

EVALUATION OF PERFLUORINATED COMPOUNDS IN SEDIMENT, WATER,  
AND PASSIVE SAMPLERS COLLECTED FROM THE BARKSDALE AIR  
FORCE BASE

by

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## ABSTRACT

Perfluorinated compounds (PFCs) are environmentally persistent surfactants that consist of fully fluorinated carbon chains and a terminal sulfonate or carboxylate polar head moiety. Due to their unique amphiphilic properties, PFCs are used in the manufacturing of products such as aqueous film forming foams (AFFFs). There is cause for concern of PFC contamination near the Barksdale Air Force Base resulting from runoff and ground infiltration of AFFFs that were used during fire training. This study analyzed water and sediment samples that were collected over a 13-month sampling period from bayous upstream and downstream of two fire training areas located on the base to determine the occurrence and magnitude of PFCs.

Liquid chromatography coupled with an electrospray ionization-triple stage quadrupole mass spectrometer was used for analysis of 6 different PFCs in sample extractions. Total PFC concentrations in the water and sediment samples ranged from non-detect to 7.1 ng/mL and non-detect to 31.4 ng/g, respectively. Two PFCs of increasing concern, perfluorooctanesulfonic acid and perfluorooctanoic acid, were quantified in 79% and 64% of water samples, respectively. Generally, PFCs containing a sulfonate polar head moiety were quantified more frequently than PFCs containing a carboxylate moiety. The perfluoroalkyl chain length of PFCs also showed significant influence on the PFC concentrations when analyzed using Spearman's rank correlation analysis. A

matrix of Spearman's rank correlation coefficients revealed that several water quality parameters (e.g., temperature, dissolved oxygen, ammonium, conductivity) may have a significant relationship with concentration of PFCs in water while parameters such as pH and organic matter content of sediment appeared to have no correlation with PFC concentrations.

Concentrations of PFCs detected in water, sediment, and fish samples were then compared to sediment and water column passive sampler data to determine if passive samplers could be used as a less invasive method for estimating PFC concentrations in the environment. The concentrations detected in sediment passive samplers were estimated to be more heavily influenced by the amount of PFCs partitioning to the aqueous phase rather than the amount partitioning to sediment. Perfluorooctanesulfonic acid was the only PFC quantified in 1 water passive sampler. The PFCs that were qualitatively detected in water column passive samplers appeared to be related to PFCs that were detected in fish samples. However, results of both types of passive samplers may be improved by longer deployment in the environment.



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## LIST OF ABBREVIATIONS

AFFF	Aqueous Film Forming Foam
BAFB	Barksdale Air Force Base
C	Conductivity ( $\mu\text{S}/\text{cm}$ )
Con at FR	Confluence at Flat River
Con	Confluence
DO	Dissolved Oxygen (ng/mL)
ExUp	Extreme Upstream
FTA-1	Fire Training Area 1
IS	Internal Standard
LCon	Lower Confluence
LFR	Lower Flat River
MeOH	Methanol
MQH <sub>2</sub> O	Milli-Q® Water
NH <sub>4</sub> <sup>+</sup>	Ammonium (mg/L)
OM	Organic Matter
PFBS	Perfluorobutanesulfonic Acid
PFC	Perfluorinated Compound
PFHpA	Perfluoroheptanoic Acid
PFHxS	Perfluorohexanesulfonic Acid
PFNA	Perfluorononanoic Acid

PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
POP	Persistent Organic Pollutant
SCB	South Cooper's Bayou
SMB	South Mack's Bayou
SUR	Surrogate
SUT	South Upper Tributary
T	Temperature (°C)
Up	Upstream
UT at SMB	Upper Tributary at South Mack's Bayou
UT	Upper Tributary
WB	Weapons Bridge
WUp	West of Upstream



## **CHAPTER I**

### **INTRODUCTION**

Organic compounds that have long environmental half-lives are typically referred to as persistent organic pollutants (POPs). These compounds do not degrade quickly and it becomes more likely for biota to be exposed to POPs as the concentration of the contaminant gradually increases in the environment. Once exposed, the interacting species may have difficulty metabolizing the POP due to its chemical stability. The accumulation of the POP within the organism is known as either bioconcentration (the contaminant is absorbed into the organism through direct contact) or bioaccumulation (the contaminant is absorbed by direct contact and ingested through dietary intake). The concern of biomagnification arises when organisms higher on the food chain consume the exposed biota. If the half-life of the POP permits, the contaminant can travel to and accumulate in destinations far removed from the production or application site via air and water currents (Jones and de Voogt 1999). For these reasons, POPs pose a potential threat to biota, humans, and the environment.

Perfluorinated compounds (PFCs) are a class of chemicals that have long half-lives and the ability to bioconcentrate, bioaccumulate, and biomagnify (Conder et al. 2008). Although perfluorooctanesulfonic acid (PFOS) is the only PFC currently on the Stockholm Convention's list of POPs, this class of chemicals, especially PFCs containing long perfluoroalkyl chains, are of

increasing concern (Stockholm Convention ; U.S. EPA 2009). Perfluorinated compounds (PFCs) are anthropogenic contaminants that consist of fully fluorinated carbon chains (perfluoroalkyl chains) and a terminal sulfonate or carboxylate moiety. Due to their unique amphiphilic properties, PFCs are used in the manufacturing of products such as fire-fighting foams, semiconductors, non-stick cookware, and waterproof clothing. In addition to PFCs being introduced to the environment through direct production, some compounds, such as perfluorooctanoic acid (PFOA), can be a result of biodegradation of PFC precursors (Prevedouros et al. 2005; U.S. Environmental Protection Agency (U.S. EPA) 2009). Consistent with other POPs, PFCs have become ubiquitous in the environment and have been found in areas far removed from any manufacturing or application site (Yamashita et al. 2005).

Human exposure can occur through multiple routes including ingestion of contaminated biota (i.e., fish). Some PFCs can take up to 8.5 years for the human body to eliminate, and can thus lead to increased chances of toxic effects (U.S. EPA 2009). While toxicity research is ongoing, a few of the current concerns resulting from PFC accumulation include immunotoxicity, developmental toxicity, and cell membrane alterations (Andersen et al. 2008; Hu et al. 2003; Lau et al. 2004). Therefore, it is important to monitor the concentrations of these contaminants in the environment in order to assess the magnitude of biota uptake.

The data resulting from this study were produced from samples collected at the Barksdale Air Force Base (BAFB) located in Bossier City, Louisiana (Figure 1.1). The base was established in 1932 in honor of Lt. Eugene Hoy Barksdale and encompasses over 22,000 acres of land including bodies of water such as rivers, bayous, and lakes (Department of the Air Force). The base provides a nutrient rich habitat in which terrestrial and aquatic species can thrive. However, these species may be subject to harmful contaminants, such as PFCs. The use of AFFFs during fire training events on the BAFB is probable cause for PFC contamination due to possible residue runoff into surrounding bayous and groundwater infiltration. Therefore, to evaluate the extent of PFC contamination, water, sediment, and fish were collected from the bayous located upstream and downstream of two fire training areas on the base and evaluated for the 6 PFCs listed in Table 1.1. These data were then compared to sediment and water column passive sampler data to determine if passive samplers could be used as a less invasive method for estimating PFC concentrations in the environment. This study is part of a larger risk assessment of PFC contamination at the BAFB location.

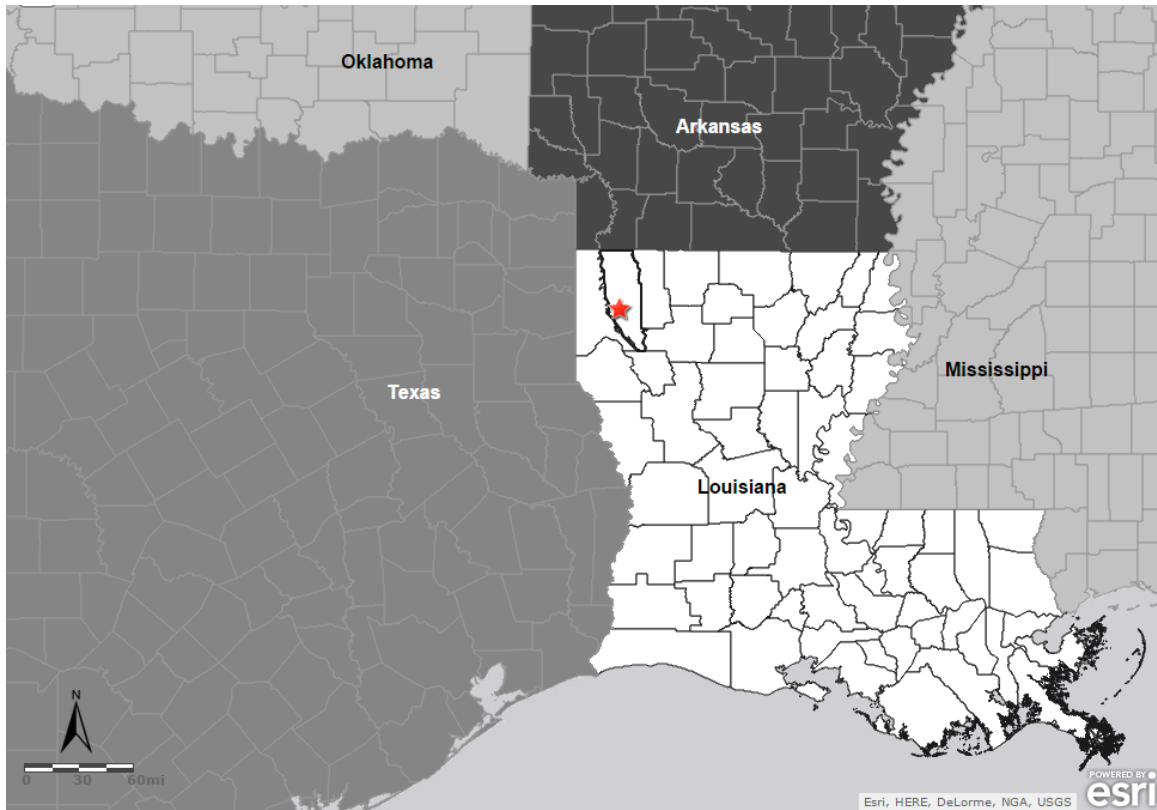


Figure 1.1 Location of Barksdale Air Force Base in relation to the state of Louisiana. The base is indicated by the star.

Table 1.1 Acronyms and structural properties of 6 perfluorinated compounds

Compound	Acronym	Molecular Formula	Molecular Weight (g/mol)	Perfluoroalkyl Chain Length	$\log K_{ow}^a$	Solubility at 25°C (mg/L) <sup>b</sup>
Perfluorobutanesulfonic acid	PFBS	C <sub>4</sub> HF <sub>9</sub> O <sub>3</sub> S	299	4	-0.3 ± 0.1	
Perfluorooctanesulfonic acid	PFOS	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	499	8	-0.7 ± 0.3	570
Perfluorohexanesulfonic acid	PFHxS	C <sub>6</sub> HF <sub>13</sub> O <sub>3</sub> S	399	6		
Perfluorooctanoic acid	PFOA	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	413	7	1.4 ± 0.2	9500
Perfluorononanoic acid	PFNA	C <sub>9</sub> HF <sub>17</sub> O <sub>2</sub>	463	8		
Perfluoroheptanoic acid	PFHpA	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>	363	6		

<sup>a</sup> Sundstrom et al. 2012<sup>b</sup> U.S. EPA 2014

## **CHAPTER II**

### **BACKGROUND**

#### **Aqueous Film Forming Foams**

The Barksdale Air Force Base (BAFB) is the host location for many fire training events (Stevanovich 2011). In the case of plane fuel ignition, foam is applied over the spill to smother existing flames and to prevent vapors from rising and igniting. Prior to 1966, fire-fighting foams were composed of proteins; the foams served their purpose of suppressing fire as long as they covered the fuel (Tuve et al. 1966). However, any disturbance or opening in the foam led to re-ignition of the fuel. The foams also degraded quickly due to the interaction with the dry chemicals that were applied before the foam to extinguish the initial fire (Tuve et al. 1966). Therefore, fire-fighting foams needed to be improved.

The first aqueous film forming foam (AFFF) was invented by Tuve, Spring, and Jablonski of the U.S. Naval Research Laboratory in the early 1960s and was patented in 1966 (Alm and Stern 1992; Tuve et al. 1966). The patent by Tuve et al. in 1966 explained that with 99% of the foam being water, the new invention allowed for easier area coverage over the fuel spill. The patent incorporates the use of perfluorinated compounds (PFCs) amounting to approximately 0.5% of the water based solution. As a result of the PFCs being hydrophobic and oleophobic, the AFFF creates a film over the fuel which lingers after the aerated foam has dissipated (Figure 2.1). This film is nearly impossible for flammable

vapors to penetrate, which prevents further vapor ignitions. The aqueous film also possesses the characteristic of quickly resealing any holes that may form to prevent re-ignition of the fuel that is concealed below the PFC film. Another benefit to this foam is that it is not susceptible to degradation by dry chemicals and was thus patented to be used after potassium bicarbonate powder was applied to the initial fire. Compounds used within this patented invention are modifications of a perfluorocarboxylic acid ( $C_7F_{15}CO^-$ ) and perfluorosulfonic acid ( $C_8F_{17}SO_2^-$ ) (Tuve et al. 1966). These compounds, without any modifications, are known as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), respectively.

The knowledge of AFFFs caught on and companies began to formulate their own foams containing fluorinated surfactants. Before long, the U.S. military comprised 75% of the AFFF market (Moody and Field 2000). One of the leading manufacturers of AFFFs was 3M and their perfluorinated surfactants were created through the process of electrochemical fluorination (Alm and Stern 1992). Electrochemical fluorination is a process that produces fully fluorinated compounds, such as PFOS (Alm and Stern 1992; Place and Field 2012). Other companies, such as National Foam and Ansul, used foams containing fluorotelomers that were created through a process called telomerization (Place and Field 2012). Although fluorotelomers are not fully fluorinated compounds, they have the potential to degrade to perfluorinated compounds, such as PFOA (Department of Defense 2011). In addition to perfluorinated surfactants, 3M also

added hydrocarbon surfactants to their AFFF concentrates to help reduce the surface tension of the hydrocarbon fuel (Alm and Stern 1992; Moody and Field 2000). These products proved to be extremely useful in the fight against hydrocarbon fuel fires. However, it was not made aware to the public until 2000 that AFFFs could pose possible threats to human health and the environment.

On May 16<sup>th</sup> of 2000, 3M announced that they were voluntarily starting a phase out process of PFOS-based AFFFs. The decision arose from the reporting of 3M data to the Environmental Protection Agency (EPA) that found PFOS to accumulate and persist in humans and the environment (U.S. EPA 2000). By 2003, 3M ceased production of PFOS and in 2006 the 2010/2015 PFOA Stewardship Program was formed. The Stewardship Program is a collaboration between the 8 leading manufacturers of fluorinated surfactant products in an attempt to eliminate PFOA and PFOA precursor compounds in products by 2015 (U.S. EPA). In 2009, PFOS was added to the persistent organic pollutants (POPs) list by the Stockholm Convention and over 100 alternative compounds were reviewed by the EPA to be used in place of long-chain PFCs (Stockholm Convention ; U.S. EPA 2009). Although actions have been set to reduce the production of long-chain PFCs, there is still no law against the use of AFFFs manufactured before the phase out in 2000 (Place and Field 2012; U.S. EPA 2009). Therefore, runoff and groundwater contamination from historical use, as well as current use of stockpiles, raises concern for environmental contamination.



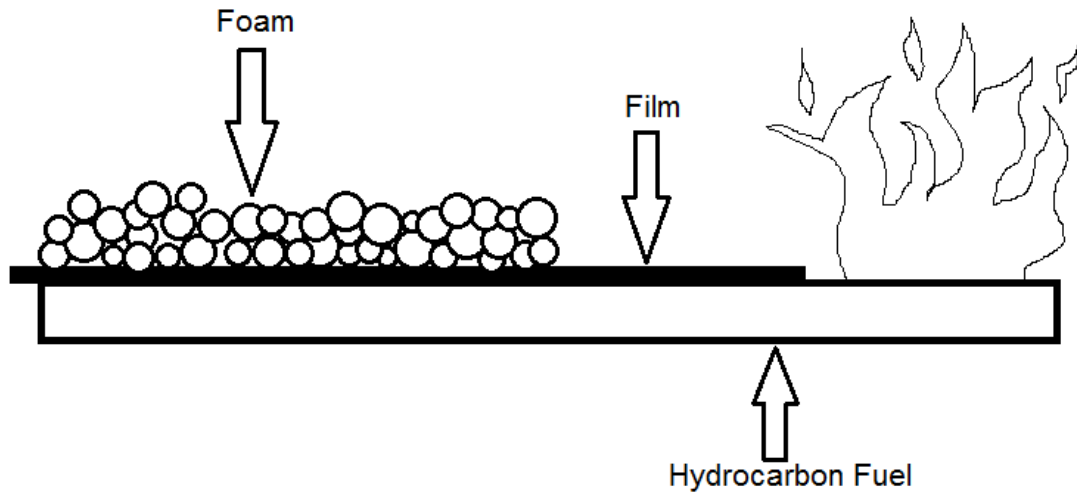


Figure 2.1 Formation of film from aqueous film forming foams over a hydrocarbon fuel spill.

## **Environmental Impacts from the Use of Aqueous Film Forming Foams**

Previous studies have evaluated concentrations of PFCs resulting from use of AFFFs. Moody et al. (2002) began monitoring concentrations of PFCs in surface water and fish from Etobicoke Creek (Toronto, ON) the day after an accidental release of AFFFs at L.B. Pearson International Airport in June 2000. Surface water was collected over the course of 3 weeks after the spill and fish were collected in June 2000 and January 2001. Perfluorinated compounds (PFCs) were determined using liquid chromatography-tandem mass spectrometry (LC/MS/MS). The liver analysis of fish collections resulted in a range of perfluorosulfonates from 0.0090 to 72.9 µg/g (n = 9) with PFOS being the predominant analyte followed by PFHxS and PFBS, respectively. Perfluorocarboxylate concentrations ranged from 0.070 to 1.02 µg/g (n = 9) with PFCs containing long perfluoroalkyl chains being the predominant analytes. The only analytes quantified in surface water samples (n = 54) were PFOS, PFHxS, and PFOA which resulted in maximum concentrations of 2210 µg/L, 2260 µg/L, and 11.3 µg/L, respectively. Maximum concentrations were detected 1 day after the spill and had decreased to < 5 µg/L 20 days after the spill (Moody et al. 2002).

Monitoring of Etobicoke and Spring Creeks was continued for 9 years after the large AFFF spill in 2000 and results were published by Awad et al. (2011). Concentrations of PFOS in water samples from the location closest to the spill in 2000 decreased from 2003 to 2009 from 690 ng/L to 290 ng/L, respectively.

Sediment samples taken from this same location retained the same concentration of PFOS from 2003 to 2009 (13 ng/g). Downstream from the spill, a 99% decrease in PFOS concentrations was observed between the years of 2000 (Moody et al. 2002) and 2009 in water samples. A 70% decline in PFOS concentrations between the years of 2003 and 2009 was observed in fish collected from a location 1.8 km from the spill (Awad et al. 2011).

Due to being the predominant analyte, PFOS was the only PFC discussed in great detail in the paper by Awad et al. (2011). However, PFOA was also a predominant analyte detected in water samples and PFHxS was found to be highly correlated with PFOS concentrations. Detection rates of PFCs other than PFOS and PFOA, were very low in sediment. Interestingly, there were no perfluorocarboxylates or short chain perfluorosulfonates detected in fish samples (Awad et al. 2011).

Toxicological effects on aquatic organisms were presented by 3M in 2000 to the Environmental Protection Agency (EPA) (3M 2000). More recently in 2010, Giesy et al. published an aquatic toxicology report for PFOS and PFBS with similar PFOS values reported by 3M in 2000. A 96 hour acute toxicity test of PFOS to fathead minnows in freshwater resulted in lowest observed effect concentrations (LOECs) of 5.4 mg/L and a 50% mortality rate ( $EC_{50}$ ) at a concentration of 9.1 mg/L. A 28 day microcosm study with fathead minnows reported a LOEC of 3 mg/L and an  $EC_{50}$  of 7.2 mg/L. The no observed effects

concentration (NOEC) of PFBS to fathead minnows after 96 hours of exposure was 888 mg/L and the EC<sub>50</sub> was reported at 1,938 mg/L (Giesy et al. 2010).

Based on previously reported toxicity values, Giesy et al. (2010) established water quality criteria for PFBS, PFOA, and PFOS. The maximum concentrations allowed in order to protect aquatic organisms from acute toxicity were calculated to be 121 mg/L, 25 mg/L, and 21 µg/L, respectively. The chronic or continuous exposure criteria were set at concentrations of 24 mg/L, 2.9 mg/L, and 5.1 µg/L, respectively (Giesy et al. 2010).

### **Physicochemical Properties and Environmental Partitioning of Perfluorinated Compounds**

Carbon-fluorine (C-F) bonds form the hydrophobic tail of PFCs and also provide most of the attributes that make these compounds appealing as surfactants. The properties created by these bonds are also the cause for concern of PFCs in the environment. The strongest covalent bond that can be formed is between carbon and fluorine (Smart 1994). This gives PFCs the stability needed to be used in events with high temperatures but it also leads to slow and incomplete degradation in the environment. Due to fluorine being the smallest halogen, second to hydrogen, complete fluorination of the carbon chain is able to occur. As the number of fluorine substitutions increase, the surface activity of the compound increases. Surface activity can be increased further by increasing the length of the C-F tail and adding a polar moiety (carboxylic or sulfonic acid) (Smart 1994). Surface activity is the ability for a compound to

orient itself in relation to a surface and create a monolayer due to having a hydrophobic and hydrophilic end. When the surface activity (the ability to form an organized layer) is increased, the surface tension of the liquid is decreased. Due to reduction of the surface tension of the aqueous film by perfluorinated surfactants and reduction of the surface tension of the hydrocarbon fuel by hydrocarbon surfactants, AFFFs are able to cover fuel spills quickly and effectively (Alm and Stern 1992; Moody and Field 2000; Smart 1994).

For most compounds, partition coefficients are able to be determined to predict the environmental fate of the contaminant. In the case of surfactants, it is difficult to calculate these partition coefficients due to their amphiphilic properties (Environmental Health Analysis Center et al. 2012). However, some literature has been published with estimations of these coefficients by using chemical structures of PFCs to model physicochemical behaviors (Bhatarai and Gramatica 2011). Partitioning has also been shown to be effected by environmental parameters, such as the pH of water and the percentage of organic matter in sediment (Ahrens et al. 2011).

It has been proposed that PFCs partition more heavily towards water than sediment (Awad et al. 2011; Prevedouros et al. 2005; Yang et al. 2011). A large contributing factor to this partitioning could be due to the high water solubility of these compounds. The Environmental Protection Agency (EPA) has reported that the solubility of PFOS and PFOA in purified water at 25°C are 570 mg/L and 9500 mg/L, respectively (U.S. EPA 2014). Therefore, PFCs are able to travel to

areas far from point sources via currents, allowing exposure to a multitude of aquatic organisms along the way.

Volatilization of PFCs is unlikely due to their low vapor pressures and anionic form, which leaves sediment as the secondary sink of these surfactants (Ahrens et al. 2009; U.S. EPA 2014). Several environmental and chemical factors influence the partitioning of PFCs to sediment. A study by Ahrens et al. (2011) showed increasing sediment sorption with decreasing levels of pH in water. An increase in concentration of PFCs was also observed with sediments that consisted of more organic matter (Ahrens et al. 2011). Sorption of PFCs has also been positively correlated with longer perfluoroalkyl chains and the presence of sulfonate functional groups (Ahrens et al. 2009; Yang et al. 2011). The partitioning of PFCs to sediment subjects benthic organisms and sediment-dwelling fish to PFCs.

### **Passive Sampling**

Passive sampling is a method that allows for an estimation of contaminants without the removal of biota or medium from the environment. Water column and sediment passive samplers were used in this study to measure PFC concentrations. In this case, semi-permeable membrane devices (SPMDs) were used as water column passive samplers. These devices measure the linear uptake of contaminants over time (Ouyang and Pawliszyn 2007). Therefore, these samplers can be used as a surrogate for pelagic fish to estimate

the bioconcentration of compounds like PFCs (Huckins et al. 1990). Semi-permeable membrane devices (SPMDs) are typically comprised of lay-flat low-density polyethylene (LDPE) tubing filled with a lipid (i.e., triolein). The lipid acts as a sorbent for hydrophobic contaminants. However, PFCs have been shown to accumulate more in serum than adipose tissue (Martin et al. 2003). The dispersion away from lipid and towards protein is most likely in part due to some PFCs having extremely low octanol/water ( $\log K_{ow}$ ) partition coefficients (Sundstrom et al. 2012; Table 1.1). Therefore, it may be beneficial to use serum proteins as the sorbent phase in the SPMDs rather than a lipid.

The concentration of contaminants in pore water can be estimated by the use of sediment passive samplers. In 1976, Hesslein developed a sampler to measure the concentration of dissolved contaminants in pore water with little disturbance to the sediment. This sampler consisted of acrylic plastic with cutout compartments. The compartments were to be filled with distilled water, covered with a membrane, and then sealed using a thin acrylic plate containing the same compartmental cutouts. The distilled water inside of the compartments measured the contaminant in pore water via equilibration (Hesslein 1976). Unlike linear uptake, equilibrium measurements only allow for an estimated concentration of PFCs at the time that samplers are removed from the environment (Ouyang and Pawliszyn 2007). Therefore, sediment passive samplers can be used to measure bioavailability of PFCs to benthic fish and organisms on a single day. These samplers were later referred to as peepers

(Teasdale et al. 1995), and will occasionally be referred to as such throughout this study.



## CHAPTER III

### RESEARCH OBJECTIVES AND HYPOTHESES

#### **Research Goals**

The goal of this study was to determine the concentrations of perfluorinated compounds (PFCs) in sediment and water at Barksdale Air Force Base (BAFB) and to determine if there are any significant relationships between PFC concentrations and environmental parameters. Perfluorinated compound (PFC) concentrations from grab samples were compared to PFC concentrations detected in sediment passive samplers deployed at BAFB to determine if passive samplers could be used as a reliable source for PFC estimations in the environment. Perfluorinated compound (PFC) concentrations detected in water column passive samplers were compared to concentrations detected in fish to determine if passive samplers could be used as a less invasive method to estimate PFC accumulation and exposure to aquatic biota.

#### **Research Hypotheses**

Question 1: Are there detectable concentrations of PFCs in water and sediment from BAFB?

Hypothesis:

H0: There are no detectable concentrations of PFCs in water and sediment from Barksdale Air Force Base.

Ha: There are detectable concentrations of PFCs in water and sediment from Barksdale Air Force Base.

Question 2: Are there any significant relationships between PFC concentrations detected in water and sediment and environmental parameters?

Hypothesis:

H0: There are no significant relationships between PFC concentrations in water and sediment and environmental parameters.

Ha: There are significant relationships between PFC concentrations in water and sediment and environmental parameters.

Questions 3: Are there detectable concentrations of PFCs in water and sediment passive samplers deployed at BAFB?

Hypothesis:

H0: There are no detectable concentrations of PFCs in water and sediment passive samplers.

Ha: There are detectable concentrations of PFCs in water and sediment passive samplers.

Questions 4: Is there a significant relationship between PFC concentrations detected in water and sediment grab samples and PFC concentrations in sediment passive samplers?

Hypothesis:

H0: There is no significant relationship between PFC concentrations detected in water and sediment grab samples and PFC concentrations in sediment passive samplers.

Ha: There is a significant relationship between PFC concentrations detected in water and sediment grab samples and PFC concentrations in sediment passive samplers.

Question 5: Is there a significant relationship between PFC concentrations detected in fish and PFC concentrations in passive samplers?

Hypothesis:

H0: There is no significant relationship between PFC concentrations detected in fish and PFC concentrations in passive samplers.

Ha: There is a significant relationship between PFC concentrations detected in fish and PFC concentrations in passive samplers.

## **Experimental Design**

The previous questions were answered using the following experimental outline:

1. Qualitative and quantitative analysis of PFCs in sediment and water grab samples from BAFB.
2. Quantitative analysis of water quality parameters at BAFB and organic matter in sediment from BAFB.

3. Qualitative and quantitative analysis of PFCs in sediment and water passive samplers deployed at BAFB.
4. Qualitative and quantitative analysis of PFCs in fish from BAFB.
5. Statistical analysis of data.

## CHAPTER IV

### MATERIALS AND METHODS

#### Reagents

Analytical standards of perfluoro-n-heptanoic acid (PFHpA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-nonanoic acid (PFNA), potassium perfluoro-1-butanesulfonate (L-PFBS), sodium perfluoro-1-hexanesulfonate (L-PFHxS), and sodium perfluoro-1-octanesulfonate (L-PFOS) in methanol (MeOH) were purchased from Wellington Laboratories. Surrogates of perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>]hexanoic acid (MPFHxA), N-ethyl-d<sub>5</sub>-perfluoro-1-octanesulfonamide (d-N-EtFOSA-M), and perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>]decanoic acid (MPFDA) in MeOH were also purchased from Wellington Laboratories. Internal standards of perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]octanoic acid (MPFOA), sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]octanesulfonate (MPFOS), and N-methyl-d<sub>3</sub>-perfluoro-1-octanesulfonamide (d-N-MeFOSA-M) in MeOH were purchased from Wellington Laboratories. All organic solvents used in this project were LC/MS grade. Nitrogen and argon was purchased as UHP grade.

#### Collection and Extraction of Surface Water Samples

Methods for water collection were adapted from EPA Method 537 (Shoemaker et al. 2009). For this study, water samples, GPS coordinants, and water quality parameters were collected upon arrival at each location. Samples

consisted of approximately 500 mL of surface water collected in a 1 L polypropylene container which contained 0.5 g of water preservative (Trizma® pre-set crystals, pH 7.4, Sigma-Aldrich). Each bottle was labeled with the sampling location and date and was transported back to the laboratory on ice.

Field reagent blanks (FRBs) were prepared in the laboratory by filling a 1 L polypropylene bottle with approximately 500 mL Milli-Q® water (MQH<sub>2</sub>O), sealed, and transported to the field site. Once arrived at the field site, the reagent water was poured into an empty 1L polypropylene bottle, labeled as the FRB, and transported on ice back to the laboratory with the other field samples.

Extraction at the laboratory was conducted by spiking an aliquot of 250 mL of the water samples and 250 mL of MQH<sub>2</sub>O (lab blank) with 5 µL of 10 ppm surrogate mixture (SUR) and then passing the water through solid phase extraction (SPE) cartridges (Bond Elut-LMS, 500 mg 6 mL, Agilent Technologies). Samples were eluted with 5 mL of MeOH, concentrated to 0.25 mL under nitrogen, and then brought to a final volume of 0.5 mL with an 80:20 MeOH:MQH<sub>2</sub>O solution. Samples were then filtered using 2 mL centrifuge tube filters (0.22 µm, cellulose acetate, Corning Incorporated) at 7000 rpm for 1 minute. An aliquot of 196 µL was transferred to a 250-µL liquid chromatography (LC) vial along with 4 µL of 5 ppm internal standard mixture (IS). All samples were extracted within one week of collection date.

## **Collection and Extraction of Sediment Samples**

Sediment samples taken from Barksdale Air Force Base (BAFB) were scraped from at least one foot away from the bank of the bayou and placed in a polypropylene jar. Each container was labeled with the sampling location and date. Samples were transported on ice to the laboratory.

After arrival to the laboratory, approximately 60-70 g of each sediment sample was weighed and set in a vacuum hood to air dry. After at least 24 hours of drying time, sediment was reweighed and a dry weight was recorded. The sediment was homogenized into smaller pieces, placed in jars, and spiked with 5  $\mu\text{L}$  of 10 ppm SUR. Enough MeOH (20-50mL) was added to each sample to cover the sediment completely. Sample jars were placed on a shaker table at a speed of 120 rpm for 5 hours. The MeOH was syringe filtered (0.2  $\mu\text{m}$ , cellulose acetate, GE Whatman) into a 15-mL polypropylene centrifuge tube. Samples were concentrated down to 0.25 mL under nitrogen and then brought back to a final volume of 0.5 mL with an 80:20 MeOH:MQH<sub>2</sub>O solution. The samples were then filtered using 2-mL centrifuge tube filters (0.22  $\mu\text{m}$ , cellulose acetate, Corning Incorporated) at 7000 rpm for 1 minute. An aliquot of 196  $\mu\text{L}$  was transferred to a 250- $\mu\text{L}$  LC vial along with 4  $\mu\text{L}$  of 5 ppm IS. All samples were extracted within one week of collection date.

## **Water Column Passive Samplers Containing Lipid**

### *Preparation and Deployment of Regenerated Cellulose*

Field samplers were prepped in the laboratory. One and a half feet of regenerated cellulose dialysis tubing was filled with 300  $\mu$ L of glyceryl trioleate (>99%, Sigma-Aldrich) and sealed 3 inches from each end with weighted clips. A fishing weight was attached to the sediment end of the dialysis tubing with fishing line. Once on the field site, thin rope was tied to the water surface end of the dialysis tubing and secured to the shore line by tying the rope to a nearby tree.

### *Preparation and Deployment of LDPE Tubing*

Field samplers were prepped in the laboratory. One and a half feet of low-density polyethylene (LDPE) dialysis tubing was filled with 300  $\mu$ L of glyceryl trioleate (>99%, Sigma-Aldrich) and heat sealed 3 inches from each end. A fishing weight was attached to the sediment end of the dialysis tubing with fishing line. Once at the field site, the sampler was placed inside of a ~3 foot PVC pipe. The PVC pipe had holes of 1 inch diameter cut out to allow for adequate water flow through the PVC pipe and sampler. The PVC pipe was anchored into the sediment, allowing for at least a foot of PVC piping and sampler to be exposed to the water column.



### *Extraction*

After 6 weeks, samplers were retrieved. Each sampler was stored in a separate bag and transferred on ice to the laboratory. Upon returning, debris was gently wiped from the samplers. The dialysis tubing was weighed and cut into ~1x1 cm fragments. The fragments were placed in a 15-mL polypropylene tube with ~20 mL of MeOH per foot of dialysis tubing. Each sample received 5  $\mu$ L of 10 ppm SUR and was then vortexed. The MeOH from each sample was syringe filtered (0.2  $\mu$ m, cellulose acetate, GE Whatman) into a new polypropylene tube and concentrated to 250  $\mu$ L under nitrogen. The samples were brought to a final volume of 0.5 mL with 80:20 MeOH:MQH<sub>2</sub>O and then centrifuge filtered (0.22  $\mu$ m, cellulose acetate, Corning Incorporated) at 7000 rpm for 1 minute. A total of 196  $\mu$ L of sample was transferred to an LC vial along with 4  $\mu$ L of 5 ppm IS.

### **Water Column Passive Samplers Containing Protein**

Field samplers were prepped in the laboratory. One and a half feet of LDPE dialysis tubing was filled with 300  $\mu$ L of Sea Block blocking buffer (Thermo Fisher Scientific) and heat sealed 3 inches from each end. A fishing weight was attached to the sediment end of the dialysis tubing with fishing line. Once at the field site, the sampler was placed inside of a PVC pipe. The PVC pipe had holes of 1 inch diameter cut out to allow for adequate water flow through the PVC pipe

and sampler. The PVC pipe was anchored into the sediment, allowing for at least a foot of PVC piping and sampler to be exposed to the water column.

After 6 weeks, samplers were retrieved. Each sampler was stored in a separate bag and transferred on ice to the laboratory. Upon returning, debris was gently wiped from the samplers. The dialysis tubing was weighed and cut into ~1x1 cm fragments. The fragments were placed in a 15-mL polypropylene tube with ~20 mL of MQH<sub>2</sub>O per foot of dialysis tubing. Each sample received 5 µL of 10 ppm SUR and was then vortexed. Samples were then passed through SPE cartridges (Bond Elut-LMS, 500 mg 6 mL, Agilent Technologies) and eluted with 10 mL of MeOH. Samples were then concentrated down to 250 µL under nitrogen. Samples were brought to a final volume of 0.5 mL with 80:20 MeOH:MQH<sub>2</sub>O and then centrifuge filtered (0.22 µm, cellulose acetate, Corning Incorporated) at 7000 rpm for 1 minute. An aliquot of 196 µL was transferred to a 250-µL LC vial along with 4 µL of 5 ppm IS. All samples were extracted within one week of collection date.

### **Sediment Passive Samplers**

Two designs of peepers were used in the field as sediment passive samplers. The first set of peepers consisted of one column of cells with each cell containing 12 mL MQH<sub>2</sub>O. The second set of peepers contained 2 columns of cells, with each cell containing 8 mL of water. Samplers were prepared upon arrival to the field site by filling 5-8 cells with MQH<sub>2</sub>O and covering the cells with a

polyether sulfone membrane (0.2  $\mu\text{m}$ , Sterlitech). The membrane was secured onto the sampler with an acrylic plate. The peeper was then deployed vertically into the sediment of the bayou, ensuring that the membrane covered cells were below the sediment line. A rope was tied from the peeper to the bank of the bayou as a location indicator for retrieval.

Peeper were removed 6 weeks later and the MQH<sub>2</sub>O from within each cell was removed using a syringe and needle and transferred to 15-mL polypropylene centrifuge tubes. The tubes were labeled with the location and date and transported on ice back to the laboratory.

Extraction at the laboratory was conducted by spiking MQH<sub>2</sub>O from each peeper with 5  $\mu\text{L}$  of 10 ppm SUR and then passing the water through SPE cartridges (Bond Elut-LMS, 500 mg 6 mL, Agilent Technologies) and eluting with 5 mL of MeOH. Samples were concentrated to 0.25 mL under nitrogen, brought to a final volume of 0.5 mL with an 80:20 MeOH:MQH<sub>2</sub>O solution, and centrifuge filtered (0.22  $\mu\text{m}$ , cellulose acetate, Corning Incorporated) at 7000 rpm for 1 minute. An aliquot of 196  $\mu\text{L}$  was transferred to a 250- $\mu\text{L}$  LC vial along with 4  $\mu\text{L}$  of 5 ppm IS. All samples were extracted within one week of collection date.

### **Instrumental Analysis**

The analytical methods for PFC determination were adapted from EPA Method 537 (Shoemaker et al. 2009). Perfluorinated compounds (PFCs) were separated using a Thermo Scientific liquid chromatograph equipped with a C-18

SecurityGuard™ column (2 x 2.1 mm) and a Gemini® NX-C18 analytical column (75 x 2 mm, 3 µm particle size). A Thermo Scientific Accela 1250 pump was operated at 300 µL/min using a mobile phase consisting of 20 mM ammonium acetate (A) and 100% MeOH (B). The elution gradient started at 60% A and 40% B and held for 1 min. The gradient was then ramped to 10:90 A:B over 24 min and held for 7 min. The gradient was then ramped to initial conditions (60:40% A:B) over 0.10 min and then held for 4.9 min. The sample injection volume was 30 µL.

A Thermo Scientific TSQ Quantum™ Access MAX triple quadrupole mass spectrometer was used to detect PFCs. The electrospray ionization source (H-ESI, Thermo Scientific) was operated in negative ion mode with capillary needle voltage set to -3 kV and cone gas flow at 98 L/hr. The flow of nitrogen desolvation gas was set to 1100 L/hr at a temperature of 350°C.

Percent organic matter for selected sediment grab samples was determined by colorimetric analysis at A & L Agricultural Laboratories, Inc. (Lubbock, TX).

### **Quality Assurance, Quality Control, and Quantification**

Fortified SUR compounds in each sample prior to the extraction process were used to estimate the percent recovery of analytes. In addition to estimating instrumental errors, labeled ISs were used to quantify analytical standards and environmental samples. A linear range was determined by a 5 point calibration

curve consisting of concentrations ranging from 10 ng/mL to 250 ng/mL. The same standard vials used for the calibration curve were injected after every 4 - 5 environmental samples to serve as quality controls. Calculated PFC concentrations were based on PFC:IS ratios and the linear equation produced by the standard calibration curve. The lowest standard of 10 ng/mL was determined to be the limit of quantification (LOQ) based on repeated measures. An analyte was considered to be detected if the area count was above 1000 units.

Calculated concentrations that were above the LOQ were back calculated to account for the volume or weight of the environmental sample. Final concentrations for water grab samples and sediment passive samplers were based on extracted volumes, the final concentrated volume (0.5 mL), and the calculated concentration. Final concentrations for sediment grab samples and water column passive samplers were determined by the dry weight of the sediment or LDPE membrane, the factor of recovery for the MeOH added to each sample, the final concentrated volume (0.5 mL), and the calculated concentration.

Some samples resulted in a final concentration of negative value. Negative values are a result of a low PFC:IS area ratio which produced a negative calculated concentration when the ratio was substituted into the standard linear equation. Perfluorinated compound (PFC) area counts for these particular samples are above the LOQ and therefore will be considered

quantifiable concentrations. However, negative values will be replaced with a 0 for statistical and graphical purposes.

### **Statistical Analysis of Data**

R statistical software (version 2.11.1) was used to compute all statistics that were run on data collected for this study. Average concentrations and ranges in concentration only consisted of values that were quantified. Shapiro-Wilk's test and Bartlett's test were used to determine if data sets were normally distributed and of equal variance, respectively. Non-normal data sets were subjected to transformations but often resulted in no improvement. Therefore, Spearman's rank correlation analysis was used to evaluate the relationship between 2 variables. Due to uneven data sets, a list-wise comparison was used for the Spearman analysis and paired deletions occurred if either the concentration or parameter were absent.

## CHAPTER V

### RESULTS

#### Sediment Grab Samples

Sediment samples were collected from Barksdale Air Force Base (BAFB) during August and November of 2013 as well as March, early May, late May, June, July, and September of 2014. Each sample was analyzed for the 6 perfluorinated compounds (PFCs) listed in Table 1.1. Fortified concentrations of surrogate analytes were added to all grab samples prior to extraction. Average recovery for surrogates PFHxA-C13, PFDA-C13, and NEtFOSAA-d5 was  $55.08 \pm 70.94\%$ ,  $36.21 \pm 51.28\%$ , and  $16.07 \pm 26.50\%$ , respectively.

A total of 55 sediment grab samples were taken from locations of concern (LOCs) (Table 5.1, Figure 5.1 - 5.2); resulting detections are listed in Table 5.2. The majority of analytes were detected but not quantified in sediment grab samples. Perfluorinated compounds (PFCs) that were quantified in sediment grab samples were PFOS, PFHxS, and PFHpA (Figure 5.3). Perfluorooctanesulfonic acid (PFOS) was quantified in 65% of sediment grab samples and resulted in the highest average concentration ( $2.75 \pm 5.28$  ng/g,  $n = 36$ ) (Table 5.3). Perfluorohexanesulfonic acid (PFHxS) was quantified in 27% of sediment grab samples with an average concentration of  $1.47 \pm 2.18$  ng/g ( $n = 15$ ) (Table 5.3). A Spearman's rank correlation analysis between the analytes that were quantified and their corresponding molecular weights resulted in a

weak but significant correlation ( $\rho = 0.27$ ,  $p = 0.05$ ,  $n = 52$ ) (Figure 5.4). When PFCs were grouped by their polar head moiety, perfluorosulfonates resulted in more frequently quantified concentrations than perfluorocarboxylates (Table 5.4, Figure 5.5). However, a little more than half (57%) of the analytes containing a carboxylic acid group were detected but not quantified.

Sediment samples were also collected from reference locations at BAFB during the same months as samples from LOCs and were analyzed for the same 6 PFCs (Table 5.1, Table 5.5, Figure 5.1). Average concentrations per month from LOCs were compared to average concentrations from reference locations of corresponding months in Figure 5.6. Late May was the only sampling period that had quantifiable concentrations of PFCs from a reference location. However, these concentrations did not exceed concentrations quantified in samples from LOCs in late May. The months of March and early May contained the highest average concentrations of PFCs ( $5.55 \pm 8.13$  ng/g,  $n = 13$  and  $5.53$  ng/g,  $n = 1$ , respectively) quantified in sediment samples from LOCs (Table 5.6). September was the only month where no PFCs were quantified in sediment samples from LOCs. Perfluorinated compound (PFC) concentrations from remaining months (August, November, late May, June, and July) did not deviate greatly from one another (Figure 5.6).

The number of analytes quantified in sediment samples from each location over the 13-month sampling period are presented in Table 5.7. The UT location had the highest average PFC concentration ( $7.29 \pm 12.11$  ng/g,  $n = 6$ ) and also



had the greatest range in concentration (0.25 - 31.38 ng/g). Location SUT had the 2<sup>nd</sup> highest average PFC concentration of  $3.39 \pm 3.54$  ng/g (n=3) and Con had the 3<sup>rd</sup> highest concentration of  $2.68 \pm 2.60$  ng/g (n = 9). Concentrations among the rest of the sampling locations did not deviate greatly from one another (Figure 5.7). However, none of the 6 PFCs were quantified in samples collected from LFR or Con at FR.

Water quality parameters (temperature (T), dissolved oxygen (DO), conductivity ( $\mu\text{S}/\text{cm}$ ), pH, and ammonium ( $\text{NH}_4^+$ )) were measured during each month of sampling (except August) and are presented in Table 5.8. Percent organic matter (OM) was also measured in some of the sediment samples (Table 5.9). Spearman's rank correlation analysis was used to determine if there were any significant relationships between water parameters, OM, and concentrations of PFCs (Table 5.10). Perfluorooctanesulfonic acid (PFOS) and PFHxS were the only 2 PFCs that were subjected to correlation analysis for sediment samples because they were the only PFCs that had more than one quantifiable data point. The number of samples used for each correlation analysis is listed in Table 5.11. There were no significant relationships between PFOS and water parameters or percent OM. However, PFHxS was estimated to be significantly influenced by T ( $\rho = -0.83$ ,  $p < 0.005$ ,  $n = 14$ ), DO ( $\rho = 0.75$ ,  $p < 0.005$ ,  $n = 14$ ), and pH ( $\rho = 0.88$ ,  $p < 0.005$ ,  $n = 9$ ) (Figure 5.8 –5.10).

## Water Grab Samples

Surface water sampling during the months of August, November, March, early May, late May, June, July, and September resulted in the collection of 58 samples from LOCs (Table 5.12) and 12 samples from reference locations (Table 5.13). A total of 8 field reagent blanks (FRBs) and 8 lab blanks (LBs) were also analyzed for each month of water sampling (Table 5.14). All water samples were fortified with surrogate analytes prior to extraction and resulted in average recoveries of  $212.20 \pm 226.60\%$ ,  $96.28 \pm 85.12\%$ , and  $100.36 \pm 86.68\%$  of PFHxA-C13, PFDA-C13, and NEtFOSAA-d5, respectively.

Perfluorinated compounds (PFCs) were quantified in every month of water collection (Figure 5.11). In the month of March, the PFC concentration quantified in the LB exceeded the average PFC concentration in water grab samples from LOCs by almost 2 times the amount. Water controls were quantified in 2 other sampling months (November and September) but did not exceed the concentrations measured in samples from LOCs. March, late May, and July had the highest average concentrations of PFCs in water grab samples from LOCs ( $0.88 \pm 1.07$  ng/mL,  $n = 3$ ;  $0.61 \pm 0.87$  ng/mL,  $n =$  and  $0.54$  ng/mL  $\pm 1.18$  ng/mL, respectively) (Table 5.6, Figure 5.11). Average PFC concentrations were lower for the months of August, November, early May, June, and September ranging from 0.01 - 2.76 ng/mL (Table 5.6, Figure 5.11).

All LOCs had at least 1 PFC that was quantified (Table 5.15). Locations WUp, UT, and SUT had the highest concentrations of all LOCs sampled at BAFB

(Figure 5.12). Concentrations from these locations averaged 0.68 ng/mL ( $n = 1$ ),  $0.90 \pm 1.99$  ng/mL ( $n = 42$ ), and  $1.73 \pm 1.77$  ng/mL ( $n = 8$ ), respectively (Table 5.15). Extreme Upstream (ExUp), SCB, LFR, and LCon all resulted in average PFC concentrations below 0.15 ng/mL (Table 5.15).

Spearman's correlation analysis was used to determine if PFC concentrations in water grab samples were influenced by water parameters (Table 5.10). It was estimated from the Spearman analysis that there was a significant relationship between the concentration of PFBS and T ( $\rho = -0.53$ ,  $p < 0.005$ ,  $n = 30$ ) (Figure 5.13). Perfluorooctanoic acid (PFOA) also showed a negative correlation with T ( $\rho = -0.44$ ,  $p < 0.05$ ,  $n = 27$ ) (Figure 5.14). Dissolved oxygen (DO) was positively correlated with concentrations of PFBS and PFOA ( $\rho = 0.69$ ,  $p < 0.05$ ,  $n = 30$ ;  $\rho = 0.40$ ,  $p < 0.05$ ,  $n = 27$ , respectively) (Figure 5.15 – 5.16). Conductivity (C) was negatively correlated with PFBS and PFNA concentrations ( $\rho = -0.44$ ,  $p < 0.05$ ,  $n = 30$ ;  $\rho = -0.56$ ,  $p < 0.05$ ,  $n = 27$ , respectively) (Figure 5.17 – 5.18). Analytes PFOS and PFHxS showed weak, positive correlations with  $\text{NH}_4^+$  ( $\rho = 0.40$ ,  $p < 0.05$ ,  $n = 30$ ;  $\rho = 0.45$ ,  $p < 0.05$ ,  $n = 30$ , respectively) (Table 5.10). Spearman's rank correlation analysis also resulted in strong positive correlation coefficients between analytes (Table 5.10). There was no significant relationship between PFC concentrations in water grab samples and location coordinates when data were subjected to an individual Spearman's correlation analysis ( $\rho = -0.03$ ,  $p = 0.57$ ,  $n = 58$ ) (Figure 5.19).

Similar to sediment grab samples, the majority of PFCs quantified in water grab samples from LOCs were sulfonic acids (Table 5.4). Perfluorosulfonates were quantified in 78% of water samples and perfluorocarboxylates were quantified in 49% of water samples (Figure 5.20). A relationship was estimated between increasing carbon chain lengths of PFCs containing a sulfonic acid and concentration of PFCs quantified in water grab samples ( $\rho = 0.40$ ,  $p < 0.005$ ,  $n = 135$ ) (Figure 5.21). However, the relationship between carbon chain length and concentration of PFCs containing carboxylic acids resulted in a negative correlation ( $\rho = -0.24$ ,  $p < 0.05$ ,  $n = 85$ ) (Figure 5.22).

Each of the 6 PFCs were quantified in at least 14 water grab samples collected from LOCs (Table 5.3, Figure 5.23). Perfluorohexanesulfonic acid (PFHxS) was the most frequently quantified analyte (86%) and had the 2<sup>nd</sup> highest average concentration ( $0.61 \pm 0.81$  ng/mL,  $n = 50$ ). Out of 46 quantified water samples, PFOS averaged the highest concentration of the 6 PFCs ( $0.98 \pm 1.38$  ng/mL) and was the 2<sup>nd</sup> most frequently detected analyte (79%). A Spearman's correlation analysis between concentrations of quantified PFCs and their corresponding molecular weights resulted in a significant positive correlation ( $\rho = 0.21$ ,  $p < 0.005$ ,  $n = 220$ ) (Figure 5.24).

### **Sediment Passive Samplers**

A total of 16 sediment passive samplers were deployed in bayous at BAFB (Table 5.16). No data (ND) indicates sediment passive samplers that were

deployed but were not found upon return 6 weeks later. Water extracted from the sediment passive samplers was fortified with surrogate analytes prior to solid phase extraction. The recoveries for surrogates PFHxA-C13, PFDA-C13, and NEtFOSAA-d5 were  $136.32 \pm 41.61\%$ ,  $106.57 \pm 40.17\%$ , and  $79.70 \pm 68.53\%$ , respectively.

Only 7 of the peepers had quantifiable concentrations of PFCs (Table 5.16). Perfluorinated compounds (PFCs) containing a sulfonic acid were quantified more frequently (26%) than PFCs containing a carboxylic acid (7.1%) (Table 5.17, Figure 5.25). Perfluorooctanesulfonic acid (PFOS) had the highest average concentration ( $1.10 \pm 1.41$  ng/mL,  $n = 5$ ) but PFHxS was the most frequently quantified analyte (43%) (Table 5.18, Figure 5.26).

Concentrations of PFOS in sediment and water grab samples were compared to sediment passive samplers (Figure 5.27). In general, as the concentration of PFOS increased in water grab samples the concentration also increased in passive samplers. In contrast, PFOS concentrations decreased in sediment grab samples with increasing concentration in passive samplers. Similar trends were observed for PFHxS concentrations in grab samples and passive samplers (Figure 5.28).

### **Water Passive Samplers**

A total of 13 water passive samplers were deployed in the bayous of BAFB (Table 5.19). No data (ND) were able to be retrieved from the water

passive sampler that was collected from WB in late May due to deterioration of the dialysis tubing. The passive sampler that was deployed at UT was lost and thus resulted in ND for the month of September. Surrogate analytes were added to water passive samplers prior to sample extraction. Recovery for PFHxA-C13, PFDA-C13, and NEtFOSAA-d5 was  $168.56 \pm 111.70\%$ ,  $162.43 \pm 106.39\%$ , and  $222.88 \pm 168.57\%$ , respectively.

Only 1 analyte (PFOS) was quantified in 1 of the passive samplers (FR in late May) (Table 5.19). More PFCs containing a sulfonic acid (39%) were above the limit of detection than PFCs containing a carboxylic acid (21%) (Table 5.17, Figure 5.29). Perfluorobutanesulfonic acid (PFBS) and PFHpA were the only 2 analytes that were not found in 100% of the samplers (Figure 5.30).

### **Fish and Passive Samplers**

Fish collected from BAFB were analyzed by another member of the lab to be used for a different segment of the ecological risk assessment of PFCs at BAFB. The results listed in Table 5.20 only consist of fish compilations that can be compared to passive sampler data and are not a representation of total fish collected from BAFB.

Perfluorooctanesulfonic acid (PFOS) was the only PFC quantified in all 3 fish compilations; 100% of fish collected from the specified locations were able to be quantified for this particular analyte. Average PFOS concentrations in fish collected in June from WB and FR were  $1885 \pm 928$  ng/g and  $175 \pm 31$  ng/g,

respectively. Fish from WB collected in June had a range of PFOS concentrations from 828 - 3787 ng/g. The range was smaller for fish collected at FR in June (143 – 231 ng/g). A total of 8 fish were compiled from WB in September resulting in an average concentration of  $876 \pm 311$  ng/g with a range of 447 – 1335 ng/g. Based on results listed in Table 5.20, no statistical comparisons were made between passive sampler data and fish data due to insufficient quantifiable data. However, detectable PFOS (area counts) in passive samplers was used for qualitative comparisons with quantified PFOS concentrations in fish (Table 5.21). Average PFOS concentrations in fish collected in June and July were plotted against average PFOS area counts in sediment passive samplers retrieved from BAFB in the months of early May through September (Figure 5.31). Similarly, average PFOS concentrations detected in fish collected in June and July were plotted against average PFOS area counts in water passive samplers retrieved from BAFB in the months of early May through September (Table 5.32).

Table 5.1 Abbreviations for sample locations at Barksdale Air Force Base

	Location	Abbreviations
Locations of Concern	Extreme Upstream	ExUp
	West of Upstream	WUp
	Upstream	Up
	Weapons Bridge	WB
	Fire Training Area-1	FTA-1
	Upper Tributary	UT
	South Upper Tributary	SUT
	Upper Tributary at South Mack's Bayou	UT at SMB
	South Cooper's Bayou	SCB
	South Mack's Bayou	SMB
	Confluence	Con
	Lower Flat River	LFR
	Confluence at Flat River	Con at FR
	Lower Confluence	LCon
Reference Locations	Flat River	FR
	Flag Lake	FL
Controls	Field Reagent Blank	FRB
	Lab Blank	LB



Table 5.2 Perfluorinated compounds detected in sediment grab samples from locations of concern at Barksdale Air Force Base

Month	Location	Concentration (ng/g dw)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
August							
	ExUp	NF	1.02	NQ	NF	NF	NF
	Up	NF	NQ	NQ	NF	NF	NF
	WB	NF	1.03	NQ	NQ	NF	NF
	UT	NF	0.43	NQ	NF	NF	NF
	SCB	NF	NQ	NQ	NQ	NF	NF
	SMB	NF	0.75	NQ	NQ	NF	NF
	Con	NF	NQ	NQ	NF	NF	NF
November							
	ExUp	NF	NF	NF	NF	NF	NF
	Up	NF	0.76	NF	NF	NF	NF
	WB	NF	1.14	NF	NF	NF	NF
	FTA-1	NF	NF	NF	NF	NF	NF
	SUT	NF	0.63	NF	NF	NF	NF
	SMB	NF	4.48	NF	NQ	NQ	0
	Con	NF	0.00	NF	NF	NF	NF
March							
	Up	NQ	0.58	NF	NQ	NQ	NQ
	WB	NQ	NQ	NF	NQ	NQ	NQ
	FTA-1	NQ	3.19	4.89	NQ	NQ	NQ
	UT	NQ	31.38	7.72	NQ	NQ	NQ
	SUT	NQ	7.39	2.16	NQ	NQ	NQ
	SCB	NQ	0.94	1.66	NQ	NQ	NQ
	SMB	NQ	2.18	2.02	NQ	NQ	NQ
	Con	NQ	6.30	1.75	NQ	NQ	NQ
Early May							
	WB	NF	NQ	NQ	NQ	NF	NF
	Con	NQ	5.53	NQ	NQ	NQ	NQ

Table 5.2 Continued

Month	Location	Concentration (ng/g dw)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
Late May							
	Up	NQ	0	0.17	NQ	NQ	NQ
	WB	NQ	2.78	0	NQ	NQ	NF
	FTA-1	NQ	0.12	0.17	NQ	NF	NQ
	SCB	NQ	1.41	0.29	NQ	NF	NQ
	SMB	NQ	2.42	0.08	NQ	NF	NQ
	Con	NQ	6.23	0.63	NQ	NQ	NQ
June							
	Up	NQ	0.18	NQ	NQ	NQ	NQ
	WB	NF	NQ	NF	NQ	NF	NF
	FTA-1	NQ	NQ	NQ	NQ	NF	NQ
	UT	NQ	1.93	0.25	NQ	NQ	NQ
	UT at SMB	NQ	1.05	NQ	NQ	NQ	NQ
	SCB	NQ	1.09	0.20	NQ	NQ	NQ
	SMB	NQ	2.33	NQ	NQ	NF	NQ
	Con	NQ	1.50	0.27	NQ	NQ	NQ
	LFR	NF	NQ	NF	NF	NQ	NF
	Lcon	NQ	4.26	NQ	NQ	NQ	NQ
July							
	Up	NQ	NQ	NQ	NQ	NF	NQ
	WB	NQ	0.61	NQ	NQ	NF	NQ
	FTA-1	NQ	0.71	NQ	NQ	NQ	NQ
	UT	NF	2.02	NQ	NQ	NQ	NQ
	SCB	NQ	0.14	NQ	NQ	NF	NQ
	SMB	NQ	0.41	NQ	NQ	NQ	NQ
	Con	NQ	1.93	NQ	NQ	NQ	NQ
	LFR	NF	NQ	NQ	NQ	NQ	NQ
	Con at FR	NF	NQ	NQ	NQ	NF	NF

Table 5.2 Continued

Month	Location	Concentration (ng/g dw)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
September	WB	NF	NQ	NF	NF	NF	NF
	FTA-1	NQ	NQ	NQ	NQ	NQ	NQ
	UT	NF	NQ	NF	NF	NF	NF
	SCB	NF	NF	NF	NF	NF	NF
	SMB	NF	NQ	NF	NQ	NF	NF
	Con	NF	NQ	NF	NF	NF	NF

NF = Not Found

NQ = Not Quantified

Table 5.3 Number of grab samples with analytes that were not found, not quantified, or quantified and average concentrations of quantified analytes from locations of concern at Barksdale Air Force Base

Sample Type	Analyte	Number of Grab Samples			Concentration of Quantified Analytes (ng/g or ng/mL)	
		Not Found	Not Quantified	Quantified	Average ± SD	Range
Sediment Grab Sample	PFBS	25	30	0		
	PFOS	3	16	36	2.75 ± 5.28	0 - 31.38
	PFHxS	16	24	15	1.47 ± 2.18	0 - 7.72
	PFOA	19	36	0		
	PFNA	29	26	0		
	PFHpA	23	31	1	0	
Water Grab Sample	PFBS	4	15	39	0.13 ± 0.17	0 - 0.92
	PFOS	2	10	46	0.98 ± 1.38	0.02 - 7.07
	PFHxS	1	7	50	0.61 ± 0.81	0 - 4.43
	PFOA	4	17	37	0.09 ± 0.10	0 - 0.37
	PFNA	11	33	14	0.01 ± 0.02	0 - 0.04
	PFHpA	5	19	34	0.08 ± 0.09	0 - 0.41

SD = Standard Deviation

Table 5.4 Number of perfluorinated compounds with a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in grab samples from locations of concern at Barksdale Air Force Base

Sample Type	Polar Head Moiety	Number of Analytes		
		Not Found	Not Quantified	Quantified
Sediment				
Grab Sample				
	Sulfonic Acid	44	70	51
	Carboxylic Acid	71	93	1
Water Grab				
Sample				
	Sulfonic Acid	7	32	135
	Carboxylic Acid	20	69	85

Table 5.5 Perfluorinated compounds detected in sediment grab samples from reference locations at Barksdale Air Force Base

Month	Reference Location	Concentration (ng/g dw)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
August	FR	NF	NQ	NQ	NF	NF	NF
	FL	NF	NQ	NQ	NF	NF	NF
November	FR	NF	NF	NF	NF	NF	NF
	March	FR	NF	NQ	NF	NF	NQ
Early May	FR	NF	NQ	NQ	NQ	NF	NF
	Late May	FL	NF	0	0	NQ	NQ
June	FR	NF	NQ	NF	NQ	NF	NF
	FL	NF	NQ	NQ	NF	NF	NQ
July	FR	NF	NQ	NQ	NF	NF	NF
	September	FR	NF	NF	NF	NF	NF

NF = Not Found

NQ = Not Quantified

Table 5.6 Number of grab samples quantified for each perfluorinated compound (PFC) and the average concentration of PFCs from each month of sampling locations of concern at Barksdale Air Force Base

Sample Type	Month	N =	Number of Grab Samples Quantified							Concentration of Quantified Analytes		
			PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA	Average ± SD	Range		
<b>Sediment Grab</b>												
Sample (ng/g)	August	7	0	4	0	0	0	0	0	0	0.81 ± 0.28	0.43 - 1.03
	November	7	0	5	0	0	0	0	1	1	1.06 ± 1.80	0 - 4.48
	March	8	0	7	6	0	0	0	0	0	5.55 ± 8.13	0.58 - 31.38
	Early May	2	0	1	0	0	0	0	0	0	5.53	
	Late May	6	0	6	6	0	0	0	0	0	1.18 ± 1.87	0 - 6.23
	June	10	0	7	3	0	0	0	0	0	1.31 ± 1.29	0.18 - 4.26
	July	9	0	6	0	0	0	0	0	0	0.97 ± 0.80	0.14 - 2.02
	September	6	0	0	0	0	0	0	0	0		
<b>Water Grab</b>												
Sample (ng/mL)	August	8	7	8	8	7	0	7	7	7	0.09 ± 0.07	0.02 - 0.30
	November	7	2	2	5	1	0	0	0	0	0.21 ± 0.12	0.06 - 0.41
	March	9	5	8	9	3	0	3	3	3	0.88 ± 1.07	0.11 - 4.43
	Early May	2	0	2	2	1	0	0	0	0	0.14 ± 0.08	0.04 - 0.26
	Late May	6	6	6	6	6	0	5	5	5	0.61 ± 0.87	0.01 - 3.39
	June	11	10	10	10	10	7	10	10	10	0.19 ± 0.44	0.01 - 2.76
	July	9	9	8	9	9	7	9	9	9	0.54 ± 1.18	0 - 7.07
	September	6	0	2	1	0	0	0	0	0	0.08 ± 0.03	0.06 - 0.12

N = Total Number of Grab Samples

Table 5.7 Number of sediment grab samples quantified for each perfluorinated compound and the average concentration of perfluorinated compounds from each location of concern at Barksdale Air Force Base

Sample Type	Location	N =	Number of Grab Samples Quantified							Concentration of Quantified Analytes (ng/g)	
			PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA	Average ± SD	Range	
Sediment Grab Sample	ExUP	2	0	1	0	0	0	0	0	1.02	0 - 0.76
	Up	6	0	4	1	0	0	0	0	1.02 ± 0.32	0 - 2.78
	WB	8	0	4	1	0	0	0	0	1.07 ± 1.09	0.12 - 4.89
	FTA-1	6	0	3	2	0	0	0	0	1.82 ± 2.13	0.25 - 31.38
	UT	5	0	4	2	0	0	0	0	7.29 ± 12.11	0.63 - 7.39
	SUT	2	0	2	1	0	0	0	0	3.39 ± 3.54	1.05
	UT at SMB	1	0	1	0	0	0	0	0	0.82 ± 0.62	0.14 - 1.66
	SCB	6	0	4	3	0	0	0	0	1.56 ± 1.57	0.00 - 6.30
	SMB	7	0	6	2	0	0	1	0	2.68 ± 2.60	
	Con	8	0	6	3	0	0	0	0		
	LFR	2	0	0	0	0	0	0	0		
	Con at FR	1	0	0	0	0	0	0	0		
	LCon	1	0	1	0	0	0	0	0	4.26	

N = Total Number of Grab Samples



Table 5.8 Universal Transverse Mercator (UTM) coordinates and water quality parameters from sampling locations at Barksdale Air Force Base

Month	Site	Coordinates	Temperature (°C)	Dissolved Oxygen (%)	Oxygen (mg/L)	Conductivity (µS/cm)	pH	Ammonium (mg/L)
November								
	ExUp	15S 0437051 3598425	15.7	49.0	4.77	641	7.60	
	Up	15S 0437829 3598274	15.9	69.0	6.83	607	7.55	
	WB	15S 0438509 3596699	14.9	61.3	6.15	482	7.72	
	FTA-1	15S 0439386 3595008	13.9	82.6	8.53	455	8.06	
	SUT	15S 0439530 3594423	13.0	74.0	7.72	557	7.93	
	SMB	15S 0439386 3594416	14.4	62.2	6.35	631	7.41	
	Con	15S 0439585 3594415	13.7	76.8	7.98	486	7.82	
	FR	15S 0440294 3598121	15.7	51.0	5.03	223	7.54	
	FL	15S 0444746 3596608	15.4	76.1	7.63	127	8.12	
March								
	Up	15S 0437786 3598273	20.2	91.4	8.33	740	7.90	1.08
	WB	15S 0438514 3596693	15.7	72.3	7.22	573	7.69	
	FTA-1	15S 0439398 3594967	19.0	145.2	13.50	591	8.80	0.98
	UT	15S 0439378 3594717	20.5	99.8	9.01	655	8.80	0.36
	SUT	15S 0439462 3594554	20.1	107.0	9.69	655	8.76	0.38
	SCB	15S 0439554 3594440	17.0	122.0	11.90	581	8.64	
	SMB	15S 0439550 3594409	16.3	101.9	9.42	680	8.03	1.53
	Con	15S 0439599 3594407	15.8	111.0	10.96	592	8.36	1.11
	FR	15S 0440305 3598127	18.3	88.2	8.14	299	8.37	1.27

Table 5.8 Continued

Month	Site	Coordinates	Temperature (°C)	Dissolved Oxygen (%)	Oxygen (mg/L)	Conductivity (µS/cm)	pH	Ammonium (mg/L)
Early May	WB	15S 0438515 3596686						
	Con	15S 0439582 3594421						
	FR	15S 0440310 3598124						
Late May	Up	15S 0437775 3598271						
	WB	15S 0438517 3596676	27.4	48.2	3.83	779	7.31	0.76
	FTA-1	15S 0439408 3594953	30.2	58.9	4.44	786	7.70	0.98
	SCB	15S 0439559 3594441	25.1	71.6	5.85	696	8.02	0.45
	SMB	15S 0439541 3594408	27.1	67.0	5.26	588	7.87	0.49
	Con	15S 0439582 3594420	23.3	66.1	5.66	662	7.60	0.42
	FL	15S 0444745 3596608	24.1	49.5	4.16	84	7.25	0.37
June	Up	15S 0437782 3598273						
	WB	15S 0438515 3596682	30.1	40.4	2.95	956	7.31	0.15
	FTA-1	15S 0439402 3594971	30.4	41.0	3.11	890	7.70	0.14
	UT	15S 0439382 3594714	32.2	40.4	3.09	847	8.02	0.16
	SCB	15S 0439554 3594441	27.2	38.5	2.96	775	7.87	0.07
	SMB	15S 0439518 3594411	27.2	41.4	3.35	828	7.60	0.11
	Con	15S 0439586 3594419	36.7	40.4	3.08	708	7.25	0.12
			26.5	38.2	3.08	815	7.55	0.11

Table 5.8 Continued

Month	Site	Coordinates	Temperature (°C)	Dissolved (%)	Oxygen (mg/L)	Conductivity (µS/cm)	pH	Ammonium (mg/L)
June	LFR	15S 0440371 3594480	29.1	30.4	2.34	678	7.40	0.16
	Con at FR	15S 0440381 3594444	28.5	30.5	2.36	911	7.42	0.13
	LCon	15S 0440293 3594430	29.9	32.0	2.40	917	7.61	0.12
	FR	15S 0440301 3598121	28.0	26.8	2.08	646	7.37	0.16
	FL	15S 0444741 3596606	29.6	25.9	1.93	117	7.00	0.17
July	Up	15S 0437783 3598270	27.7	42.3	3.25	978	7.18	0.54
	WB	15S 0438522 3596676	29.7	39.1	2.96	957	7.63	0.56
	FTA-1	15S 0439399 3594957	26.1	38.7	3.11	941	7.71	0.51
	UT	15S 0439381 3594719	24.1	39.8	3.31	687	7.86	1.93
	SCB	15S 0439600 3594493	25.2	32.1	2.65	962	7.79	0.46
	SMB		24.2	35.9	2.99	1005	7.40	0.67
	Con	15S 0439580 3594417	25.1	31.2	2.54	962	7.38	0.59
	LFR	15S 0440352 3594485	29.1	29.9	2.29	625	7.56	0.68
	Con at FR	15S 0440367 3594442	26.1	30.8	2.47	1039	7.40	0.52
	FR	15S 0440306 3598122	30.7	38.0	2.80	637	7.76	0.76
FL	15S 0438520 3596675	31.0	25.5	1.89	155	7.42	0.95	

Table 5.8 Continued

Month	Site	Coordinates	Temperature (°C)	Dissolved Oxygen (%)	Oxygen (mg/L)	Conductivity (µS/cm)	pH	Ammonium (mg/L)
September	WB	15S 0438512 3596679	29.9	82.5	6.24	893	7.54	0.09
	FTA-1	15S 0439405 3594952	30.1	98.0	7.30	853	7.92	0.12
	UT	15S 0439370 3594714	26.4	64.5	5.12	483	7.47	0.05
	SCB	15S 0439556 3594445	28.0	87.1	6.77	834	7.60	0.04
	SMB	15S 0439532 3594405	26.4	80.2	6.27	918	7.20	0.09
	Con	15S 0439579 3594420	27.6	66.6	5.25	846	7.38	0.09
	FR	15S 0440299 3598124	29.1	73.2	5.61	802	7.40	0.09

Table 5.9 Percent organic matter in sediment grab samples from Barksdale Air Force Base

Location	Month	Percent Organic Matter
Weapons Bridge	November	0.3
	June	0.2
	September	0.4
Upper Tributary	November	0.6
	June	0.3
	September	0.3
South Cooper's Bayou	March	0.7
	June	0.6
	September	0.9
FTA-1	November	0.5
	June	0.5
	September	0.7
Flat River	November	0.8
	June	0.3
	September	0.6
Confluence	November	1.1
	June	0.6
	September	0.6
Upstream	November	1.3
	March	2
	June	3.2
South Mack's Bayou	November	1.2
	June	1.7
	September	0.5

Table 5.10 Spearman's rank correlation coefficients between perfluorinated compounds (PFCs) quantified in water (PFC<sub>w</sub>) and sediment (PFC<sub>s</sub>) grab samples, water column parameters, and percent organic matter from locations of concern at Barksdale Air Force Base

Parameters	PFBS <sub>w</sub>	PFOS <sub>w</sub>	PFHxS <sub>w</sub>	PFOA <sub>w</sub>	PFNA <sub>w</sub>	PFHpA <sub>w</sub>	PFOS <sub>s</sub>	PFHxS <sub>s</sub>	T (°C)	DO (ng/mL)	C (µS/cm)	pH	NH <sub>4</sub> <sup>+</sup> (mg/L)	OM (%)
PFBS <sub>w</sub>	1													
PFOS <sub>w</sub>	0.65**	1												
PFHxS <sub>w</sub>	0.82**	0.86**	1											
PFOA <sub>w</sub>	0.78**	0.73**	0.79**	1										
PFNA <sub>w</sub>	0.17	0.38	0.15	0.32	1									
PFHpA <sub>w</sub>	0.82**	0.67**	0.77**	0.91**	0.35	1								
PFOS <sub>s</sub>	0.46*	0.48**	0.33	0.45*	0.41	0.43*	1							
PFHxS <sub>s</sub>	0.64*	0.04	0.39	0.75*	-1.00**	0.72*	0.57*	1						
T (°C)	-0.53**	-0.07	-0.22	-0.44*	0.23	-0.36	-0.11	-0.83**	1					
DO (ng/mL)	0.69**	-0.05	0.27	0.40*	0.50	0.33	0.28	0.75**	-0.62**	1				
C (µS/cm)	-0.44*	-0.03	-0.02	-0.20	-0.56*	-0.16	-0.29	-0.50	0.61**	-0.61**	1			
pH	0.29	0.14	0.30	0.37	0.04	0.34	0.31	0.88**	-0.41*	0.62**	-0.49**	1		
NH <sub>4</sub> <sup>+</sup> (mg/L)	0.31	0.40*	0.45*	0.10	-0.28	0.02	-0.06	0.10	-0.45*	0.09	-0.12	0.33	1	
OM (%)	0.28	-0.22	0.08	-0.09	-0.71	0.14	-0.35	0.63	-0.05	0.23	0.01	-0.17	0.38	1

Significant levels below p < 0.05 are indicated by \*

Significant levels below p < 0.005 are indicated by \*\*

T = Temperature

DO = Dissolved Oxygen

C = Conductivity

NH<sub>4</sub><sup>+</sup> = Ammonium

OM = Organic Matter

Table 5.11 Number of samples compared in spearman's rank correlation analysis between perfluorinated compounds (PFCs) quantified in water (PFC<sub>w</sub>) and (PFC<sub>s</sub>) sediment grab samples, water column parameters, and percent organic matter from locations of concern at Barksdale Air Force

Parameters	PFBS <sub>w</sub>	PFOS <sub>w</sub>	PFHxS <sub>w</sub>	PFOA <sub>w</sub>	PFNA <sub>w</sub>	PFHpA <sub>w</sub>	PFOS <sub>s</sub>	PFHxS <sub>s</sub>	T (°C)	DO (ng/mL)	C (μS/cm)	pH	NH <sub>4</sub> <sup>+</sup> (mg/L)	OM (%)
PFBS <sub>w</sub>	58													
PFOS <sub>w</sub>	36	58												
PFHxS <sub>w</sub>	39	45	58											
PFOA <sub>w</sub>	34	36	37	58										
PFNA <sub>w</sub>	14	14	14	14	58									
PFHpA <sub>w</sub>	33	33	34	34	14	58								
PFOS <sub>s</sub>	28	33	35	27	11	24	58							
PFHxS <sub>s</sub>	13	15	15	12	2	11	15	58						
T (°C)	30	34	37	27	13	26	29	14	58					
DO (ng/mL)	30	34	37	27	13	26	29	14	45	58				
C (μS/cm)	30	34	37	27	13	26	29	14	45	45	58			
pH	25	29	32	22	13	26	23	9	36	40	40	58		
NH <sub>4</sub> <sup>+</sup> (mg/L)	28	30	30	26	13	26	23	13	36	36	36	31	58	
OM (%)	9	13	14	8	5	7	12	4	21	21	21	21	14	58

T = Temperature  
 DO = Dissolved Oxygen  
 C = Conductivity  
 NH<sub>4</sub><sup>+</sup> = Ammonium  
 OM = Organic Matter

Table 5.12 Perfluorinated compounds detected in water grab samples from locations of concern at Barksdale Air Force Base

Month	Location	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
August							
	ExUp	NQ	0.02	0.04	0.03	NQ	0.02
	Up	0.03	0.06	0.10	0.03	NQ	0.02
	WB	0.03	0.18	0.19	0.05	NQ	0.03
	FTA-1	0.03	0.15	0.19	0.06	NQ	0.04
	UT	0.12	0.05	0.30	NQ	NF	NQ
	SCB	0.03	0.18	0.16	0.05	NQ	0.03
	SMB	0.05	0.17	0.17	0.04	NQ	0.03
	Con	0.06	0.14	0.22	0.05	NQ	0.04
November							
	ExUp	0.21	NQ	0.18	NQ	NQ	NQ
	Up	NQ	NQ	NQ	NQ	NQ	NQ
	WB	NQ	NQ	0.17	NQ	NF	NQ
	FTA-1	NQ	NQ	NQ	NF	NF	NF
	SUT	NQ	0.41	0.39	0.06	NQ	NQ
	SMB	0.22	NQ	0.26	NQ	NQ	NQ
	Con	NQ	0.07	0.10	NQ	NF	NQ
March							
	WUp	NQ	NQ	0.68	NQ	NF	NQ
	Up	0.11	0.11	0.38	NQ	NQ	NQ
	WB	NQ	0.24	0.40	NQ	NQ	NQ
	FTA-1	NQ	0.25	0.24	NQ	NQ	NQ
	UT	0.28	2.48	2.79	0.37	NQ	0.27
	SUT	0.92	2.58	4.43	0.30	NQ	0.41
	SCB	NQ	0.21	0.22	NQ	NQ	NQ
	SMB	0.52	0.55	1.45	NQ	NQ	NQ
	Con	0.37	1.64	2.00	0.20	NQ	0.22
Early May							
	WB	NQ	0.12	0.11	NQ	NQ	NQ
	Con	NQ	0.26	0.17	0.04	NQ	NQ



Table 5.12 Continued

Month	Location	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
Late May							
	Up	0.07	0.91	0.49	0.04	NQ	NQ
	WB	0.04	0.86	0.48	0.02	NQ	0.01
	FTA-1	0.14	1.39	0.77	0.05	NQ	0.03
	SCB	0.06	2.08	0.48	0.04	NQ	0.01
	SMB	0.25	3.39	1.31	0.08	NQ	0.07
	Con	0.19	2.71	1.36	0.15	NQ	0.09
June							
	Up	0.02	0.13	0.09	0.02	0.01	0.03
	WB	0.02	0.09	0.08	0.02	NQ	0.02
	FTA-1	0.03	0.27	0.12	0.03	0.01	0.03
	UT	0.09	1.91	0.68	0.15	0.03	0.10
	UT at SMB	0.07	2.76	0.67	0.14	0.04	0.10
	SCB	0.02	0.09	0.08	0.03	NQ	0.02
	SMB	0.13	0.30	0.33	0.04	0.01	0.05
	Con	0.04	0.24	0.19	0.04	0.01	0.04
	LFR	NQ	NQ	NQ	NQ	NQ	NQ
	Con at FR	0.04	0.38	0.18	0.05	NQ	0.04
	LCon	0.05	0.45	0.24	0.06	0.01	0.04
July							
	Up	0.25	3.58	1.71	0.36	0.03	0.25
	WB	0.16	1.11	1.21	0.18	0	0.13
	FTA-1	0.10	1.24	1.03	0.13	0.00	0.10
	UT	0.11	7.07	1.72	0.34	0.03	0.23
	SCB	0.01	0.16	0.24	0.03	0	0.02
	SMB	0.11	0.41	0.53	0.02	NQ	0.03
	Con	0.01	0.42	0.22	0.03	0	0.01
	LFR	0	NQ	0	0	NF	0
	Con at FR	0.16	2.99	0.77	0.20	0	0.12

Table 5.12 Continued

Month	Location	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
September	WB	NF	NF	NF	NF	NF	NF
	FTA-1	NF	NQ	NQ	NQ	NF	NQ
	UT	NF	NQ	NQ	NF	NF	NF
	SCB	NQ	0.06	0.06	NQ	NF	NQ
	SMB	NQ	0.12	NQ	NQ	NQ	NQ
	Con	NF	NF	NQ	NF	NF	NF

NF = Not Found

NQ = Not Quantified

Table 5.13 Perfluorinated compounds detected in water grab samples from reference locations at Barksdale Air Force Base

Month	Reference Location	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
August	FR	NQ	NQ	NQ	NQ	NQ	NQ
	FL	NF	NQ	NF	NQ	NQ	0.07
November	FR	0.18	NQ	0.16	NQ	NQ	NQ
	FL	NQ	NQ	NQ	NF	NF	NF
March	FR	NQ	NQ	0.36	NQ	NQ	NQ
Early May	FR	NQ	NQ	NQ	NQ	NQ	NQ
Late May	FL	NQ	NQ	NQ	NQ	NQ	NQ
	FR	NQ	NQ	NQ	NQ	NQ	NQ
June	FR	NQ	NQ	NQ	NQ	NQ	NQ
	FL	NQ	NQ	NQ	NQ	NQ	NQ
July	FR	0	NQ	0	0.00	NQ	NQ
	FL	NQ	0.01	NQ	0	NQ	0
September	FR	NF	NF	NQ	NQ	NF	NF

NF = Not Found

NQ = Not Quantified

Table 5.14 Perfluorinated compounds detected in field reagent blanks and lab blanks

Month	Sample	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
August	FRB	NF	NF	NF	NF	NF	NF
	LB	NF	NF	NF	NF	NF	NF
November	FRB	0.21	NQ	0.18	NQ	NQ	NQ
	LB	NQ	NQ	NQ	NQ	NQ	NQ
March	FRB	NF	NQ	NF	NQ	NQ	NF
	LB	NF	NF	1.63	NF	NF	NF
Early May	FRB	NF	NF	NF	NQ	NQ	NF
	LB	NF	NF	NF	NF	NQ	NF
Late May	FRB	NQ	NQ	NQ	NQ	NQ	NQ
	LB	NF	NQ	NF	NQ	NQ	NF
June	FRB	NF	NF	NF	NF	NQ	NF
	LB	NF	NF	NF	NF	NF	NF
July	FRB	NF	NF	NF	NF	NF	NF
	LB	NF	NF	NF	NF	NF	NF
September	FRB	NF	0.12	NQ	NF	NF	NF
	LB	NF	NF	NF	NF	NF	NF

NF = Not Found

NQ = Not Quantified

Table 5.15 Number of water grab samples quantified for each perfluorinated compound and the average concentration of perfluorinated compounds from each location of concern at Barksdale Air Force Base

Sample Type	Location	N =	Number of Grab Samples Quantified										Concentration of Quantified Analytes (ng/mL)	
			PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA	Average ± SD	Range				
Water Grab Sample	ExUp	2	1	1	2	1	0	1	0	1	0	1	0.08 ± 0.09	0.02 - 0.21
	WUp	1	0	1	0	0	0	0	0	0	0	0	0.68	
	Up	6	5	5	5	4	4	2	2	3	3	3	0.37 ± 0.78	0.01 - 3.58
	WB	8	4	6	7	4	4	1	1	4	4	4	0.23 ± 0.33	0 - 1.21
	FTA-1	7	4	5	5	4	4	2	2	4	4	4	0.27 ± 0.40	0.00 - 1.39
	UT	5	4	4	4	3	2	2	2	3	3	3	0.90 ± 1.99	0.03 - 7.07
	SUT	2	1	2	2	2	2	0	0	1	1	1	1.73 ± 1.77	0.30 - 4.43
	UT at SMB	1	1	1	1	1	1	1	1	1	1	1	0.63 ± 1.07	0.04 - 2.76
	SCB	6	4	6	6	4	4	1	1	4	4	4	0.17 ± 0.41	0 - 2.08
	SMB	7	6	6	6	4	4	1	1	4	4	4	0.39 ± 0.70	0.01 - 3.39
	Con	8	5	7	7	6	6	2	2	5	5	5	0.35 ± 0.64	0 - 2.71
	LFR	2	1	0	1	1	1	0	0	1	1	1	0 ± 0.00	0 - 0
	Con at FR	2	2	2	2	2	2	1	1	2	2	2	0.45 ± 0.87	0 - 2.99
	LCon	1	1	1	1	1	1	1	1	1	1	1	0.14 ± 0.17	0.01 - 0.45

N = Total Number of Grab Samples

Table 5.16 Perfluorinated compounds detected in sediment passive samplers deployed at Barksdale Air Force Base

Month	Location	Concentration (ng/mL)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
Early May	WB	NF	NQ	NQ	NQ	NQ	NF
	Con	NQ	0.36	0.30	NQ	NQ	NQ
Late May	Up	NQ	0	0.01	NQ	NQ	NQ
	June	WB	NQ	0.15	NQ	NQ	NF
June	Con	ND	ND	ND	ND	ND	ND
	FR	NQ	NQ	NQ	NQ	NQ	NF
	July	WB	NQ	NQ	0.25	NQ	NQ
July	FTA-1	NQ	NQ	0.24	NQ	NQ	NQ
	UT	NQ	1.66	0.82	0.32	NQ	NQ
	Con	NQ	NQ	NQ	NQ	NQ	NQ
	FR	NQ	NQ	NQ	NF	NF	NQ
	September	WB	NF	NF	NF	NQ	NF
September	FTA-1	ND	ND	ND	ND	ND	ND
	UT	NQ	3.32	0	0	NQ	0
	Con	NQ	NF	NQ	NF	NF	NQ
	FR	NF	NF	NQ	NQ	NF	NF

ND = No Data

NF = Not Found

NQ = Not Quantified

Table 5.17 Number of perfluorinated compounds with a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in passive samplers deployed at Barksdale Air Force Base

Sample Type	Polar Head Moiety	Number of Analytes		
		Not Found	Not Quantified	Quantified
Sediment Passive Sampler				
	Sulfonic Acid	7	24	11
	Carboxylic Acid	10	29	3
Water Passive Sampler				
	Sulfonic Acid	19	13	1
	Carboxylic Acid	26	7	0

Table 5.18 Number of passive samplers with analytes that were not found, not quantified, or quantified and average concentrations of quantified analytes from locations of concern at Barksdale Air Force Base

Sample Type	Analyte	Number of Passive Samplers		Concentration of Quantified Analytes		
		Not Found	Not Quantified	Quantified	Average ± SD	Range
Sediment Passive Sampler (ng/mL)	PFBS	3	11	0		
	PFOS	3	6	5	1.10 ± 1.41	0 - 3.32
	PFHxS	1	7	6	0.27 ± 0.30	0 - 0.82
	PFOA	2	10	2	0.16	0 - 0.32
	PFNA	5	9	0		
	PFHpA	3	10	1	0	
Water Passive Sampler (ng/g)	PFBS	11	0	0		
	PFOS	4	6	1	0	
	PFHxS	4	7	0		
	PFOA	7	4	0		
	PFNA	8	3	0		
	PFHpA	11	0	0		

SD = Standard Deviation



Table 5.19 Perfluorinated compounds detected in water passive samplers deployed at Barksdale Air Force Base

Month	Location	Concentration (ng/g)					
		PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA
Late May							
	WB	ND	ND	ND	ND	ND	ND
	FR	NF	0	NQ	NQ	NF	NF
July							
	WB	NF	NQ	NQ	NQ	NF	NF
	FTA-1	NF	NQ	NQ	NF	NQ	NF
	UT	NF	NQ	NQ	NQ	NQ	NF
	SCB	NF	NQ	NQ	NF	NF	NF
	Con	NF	NQ	NQ	NF	NF	NF
	FR	NF	NQ	NQ	NF	NQ	NF
September							
	WB	NF	NF	NF	NQ	NF	NF
	FTA-1	NF	NF	NF	NF	NF	NF
	UT	ND	ND	ND	ND	ND	ND
	Con	NF	NF	NF	NF	NF	NF
	FR	NF	NF	NF	NF	NF	NF

ND = No Data

NF = Not Found

NQ = Not Quantified

Table 5.20 Perfluorinated compounds detected in fish, water passive samplers (WPS), and sediment passive samplers (SPS) from Barksdale Air Force Base

Month	Location	Sample Type	Concentration						
			PFBS	PFOS	PFHxS	PFOA	PFNA	PFHpA	
June	WB	Fish (ng/g)	8 (NF)	1885 ± 928	8 (NQ)	8 (NF)	8 (NF)	8 (NF)	
		WPS (ng/g)	ND	ND	ND	ND	ND	ND	
		SPS (ng/mL)	NQ	0.15	NQ	NQ	NF	NQ	
	FR	Fish (ng/g)	7 (NF) + 1 (NQ)	175 ± 31	8 (NQ)	3 (NF) + 5 (NQ)	2 (NF) + 6 (NQ)	7 (NF) + 1 (NQ)	
		WPS (ng/g)	ND	ND	ND	ND	ND	ND	
		SPS (ng/mL)	NQ	NQ	NQ	NQ	NQ	NF	
September	WB	Fish (ng/g)	8 (NF)	876 ± 311	8 (NQ)	8 (NF)	5 (NF) + 3 (NQ)	8 (NF)	
		WPS (ng/g)	NF	NF	NF	NQ	NF	NF	
		SPS (ng/mL)	NF	NF	NF	NQ	NF	NQ	

NF = Not Found  
 NQ = Not Quantified  
 ND = No Data

Table 5.21 Average PFOS area counts detected in passive samplers collected in early May through September and average PFOS concentrations detected in fish collected in June and July

Location	Sediment Passive Sampler			Water Passive Sampler			Fish (ng/g)		
	Average Area	SD	n =	Average Area	SD	n =	Average Concentration	SD	n =
Con	331325	455317	2	10305		1	1664	785	3
WB	44734	718526	3	11971		1	1885	869	17
FR	7539		1	57517	66402	2	180	31	7
FTA-1	49890		1	9225		1	1135	887	5
SCB				21221		1	1127	450	9

SD = Standard deviation

n = Number of samples used to calculate average

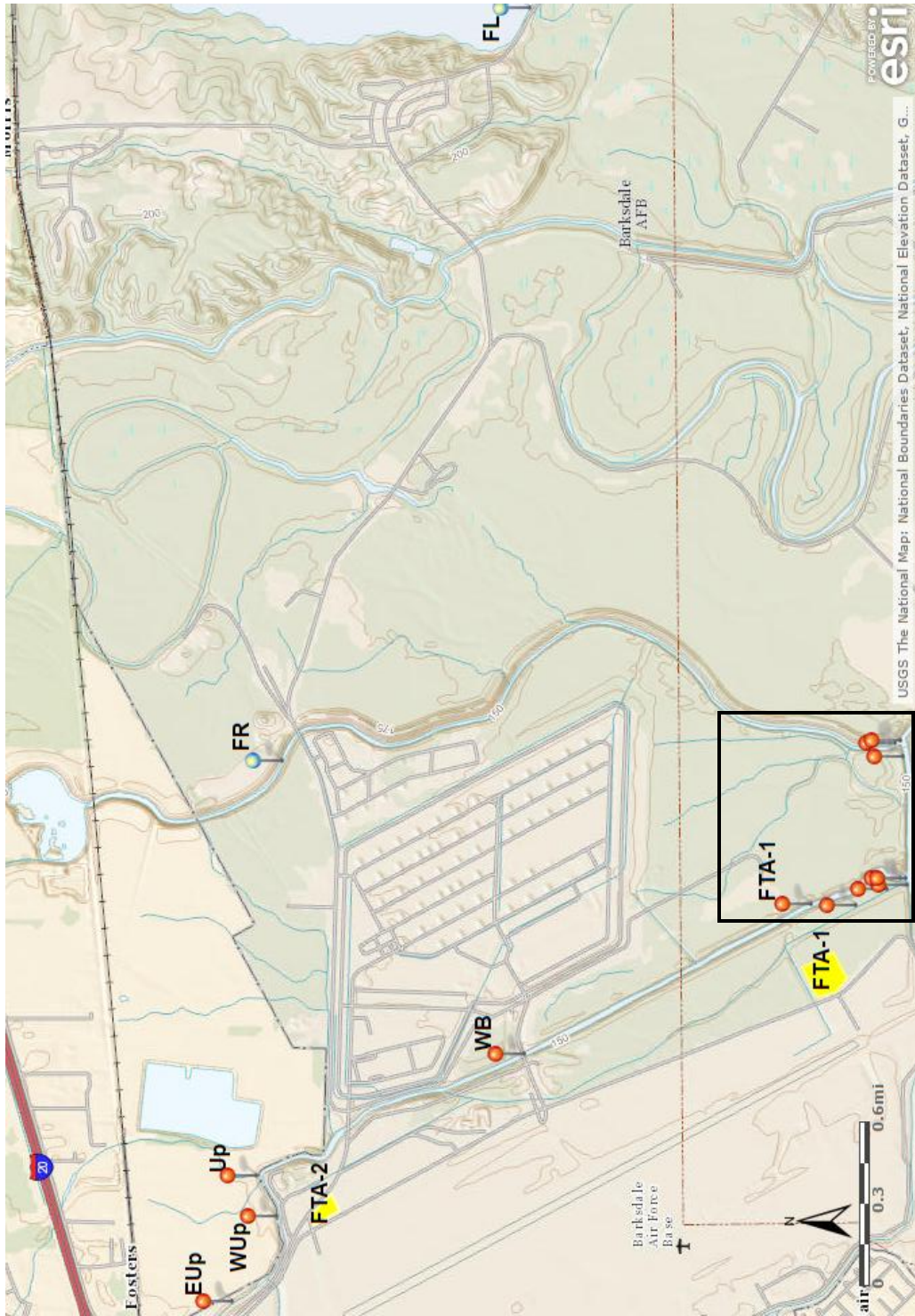


Figure 5.1 Sampling locations at Barksdale Air Force Base. Locations within the black box are shown in Figure 5.2.

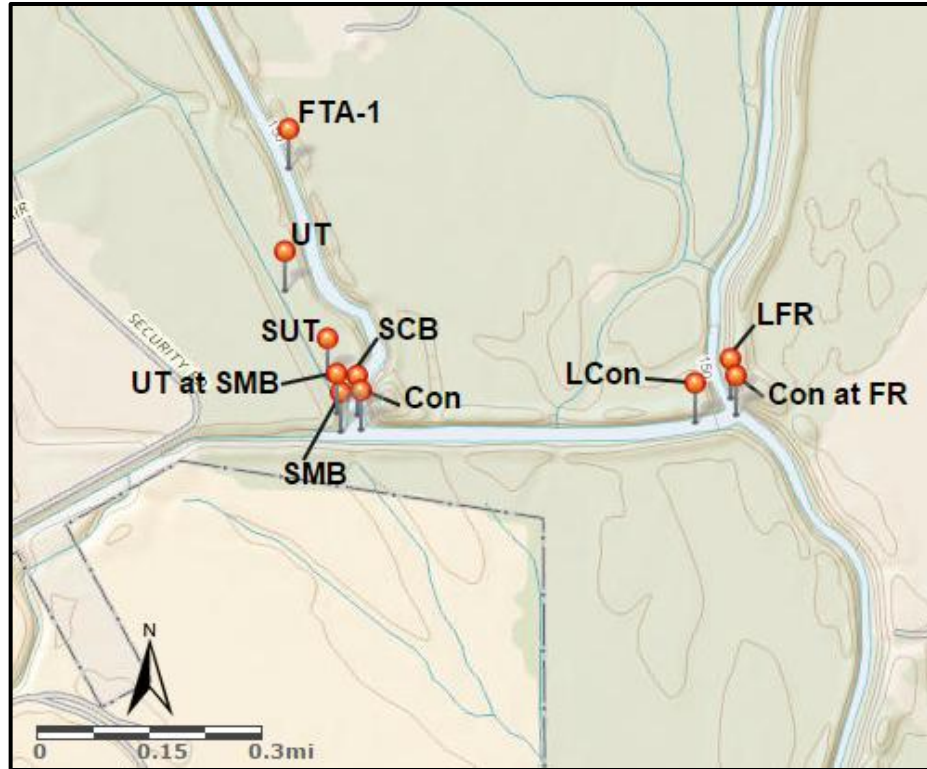


Figure 5.2 Sampling locations at Barksdale Air Force Base.

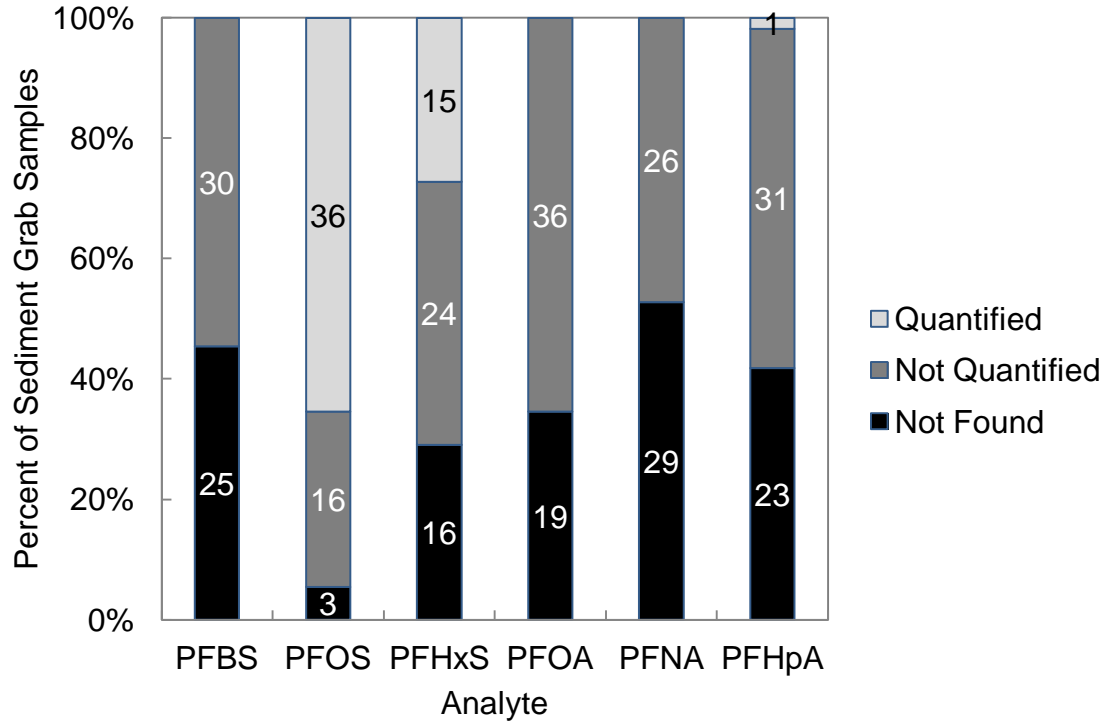


Figure 5.3 Percent of sediment grab samples from locations of concern at Barksdale Air Force Base for which a perfluorinated compound was quantified, not quantified, or not found.

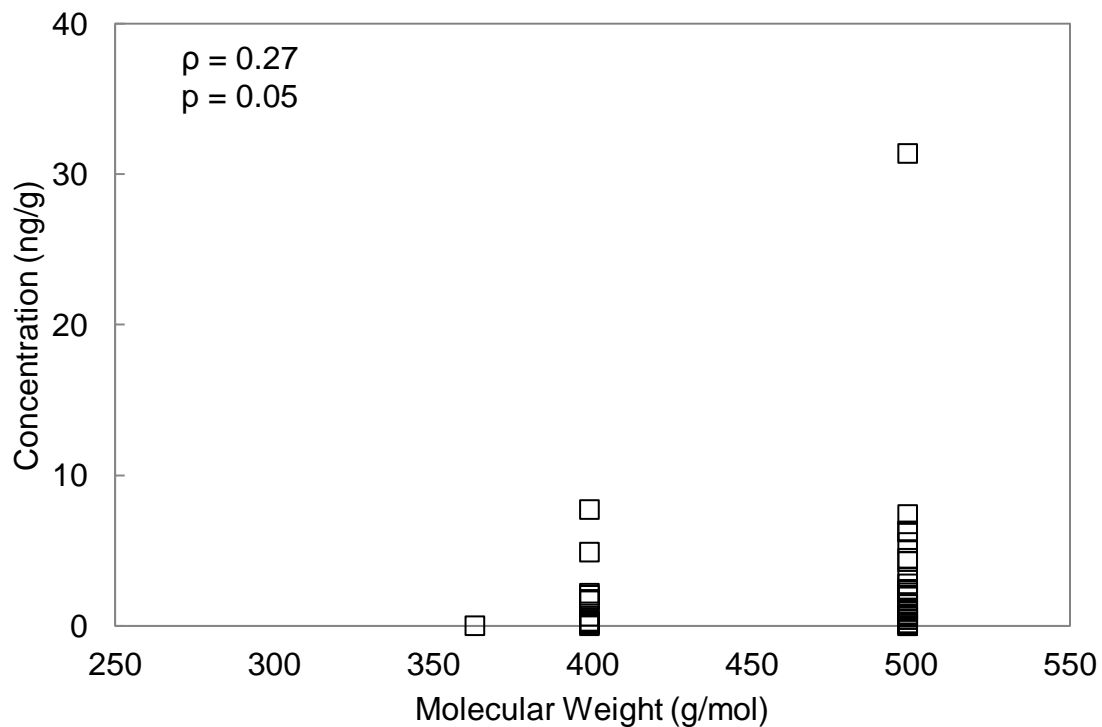


Figure 5.4 Correlation between molecular weight (g/mol) and concentrations (ng/g) perfluorinated compounds quantified in sediment grab samples from locations of concern at Barksdale Air Force Base.

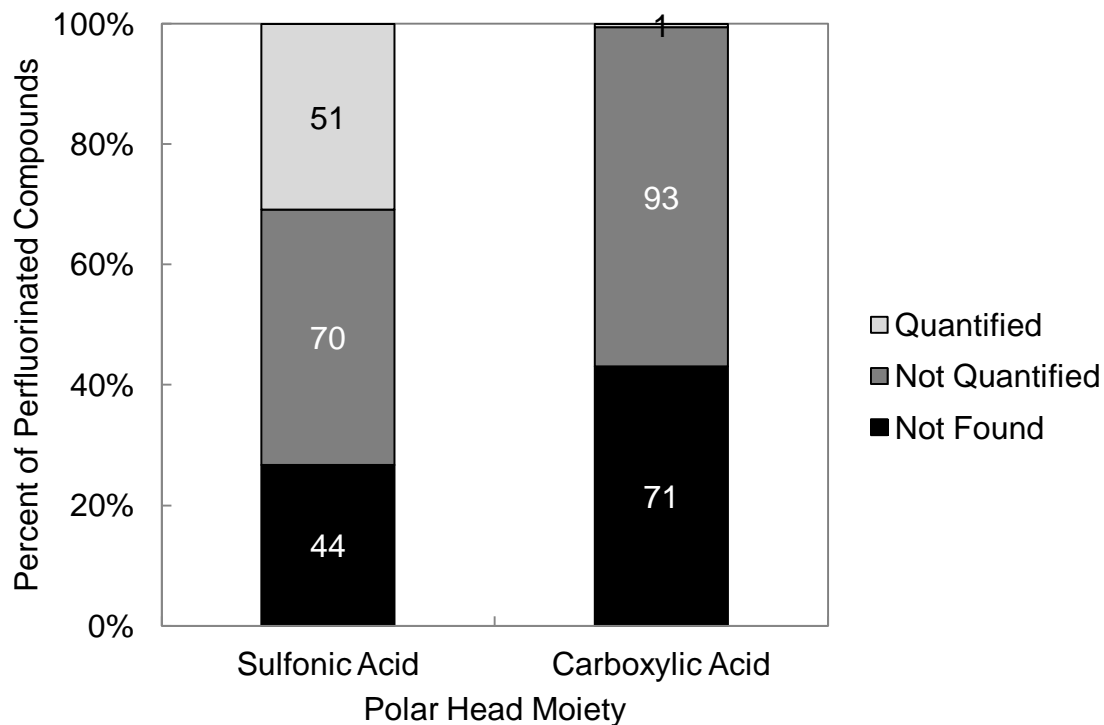


Figure 5.5 Percent of perfluorinated compounds containing a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in sediment grab samples from locations of concern at Barksdale Air Force Base.



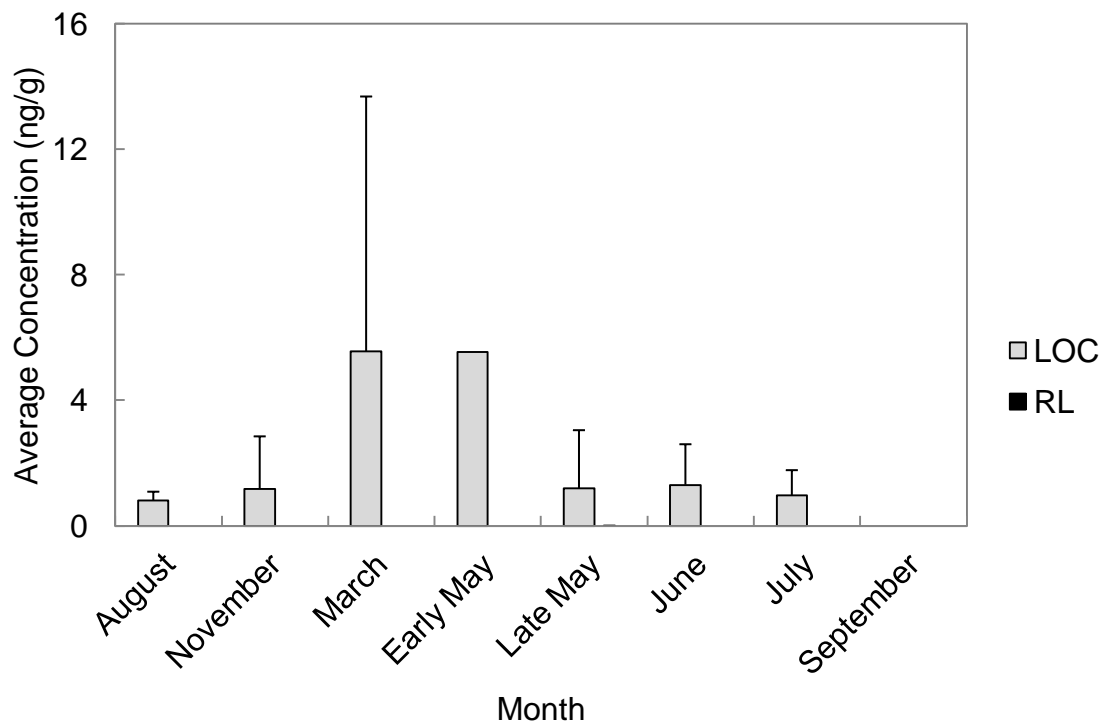


Figure 5.6 Average concentrations (ng/g) of perfluorinated compounds per month in sediment grab samples from locations of concern (LOC) compared to reference locations (RL) at Barksdale Air Force Base.

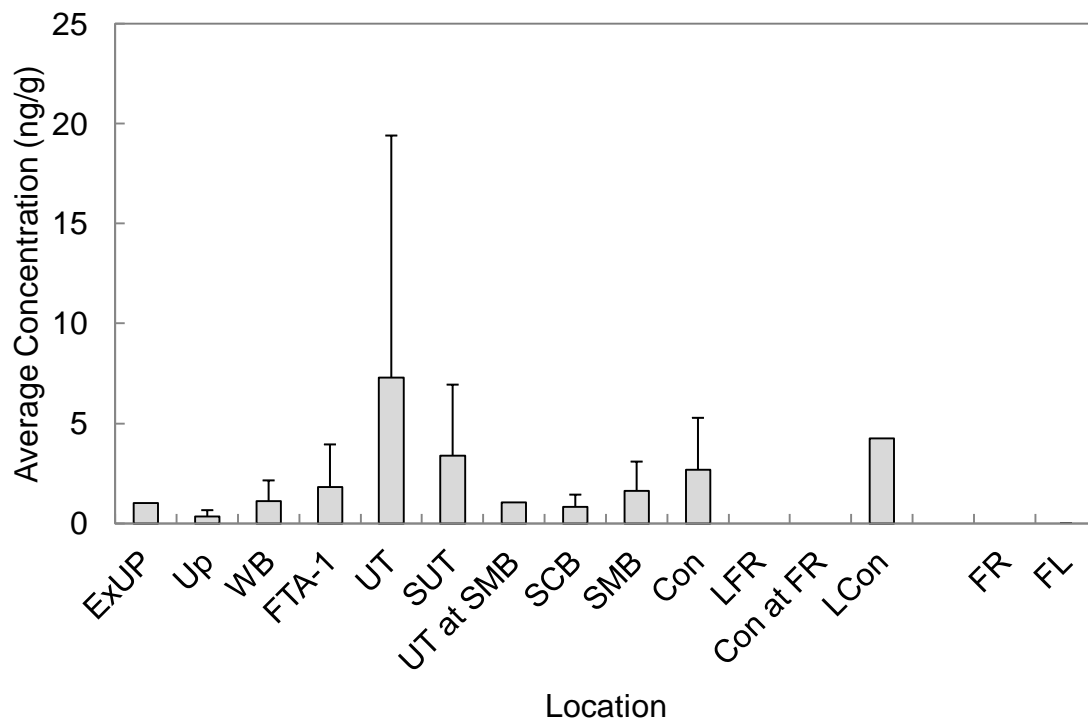


Figure 5.7 Average concentrations (ng/g) of perfluorinated compounds quantified in sediment grab samples from each location of concern and reference location at Barksdale Air Force Base.

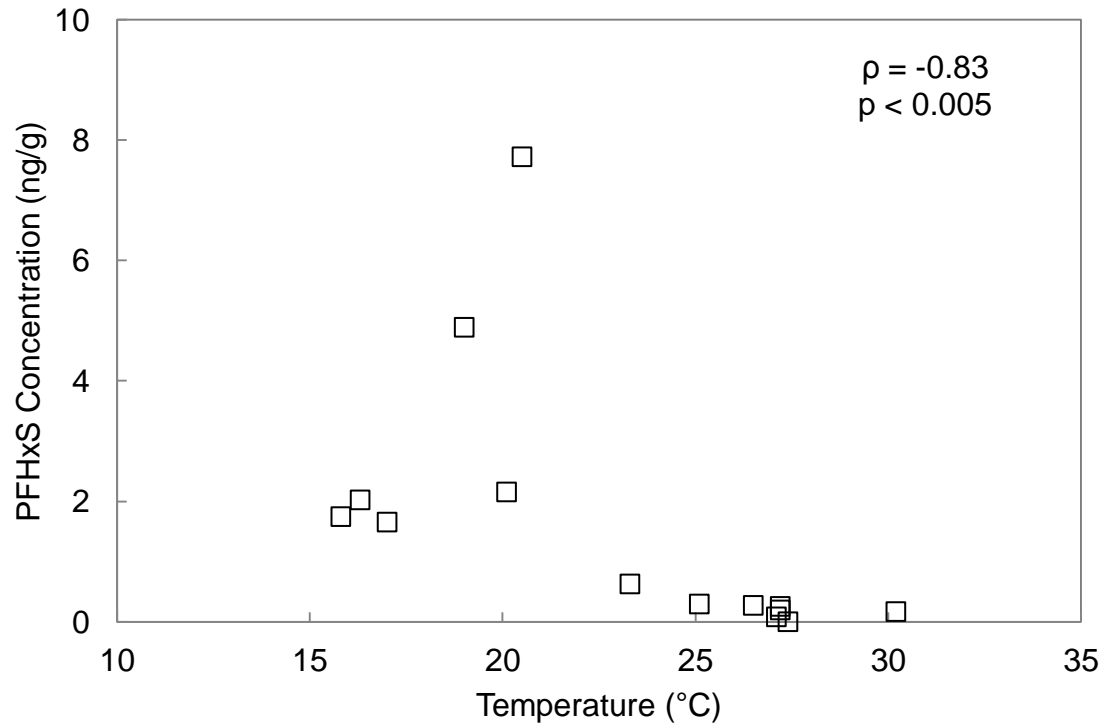


Figure 5.8 Correlation between temperature (°C) and concentration (ng/g) of perfluorohexanesulfonic acid (PFHxS) quantified in sediment grab samples from locations of concern at Barksdale Air Force Base.

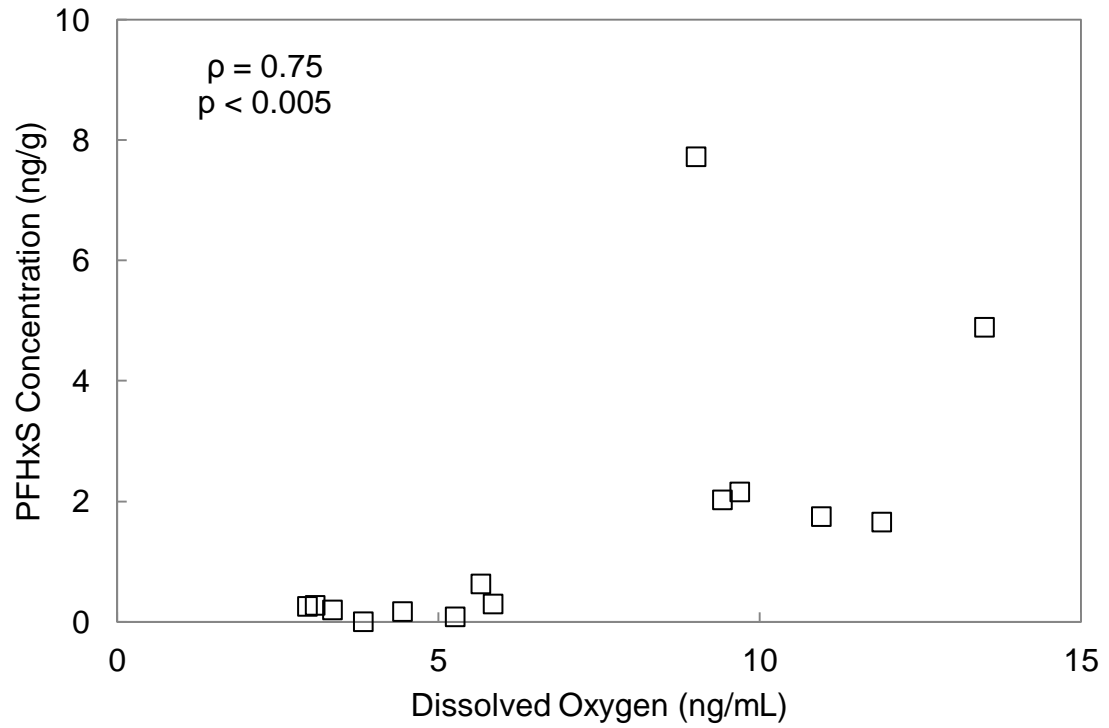


Figure 5.9 Correlation between dissolved oxygen (ng/mL) and concentration (ng/g) of perfluorohexanesulfonic acid (PFHxS) quantified in sediment grab samples from locations of concern at Barksdale Air Force Base.

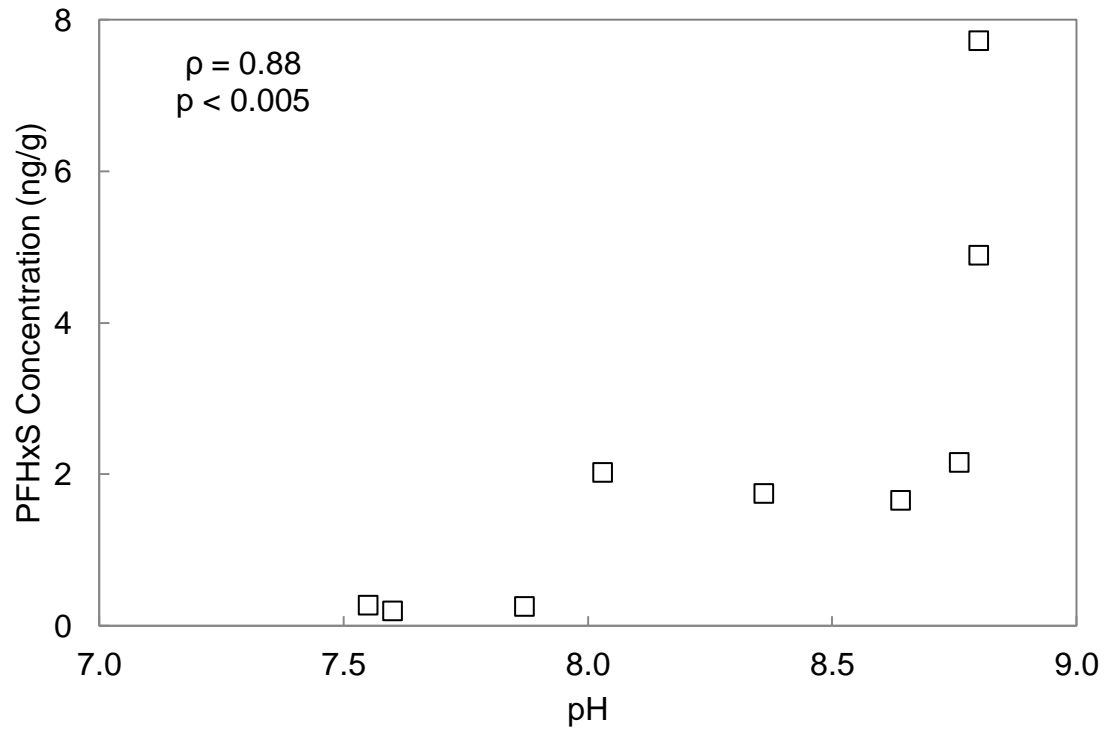


Figure 5.10 Correlation between pH and concentration (ng/g) of perfluorohexanesulfonic acid (PFHxS) quantified in sediment grab samples from locations of concern at Barksdale Air Force Base.

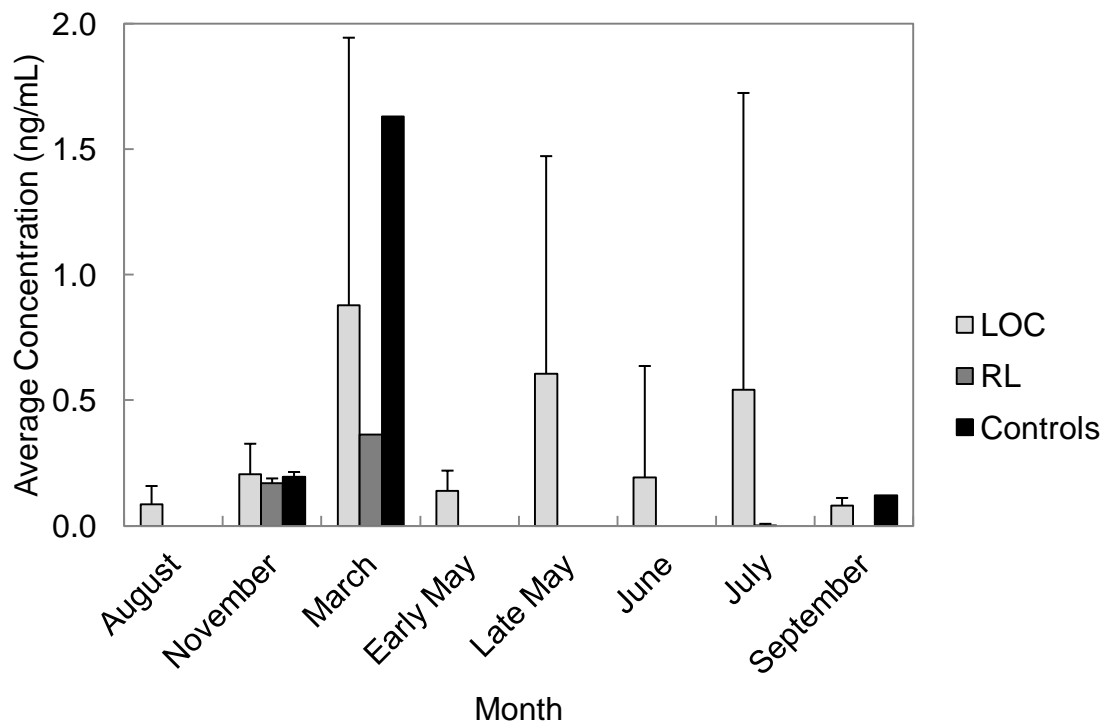


Figure 5.11 Average concentrations (ng/mL) of perfluorinated compounds per month in water grab samples from locations of concern (LOC) compared to reference locations (RL) and controls (field reagent blanks and lab blanks) at Barksdale Air Force Base.

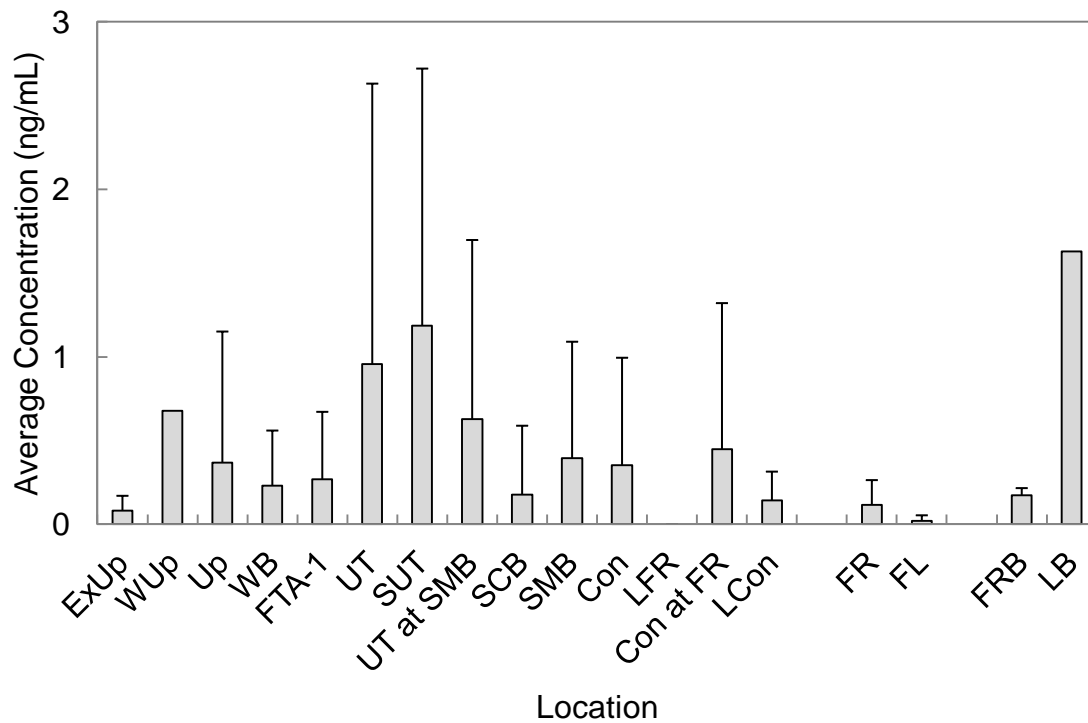


Figure 5.12 Average concentrations (ng/mL) of perfluorinated compounds quantified in water grab samples from each location of concern, reference locations, and controls at Barksdale Air Force Base.

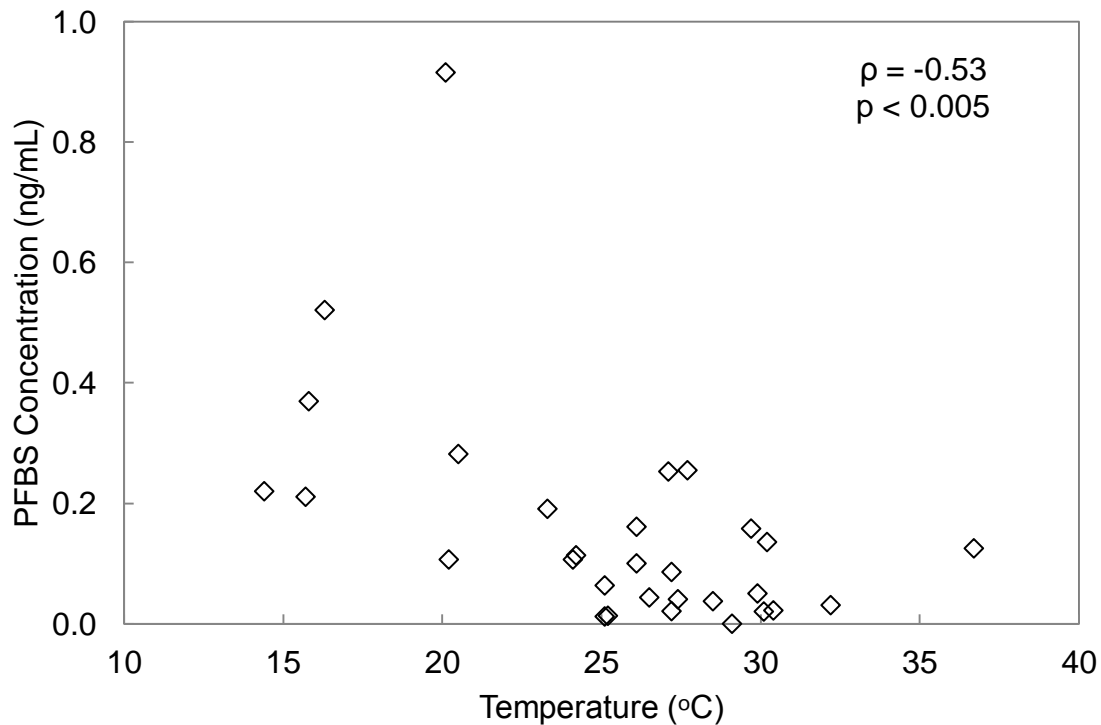


Figure 5.13 Correlation between temperature (°C) and concentration (ng/g) of perfluorobutanesulfonic acid (PFBS) quantified in water grab samples from locations of concern at Barksdale Air Force Base.



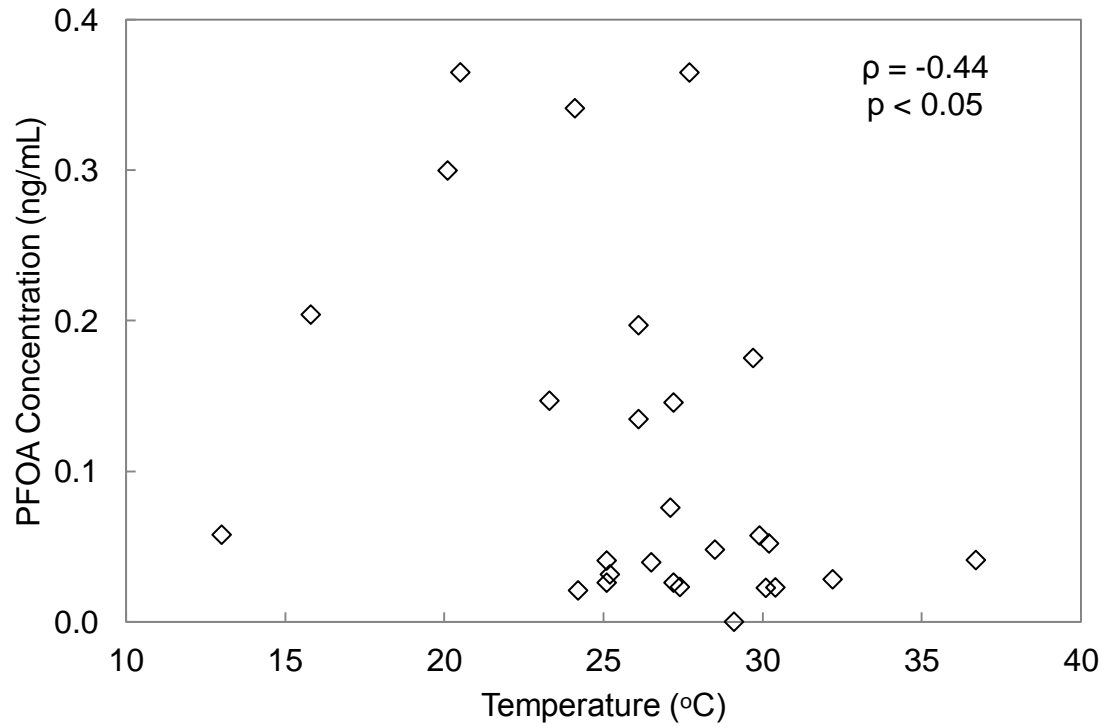


Figure 5.14 Correlation between temperature (°C) and concentration (ng/g) of perfluorooctanoic acid (PFOA) quantified in water grab samples from locations of concern at Barksdale Air Force Base.

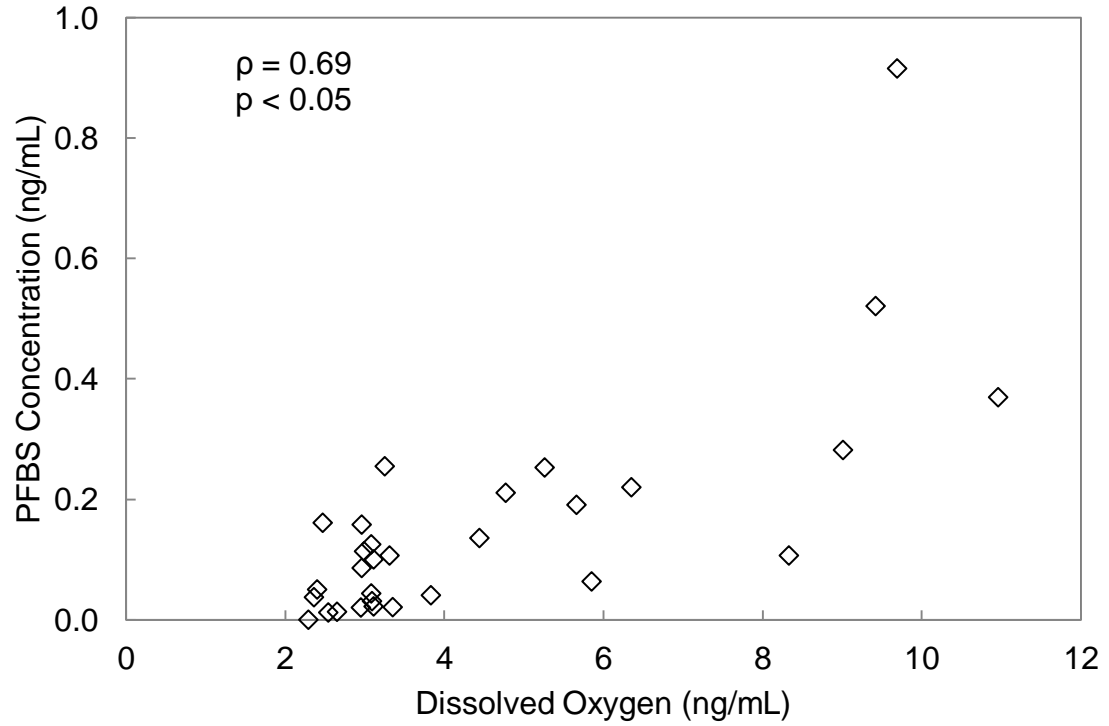


Figure 5.15 Correlation between dissolved oxygen (ng/mL) and concentration (ng/g) of perfluorobutanesulfonic acid (PFBS) quantified in water grab samples from locations of concern at Barksdale Air Force Base.

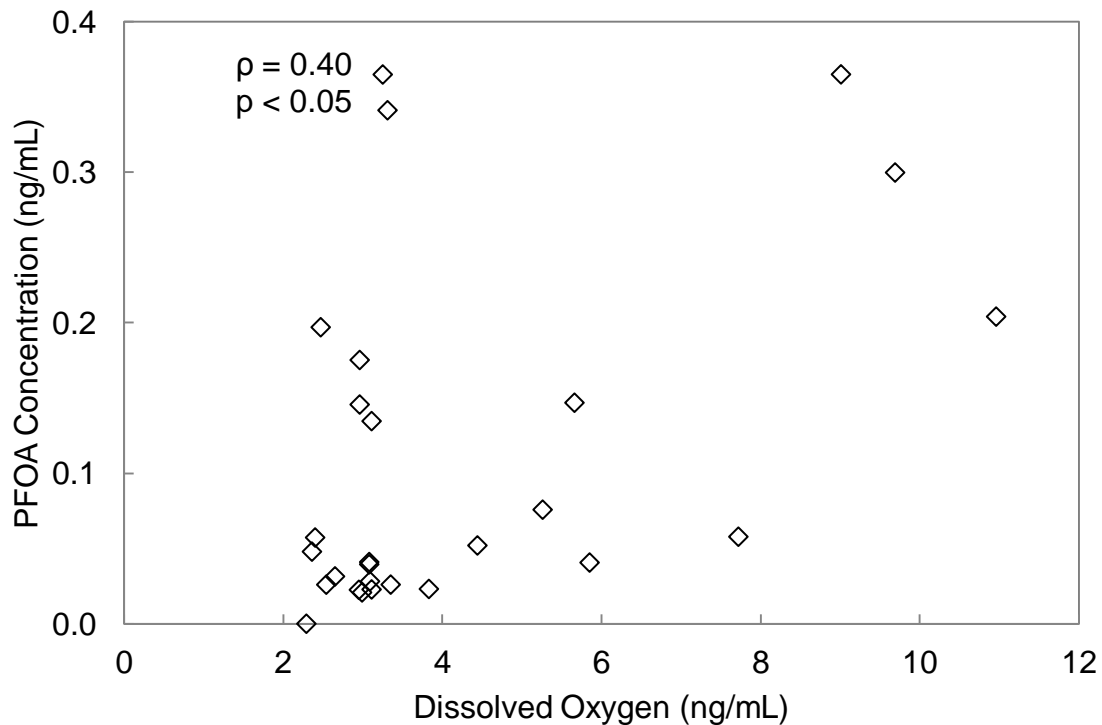


Figure 5.16 Correlation between dissolved oxygen (ng/mL) and concentration (ng/g) of perfluorooctanoic acid (PFOA) quantified in water grab samples from locations of concern at Barksdale Air Force Base.

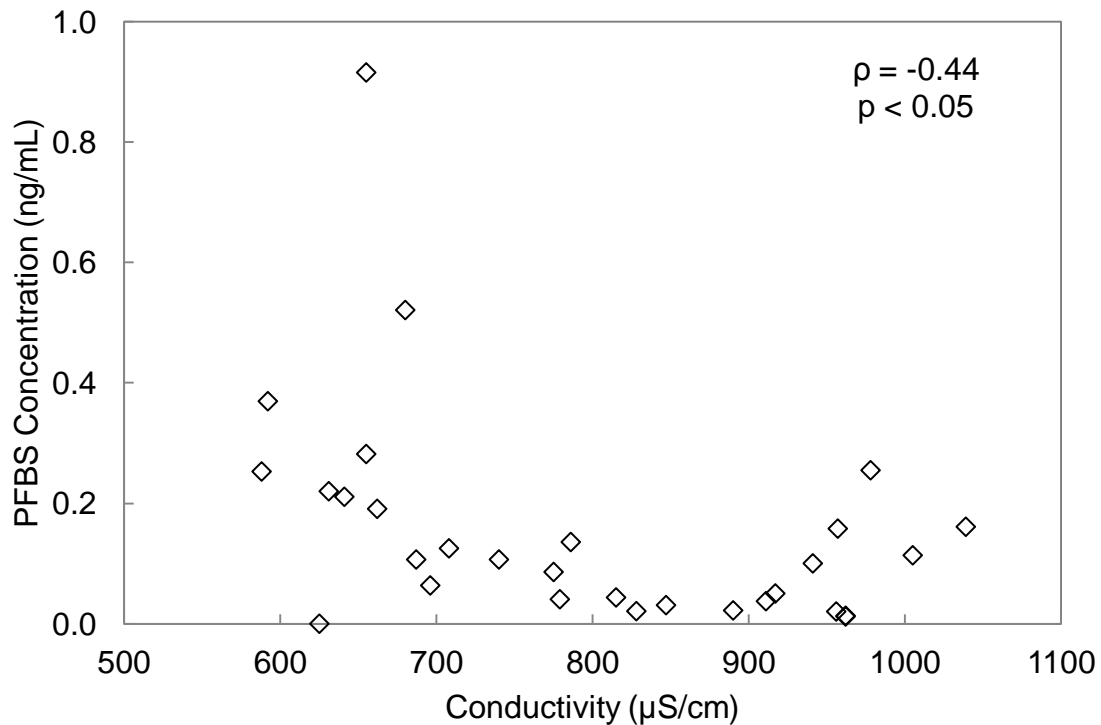


Figure 5.17 Correlation between conductivity ( $\mu\text{S}/\text{cm}$ ) and concentration (ng/g) of perfluorobutanesulfonic acid (PFBS) quantified in water grab samples from locations of concern at Barksdale Air Force Base.

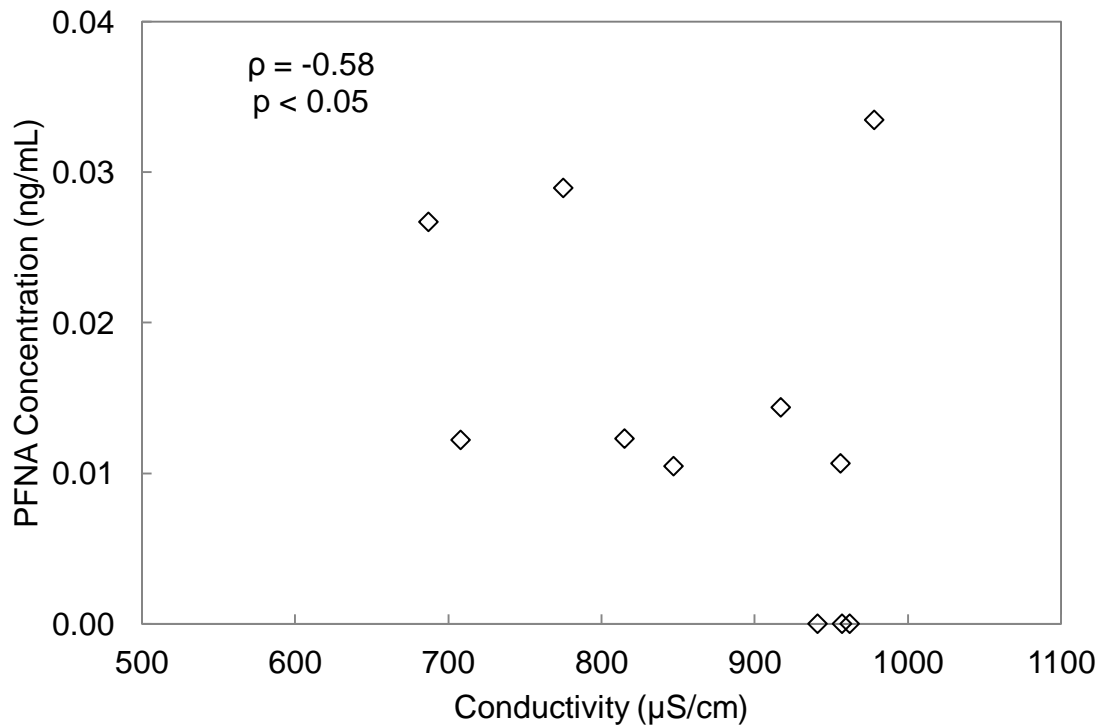


Figure 5.18 Correlation between conductivity (µS/cm) and concentration (ng/g) of perfluorononanoic acid (PFNA) quantified in water grab samples from locations of concern at Barksdale Air Force Base.

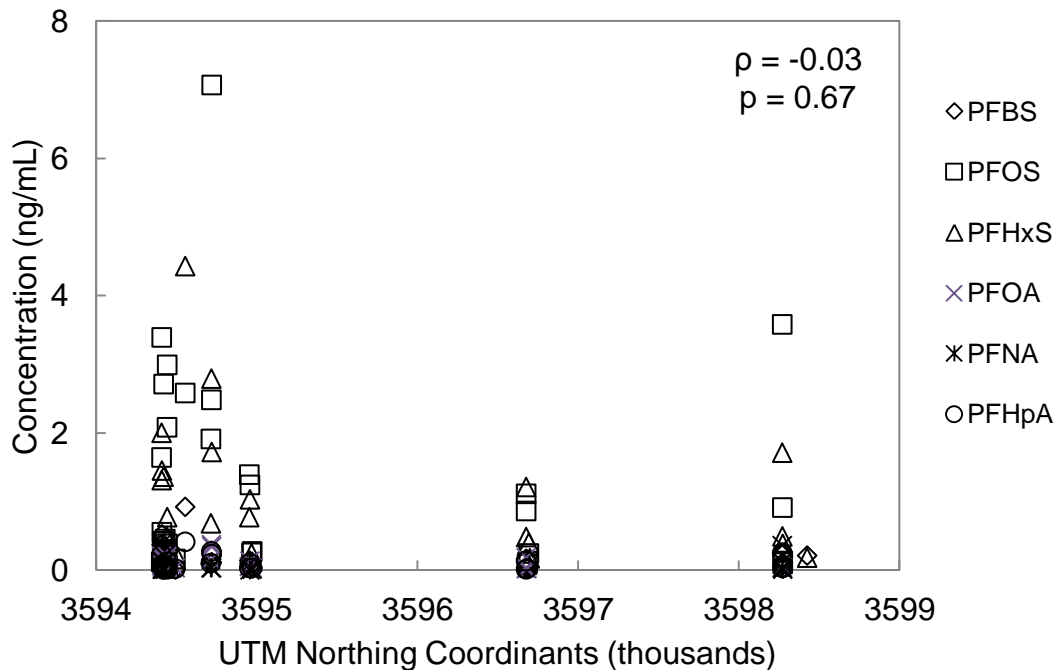


Figure 5.19 Correlation between Universal Transverse Mercator (UTM) northing coordinates and concentration (ng/mL) of quantifiable perfluorinated compounds in water grabs samples from locations of concern at Barksdale Air Force Base. Coordinates increase northward as the x-axis moves to the right.

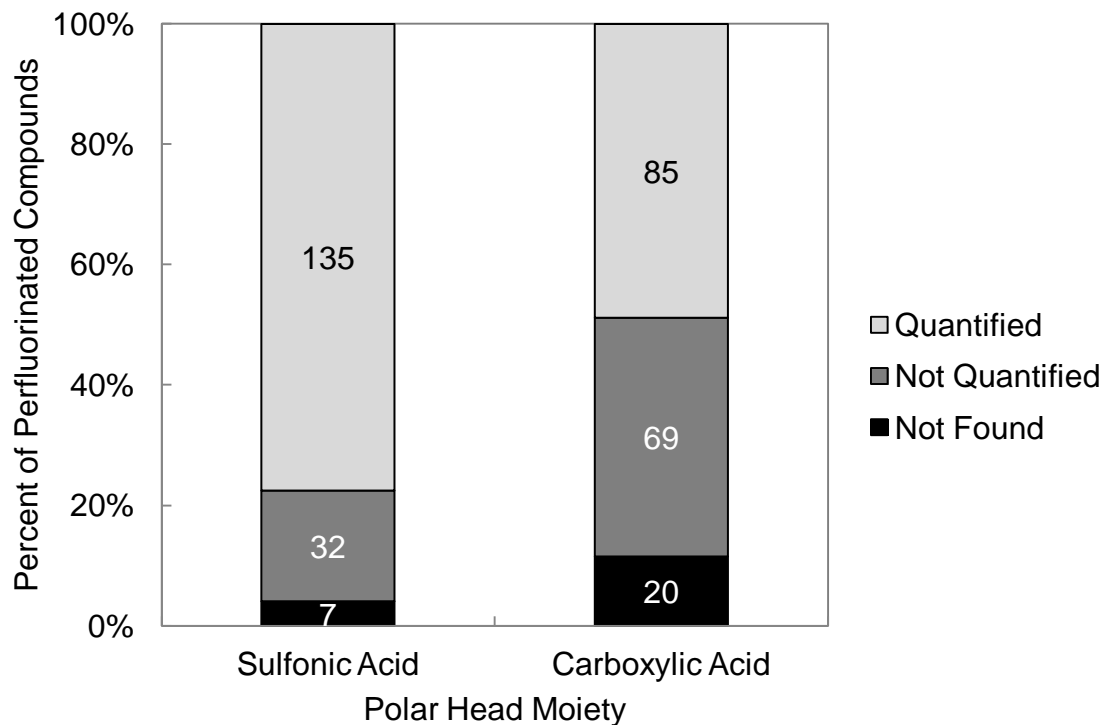


Figure 5.20 Percent of perfluorinated compounds containing a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in water grab samples from locations of concern at Barksdale Air Force Base.

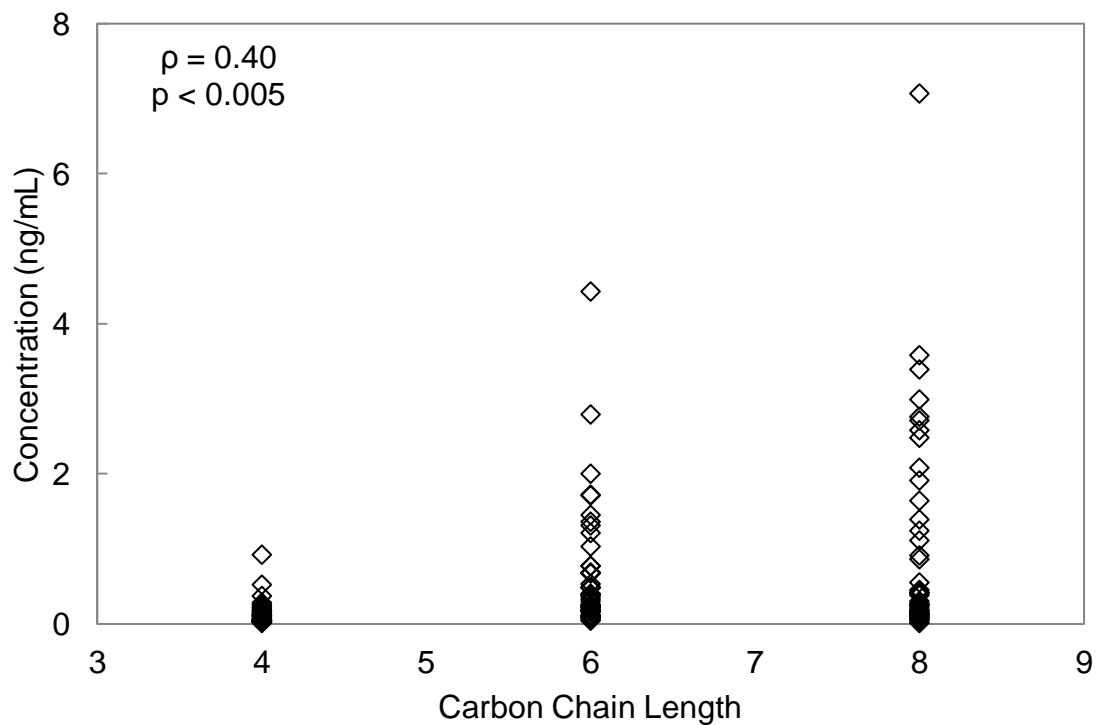


Figure 5.21 Correlation between carbon chain length and concentration (ng/mL) of quantifiable perfluorinated compounds that contain a sulfonic acid polar head moiety in water grab samples from locations of concern at Barksdale Air Force Base.



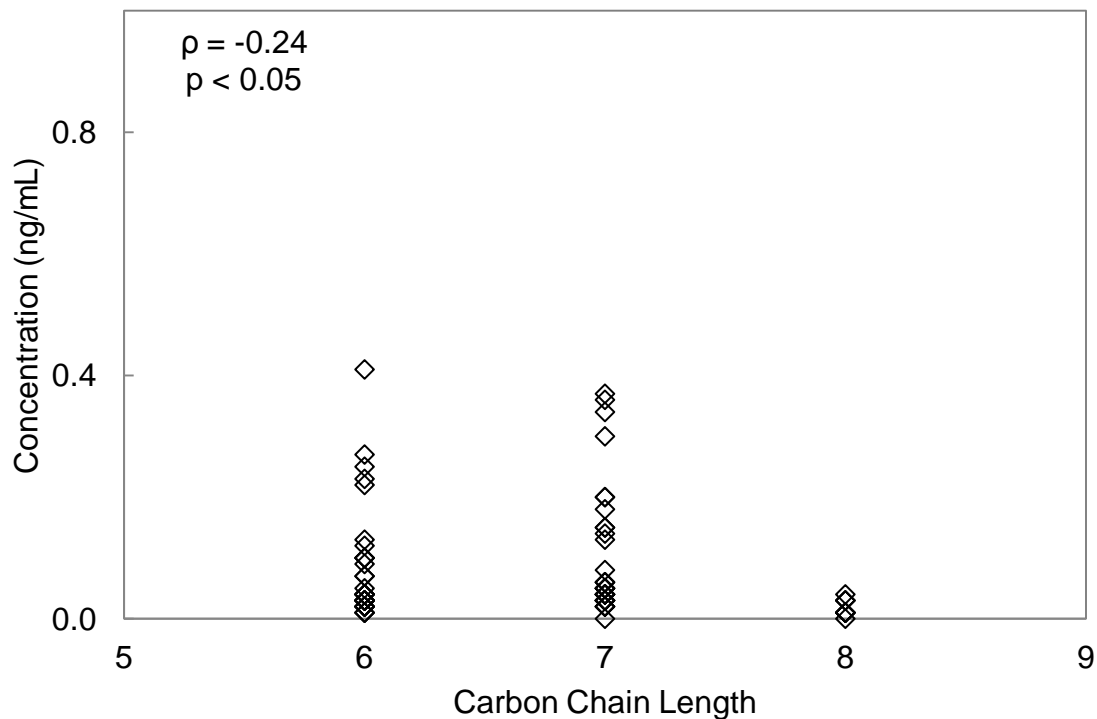


Figure 5.22 Correlation between carbon chain length and concentration (ng/mL) of quantifiable perfluorinated compounds that contain a carboxylic acid polar head moiety in water grab samples from locations of concern at Barksdale Air Force Base.

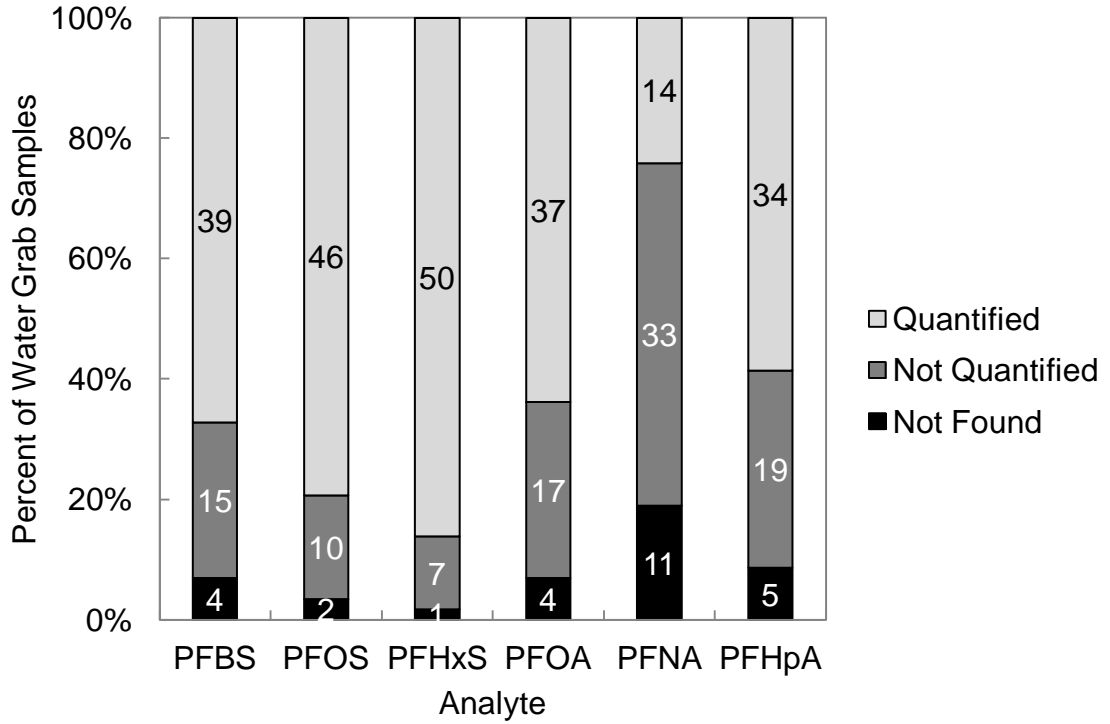


Figure 5.23 Percent of water grab samples from locations of concern at Barksdale Air Force Base for which a perfluorinated compound was quantified, not quantified, or not found.

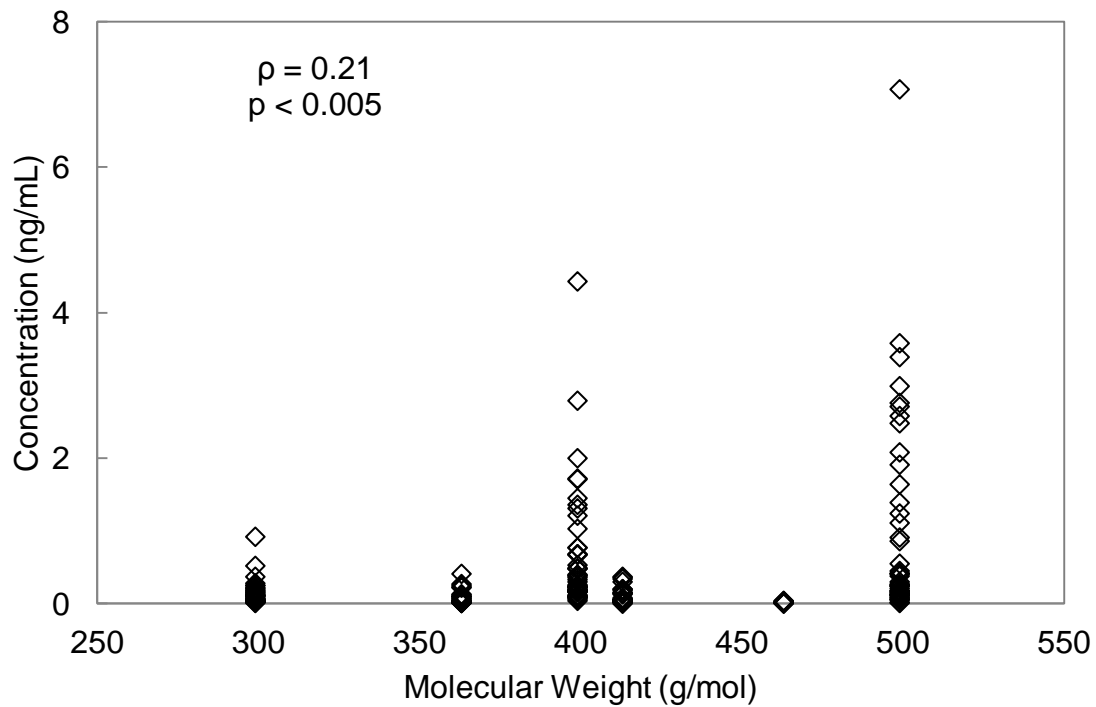


Figure 5.24 Correlation between molecular weight (g/mol) and concentration (ng/mL) of perfluorinated compounds quantified in water grab samples from locations of concern at Barksdale Air Force Base.

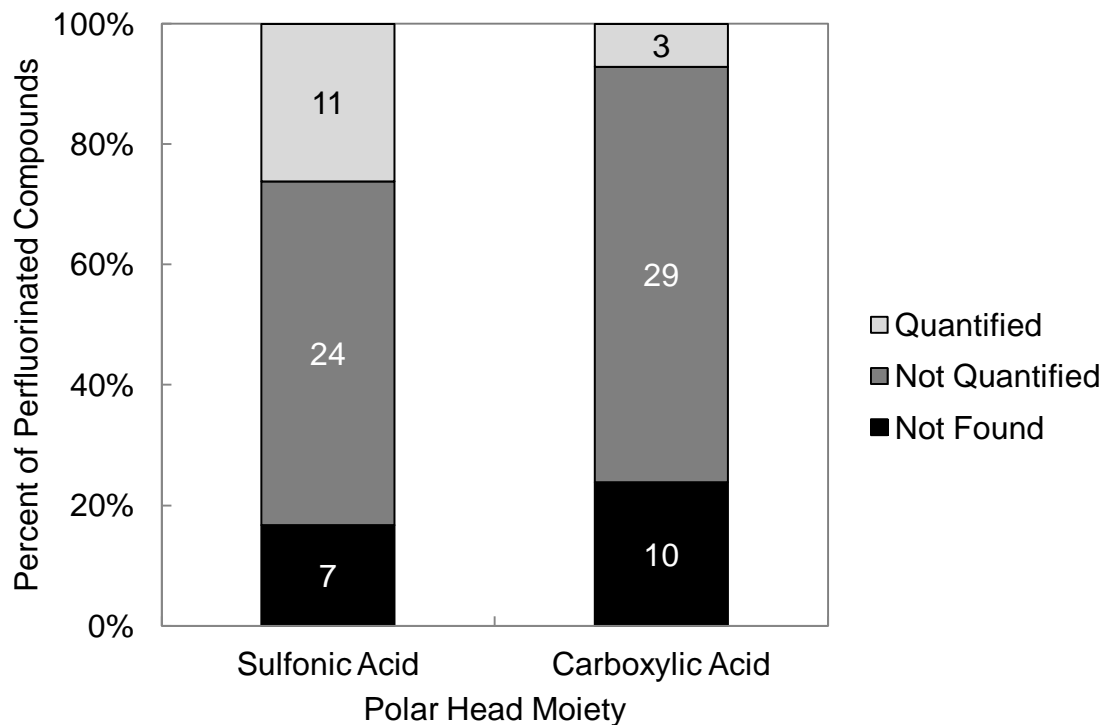


Figure 5.25 Percent of perfluorinated compounds containing a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in sediment passive samplers from all sample locations at Barksdale Air Force Base.

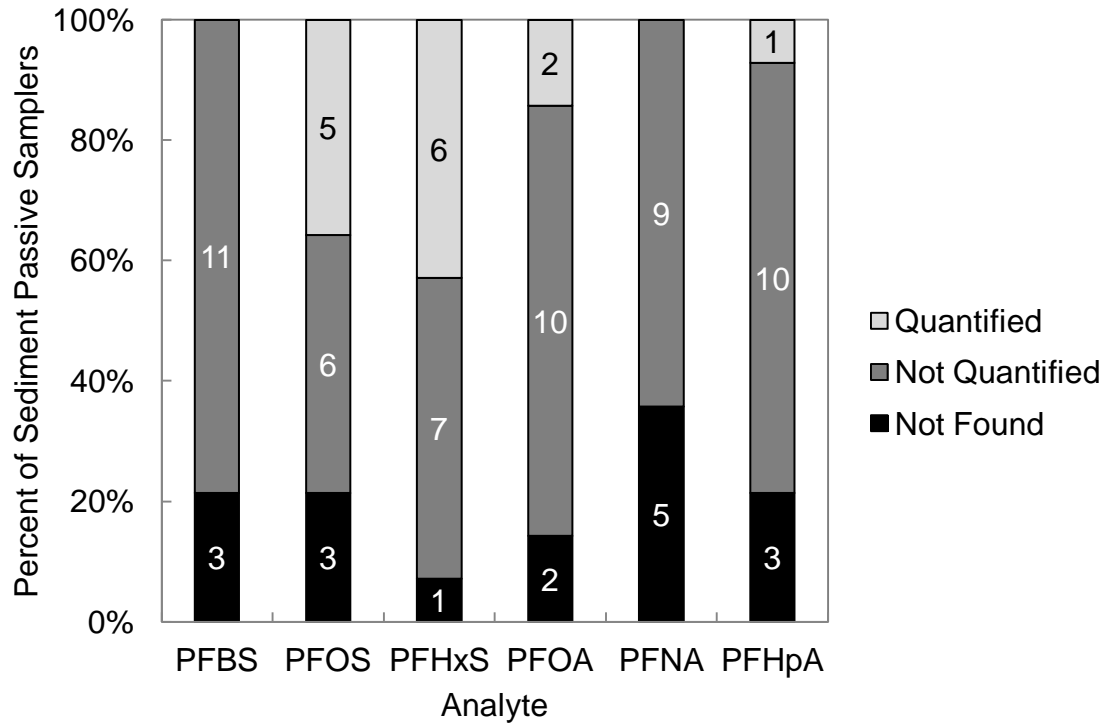


Figure 5.26 Percent of sediment passive samplers from all sample locations at Barksdale Air Force Base for which a perfluorinated compound was quantified, not quantified, or not found.

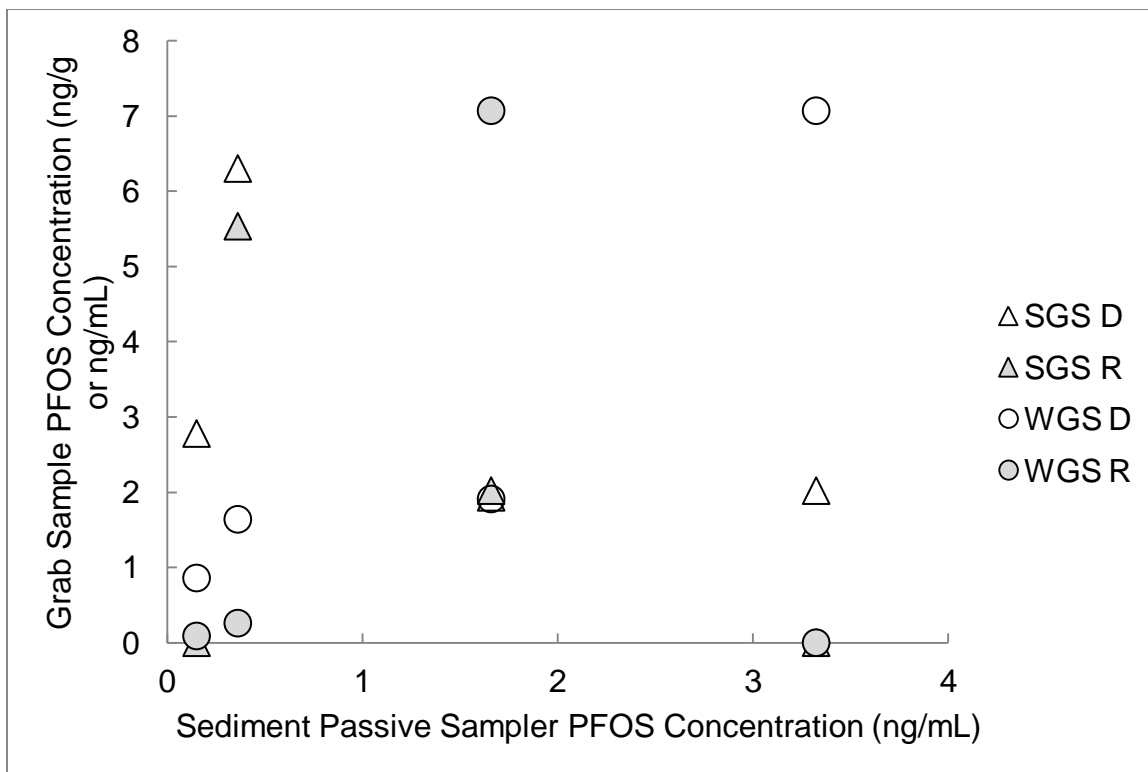


Figure 5.27 Distribution plot for PFOS concentrations quantified in sediment and water grab samples at the time of sediment passive sampler deployment and removal versus PFOS concentrations quantified in sediment passive samplers (ng/mL). Abbreviations: sediment grab sample at time of deployment (SGS D, ng/g); sediment grab sample at time of removal (SGS R, ng/g); water grab sample at time of deployment (WGS D, ng/mL); water grab sample at time of removal (WGS R, ng/mL).

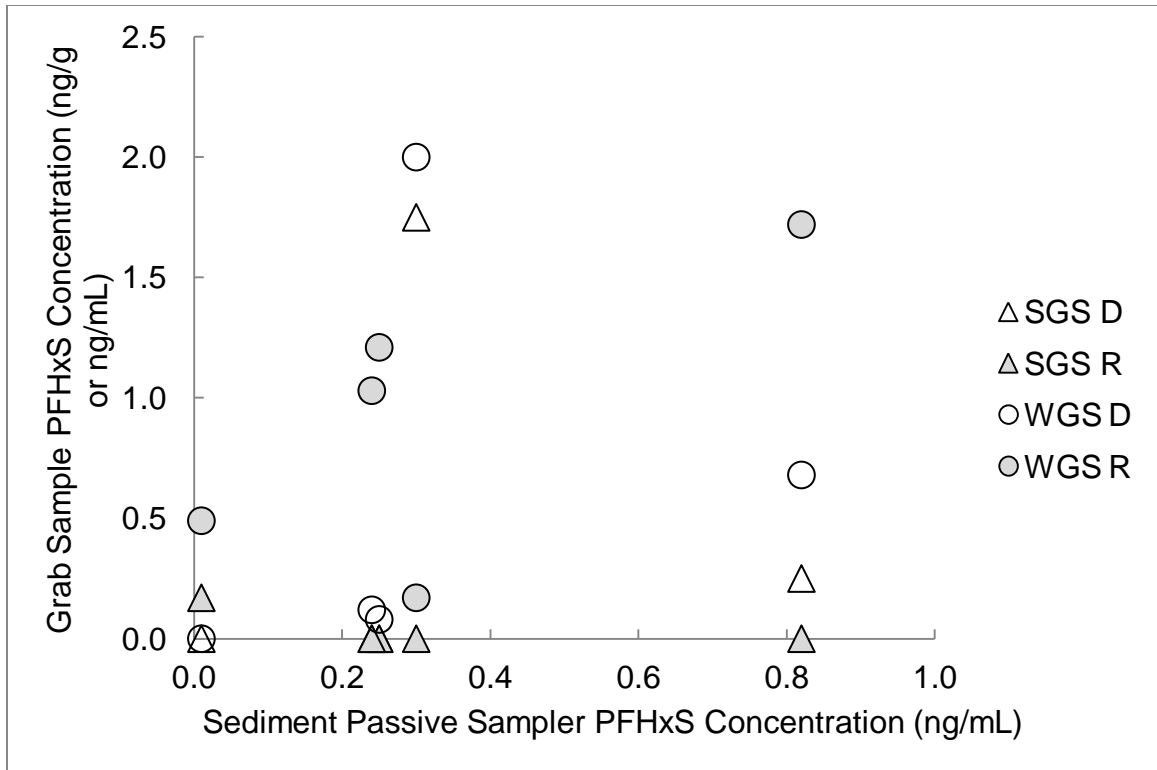


Figure 5.28 Distribution plot for PFHxS concentrations quantified in sediment and water grab samples at the time of sediment passive sampler deployment and removal versus PFHxS concentrations quantified in sediment passive samplers (ng/mL). Abbreviations: sediment grab sample at time of deployment (SGS D, ng/g); sediment grab sample at time of removal (SGS R, ng/g); water grab sample at time of deployment (WGS D, ng/mL); water grab sample at time of removal (WGS R, ng/mL).

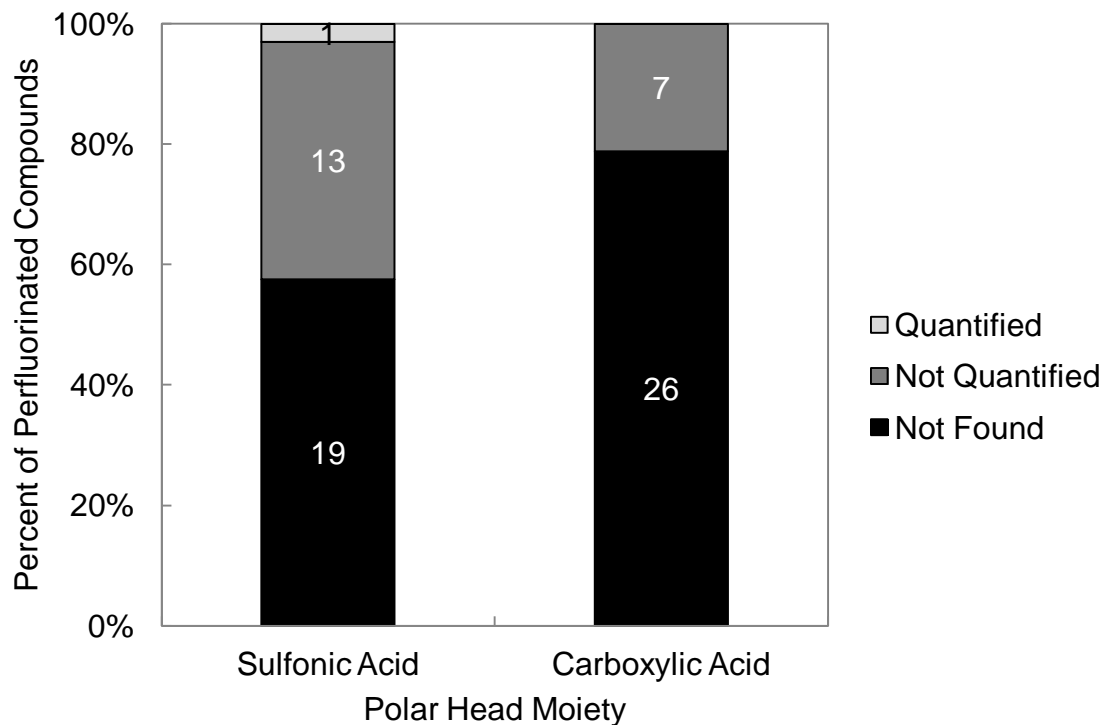


Figure 5.29 Percent of perfluorinated compounds containing a sulfonic or carboxylic acid polar head moiety that were quantified, not quantified, or not found in water passive samplers from all sample locations at Barksdale Air Force Base.



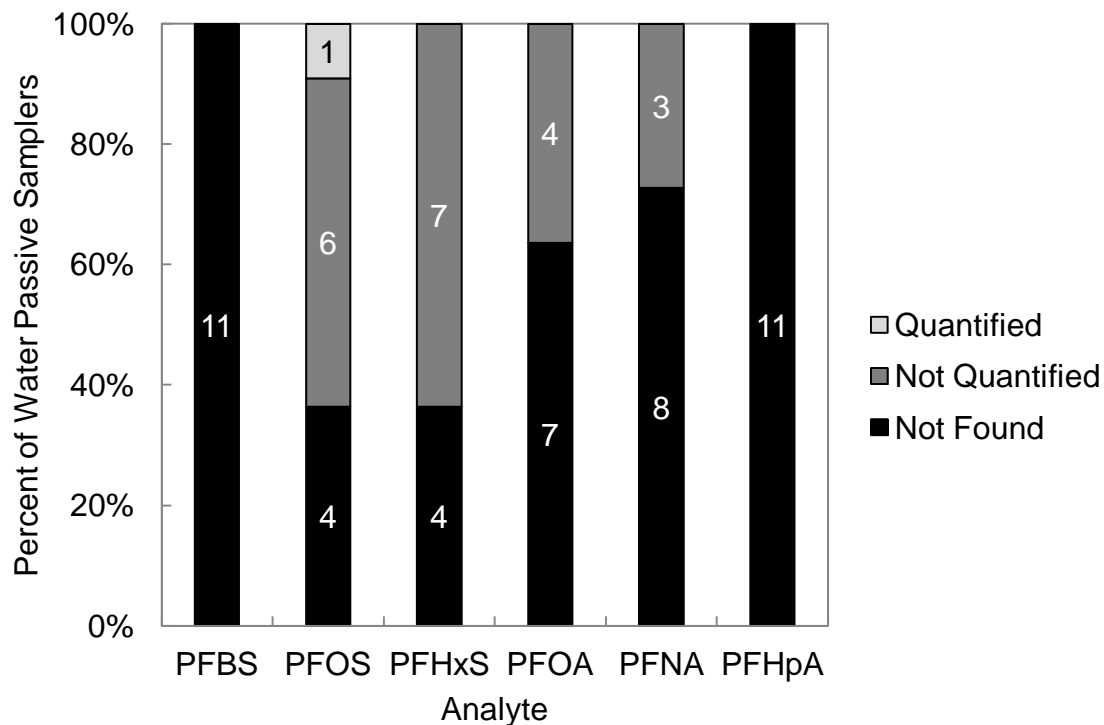


Figure 5.30 Percent of water passive samplers from all sample locations at Barksdale Air Force Base for which a perfluorinated compound was quantified, not quantified, or not found.

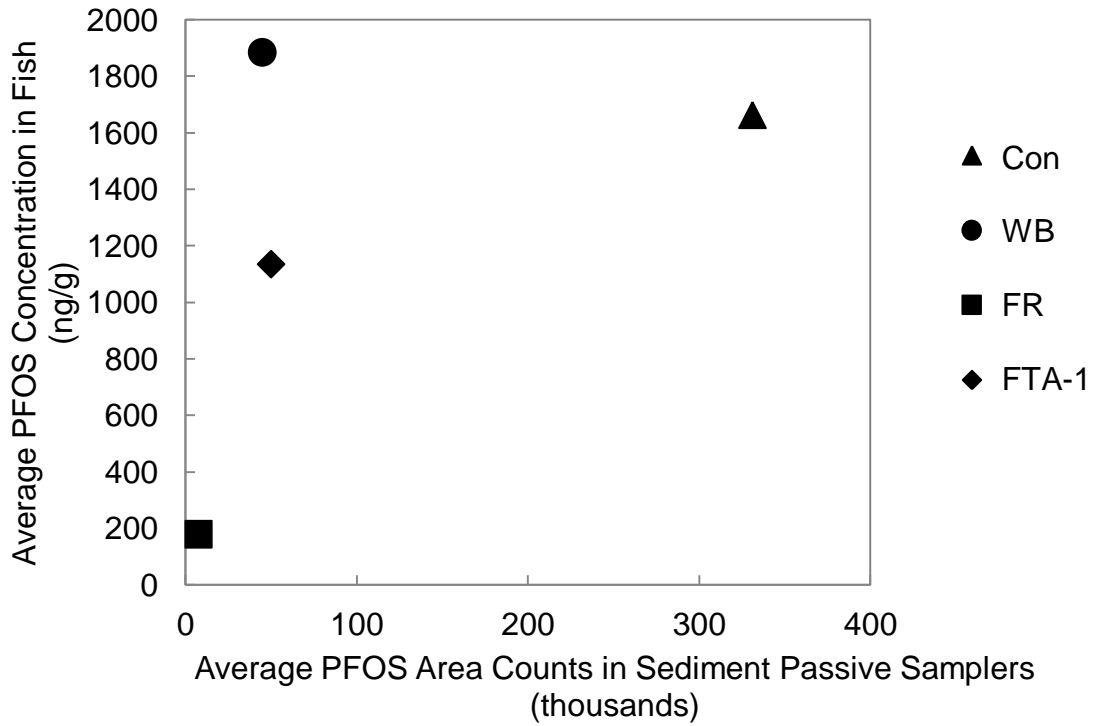


Figure 5.31 Average PFOS concentrations detected in fish collected in June and July compared to average PFOS area counts detected in sediment passive samplers collected in early May through September.

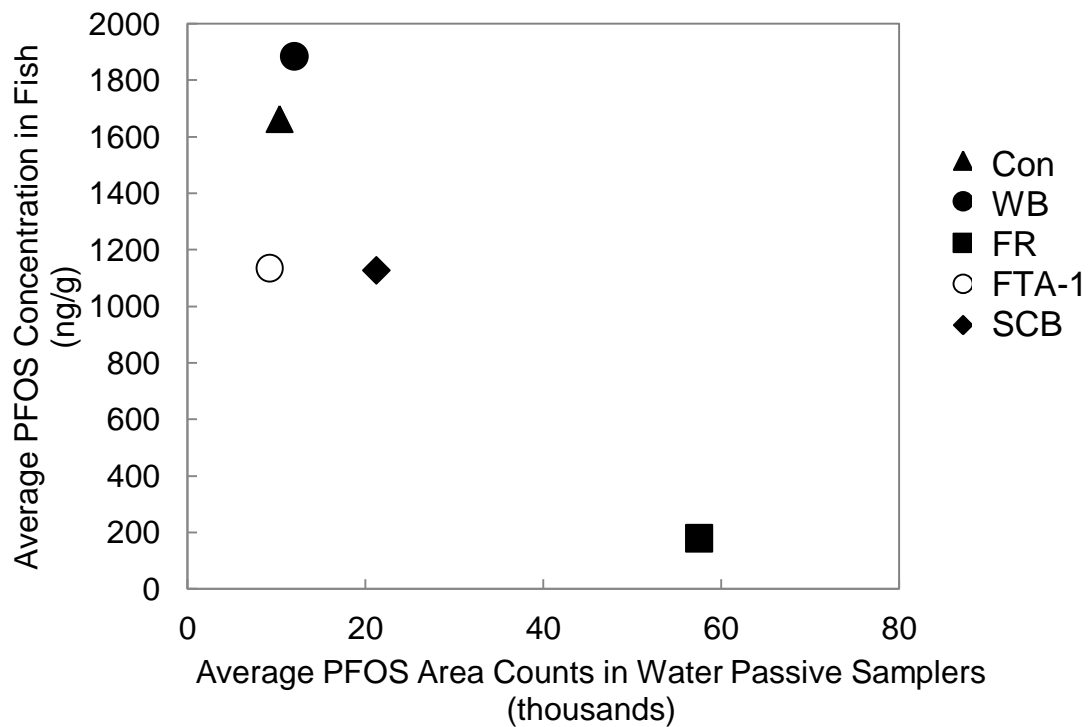


Figure 5.32 Average PFOS concentrations detected in fish collected in June and July compared to average PFOS area counts detected in water passive samplers collected in late May through September.

## CHAPTER VI

### DISCUSSION

Perfluorinated compounds (PFCs) were detected in sediment and water grab samples, sediment and water passive samplers, and fish samples. Overall, perfluorosulfonates were the most frequently detected PFCs and had the highest concentrations across all media types.

Perfluorinated compounds (PFCs) persist in the environment in their anionic form and can thus participate in electrostatic interactions with cationic species lining the surface of sediments. Perfluorosulfonates may have been quantified more frequently than perfluorocarboxylates in sediment samples due to their physical properties. Sulfonic acids are stronger and heavier acids than carboxylic acids and therefore their negatively charged conjugate bases are stronger than carboxylates and can saturate the cationic sediment surface, preventing the perfluorocarboxylates from binding.

A study by Zhao et al. (2014) depicts an increase in protonation of the sediment surface when the surrounding solution is at a low pH, leading to a strong electrostatic attraction between the sediment surface and anionic PFCs. When pH was increased to form a more basic solution, the sediment surface lost some of its positive charge and PFCs were no longer able to bind as frequently (Zhao et al. 2014). In the current study, PFHxS was the only PFC that showed a significant positive correlation with pH ( $\rho = 0.88$ ,  $p < 0.005$ ,  $n = 9$ ) which is the

opposite of the trend described by Zhao et al. (2014). However, the pH range (7.18 – 8.80) that was observed in the environment may not have deviated enough to provide a true representation of the trend between PFCs and pH. In addition, low organic matter (OM) content typically correlates with a decrease in positively charged metal species on the sediment surface which can result in a decrease in binding of anionic species. The low OM content detected in a subset of sediment samples collected from Barksdale Air Force Base (BAFB) could be an explanation for the low number of PFCs binding to sediment in the bayous.

A study by Ahrens et al. (2011) indicated that the perfluoroalkyl chain length has a strong influence on sorption of PFCs to sediment. It was also found that perfluorosulfonates with the same carbon-fluorine chain length as perfluorocarboxylates were detected more frequently and at higher concentrations (Ahrens et al. 2011). A similar trend was observed in the current study among PFCs that were quantified in sediment grab samples. Correlation analysis between PFC concentrations and molecular weight (which corresponds to perfluoroalkyl chain length) resulted in a significant positive correlation coefficient ( $\rho = 0.27$ ,  $p < 0.05$ ,  $n = 52$ ). Perfluoroheptanoic acid (PFHpA) has a carboxylic head group, a perfluoroalkyl chain length of 6, and was quantified at the lowest concentration in sediment grab samples. Perfluorohexanesulfonic acid (PFHxS) also has a 6 carbon perfluoroalkyl chain length. However, the concentration ( $1.47 \pm 2.18$  ng/g) and frequency that PFHxS was quantified (27%) increased in comparison to PFHpA possibly due to the replacement of the

carboxylic acid with a sulfonic acid polar head moiety. Average concentration increased further to  $2.75 \pm 5.28$  ng/g when the perfluoroalkyl chain length was extended by 2 carbon-fluorines. This average concentration is the result of PFOS being quantified in 65% of sediment grab samples.

It is possible that concentrations of PFCs and the number of PFCs quantified in sediment grab samples may have been underestimated given the low percent recovery of surrogates. Low surrogate recovery and low detection frequency of PFCs, particularly carboxylic acids, could be the result of matrix effects with competing compounds in sediment. A study published by Powley et al. (2005) attempted to improve recovery of perfluorinated carboxylic acids in solid environmental samples. This enhancement was achieved by purifying the crude extract from sediment samples with a dispersive solid-phase extraction process. This method allowed for matrix components to be removed and increased recovery of the desired analytes (Powley et al. 2005). Underestimated concentrations are also possible if PFCs are not desorbing completely from sediment samples. The desorption coefficient of PFOS was determined to be  $< 0.001$  L/g for all soil types even when extracted with an organic solvent (Giesy et al. 2010).

The higher quantification rate of PFCs in water grab samples could be due to the physicochemical properties of PFCs. The strong polarity of sulfonic and carboxylic acids increases the solubility of PFCs and results in preferable partitioning to aqueous media. The 3 PFCs with sulfonic acid polar head

moieties were the most frequently quantified and had higher average concentrations compared to any of the perfluorocarboxylates.

Perfluorohexanesulfonic acid (PFHxS) was the most frequently quantified analyte (86%) but PFOS had the highest average concentration ( $0.98 \pm 1.38$  ng/mL) and was quantified in 79% of water samples. A study by Moody et al. (2002) also showed PFOS and PFHxS as predominant analytes detected in water samples in areas contaminated from AFFFs. In the current study, Perfluorobutanesulfonic acid (PFBS) was also quantified more frequently (67%) and at higher concentrations ( $0.13 \pm 0.17$  ng/mL) than any of the perfluorocarboxylates. In comparison, PFOA was the most frequently quantified (64%) and had the highest concentration ( $0.09 \pm 0.10$  ng/mL) of the PFCs containing a carboxylic acid. These results indicate that the polar head moiety has a major influence on which PFCs persist in water.

In addition to the polar head moiety, concentrations in water grab samples were influenced by molecular weight and carbon chain length of PFCs. The results from a Spearman's rank correlation analysis indicated a significant positive correlation between concentration of PFCs and their corresponding molecular weights ( $\rho = 0.21$ ,  $p < 0.005$ ,  $n = 220$ ). This relationship is heavily influenced by the correlation between concentration and chain length of perfluorosulfonates ( $\rho = 0.40$ ,  $p < 0.005$ ,  $n = 135$ ). A paper identifying PFC components in 3M AFFF indicated only perfluorosulfonates in surfactants produced between 1988 and 2001 (Place and Field 2012). Therefore,

perfluorosulfonates may be the predominant PFCs in water grab samples due to historical use of AFFFs produced by electrochemical fluorination.

Perfluorosulfonate concentrations may increase with chain length because PFOS may have been the key component in the surfactant, with shorter chain PFCs at lower concentrations. The quantification of perfluorocarboxylates could result from use of another surfactant produced by a separate company.

There did not appear to be any temporal influence on the concentrations of PFCs over the 13-months of sampling. Alternatively, sampling location appeared to have an influence on detection of PFCs. Upon qualitative analysis, there was an increase in PFC concentration as sampling locations moved south of the fire training areas. This trend would be expected due to southward groundwater flow. Low concentrations of PFCs (0.01 – 3.58 ng/mL) were quantified in water samples collected upstream of fire training areas, indicating that PFC concentrations may be influenced by some urban input. However, an increase in PFC concentrations downstream of fire training areas signifies that the majority of PFC contaminants may be a result of runoff and/or contaminated groundwater infiltration from use of AFFFs. However, when subjected to a Spearman's rank correlation analysis a non-significant ( $p = 0.67$ ) trend was observed between PFC concentration and southward movement of sampling locations.

Temperature (T), DO, C, and  $\text{NH}_4^+$  were identified as parameters co-varying with concentration of PFCs in the water column. Dissolved oxygen (DO)



and  $\text{NH}_4^+$  are negatively correlated with T ( $\rho = -0.62$ ,  $p < 0.005$ ,  $n = 45$ ;  $\rho = -0.45$ ,  $p < 0.05$ ,  $n = 36$ , respectively) while C is positively correlated with T ( $\rho = 0.61$ ,  $p < 0.005$ ,  $n = 45$ ). Concentrations of PFCs in water samples parallel these trends when analyzed using Spearman's rank correlation test. Analytes PFBS and PFOA are negatively correlated with T ( $\rho = -0.53$ ,  $p < 0.005$ ,  $n = 30$ ;  $\rho = -0.44$ ,  $p < 0.05$ ,  $n = 27$ , respectively) and PFBS and PFNA are negatively correlated with C ( $\rho = -0.44$ ,  $p < 0.05$ ,  $n = 30$ ;  $\rho = -0.56$ ,  $p < 0.05$ ,  $n = 13$ , respectively). As expected, PFBS and PFOA have significant positive correlations with DO ( $\rho = 0.69$ ,  $p < 0.005$ ,  $n = 30$ ;  $\rho = 0.40$ ,  $p < 0.05$ ,  $n = 27$ , respectively) and PFOS and PFHxS are positively correlated with  $\text{NH}_4^+$  ( $\rho = 0.40$ ,  $p < 0.05$ ,  $n = 30$ ;  $\rho = 0.45$ ,  $p < 0.05$ ,  $n = 30$ , respectively). Since DO, C, and  $\text{NH}_4^+$  are dependent on T, they may only reflect the concentrations of PFCs while T may influence the concentrations.

The results published by Awad et al. (2011) from monitoring an accidental release of AFFFs in Toronto make it evident that PFC concentrations decrease significantly over time in the environment. The average PFOS concentration ( $0.98 \pm 1.38$  ng/mL and  $1.73 \pm 1.77$  ng/mL) detected in water grab samples at BAFB were similar to the PFOS concentration (0.69 ng/mL) detected in the water sample 3 years after the accidental spill in Toronto (Awad et al. 2011). However, the average PFOS concentration at BAFB was at least 3 times greater than the PFOS concentration (0.29 ng/mL) collected in a water sample 9 years after the accidental AFFF spill in Toronto (Awad et al. 2011). Therefore, since average

concentrations of PFCs are still higher than concentrations monitored 9 years after a large release of AFFFs, there is most likely a continuous release of PFCs at BAFB from groundwater that was heavily contaminated by the use of AFFFs. If concentrations similar to the maximum PFOS concentration (7.07 ng/mL) are being continuously released into the tributary at BAFB, than biota may not be protected from chronic toxicity based on the chronic criteria concentration of 5.1 ng/mL (Giesy et al. 2010).

Due to insufficient data, the majority of concentrations quantified in grab samples could not be compared to passive samplers. Four analytes (PFOS, PFHxS, PFOA, and PFHpA) were quantified in sediment passive samplers but only PFOS and PFHxS were compared with grab samples. Qualitative positive trends for PFOS and PFHxS concentrations were observed between water grab samples and peepers. However, qualitative negative trends for PFOS and PFHxS concentrations were observed between sediment grab samples and peepers. This is an indication that peepers were more sensitive towards PFC concentrations in water versus PFCs partitioning to sediment and therefore may be more beneficial for estimating environmental water concentrations versus sediment concentrations.

Qualitatively, PFCs detected in water passive samplers were similar to those detected in fish samples from BAFB. Similar to results published by Awad et al. (2011), there were no perfluorocarboxylates quantified in fish samples. The only analyte that was quantified in either media was PFOS. This analyte was

only quantified in 1 passive sampler but was quantified in 100% of fish samples. An increase in accumulation and a more comparable concentration may occur if passive samplers are deployed for longer than 6 weeks. The sorbent material within the dialysis tubing (trioleate or serum protein) did not appear to impact PFC concentrations. However, a statistical difference may have been observed if the duration of deployment was increased. The possibility of cellulose tubing degradation has been noted in previous studies (Alvarez et al. 2004; Ehlke et al. 2004). The current study also demonstrated that low-density polyethylene (LDPE) dialysis tubing is more durable in comparison to regenerated cellulose tubing due to the cellulose degrading to an almost non-existent form after a 6-week deployment in late May at BAFB.

Sediment passive samplers collect PFCs until equilibrium is reached between cell concentration and pore water concentration and can therefore estimate the concentration that aquatic biota may be exposed to. Water passive samplers accumulate PFCs exponentially over time and can potentially be used as surrogates for fish. In general, average area counts detected in sediment passive samplers were higher than area counts detected in water passive samplers. This could imply that fish are being exposed to PFOS but may take longer than 6 weeks to accumulate quantifiable concentrations.

In comparison to other sampling locations, FR had the lowest area count detected in peepers as well as the lowest average concentration detected in fish. However, FR had the highest average area count detected in water passive

samplers. The low area count detected in peepers and fish is expected due to being a reference location. The high average area count detected in water passive samplers for FR may not be a true representation and could be driven by a water passive sampler collected in late May which had a quantifiable PFOS concentration.

Confluence (Con) consisted of the largest average PFOS area count in sediment passive samplers and therefore the chances of biota being exposed may be heightened at this location. However, this location did not have the largest average area count in water passive samplers, indicating that even if fish were to linger at this location for roughly 6 weeks they would not accumulate as much PFOS as they would if lingering near SCB. Concentrations detected in fish also indicate that fish may not be at the Con location long enough for exposure to be of concern. Alternatively, fish collected from WB have the highest average concentration of PFOS. It was observed that larger fish were collected from this location during spawning season and concentrations may be the result of fish remaining in this area for long periods of time.

## **CHAPTER VII**

### **CONCLUSION**

It can be concluded that water and sediment within the bayous at Barksdale Air Force Base (BAFB) contain quantifiable concentrations of perfluorinated compounds (PFCs). Average PFC concentrations were below acute and chronic concentration criteria established to protect aquatic organisms but the maximum concentration of PFOS was greater than the established chronic criteria (Giesy et al. 2010). It is suspected that the contamination at BAFB is the result of run off and ground infiltration from historical use of aqueous film forming foams (AFFFs). Some contamination could be a result of city runoff from the production of other PFC-containing products but AFFFs are a probable cause given the close proximity of the fire training areas in relation to the contaminated bayous.

As a result of Spearman's rank correlation analysis, it was estimated that temperature is the most influential water parameter on concentration of PFCs. Due to known dependencies of dissolved oxygen, conductivity, and ammonium on temperature, these parameters are thought to only parallel the increase or decrease of PFCs. The partitioning of PFCs between environmental media also appears to be heavily influenced by the polar head moiety attached to the PFC. Perfluorosulfonates partition more readily to all media types that were observed including sediment and water grab samples, sediment and water passive

samplers, and fish. An increase in perfluoroalkyl chain length attached to the sulfonic polar head moiety correlates strongly with an increase in magnitude of perfluorosulfonates. Organic matter content of sediment grab samples did not significantly correlate with PFC concentrations. However, the low organic matter content could be an indication of low cationic metal species on the sediment surface and could therefore provide a reasonable explanation for infrequent quantifications of PFCs bound to sediment given insufficient electrostatic interactions between cationic metal species and anionic PFCs.

Perfluorinated compound (PFC) concentrations detected in water grab samples were related to the magnitude of PFCs collected within sediment passive samplers. When PFC concentrations in the water column are low, concentrations in pore water are also most likely low, and therefore influencing the amount that is collected within the passive sampler. Peepers may be useful as water column passive samplers in future studies. Semi-permeable membrane devices provided a semi-qualitative representation of PFCs detected in fish samples. The only PFC that was able to be quantified within water passive samplers and fish samples was PFOS. It is suggested from the results of this study to allow accumulation within passive samplers for longer than 6 weeks if environmental conditions permit. More data are needed to provide a definitive conclusion that passive samplers could provide a reliable estimation of PFCs in the environment.

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