organic acids from aqueous solution (Pan et al. 2009). Cross-linked β-cyclodextrin (β-CD) polymers have been used to remove pesticides and pharmaceuticals, and show promise for PFAS sorption (Alsbaiee et al. 2016, Xiao et al. 2017, Xiao et al. 2019). Xiao et al. (2017) studied the effect of polymer structure on PFAS sorption by conducting batch tests with of 1 µg/L PFOA and four β-CD polymers with varied degrees of crosslinking to decafluorobiphenyl (DFB-CDP). In a subsequent study, Xiao et al. (2019) determined the effect of polymer surface charge on PFAS sorption using three DFB-CDP polymers containing anionic phenolate concentrations ranging from 0.0063 to 0.25 mmol/g. DFB-CDP sorbents removed over 70% of long chain PFAS, but less than 30% of PFAS with < 7 carbons. Sorption capacity for the DFB-CDP was greatest when there was a
moderate degree of cross-linking and the low phenolate concentration (Fig 10a) (Xiao et al. 2019). At greater degrees of crosslinking, the polymer frame is too rigid to support intraparticle diffusion of PFAS, reducing overall sorption (Fig. 10b). Greater concentrations of phenolate result in more negatively charged functional groups, increasing electrostatic repulsion of anionic PFAS and reducing sorption. The crosslinkers tetrafluoroterephthalonitrile (TFN-CDP), epichlorohydrin (EPI-CDP), and urethane-containing methacrylate (IEM-CDP) were studied in comparison to DFB-CDP and did not have a strong affinity for PFAS sorption.

![Crosslinked Polymer Network](image)

Figure 10. a. Crosslinked polymers can provide increased hydrophobic surface area that promotes PFAS partitioning. b. Greater degrees of crosslinking in the polymer network may inhibit PFAS access to inner pore space and reduce sorption.

Polymer adsorbents with cationic functional groups may provide greater sorption for short chain PFAS that typically have higher solubility and are more strongly controlled by electrostatic forces. Ji et al. (2018) studied the use of a covalent organic framework (COF) containing positively charged amine groups to sorb 12 PFAS compounds at initial concentrations of 1 µg/L. The polymer removed > 80% of all PFAS compounds except PFBA, which has the shortest carbon chain length (n=4) (removal = 63%). Stebel et al. (2019) also report greater sorption of short chain PFAS for sorbents containing cationic polymers, based on sorption experiments using long and short chain PFAS and four organically modified silica (SOM) sorbents. SOM that incorporated a
cationic polymer removed over 80% of PFBS and PFBA (n=4), whereas there was low or no removal of PFBA and PFBS for SOM without cationic polymer (Stebel et al. 2019).

Ateia et al. (2019) studied sorption of 16 PFAS compounds at 1 µg/L to a crosslinked cationic hydrogel (poly (N-[3-(dimethylamino)propyl]acrylamide, methyl chloride quaternary, DMAPAA-Q), to assess the relative effectiveness to sorb short chain vs. long chain PFAS. DMAPAA-Q removed both short chain and long chain PFAS rapidly, reaching equilibrium in under two hours (Fig. 11). Over 80% removal of PFAS was achieved for pH ranging from 4 to 10, indicating that sorption to the polymer was not strongly affected by pH. Additionally, PFAS sorption was only marginally affected by changes in DOM concentration. Sorption capacity decreased only 5-10% when DOM was doubled from 2.5 mg/L to 5.0 mg/L. Ateia et al. (2019) conclude that DMAPAA-Q is an effective sorbent for long and short chain PFAS.

![Figure 11. Removal of PFAS by polymer adsorbents. PFBA showed no sorption to SOMS or F-SOMS. PFBS showed no sorption to F-SOMS. Initial PFAS concentrations were 2000 µg/L (Stebel et al. 2019), 1 µg/L (Xiao et al. 2019), and 1 µg/L (Ateia et al. 2019).](image-url)

5. Proposed Methods for Quantifying PFAS Sorption to Barrier Materials

5.1. Background
An experimental method was developed for bench-scale sorption batch tests to quantify the sorption of PFAS to engineered barrier components. Lab tests were not completed due to unforeseen difficulties in instrumentation and a global pandemic. Proposed sorption batch test methods, PFAS quantification methods and lessons learned during method development are reported below.

5.1. Materials

PFAS standards were purchased from Wellington Laboratories. Sodium bentonite clay, an ammonium modified bentonite clay manufactured for PFAS removal (Commercial name: FLUORO-SORB), nonwoven geotextile, and high-density polyethylene (HDPE) geomembrane were obtained from CETCO (Minerals Technology, Inc). All analytical reagents were HPLC grade and purchased from Thermo Fisher Scientific.

5.3. Sorption Batch Test Methods

Batch adsorption tests were conducted using a method modified from the EPA method OECD 106. Five stock solutions (100, 200, 300, 400, and 500 ng/L) of PFAS were prepared in a 50% methanol solution and were stored in polypropylene bottles at below 7°C. For sodium bentonite and FLUORO-SORB batch tests, clay was ground to pass a 2µm sieve and 400 mg (dry weight) was added to a 50 mL polypropylene centrifuge tube. For geotextile and geomembrane batch tests, the material was cut into 7cm x 2 cm strips and added to centrifuge tube. 40 mL of stock solution was added to the centrifuge tubes and shaken by hand to ensure contact between solution and test materials. Samples were then placed on a rotating shaker at 30 rpm for 72 hours to reach equilibrium. 72 hours has been shown to be sufficient for PFAS compounds to reach equilibrium (Ahrens et al, 2011, Li et al. 2019). Duplicates were run for each concentration level, and solution blanks and sorbent blanks were run for quality assurance and estimation of PFAS loss to lab materials.
After shaking, samples were centrifuged for 20 minutes at 4000 rpm and a 10 mL aliquot of the supernatant was added to a 15 mL polypropylene centrifuge tube. For sodium bentonite batch tests, samples were centrifuged again at 4000 rpm for 20 minutes to ensure clarity of analytical sample. All samples were filtered with a 0.45 μm polyethersulfone (PES) syringe filter into a 300 μL polypropylene autosampler vial for analysis. Lath et al. (2019) recommends against filtering PFAS through a syringe filter to limit loss to the filter membrane, but filtration was considered necessary to ensure a clean sample for analysis.

5.4. Analytical Method Development

Quantification of PFAS was conducted with a Thermo Scientific Vanquish Liquid Chromatographer coupled to a Thermo Scientific Altis Triple Quadripole Tandem Mass Spectrometer (LC-MS/MS) in negative ion mode. The instrument used a Thermo Scientific TriPlus autosampler to inject samples. The LC method was developed to provide separation of compounds of interest using a Thermo Accucore RP analytical column (2.1 x 100 mm, 2.6 μm). The mobile phases for LC flow consisted of water with 2mM ammonium acetate, 2% methanol and 0.1% acetic acid (Solvent A), and methanol with 2mM ammonium acetate, 2% water and 0.1% acetic acid (Solvent B). Mobile phases were made with HPLC grade solvents to reduce impurities. A mobile phase gradient established by Thermo Scientific was utilized to move the sample across the column during each injection (Table 5).

Table 5. LC mobile phase gradient developed by Thermo Scientific to achieve quantification of PFAS.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Solvent B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
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<tr>
<td>13</td>
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<td>14</td>
<td>100</td>
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<td>18</td>
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</tr>
<tr>
<td>21</td>
<td>0</td>
</tr>
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The LC flow rate was set at 500 µL/min and the sample injection volume was 25 µL. Selected reaction monitoring (SRM) method was used for MS/MS analysis for PFAS compounds using pre-determined precursor and product ions (Table 6). Run time per injection was 22 minutes, including injection, chromatographic separation, and MS/MS detection. Linear calibration was established for a range of 50 – 250 ng/L for PFOA (Fig. 12b).

Table 6. MS Conditions for SRM method of quantifying PFAS compounds. “L-” designates a linear isomer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time (min)</th>
<th>Precursor (m/z)</th>
<th>Product (m/z)</th>
<th>Collision Energy (V)</th>
<th>RF Lens (V)</th>
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<tr>
<td>L-PFBS</td>
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<td>298.95</td>
<td>79.958</td>
<td>31.24</td>
<td>105</td>
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<tr>
<td>L-PFBS</td>
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<td>298.95</td>
<td>98.958</td>
<td>29.43</td>
<td>105</td>
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<td>PFHxA</td>
<td>7.18</td>
<td>312.962</td>
<td>119</td>
<td>19.79</td>
<td>34</td>
</tr>
<tr>
<td>PFHxA</td>
<td>7.18</td>
<td>312.962</td>
<td>268.97</td>
<td>8.16</td>
<td>34</td>
</tr>
<tr>
<td>PFHpA</td>
<td>9.3</td>
<td>362.962</td>
<td>169.042</td>
<td>16.29</td>
<td>39</td>
</tr>
<tr>
<td>PFHpA</td>
<td>9.3</td>
<td>362.962</td>
<td>318.97</td>
<td>8.54</td>
<td>39</td>
</tr>
<tr>
<td>PFHxSK</td>
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<td>399</td>
<td>79.958</td>
<td>36.59</td>
<td>146</td>
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<tr>
<td>PFHxSK</td>
<td>9.57</td>
<td>399</td>
<td>98.988</td>
<td>34.23</td>
<td>146</td>
</tr>
<tr>
<td>PFOA</td>
<td>10.7</td>
<td>412.95</td>
<td>168.97</td>
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<tr>
<td>PFOA</td>
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<td>412.95</td>
<td>369.042</td>
<td>9.04</td>
<td>44</td>
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<tr>
<td>N-EtFOSAA</td>
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<td>584.05</td>
<td>418.964</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>N-EtFOSAA</td>
<td>11</td>
<td>584.05</td>
<td>526.03</td>
<td>19.53</td>
<td>100</td>
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<tr>
<td>PFNA</td>
<td>11.7</td>
<td>462.95</td>
<td>218.97</td>
<td>16.08</td>
<td>49</td>
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<tr>
<td>PFNA</td>
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<td>462.95</td>
<td>419.042</td>
<td>9.55</td>
<td>49</td>
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<tr>
<td>PFOSK</td>
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<td>499</td>
<td>79.97</td>
<td>41.94</td>
<td>146</td>
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<tr>
<td>PFOSK</td>
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<td>499</td>
<td>229.929</td>
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<td>L-PFOS</td>
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<td>499.167</td>
<td>79.988</td>
<td>39.96</td>
<td>103</td>
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<tr>
<td>L-PFOS</td>
<td>11.88</td>
<td>499.167</td>
<td>98.958</td>
<td>39.84</td>
<td>103</td>
</tr>
<tr>
<td>PFDA</td>
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<td>512.95</td>
<td>218.97</td>
<td>16.84</td>
<td>54</td>
</tr>
<tr>
<td>PFDA</td>
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<td>512.95</td>
<td>468.97</td>
<td>9.8</td>
<td>54</td>
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<tr>
<td>N-MeFOSAA</td>
<td>13</td>
<td>570</td>
<td>419.03</td>
<td>19.66</td>
<td>103</td>
</tr>
<tr>
<td>N-MeFOSAA</td>
<td>13</td>
<td>570</td>
<td>512</td>
<td>19.55</td>
<td>103</td>
</tr>
<tr>
<td>PFUdA</td>
<td>13.3</td>
<td>563</td>
<td>269.042</td>
<td>17.55</td>
<td>59</td>
</tr>
<tr>
<td>PFUdA</td>
<td>13.3</td>
<td>563</td>
<td>518.97</td>
<td>10.48</td>
<td>59</td>
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<tr>
<td>PFDoA</td>
<td>13.9</td>
<td>612.95</td>
<td>318.97</td>
<td>18.56</td>
<td>66</td>
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<tr>
<td>PFDoA</td>
<td>13.9</td>
<td>612.95</td>
<td>569.042</td>
<td>10.98</td>
<td>66</td>
</tr>
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<td>PFTrDA</td>
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<td>662.95</td>
<td>368.988</td>
<td>19.24</td>
<td>80</td>
</tr>
<tr>
<td>PFTrDA</td>
<td>14.4</td>
<td>662.95</td>
<td>619.042</td>
<td>11.23</td>
<td>80</td>
</tr>
<tr>
<td>PFTeDA</td>
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<td>712.95</td>
<td>630.917</td>
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<td>89</td>
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<tr>
<td>PFTeDA</td>
<td>14.7</td>
<td>712.95</td>
<td>669.042</td>
<td>11.7</td>
<td>89</td>
</tr>
</tbody>
</table>
Appendix B was developed over the course of this thesis work and provides a step by step guide for operating and troubleshooting the LC-MS/MS. A lengthy troubleshooting period occurred during which several analytical columns were consumed. The source of the issue was eventually identified as a manufacturing error from the Thermo BDS Hypersil C18 isolator column (2.1 x 50 mm, 5µm) that was initially used to remove PFAS within the mobile phase solvents and decrease background noise in samples. The BDS Hypersil C18 isolator column consistently released particulates into the LC flow, clogging the analytical column. Removing the isolator column from the LC flow path has been an effective step in eliminating time consuming column errors. While the isolator column is not necessary to successfully run the instrument, background PFAS contamination is difficult to eliminate in a lab setting, and contamination of blanks is a possibility. The use of the isolator column resulted in linear calibrations of PFOA down to 10 ng/L, which may not be an achievable calibration level without the isolator column. Considering the regulatory levels of PFAS compounds are as low as 6 ng/L, building an LC-MS/MS method that can quantify PFAS down to below 10 ng/L may be necessary (Cal EPA 2019). A Thermo Hypersil Gold column (3.0x50 mm, 1.9 µm) was recommended by Thermo Scientific technicians as an alternative isolator column to reach lower detection limits.

![Graph a](image1.png)  ![Graph b](image2.png)

**Figure 12.** a. Linear calibration was achieved for PFOA ranging 25 – 750 ng/L when an LC isolator column was installed before the analytical column. b. Linear calibration was achieved for PFOA ranging 50 – 250 ng/L without the use of an isolator column.
5.5. Preliminary Results

Complete results of sorption batch tests between PFOA and liner materials was not possible to obtain due to the previously discussed laboratory issues. An equilibrium aqueous concentration was determined for a single initial PFOA concentration of 100 ng/L (Table 7). The equilibrium PFOA concentration after shaking with sodium bentonite was not different from the equilibrium PFOA concentration in the sorbent blank Sample 3. This result indicates that there was no significant sorption of PFOA to sodium bentonite. The solution blanks (Samples 4 and 5) also had no substantial concentration of PFOA at equilibrium, indicating that there is little to no PFOA contamination from lab materials or sodium bentonite.

The equilibrium PFOA concentrations for Samples 1-3 appear to be greater than the initial concentration, which would indicate desorption from either the sodium bentonite or the lab materials. The negligible concentrations of PFOA in the sorbent blanks do not support this desorption theory. A more likely explanation is that there was some amount of human error in the creation of the PFOA stock solutions that resulted in slightly greater initial PFOA concentrations.

Table 7. Preliminary results from sorption batch test with PFOA and sodium bentonite. Initial aqueous concentration is assumed based on lab dilution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Aqueous PFOA Concentration (ng/L)</th>
<th>Sodium Bentonite - Dry Mass (g)</th>
<th>Equilibrium Aqueous PFOA Concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0.4</td>
<td>121</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.4</td>
<td>116</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0</td>
<td>121</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.4</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
</tr>
</tbody>
</table>

Despite there being little data to report from these sorption batch tests, the preliminary conclusion that PFOA shows little to no sorption to sodium bentonite agrees with the studies discussed in Sections 3 and 4. Bentonite clay does not appear to be a strong sorbent of PFOA.
Additionally, the laboratory method developed for testing PFOA sorption showed limited loss to lab materials and can hopefully continue to be used to determine PFAS sorption to liner materials.

5.6. Future Work

Continued work on PFAS sorption to liner materials should include the successful completion of sorption batch tests and analysis. Given the previous discussion of PFAS sorption behavior and the preliminary results from Section 5.5, there will likely be little to no PFAS sorption onto sodium bentonite due to electrostatic repulsion and the lack of hydrophobic organic matter. The geotextile and geomembrane samples may show small amounts of PFAS sorption based on the hydrophobic attraction to polymeric materials. Fluorosorb, which contains a cationic functional group, promises to be an effective sorbent for anionic PFAS compounds and should show significant PFAS removal through electrostatic attraction.

6. Summary and Conclusions

Predicting the efficacy of engineered barriers to contain PFAS within leachate depends on a complete understanding of the drivers of PFAS sorption. Sorption of PFAS on barrier materials should be considered in the context of how each PFAS species will interact with the sorbent and with the other leachate constituents. Environmental properties and PFAS structure can impact both the mechanism and magnitude of sorption (Fig. 13).
Figure 13. Environmental properties and PFAS structure should both be considered when assessing PFAS sorption. PFAS sorption is most favorable at high organic content and low pH (indicated by star).

Hydrophobic partitioning into organic matter is the primary factor controlling long chain PFAS sorption in environments where there is sufficient organic content. Attraction of the hydrophobic PFAS tail to hydrophobic organic matter is strong enough to overcome electrostatic repulsion between the anionic PFAS head and negatively charged surfaces, allowing PFAS to partition out of solution and bind to the solid. Organic matter in solution can also associate to a soil surface and provide sites for PFAS partitioning, increasing the sorption capacity. In contrast, low concentrations of organic matter in soil or solution may instead compete with PFAS for mineral sorption sites and be insufficient to promote hydrophobic partitioning.

Soil surface charge impacts PFAS sorption through influencing the electrostatic behavior, specifically in the absence of sufficient organic content to support hydrophobic partitioning. Solution pH, ionic strength, and composition of the soil surface (i.e. pH_pzc) affect the net soil surface charge, which determines whether there will be electrostatic repulsion of PFAS. PFAS sorption typically increases with decreasing pH and increasing cation concentration due to the decrease in net negative surface charge. The composition of landfill leachate varies, but can include ion and DOM concentrations at hundreds of milligrams per liter (Kjeldsen et al. 2010). Depending on the leachate conditions, ions and dissolved organic matter may compete with PFAS for sorption sites or augment PFAS sorption by reducing electrostatic repulsion.
Electrostatic interactions are likely to have an observable effect on PFAS containment in landfills considering there is little to no organic content within bentonite mixtures used in GCLs. Li et al. (2015) reported no PFAS sorption to bentonite mixtures, which suggests that containment of PFAS in leachate will not be a result of chemical sorption to bentonite GCLs. Polymeric components of barrier systems such as geomembranes and geotextiles may provide sorption of long chain PFAS through hydrophobic interaction. Short chain PFAS are unlikely to sorb to existing polymeric liner surfaces due to their lower hydrophobicity. Cationic or cross-linked polymers may be a useful additive to bentonite GCLs to effectively contain PFAS. Bentonite polymer composite GCLs are already used to increase the impermeability of a liner system and increase resistance to chemical decay (Scalia et al. 2018). Considering specific GCL amendments for containing trace contaminants like PFAS is a promising research direction.

The ubiquity of PFAS compounds in manufactured goods ensures that PFAS will continue to enter waste streams and present challenges for containment and removal. Laboratory-scale experiments quantifying PFAS sorption to barrier components is a necessary next step to understand how these compounds will interact with and affect liner systems. This review hopefully provides an indicator of how PFAS sorption may be affected by leachate conditions and barrier materials. Continued research should quantify PFAS sorption to barriers and explore the development of enhanced barriers for PFAS containment.
References

3M. 2000. “Soil Adsorption/Desorption Study of Potassium Perfluorooctanesulfonate (PFOS).”


## Appendix A. Data used to generate Fig. 6 comparing $K_{oc}$ and PFAS chain length.

<table>
<thead>
<tr>
<th>PFAS</th>
<th>PFAS Class</th>
<th>Carbon Chain Length (n)</th>
<th>log $K_{oc}$ (ml/g OC)</th>
<th>Std Dev</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>PFCA</td>
<td>4</td>
<td>1.88</td>
<td></td>
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<td>Campos Pereira et al. 2018</td>
</tr>
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Appendix B. Unofficial Users Guide for Operating Thermo Scientific TSQ Altis LC-MS/MS

Serial Number: TSQ-A-10416
Location: Thornton D106, UVA SEAS
Updated 8/2/2020 by Julie Bridstrup

Contents:

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   d. Gases

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    b. TraceFinder 4.1
    c. Freestyle

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    b. Turning on Vanquish HPLC
    c. Running MS/MS with LC flow

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    b. Setting up a Sample Batch
    c. Submitting a Sample
    d. Submit an Existing Batch
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    b. LC Errors
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I. LC-MS/MS Components

a. LC TriPlus Auto Sampler
   • The auto sampler controls the sample acquisition and injection into the HPLC. You can manually control the autosampler using the “Gameboy” on the left side of the auto sampler. (Gameboy can be remote accessed through TraceFinder software (Realtime status→Instrument Controls→Virtual Terminal)
The Peltier Stack: This is where you load your samples to be run.
- There are three drawers with two slots each – top drawer is 1, bottom drawer is 3
- Each tray has numbers next to each vial position. A vial in the top drawer in the back tray (1) will have the vial location: Drawer1:Slot1:1
- LS1 and LS2: the sample loading syringes. Use LS1 (100 µL) unless you are performing large volume injections.
- Valve drives (labeled on the instrument as “Injectors”): Where the sample is injected to combine with LC flow.

b. Vanquish HPLC
- [pic insert]
- Binary Pump
- Quaternary Pump (for Large Volume Injection)

c. Altis Triple-Quad Tandem Mass Spectrometer
• Source
• Power switches
d. Gases
• Nitrogen
  o Needs to be at 120 psi – always running when main MS/MS power is on
  o Sheath gas – used to create vacuum
  o Will need to be replaced about every ~12 days during regular use
  o When replacing, connect to gas valve and open valve, then open pressure builder valve
• Argon
  o Collision gas – needs to be at 20 psi – pumps into Q2 where fragmentation happens
  o One cylinder should last ~18 months

II. Software for LC-MS/MS Use:

a. **TSQ Altis Tune**
  o Direct control of the Altis MS/MS
  o Uses: Calibrate Altis, optimize for new chemicals, monitor Altis parameters/settings

b. **TraceFinder**
  o Uses: Creating instrument methods, creating master methods, running samples, analyzing data, direct control of LC
  o Will be your most used software
  o Three main views: Acquisition, Analysis, Method Development
    o Switch views in bottom right corner of screen
    o Can always click “Real Time Status” in top right corner to see current instrument status
c. **Freestyle**
   - Look at raw data files
   - Used in creating instrument methods

### III. Turning on the LC-MS/MS

a. **Starting the Altis MS/MS from full power down**

**NOTE:** Instrument should only be fully powered down if there is a planned power outage or if you will not be using it for an extended period of time (e.g. a global pandemic hits and you are out of the lab for four months). During regular use, the instrument should remain in Operating Mode.

- On the right side of the Altis MS/MS, you should see:
  - Main Power Switch – Off.
  - Electronics Switch – Service mode.
• Check Nitrogen tank levels. Gas valve and pressure builder valves should be open and pressure should be at around 120 psi
• Switch Main Power to “On.” You should hear the vacuum pumps turn on. They are both plugged into the ceiling (they have come loose before, so make sure they are both humming)
• On the computer, open up the TSQ Altis Console from the start menu
  
  ![TSQ Altis Console](image)
  
• Switch the electronics switch to “Operating Mode”
• Wait to see the start-up process on the TSQ Console. It will go through several steps over a few minutes.
• When you start to see the monitoring for the current ion gauge pressure, the MS/MS vacuum is pumping down and you will need to wait at least overnight to continue use.
• Ideal vacuum pressure for operating is < 4e-6

```plaintext
0 USB Turbo 1 Speed: 703
1 USB Turbo 1 Speed: 703
2 USB Turbo 1 Speed: 703
3 USB Turbo 1 Speed: 722

5 ............Convection Pressure (Torr): 2.69503
6 USB Turbo 1 Speed: 722
7 ............Convection Pressure (Torr): 2.69314
8 USB Turbo 1 Speed: 722
9 ............Convection Pressure (Torr): 2.69503
0 USB Turbo 1 Speed: 722
1 ............Convection Pressure (Torr): 2.69314
2 USB Turbo 1 Speed: 722
3 ............Convection Pressure (Torr): 2.69503
4 Enabling ion gauge, Please wait 5 seconds ...
5 Enabling ion gauge, Please wait 5 seconds ...
6 Ion gauge is enabled.
7 ...Monitoring ion gauge pressure
0 ...Current ion gauge pressure (Torr): 2.19047e-05
1 ...Current ion gauge pressure (Torr): 2.10998e-05
0 ...Current ion gauge pressure (Torr): 2.02611e-05
1 ...Current ion gauge pressure (Torr): 1.95759e-05
2 ...Current ion gauge pressure (Torr): 1.89261e-05
3 ...Current ion gauge pressure (Torr): 1.83628e-05
```
• If you don’t get to this point, first try the whole process again, switching back to service mode first, then main power off, then main power back on, back to operating mode. If after a few tries it is not able to start pumping down, call tech support.

• When the ion gauge pressure reaches < 9 e-6, the system will enter standby and you can go to the Altis Tune software to control the instrument.

• In Altis Tune software, continue to monitor Analyzer Pressure (i.e. ion gauge pressure) as it decreases. It will slowly decrease over a few days. You can speed up the process by running the instrument fully. (continue following steps below)

b. Turning on the Vanquish HPLC
• Check solvent levels:
  o Solvents (i.e. mobile phases) A and B on the left side rack of the LC
  o Rear seal wash – 10% methanol – on top of LC
• Open TraceFinder software
  o Access Direct Control of LC:
    ▪ Open Real Time Status by clicking in the upper right corner:
      ▪ Go to the Instrument Controls Tab→ThermoScientific SII for Xcalibur Tab
- Click the button for Direct Control

- In the “Pump” tab, check that module is Connected and Ready in upper left corner

- Purge the lines
  - In the Direct Control Screen turn on the motor by clicking the checkbox in the commands section on the left side of the screen
  - Set the flow to 5 mL/min and the Eluent (mobile phases) to 50/50%
Click the checkbox to turn on Purge
  • A pop up will come up. DON'T CLICK EXECUTE YET.
  • On the LC, open the purge valve by turning counter clockwise
  • Return to computer, now click “execute despite warnings”

Purge runs for a few minutes and turns itself off when done (or you can uncheck the box to turn off sooner).
  • CLOSE THE PURGE VALVE – on LC, turn clockwise until finger-tight
    In the ColumnComp tab, turn on Column chamber and set temperature to 45 C. Actual value will be in red until it is at the Nominal Temperature you set.
    In Pump tab, pressure should start to stabilize around 400-500 bar.

c. Run LC-MS/MS fully with flow on
  • In Tune software, click the Valve button to switch to “1-2”. This allows the flow to go into the Altis. (“1-6” goes to waste)
  • Click the big Play button to turn to on scanning mode
The top right status button will turn orange as it changes the settings to scan mode, then turn green and say Normal.

Continue monitoring analyzer pressure and HPLC pump pressure. When the pressure is < 5 e-6, you can start running samples.

IV. Regular Use of LC-MS/MS

a. Preparing for use
   - Check Nitrogen level (120 psi), Mobile Phase level, Rear seal wash level
     - If using regularly, nitrogen tank will last about 2 weeks.
     - Rear seal wash is used whether or not there is flow through the HPLC. Runs out fairly frequently.
     - Mobile phase composition depends on method. See PFAS method below.
   - Check MS/MS analyzer pressure in Altis Tune software (< 5e-6)
   - Purge LC lines and turn on flow to 5 ml/min using TraceFinder direct control (See III.b)
   - Divert flow to waste in Altis Tune (Valve set to 1-6)

b. Setting up Sample Batch Using an Existing Master Method (TraceFinder Software)
   - Click Acquisition in the bottom left corner
   - Select “Create a new batch”
   - Choose containing folder and name your batch
   - Choose Master Method and click Next to continue to sample definition
   - Insert your sample information. You can add them individually, use the Fill Down function by right clicking a text square, or import a CSV of your sample definitions (see template in training folder)
- Vial position must be in the format [Drawer 1:Slot1:29]. Easiest to use fill down function or template for vial position.

- Sample Types
  - Solvent: blank
  - Cal Std: Calibration standard (will pick calibration level in “Level” column as defined by Master Method)
  - Unknown: unknown

- Each file name must be unique (i.e. cannot have multiples named ‘Blank’)

- A raw data file will be generated for each row and stored under 
  C:\TraceFinderData\4.0\Projects\[BATCH_FOLDER]\[BATCH_NAME]\Data

- Click the next arrow, select any reports you want generated, click next again to reach Finish page.

- You can choose to submit now or save your batch to submit later.

  **c. Submitting A Batch**
  - Click Submit on the Finish page.
  - Make sure the Acquire and Process data boxes are checked. You can select whether to leave the system ‘On” or in “Standby” after the batch is complete.
  - When you see “Thank you! Batch Submitted”, you’re all set!
  - It will take a few minutes after submitting the back before the first sample is collected. Wait for that to happen before leaving the instrument unattended.

  **d. Submit Existing Batch**
  - If you have already created a saved batch, you can run it by clicking on “Submit a prepared batch” in the Acquisition page. This will take you directly to the Finish page.
  - You can edit Sample Definitions before submitting but clicking the previous arrow

  **e. Quick Acquire Sample Data:**
  - At any time, you can click the three test tube icon to “quick acquire” a sample.
  - This does NOT use a Master Method, but does require an instrument method
  - Label your samples with a unique file name. These raw data files will be saved under C:/TraceFinder Data/Sequences
  - Click either Acquire highlighted samples or submit sequence to run samples
  - Creates only the raw data file (can later be associated to a quantification method)
f. Analyzing Results
   - In the Analysis view, open your submitted batch
   - Your samples are listed along with their status. Hover over the circle to see what the color means. (Green means sample had been acquired and processed)

   - The Data Review sections show you the calculated results either by sample or by compound. Compound view will show you the results from all samples for only one compound.

   - The top panel is the calculated data for all samples – scroll to the right to see all the calculated fields
   - CompoundCentric Plot view shows the chromatographic peaks for each injection.
If you click on one of the compound centric plots, the compound details will open where you can see the peaks for each confirming ion. You can manually adjust the peak edges or right click and adjust the local method for peak detection. (this will not change the master method)

The Calibration curve is calculated based on the standards you made. If one isn’t made, be sure that you have selected “External” as the calibration type by right clicking the graph.

Report View generates reports in pdf of excel file format.

V. Method Development

a. Instrument Methods

i. Optimizing MS/MS for a new compound

- Use Tune software
- Need T piece to direct inject into the MS and LC flow on
- Concentration should be between 100-1000 ng/L (low enough that background noise can still be observed if the syringe is off
- Define Scan Optimization tab

ii. Creating an Instrument Method

- Under the Method Development view in Tracefinder, you can open or create a new Instrument Method
Define instrument parameters for Autosampler, Vanquish LC, and Altis MS/MS in each screen.

You can also open an existing instrument method and save as new to not reinvent the wheel.

b. Master Method Development
   i. Quick acquire a sample using an existing method
   ii. In Method development view in TraceFinder, choose file→new→Master Method
   iii. Use the method forge wizard to walk through the method development using the raw data file from your quick acquire
   iv. Detailed instructions available in TraceFinder training powerpoint from Thermo

VI. Troubleshooting & Tips

- Common LC errors
  - “Piston Seal Leakage Exceeds Limit”: check for leaks. Remove white cylinder containing electrode in bottom right corner of LC pump and dry with a paper towel. That liquid is supposed to flow into waste but sometimes builds up.
  - “Pressure exceeds limit”: There is a clog somewhere along the LC tubing or in the column.
  - Always check that you have enough of your mobile phases to get through your run. Not good to run out during the run.

- MS/MS errors
  - “Sheath gas unstable”: check the nitrogen tank. Pressure should be ~120 psi and flowing.
  - Do not turn the MS/MS power off unless you are planning an extended down time for the instrument (i.e. several weeks). Main power should remain on and electrics should remain in Operational mode.

- Other errors
Always make sure you get through your first injection before leaving to make sure the method is running correctly. If the method is going to mess up, it will happen in the first sample (unless a clog comes later).

Make sure to close the purge valve on the LC after purge cycle.

**LC-MS/MS Methods for PFAS Detection (Based on Thermo Method)**

**Columns for Vanquish HPLC:**

- Analytical Column: Thermo Accucore RP, 2.1 x 100 mm, 2.6 µm
- Guard/Isolator Column: Thermo Hypersil Gold, 50 x 3 mm, 1.9 µm
  - Isolator column used to separate any contamination from mobile phases. Not strictly needed. (Not installed as of 7/22/2020).

**Mobile Phases:**

- Mobile Phase A:
  - LC grade water, 20 % Methanol, 2mM ammonium acetate, 0.1% acetic acid
  - Recipe: 979 mL LC grade water, 20 mL methanol, 1 mL acetic acid, 0.1542 g ammonium acetate
- Mobile Phase B:
  - Methanol, 20% LCMS grade water, 2mM ammonium acetate, 0.1% acetic acid
  - Recipe: 979 mL methanol, 20 mL LCMS grade water, 1 mL acetic acid, 0.1542 g ammonium acetate