Enhanced Sorption of Perfluoro-alkyl Substances (PFASs) onto Ottawa Sand

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Dedication

This thesis is dedicated to my wife, Alaa Koleilat, who has shown me what true hard work and dedication look like. Her endless support has kept me motivated and focused through long hours of the night.

I would like extend my deepest appreciation to my parents Hussein Aly and Mai Abdel-Salam, and their support and years of encouragement Any success that I have earned is due to their advice and direction.

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Abstract

Sorption to mineral surfaces is an important process in controlling the fate, mobility, and bioavailability of perfluoroalkyl substances (PFASs) in aquatic systems. Unlike other persistent organic pollutants, PFASs are highly water-soluble due to their hydrophilic head group and thus their solid-phase partitioning is limited under natural conditions. However, recent research has shown that sorption of PFASs to suspended solids in surface water can be enhanced by addition of cationic coagulants, through a combination of electrostatic and hydrophobic effects. Whether coagulant-enhanced sorption can be adapted for in situ remediation of PFAS-contaminated groundwater remains an open question. We investigated sorption of six PFASs at environmentally relevant concentrations in the presence of four cationic coagulants: polyaluminum chloride, polyamine, polydiallyldimethyl ammonium chloride (polyDADMAC), and a tannin-based cationic polymer. PFAS adsorption isotherms were determined on Ottawa sand and on aquifer material from a known PFAS-contaminated site. Preliminary results suggest that this method shows promise for in situ remediation of PFAS-contaminated groundwater.

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Introduction

Perfluoroalkyl substances (PFASs) have been a topic of increasing concern in recent years. PFASs are a group of persistent organic pollutants (POPs) that have been produced and used in large amounts and thus, are being found regularly in the environment. (Buck *et al.*, 2011; Kallenborn *et al.*, 2004; Xiao *et al*., 2015) PFASs were produced for many uses in industry such as aqueous film-forming foam (AFFF), non-stick cookware, pesticides, water repellent coatings, and many other uses people encounter on a daily basis. (EPA, 2015; Fernández-Sanjuan *et al.*, 2010; Lindstrom *et al.*, 2011) The source of the exposure this project will focus on is the use of AFFF in the emergency and training exercises at many military institutions around the United States. The goal of this research is to develop a novel remediation method of PFAS for contaminated groundwater. Specifically, this project will focus on sites at which AFFF was used for fire fighting training purposes. AFFF, which contained many PFASs and their pre-cursors, seeped into ground water beneath where they were applied, causing contamination of water used for irrigation, municipal services and drinking. In the United States alone, AFFF is used in over 90 airports including many more Air Force Fire Training sites and civilian fire departments (nrl.navy.mil). This is a strong cause for alarm since PFASs have been shown to be wide spread and highly persistent in the environment; as well as bio-accumulative and toxic to wildlife and human beings.

Despite being produced since the mid 1950's, PFASs were initially detected in the environment in the first decade of the 21st century (Giesy and Kannan, 2001). Since their

initial discovery, they have been found in wide-spread locations across the world including the Canadian Arctic, South America and the Scandinavian Peninsula (Calafat *et al.* 2007; Karrman *et al.* 2011). As a result of their high water solubility and high stability, PFAS are common contaminants found in water through many trophic levels including fish, birds and even polar bear liver samples (Martin *et al.,* 2004; Suja *et al.,* 2009). PFASs contamination of water has been found to lead to corresponding contamination of ground and drinking water supplies, which contribute to an important source of human exposure to PFASs (Takagi *et al.,* 2008; Wilhelm *et al.,* 2010). Moody *et al.* 2002 reported some of the highest levels of PFAS contamination of ground water in sites where AFFF has been applied. The levels of PFOS and three other PFASs **(**perfluorohexanesulfonate (PFHxS); perfluorooctanoate (PFOA); and perfluorohexanoate (PFHxA) ranged from 3 to 120 ng/mL (Moody *et al.* 2003). The the chronic health limit proposed by the Minnesota Department of Health (MDH) is 0.3 ng/mL (MDH.gov). Filipovic *et al.* 2015 found that in 2014, a site where AFFF was historically used in 1994 may still be a point source PFASs, suggesting that even after 20 years, AFFF use may still be source of PFAS contamination.

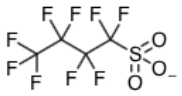
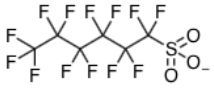
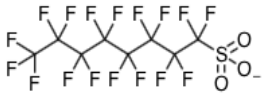
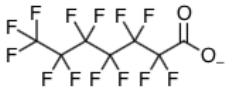
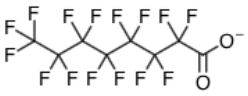
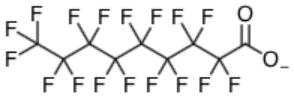
PFASs have also been shown to be bio-accumulative. Rather than binding to lipids like most other persistent organic pollutants, PFASs attach to proteins (Cui *et al,.* 2009; Yeung *et al.,* 2009). Through this, they can can accumulate in wildlife through and up trophic levels. Haukas *et al.* 2007 found that out of a suite of PFAS consisting of PFOS, PFOA, perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDcA), all were found in a variety of wildlife ranging from fish

to birds to amphipods. PFOS was found at the highest concentration in all species with the highest reported value of 225 ng/g in a glaucous gull. Martin *et al.* 2003 showed bioaccumulation factors of PFAS increase with carbon-fluorine chain length for both sulfonates and carboxylic acids, with sulfonates accumulating to a greater extent. Additionally, this study noted that higher trophic levels exhibited the highest concentration of PFOS, indicating its strong potential for accumulation and bio-magnification in a food web. PFASs also display significant half-lives in the serum of rats, mice, monkeys and humans with the latter the longest of 2-8 years (EPA, 2009).

Many studies have shown perfluorinated substances to be toxic to animals as well. Lee *et al.* 2013 analyzed PFOS, PFOA, and PFHxS in maternal and umbilical samples. High concentrations of these chemicals were shown to have a strong correlation with lower birth weights, birth length and ponderal index, which are all associated with infantile health. It was also shown that these chemicals transport across the umbilical chord to a fetus and exposure to PFOS and PFOA can lead to a decrease in fecundity in women (Fei *et al.,* 2009). Besides fetal and maternal health effects, several other studies have linked exposure to long chain PFASs to attention deficit disorder, peroxisome proliferation**,** and carcinogenicity through inhibition of cellular communication in livers (Hoffman *et al.,* 2010; Stock *et al.,* 2010). Some more severe effects were observed in the way of reduced lipid metabolism, impeded immune and endocrine pathways, and tumors across organ systems (Wang *et al.,* 2014; Lau *et al.,* 2002; Post *et al.,* 2012). It is important to understand the effects of this class of chemicals in order to develop new methods of limiting exposure to the environment and the humans that inhabit it.

PFASs are quite mobile once they enter the aqueous environment, with up to 26% remaining in the dissolved phase. (Johnson *et al.,* 2007) This may lead to exposure through drinking water in places near sites where AFFF is used. Although these fire-fighting foams contain many chemicals of interest, this work focuses on the six perfluorinated compounds listed under the United States Environmental Protection Agency Unregulated Contaminant Monitoring Rule 3 List (UCMR3). This group consists of commonly found and highly persistent carboxylic acids; perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluoroheptanoic acid (PFHpA), and sulfonates; perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate (PFBS) and perfluorohexane sulfonate. (PFHxS) (Table 1).

Table 1) Names, acronyms, structures and m/z ratios of all six PFASs on the UCMR3 List.

Name **(Acronym)**	Structure*	m/z Ratio
Perfluorobutane Sulfonate **(PFBS)**		299
Perfluorohexane sulfonate **(PFHxS)**		399
Perfluorooctane sulfonate **(PFOS)**		499
Perfluoroheptanoic Acid **(PFHpA)**		363
Perfluorooctanoic Acid **(PFOA)**		413
Perfluorononanoic Acid **(PFNA)**		463

*** All structures drawn on *chemdoodle.com***

At 130 kcal/mol, the C-F bond is the strongest covalent bond (Lemal, 2004). Because the C-F bond is a defining characteristic of all PFASs, they are extremely

difficult to destroy in the environment. There has been some work to investigate what kind of interactions will destroy these resilient fluorinated carbon chains. Ochoa-Herrera *et al.* 2008 found that defluorination requires a catalyst, a powerful reductant and high temperatures. In 2012, Liu *et al.* demonstrated that the destruction of perfluorooctanoic acid (PFOA) requires a strong oxidizing agent and high temperatures as well. As a consequence of their stability and persistence, most conventional water treatments, such as hydrolysis, photolysis and biodegradation are ineffective when applied to remove PFASs from contaminated water. (Armitage *et al.,* 2006; Tabtong *et al.,* 2015). Other common and suggested methods include filtration, reverse-osmosis and boron doped diamond (BDD) anodes, sono-chemical degradation, electro-chemical coagulation and treatment, adsorption to carbon nano-tubes, ball milling, a range of powerful oxidants and bio-degradation (Urtiga *et al,.* 2015; Carter and Farell, 2008; Thompson *et al.,* 2010; Lin *et al*., 2012; Cheng *et al.,* 2008; Vecitis *et al.,* 2009; Zhang *et al.,* 2014; Schaefer *et al.,* 2015; Xioana *et al.,* 2015; Zhang *et al.,* 2013; Santos *et al., 2015;* Kwon 2015). Only a few of these methods have been shown to be efficient. Thompson *et al.* reported that all PFASs tested for at a plant that used reverse-osmosis were removed to levels below detection limits. However, all these methods are costly and time consuming and none have been tested as a possible *in-situ* remediation method. There is a need for the development of a novel remediation method of PFASs that can be implemented directly at the site of contamination.

An alternate method to destruction is the sequestration of PFASs from water. This can be a valuable innovation if it can be applied *in situ.* Sorption can be enhanced

through the use of coagulants with sorption enhancing capabilities, thus removing them from the mobile phase, preventing their migration. Previous work has shown that PFAS sorption is correlated with soil organic matter (Higgins and Luthy, 2006) Many others have found PFAS sorption to be correlated to soil organic matter. Yet others found PFAS sorbing onto minerals with relatively low organic content such as iron oxide, sand, boehmite and kaolinite (Johnson *et al.*, 2007, Shih and Wang, 2013; Xiao *et al.*, 2011). This, along with the relationship between PFAS sorption and pH and ionic strength, indicates that ion exchange occupies an important role in PFAS sorption as well. (Higgins and Luthy, 2007**;** Xiao *et al.*, 2011).

Previous work has corroborated that enhanced coagulation can decrease PFAS content in water. Xiao *et al.* investigated the removal of PFOS and PFOA by conventional and enhanced coagulation (2013). Coagulation with Alum results in the particles' attraction to one another, thus rendering them more susceptible to sorption onto the surrounding soil and sediments. Xiao *et al.* showed that the dose of alum ($Al_2(SO_4)_3 \cdot 18H_2O$), a common coagulant used in conventional water treatment, has a positive effect on the removal percentage of PFOS and PFOA. This correlated with a decrease in turbidity and natural organic matter (NOM) represented by UV_{254}. The authors suggest that the mechanism for PFAS removal is that they sorb to Alum flocs. This introduces the possibility that other coagulants may have a similar effect on the removal of PFASs from water.

These results indicate that coagulation and thus enhanced sorption may lead to increased removal of PFOS, PFOA and even other PFASs from water possibly by

enhancing sorption to the particle surface. This is the premise around this project. A selection of 3 coagulants representing a wide range of characteristics were tested. An inorganic positively charged polymer, polyaluminum chloride (PAl-Cl); a cationic polymer of approximately 750 thousand Daltons, polyamine (PA); and a cationic polymer polydimethylamine diallyldimethyl ammonium chloride (poly-DADMAC), of 2-3 mega Daltons, were selected as potential enhancers for this project. They were selected for their wide use in the water treatment process. PAl-Cl is commonly used as a coagulant in water and wastewater treatment to remove dissolved organic matter (DOM) and colloidal particles. Polyamine, an organic coagulant, has been shown to be an effective color remover and is also used regularly in the wastewater treatment process. Poly-DADMAC is an organic coagulant shown to neutralize negatively charged particles. These three coagulants were tested and their ability to remove PFASs from water through their enhanced sorption were evaluated.

Materials and Methods

Determining Optimal Coagulant Dosage

Sorption enhancers polyDADMAC and PA were purchased from Accepta in Manchester, United Kingdom, and polyaluminum chloride (PAl-Cl) was purchased from Sielder Chemical in Newark, New Jersey, U.S.A. All three were stored at room temperature. Starting concentrations of sorption enhancers were based on previous experiments with the enhancers alone on Ottawa Sand performed by post-doctoral fellow, Daniel McInnis. (U.S. Silica, Berkeley Springs, West Virginia) In general, Dan's isotherms were constructed for poly-DADMAC and polyamine by filling 50 mL polypropylene centrifuge tubes with 5 grams of 40-60 mesh Ottawa sand, 25 mL of reverse osmosis (RO) water with 0.1 M potassium nitrate (KNO_3), and added masses of coagulant to reach starting concentrations of 0, 1, 5, 10, 50, 100, 200, 300, 500, 600, 800, and 1000 mg/L as total coagulant. Calibration curves were prepared in the same way with the exception that no Ottawa Sand was added to tubes. Solution pH was adjusted and fixed to 7 with a sodium bicarbonate ($NaHCO_3$) buffer. After 24 hours on a wrist action shaker to reach equilibrium, test tubes were centrifuged for 15 minutes at 2000 RPM on a Dynac Centrifuge. Approximately 10 mL of supernatant was decanted into 19 × 65 mm glass tubes and analyzed via a Shimadzu TOC-L. The amount sorbed, q, in mg of enhancer/g of sand, was calculated using Equation 1, where C_0 is the TOC reading for the coagulant solution alone, C is the TOC reading for the coagulant and sand, V is the volume of the solution (.025 L), and m is the mass of the sand in the batch samples (5 g).

Equation 1) $$q = \frac{(C_o - C) \times V}{m}$$

Collaborators at the Tufts University Department of Civil and Environmental Engineering in Medford, Massachusetts, U.S.A., performed isotherm experiments for polyaluminum chloride on Ottawa Sand. The starting concentrations selected for polyaluminum chloride were 500, 1000, 2000, 3000, 4000, mg polyaluminum chloride/L water. Final concentrations were measured as mg Al/L via ICP-OES to detect aluminum at a wavelength of 308.215 nm. Optimal dosages of the enhancers were then selected based on q_{max} (maximum adsorption) to achieve a monolayer coverage of the sorption enhancers on the surface of sand particles.

Sorption Batch Experiments with PFASs

Similar isotherm batch experiments were also performed on the suite of PFASs in USEPA's UCMR3 list, consisting of three sulfonates and three acids as follows; perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluoroheptanioc acid (PFHpA), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA). Unlabeled compounds used for analytes were purchased from Cambridge Isotope Laboratories, Andover, Massachusetts (PFOS and PFOA) and Wellington Laboratories, Ontario, Canada (PFBS, PFHxS, PFHpA, and PFNA). Isotopically labeled isotopes used for quantification were purchased from Cambridge Isotope Laboratories, Andover, Massachusetts ($^{13}C_8$-PFOA and $^{13}C_8$-PFOS) s and Wellington Laboratories, Ontario, Canada ($^{18}O_2$-PFHxS, $^{13}C_3$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFHpA, $^{13}C_5$-PFNA and $^{13}C_9$-PFNA). No isotopically labeled PFBS was available,

therefore $^{13}C_3$-PFHxS was used instead. All compounds were received in a solution of 50 μg/mL in methanol and stored at room temperature. Analytes were later diluted by a factor of 100 with Optima Grade methanol from Fisher Scientific to 0.5 μg/mL, a more applicable concentration for sample preparation. After dilution, all PFAS stock solutions were stored at -20 °C. Internal standards were diluted by a factor of 10 to 5 μg/mL. Protocol for the batch experiments on the USEPA UCMR3 List was based on the methods described in Johnson et al. (2007). The solution placed in the 50 mL polypropylene centrifuge tubes consisted of varying volumes of 5 μg/mL PFAS solution to reach starting concentrations of 10, 20, 40, 50, 75 and 100 ng/mL, 1 mL of coagulant solution to reach desired dosage, and (reverse osmosis) RO water was added to bring final solution volume to 10 mL. 25 g of Ottawa sand was added to each test tube before they being placed on a wrist action shaker for 24 hours. Control samples were created by adding only contaminant and sand and no coagulant to the solution. Procedural blanks were prepared by adding 25 grams of sand and 10 mL of RO water to test tubes and analyzing the solution to detect possible PFAS contamination sources from the materials being used. All enhancers were analyzed for PFAS contamination as well. These quantities of sand and water were selected to represent the low end of a solid to liquid ratio representative of ground water systems (Schwarzenbach et al. 2003). A scheme for the preparation of six-sample batches for control and coagulant solutions as shown in Table 2. After 24 hours, test tubes were centrifuged for 15 minutes and 1 mL of the supernatant was extracted and placed, along with 20 uL of 5 μg/mL internal standard

solution in a 2 mL glass LC/MS auto-sampler vial. Plastic caps and viton septa were used instead of crimp-on caps to avoid PFAS contamination from PTFE.

Table 2) a) Preparation scheme for control batch experiments where no coagulant was added. b) Preparation scheme for batch experiments with coagulant included.

a)

Control Samples (Concentration)	uL PFAS (0.5 ug/mL)	mL Coagulant (1000 mg/L)	mL RO Water (pH 7, $NaHCO_3$)
10 ng/mL	200	0	9.8
20 ng/mL	400	0	9.6
40 ng/mL	800	0	9.2
50 ng/mL	1000	0	9.0
75 ng/mL	1500	0	8.5
100 ng/mL	2000	0	8.0

b)

Coagulant Samples (Concentration)	uL PFAS (0.5 ug/mL)	mL Coagulant (1000 mg/L)	mL RO Water (pH 7, $NaHCO_3$)
10 ng/mL	200	1	8.8
20 ng/mL	400	1	8.6
40 ng/mL	800	1	8.2
50 ng/mL	1000	1	8.0
75 ng/mL	1500	1	7.5
100 ng/mL	2000	1	7.0

Calibration standards were prepared for quantification purposes by adding 20 μL of each 5 μg/mL PFAS solution and 20 μL of their respective 5 μg/mL internal standard solution to have 100 ng of each chemical in each LCMS vial. 1 mL of methanol was added for ease of analysis. To determine a relative response factor for each PFAS, Equation 2 was applied where $MASS_{analyte}$ was the mass of the unlabeled PFAS in each vial (100 ng) and $MASS_{int.std.}$ was the mass of the internal standard in the vial (100 ng). A RRF was used as an alternative to a traditional linear calibration curve in order to account for small fluctuations in injection volume of sample into the liquid chromatograph.

Equation 2) $\text{RRF} = \frac{MASS_{analyte} / PEAK\ AREA_{analyte}}{MASS_{Int.Std.} / PEAK\ AREA_{Int.Std.}}$

Samples were then analyzed for equilibrium PFAS concentration by a Hewlett Packard model 1090 high-performance liquid chromatograph (HPLC) along with a Hewlett Packard 1100 MSD mass spectrometer using electrospray ionization source. Between sample sets, the system was flushed with acetonitrile to remove any residual buffer out of the column to avoid precipitation. The analytical column used was a 50×21 mm Betasil C18 column (Thermo-Scientific, Waltham MA). A Betasil C18 10×2.1 mm guard column was used in conjunction with the analytical column. Mobile Phase A was a 2mM ammonium acetate ($NH_4C_2H_3O_2$) 9:1 ratio solution of RO water and filtered Optima Grade Methanol (Fisher Scientific) and Mobile Phase B was 2 mM ammonium acetate ($NH_4C_2H_3O_2$) in filtered Optima Grade Methanol (Fisher Scientific). Parameters for LC-MS operation and method and a sample sequence table are tabulated below. (Table 3) Parameters not listed in Table 3 include; injection volume of 5 μL, flow rate of 0.2 mL/minute. Ionization of analytes was accomplished with an electro-spray ionization (ESI) in negative polarity. The mass spectrometer was operated in elective ion monitoring mode (SIM) according to the mass to charge rations (m/z) given in Table 3a. Mobile phase gradients for the LC pump are given in Table 3b.

Table 3) a) List of m/z charges of all PFAS analytes and internal standards used in the UCMR# method. b) Mobile phase gradient through all 25 minutes of injection time.

a

Minutes	% B
0	22
3	67
4	67
8	100
15	100
20	22
25	22

b

Acronym	SIM Ion (m/z)
PFBS	299
PFHpA	362
$^{13}C_4$-PFHpA	367
PFHxS	399
$^{13}C_3$-PFHxS	402
$^{18}O_2$-PFHxS	403
PFOA	413
$^{13}C_4$-PFOA	417
$^{13}C_8$-PFOA	421
PFNA	463
$^{13}C_5$-PFNA	468
$^{13}C_9$-PFNA	472
PFOS	499
$^{13}C_4$-PFOS	503
$^{13}C_8$-PFOS	507

To quantify PFAS mass in LCMS vials, rearranging Equation 2 gives the mass of analyte in each glass vial (Eq. 2) and dividing by 1 mL, the volume placed in the vial, gives the final concentration of PFAS in solution.

Equation 3) a) $$MASS_{analyte} = \frac{RRF \times PEAK\ AREA_{analyte} \times MASS_{Int.Std.}}{PEAK\ AREA_{Int.Std.}}$$

Equation 3) b) $$C_{equilibrium} = \frac{MASS_{analyte}}{Volume_{vial}}$$

The q in ng of PFAS sorbed/g Ottawa Sand was measured by difference (Eq. 1) and isotherms were constructed with linear fits in Microsoft Excel. The solid water distribution coefficient (K_d) was estimated by the slope of the linear fits for the isotherms constructed. Linear fits were used as opposed to Freundlich, Langmuir, or BET because the data was linear. K_d values were compared across experiments with the same PFAS in

the presence of different sorption enhancers to deduce which enhancer was the most effective at increasing the sorption over the control conditions.

Background Subtraction and Order of Addition Experiments

In the case that background PFAS levels were detected in the LC-MS system, a background subtraction was performed. The background peak area of the PFAS in question was averaged across all the blanks in the run then was subtracted from the peak areas of the analyte. This was done for both calibration standards and samples. Two sets of calculation were then performed in which the RRF with the area subtracted was applied to the samples with the area subtracted and vice versa. The case in which q was found to be negative (i.e. where the mass analyzed was below that in the blanks) was neglected.

To further describe enhanced sorption of PFASs in groundwater system, order of addition experiments were preformed with PFOS and polyDADMAC. In one set of experiments, the sorbates were added prior to the sorption enhancer. Before and after the addition of the sorption enhancer, the centrifuge tubes were placed on a wrist shaker for 24 hours. The converse was done as well where the enhancer was added first and the analyte 24 hours later.

Results & Discussion

Enhancer Isotherms

Results from Dr. Daniel McInnis' experiments revealed isotherms of sorption enhancers that were best fit using the Langmuir equation. The maximum adsorption (q_{max}), representative of the concentration at which form a monolayer coverage on the sand particles, was estimated using equation 4. Figure 1 shows isotherms constructed with polyDADMAC, polyamine and polyaluminum-chloride on Ottawa Sand.

Equation 4) $$q = \frac{q_{max} * K_l * C_{equilibrium}}{1 + K_l * C_{equilibrium}}$$

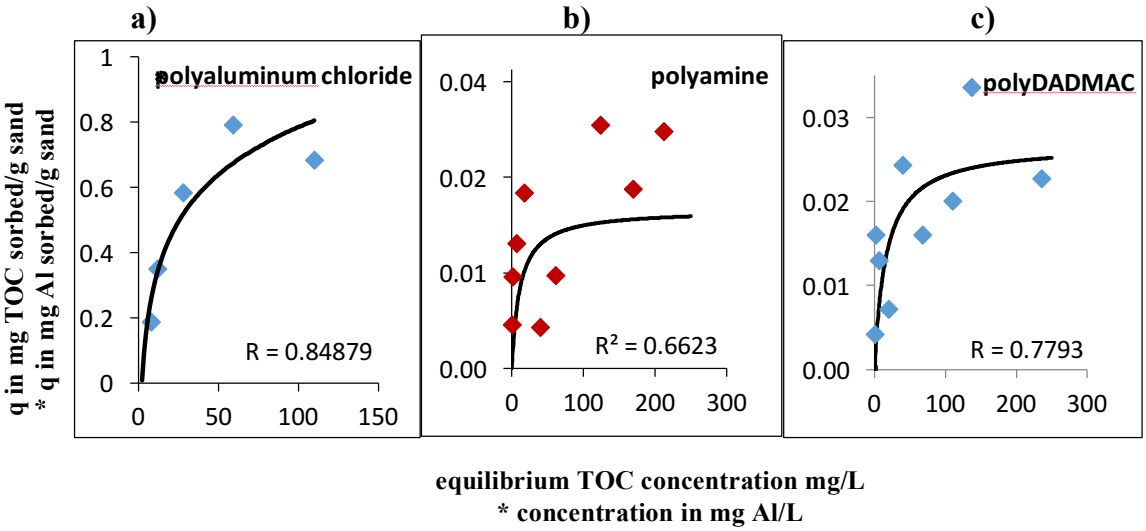


Figure 1) a) polyaluminum chloride adsorption isotherm; optimal dose 100 mg Al/L (courtesy of Tufts University) b) polyamine adsorption isotherm; optimal dose 100 mg polyamine/L c) polyDADMAC adsorption isotherm; optimal dose 100 mg polyDADMAC/L

The q_{max} for PAl-Cl, PA and polyDADMAC were found to be 0.68, .019, and .025 ng enhancer/g sand respectively. The starting dosage for each enhancer was selected at the concentration where q_{max} was reached, 100 mg Al/L for polyaluminum chloride, 100 mg of enhancer for both polyamine and polyDADMAC. Although the isotherm for polyaluminum chloride fits quite well, it would be worthwhile to perform a similar experiment with higher starting concentrations to determine if q_{max} was actually reached. This should be done for polyamine and polyDADMAC as well because their respective isotherms are not quite well as fitted as expected.

Batch Experiments

At the enhancer dosages determined by Daniel McInnis, adsorption batch experiments with the enhancers present were preformed with the six analytes. Linear isotherms were constructed by fitting linear trend-lines in Excel because the data was best fit by a linear equation. K_d was estimated to be the slope of the line using equation 5. K_d's were then compared between the three enhancers and control conditions of no enhancer added. Figure 2 contains graphs of the isotherms constructed with each PFAS and each enhancer. Table 4b shows the % increase in the value of K_d over the control conditions for each PFAS. In all cases, polyDADMAC exhibited the highest increase in sorption for each PFAS. Both polyamine and polyaluminum chloride showed an increase in most cases. Some K_d's, however, were found to be comparable to control conditions and in fewer cases, slightly less.

Equation 5) $q = K_d * C_{equilibrium}$

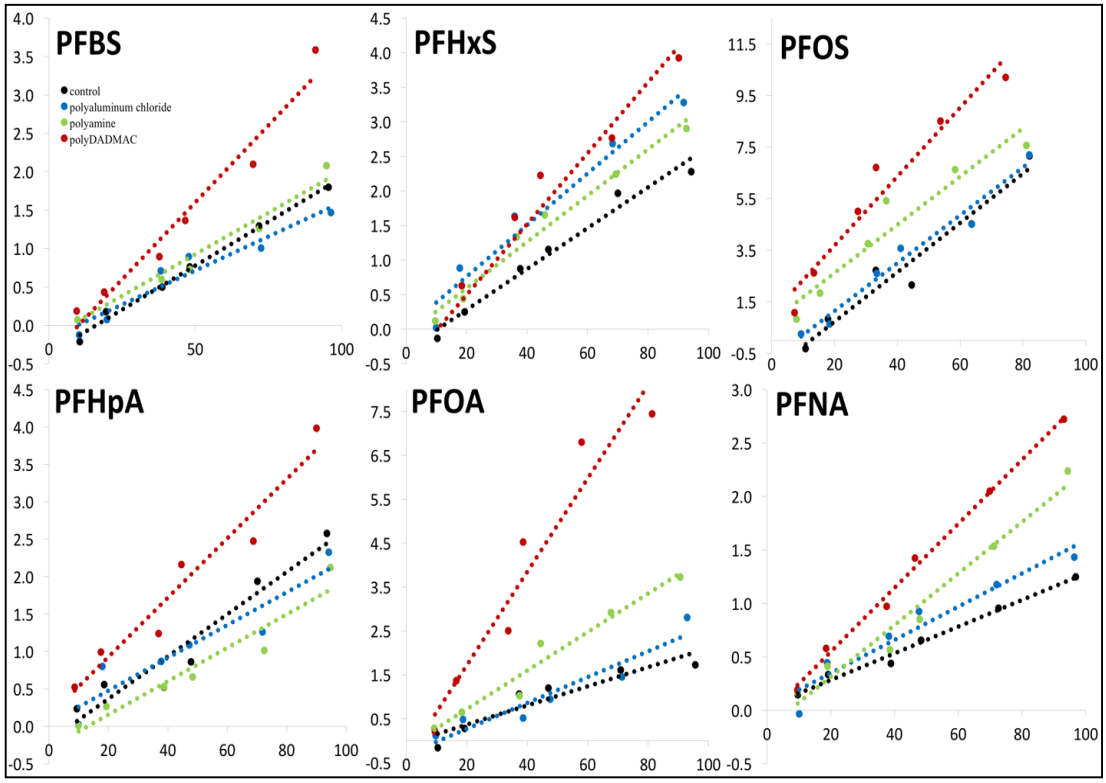


Figure 2) Isotherms for all 6 PFAS on the USEPA UCMR3 List in the presence of polyaluminum chloride, polyamine, polyDADMAC, or no enhancer. Equations for linear fit in appendix a.

Table 4) a) K_d for each sorption batch experiment. b) % increase in K_d over control conditions for all 6 PFASs in the presence of sorption enhancers

a)

K_d (mL/g)	PFBS	PFHxS	PFOS	PFHpA	PFOA	PFNA
Control	.0229 ± .002	.0295 ± .006	.0957 ± .029	.0282 ± .011	.0218 ± .011	.0105 ± .002
POLYDADMAC	.0402 ± .01	.0513 ± .017	.1338 ± .046	.0396 ± .013	.1064 ± .037	.0299 ± .003
PA	.0217± .006	.0335 ± .006	.0935 ± .031	.02 ± .009	.0493 ± .012	.0241 ± .006
PAlC	.0178± .007	.0373 ± .01	.0929 ± .029	.0219 ± .011	.0294 ± .006	.0156 ± .006

b)

% increase in K_d over control	**polyDADMAC (POLYDADMAC)**	**Polyamine (PA)**	**polyaluminum chloride (PAlC)**
PFBS	95%	12%	-13%
PFHxS	73%	31%	52%
PFOS	105%	43%	7%
PFHpA	66%	-29%	-11%
PFOA	378%	100%	18%
PFNA	124%	65%	24%

It is apparent from Figure 2 and Table 4 that polyDADMAC performed the best in terms of enhancing PFAS sorption. At the low end, with PFHpA, K_d was increased by 66% reaching a q_{max} of 3.58 ng PFHpA/g sand as opposed to 1.80 ng PFHpA/g sand without any enhancement of sorption. PFOA displayed the greatest increase in K_d at 378%. PFOA reached a q value of 7.44 ng PFOA/g sand compared to 1.73 ng PFOA/g

sand with no enhancer. Comparing these numbers with a t-test resulted in a p-value of .0012, indicating that they are statistically different. In fact, upon comparing all polyDADMAC experiments with controls, all p-values were <.05. Polyamine increased the sorption in all cases but PFHpA with a decrease of K_d of -29%. However, some increases of sorption by polyamine may not be significant, showing an increase of 12% for PFBS. Polyaluminum chloride showed an increase for all but two PFASs, PFBS and PFHpA. These showed a decrease of -13% and -11% respectively. And yet, even in the cases where polyaluminum chloride was increased, some may not be considered as significant, such as PFOS which showed an increase of only 7%.

PolyDADMAC and polyamine are both organic compounds while polyaluminum chloride is inorganic and contains metals. Organic matter sorption is closely correlated to organic carbon content of the sorbent. Therefore, it is reasonable to expect less sorption using an inorganic enhancer when compared to organic substances such as polyDADMAC or polyamine. One reason that polyamine may not be as effective a sorption enhancer may have to do with the mechanism by which sorption is enhanced. Both polyDADMAC and polyamine are cationic, having a positive charge. This charge is the proposed component that increases sorption by electrostatically attracting the anionic PFASs. However, the nitrogen that produces the positive charge in polyamine is adjacent to two methyl (CH_3) groups and a polar hydroxide (OH) which may introduce steric hindrance.

It is also widely known that longer chain perfluorinated compounds and sulfonates are generally more effective at partitioning to surfaces and organic matter than

their shorter chained and acid head-group counterparts. This may be in part what is contributing to PFOS showing the highest sorption under control conditions and in the presence of enhancers amongst all six PFASs investigated. Amongst all acids, the longer chain PFOA, although not the longest, shows the strongest sorption both under control conditions and in the presence of polyDADMAC among the three acids. PFNA sorption is increased in the presence of polyDADMAC, though not nearly as much as PFOA. This may indicate a maximum chain-length of PFASs at which the enhancers' efficacy decreases.

Order of Addition

Because polyDADMAC was determined to be most effective enhancer based (Table 4), order of addition batch experiments were performed with PFOS and polyDADMAC. Two different isotherms were constructed and compared, one in for which the analyte (PFOS) was added before the enhancer and vice-a-versa. Figure 3 shows the two different cases as well as control sorption of PFOS and simultaneous addition of PFOS and POLYDADMAC. In Figure 3, it is apparent at first glance that adding the analyte first may have slightly more enhanced sorption, especially at lower PFOS concentrations. However, a two tailed t-test resulted in a p-value of .29, indicating that the two cases are not significantly different. Additionally, in later order of addition batch experiments where the initial concentration of polyDADMAC was increased, it can be clearly seen that any effect the order in which enhancer and analyte are added has on PFOS sorption seems to diminish.

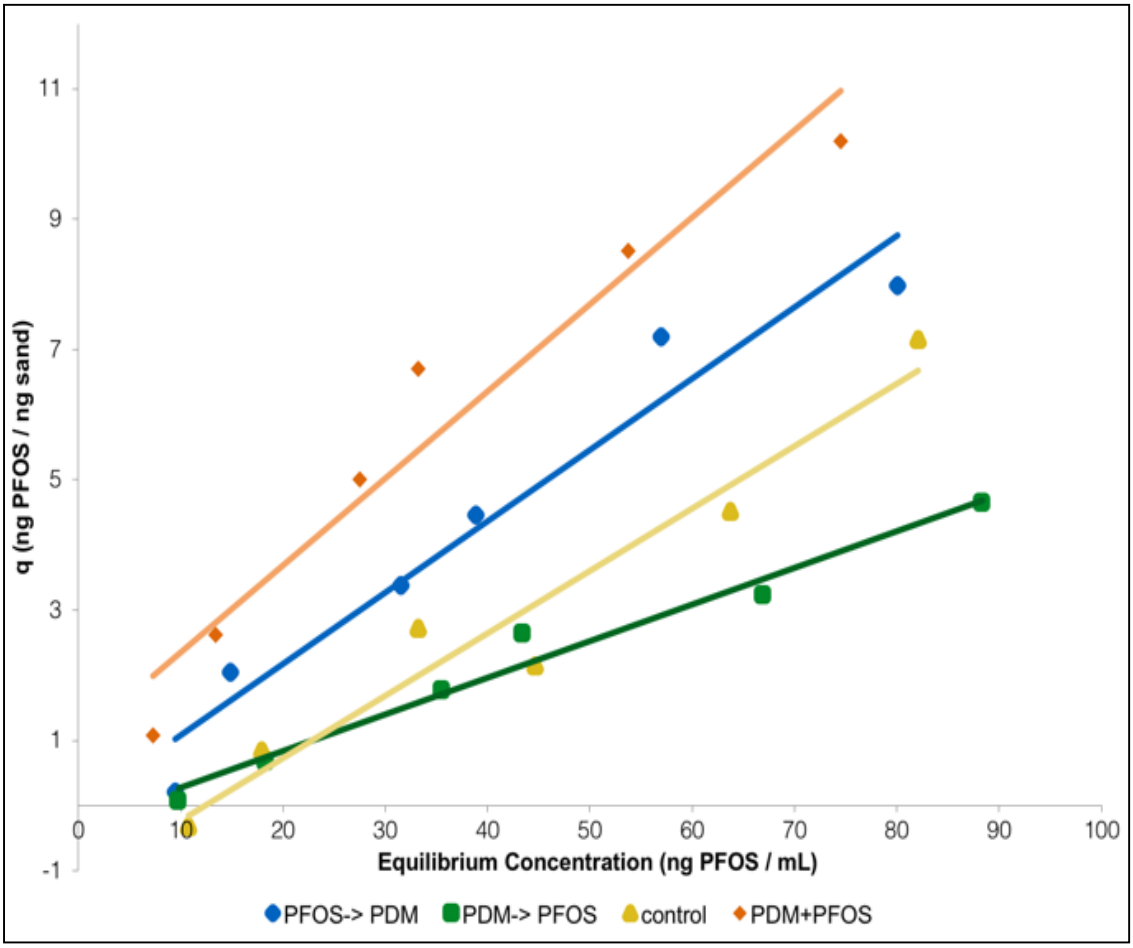


Figure 3) Isotherm for order of addition batch experiments for PFOS and polyDADMAC. Including isotherms for control PFOS sorption and simultaneous addition of POLYDADMAC and PFOS. Equations for linear fits in appendix B.

Table 5) Isotherm for order of addition batch experiments for PFOS and polyDADMAC. Including isotherms for control PFOS sorption and simultaneous addition of POLYDADMAC and PFOS. Equations for linear fits in appendix B.

Experiment	K_d (mL/g)
Control	.0957± .029
PFOS → POLYDADMAC	.1096 ± .034
POLYDADMAC → PFOS	.0563 ± .011
PFOS + POLYDADMAC	.1338 ± .041

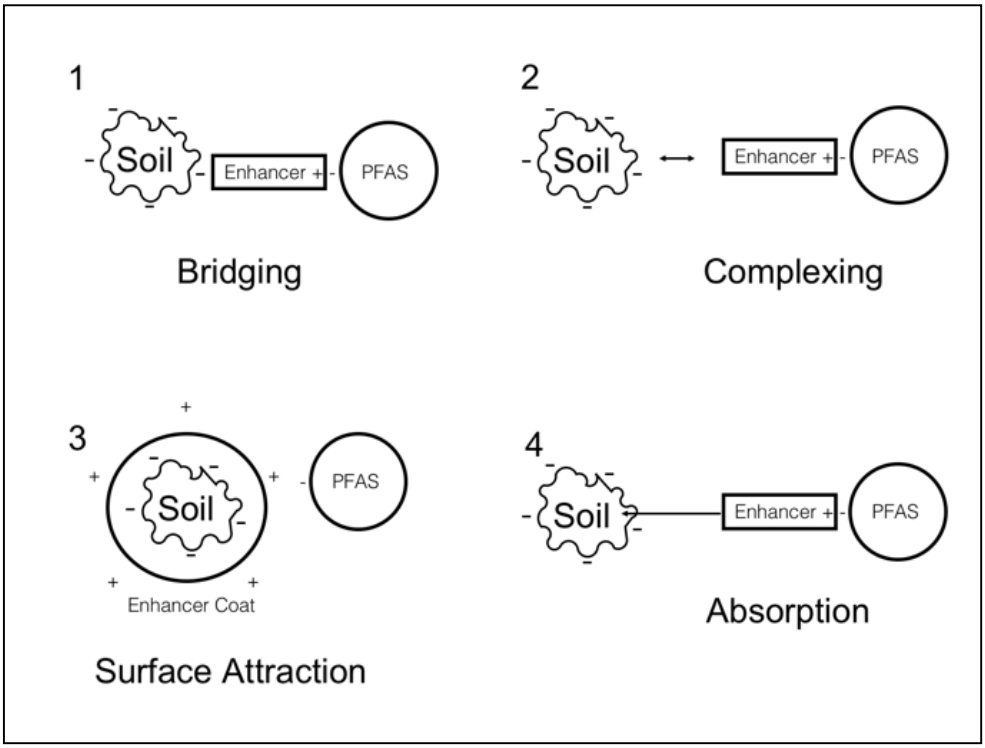


Figure 4) Proposed mechanisms for enhancement of PFAS sorption. 1) POLYDADMAC bridge to overcome negative charge on soil particle. 2) PFOS-POLYDADMAC complex sorbing onto soil complex. 3) POLYDADMAC coat around soil particle attracting PFAS. 4) absorption of PFAS into soil associated organic matter.

The order of addition isotherms revealed that the order in which the components of the experiments have a significant effect on the sorption of PFOS. Absorption can be ruled out as a main driver of PFAS sorption Ottawa sand is very low in organic content, so there is no organic matter for PFASs to sorb into. Figure 3 shows that there is a significant increase in Kd when POLYDADMAC is added before the PFOS. The addition of PFOS before POLYDADMAC resulted in a K_d of 0.1302 mL/g as opposed to .0563 mL/g for the case where POLYDADMAC was added before PFOS, which is an increase of approximately 131%. Because adding enhancer first does not increase the

sorption of PFOS, this provides insight in to the mechanism of enhanced sorption of PFOS. When adding polyDADMAC to the solution first, POLYDADMAC molecules may sorb to available sites on the Ottawa sand particles. Then, when the PFOS is added, available sites are occupied by the more strongly sorbed POLYDADMAC. This would explain why we see a substantial decrease in K_d for POLYDADMAC → PFOS experiments relative to the PFOS → POLYDADMAC. It would also explain why the K_d of the control experiments is greater than the POLYDADMAC → PFOS. In terms of mechanisms, this rules out bridging and coating because an increase of sorption when POLYDADMAC is added first would be expected if either of these mechanisms are the main driver of PFOS sorption. Comparing these results to simultaneous addition results also provide some insight into the mechanism of sorption. Simultaneous addition of the enhancer resulted in both slightly higher q values and a greater K_d than PFOS → POLYDADMAC experiments. This points to complexing being the main driver of enhanced sorption.

Finally, even though there was greatly increased sorption in some cases in the presence of polyDADMAC, none of the isotherms showed a decrease in equilibrium concentrations of PFAS under the suggested health limit of 0.3 ng/mL. However, these experiments were performed on Ottawa Sand, a mineral with less surface area and organic carbon content than natural soils, such as the material from the site on which this project focuses. Both of these properties are correlated with PFAS sorption. We hypothesize that repeating this process with material from an actual site will result in not only stronger sorption of enhancers, but PFASs sorption stronger still in the presence of

enhancers. In fact, preliminary tests have shown that enhancer sorption on the soil is greatly increased relative to Ottawa Sand (Figure 5). On Tinker Air Force Base (TAFB) soil, q_{max} for polyDADMAC and poly amine are 6.99 and 8.11mg enhancer /g soil respectively, two orders of magnitude greater than q_{max} values on sand.

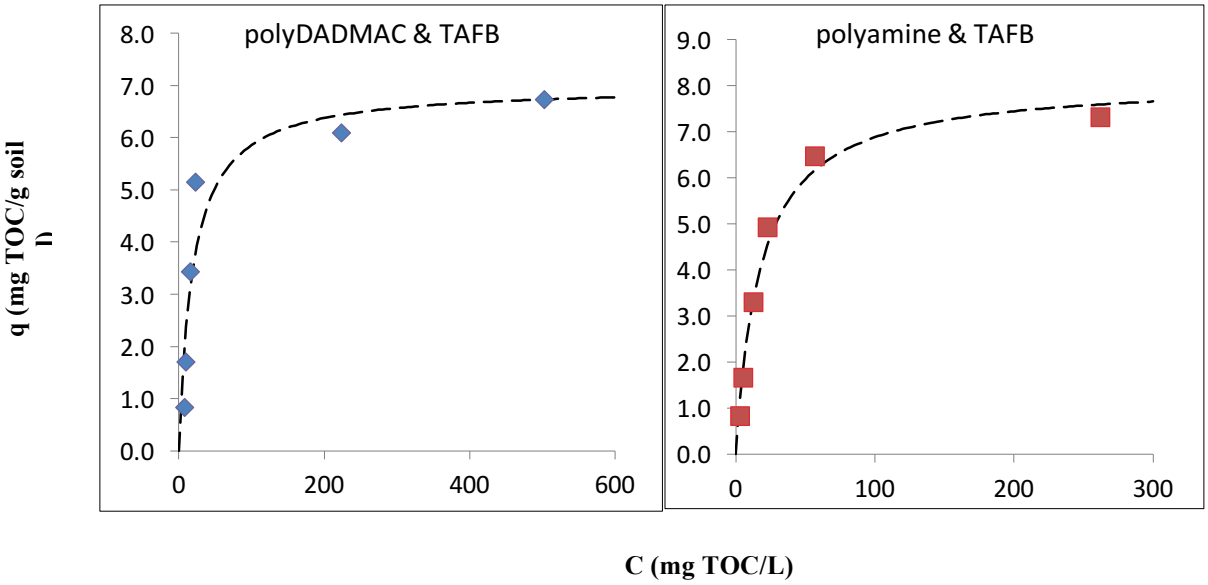


Figure 5) Isotherms polyDADMAC and polyamine on Tinker Air Force Base Soil. q_{max} polyDADMAC; 6.99 mg polyDADMAC/ g soil q_{max} polyamine; 8.11 mg polyamine/g soil.

Conclusion & Future Work

PFASs have all the necessary components to warrant environmental concern; they are toxic, bio-accumulative and highly persistent. Water is one of the most important reserves of PFASs in the environment due to their high solubility. Ground water contamination is of the utmost importance given ground waters' ubiquitous and direct use by humans for drinking, agriculture, municipal services and industry. This contributes to a large source of exposure to these harmful chemicals. Some widely used treatment methods have been shown to be effective to remove PFASs from water. New technologies have been tested showing a range of outcomes. There is still a need, however, for the development of an *in-situ* remediation technique of PFASs in groundwater.

Enhanced sorption may be a viable technology and solution to this problem. By enhancing sorption of PFASs and thus sequestering them onto aquifer materials, their aqueous concentrations can be decreased rendering contaminated water once again safe. Of the three enhancers investigated, polyDADMAC performed the best in terms of enhancing sorption for all 6 PFAS on the USEPA UCMR3 List. We also investigated whether or not the order of addition of enhancer (polyDADMAC) and PFAS (PFOS) had an effect on the enhancement of the sorption. It was found that as polyDADMAC starting dose increased, the slight advantage of adding the PFAS first diminished. These order of addition experiments also revealed that as the starting dose of polyDADMAC increased past what was predetermined at the optimal starting dose, equilibrium PFOS concentration decreased. This may indicate that monolayer coverage was not in fact

achieved, or additional layers on the surface of the sand were formed by the increased concentration. A recommendation for future work, as previously stated, would be to construct isotherms for enhancers at higher concentrations above what was initially done in order to see if we had truly captured maximum adsorption for each enhancer.

The results from this project holds implications for the *in-situ* remediation of PFAS contaminated groundwater. Before any further steps are taken, however, we will repeat these batch adsorption experiments on soil excavated from Tinker Air Force Base in Oklahoma. This will be done in order to determine if these enhancers are at least as effective on soil with higher surface area and higher organic carbon content than Ottawa Sand. Once this is done, we will conduct further studies in order to inquire into the environmental fate and transport of PFAS in the absence and presence of enhancers. This will be accomplished by constructing one-dimensional columns to determine breakthrough curves for PFASs in the presence of enhancers, developing a slow release system to deliver a constant dose of enhancer and examine the effects of co-contaminants likely to be found in similar sites such as diesel. PFASs are a proven hazard to environmental and human health. And so they present an important target for environmental chemistry research. This project is a small step towards developing important technology for the viable and effective treatment of ground water contaminated with PFASs and other persistent organic pollutants.

Bibliography

- Armitage, James, Ian T. Cousins, Robert C. Buck, Konstantinos Prevedouros, Mark H. Russell, Matthew Macleod, and Stephen H. Korzeniowski. "Modeling Global-Scale Fate and Transport of Perfluorooctanoate Emitted from Direct Sources." Environmental Science & Technology Environ. Sci. Technol. 40.22 (2006): 6969-975.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. and van Leeuwen, S.P. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integrated Environmental Assessment and Management 7 (4), 513–541.
- Calafat, A.M., Kuklenyik, Z., Reidy, J.A., Caudill, S.P., Tully, J.S. and Needham, L.L. 2007. Serum concentrations of 11 polyfluoroalkyl compounds in the U.S. population: Data from the national health and nutrition examination survey (NHANES). Environmental Science & Technology 41 (7), 2237–2242.
- Carter, Kimberly E., and James Farrell. "Oxidative Destruction of Perfluorooctane Sulfonate Using Boron-Doped Diamond Film Electrodes." Environmental Science & Technology Environ. Sci. Technol.42.16 (2008): 6111-115
- Cheng, Jie, Chad D. Vecitis, Hyunwoong Park, Brian T. Mader, and Michael R. Hoffmann. "Sonochemical Degradation of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Landfill Groundwater: Environmental Matrix Effects." *Environmental Science & Technology Environ. Sci. Technol.* 42.21 (2008): 8057-063
- Cui, L., Zhou, Q.-F., Liao, C.-Y., Fu, L.-J. and Jiang, G.-B. 2009. Studies on the toxicological effects on PFOA and PFOS on rats using histological observation and chemical analysis. Archives of Environmental Contamination and Toxicology 56 (2), 338–349.
- Epa, Us. Long-Chain Perfluorinated Chemicals (PFCs) Action Plan (n.d.): n. pag.

- Fei, C., McLaughlin, J.K., Lipworth, L. and Olsen, J. 2009. Maternal levels of perfluorinated chemicals and subfecundity. Human Reproduction 1 (1), 1–6
- Fernández-Sanjuan, María, Johan Meyer, Joana Damásio, Melissa Faria, Carlos Barata, and Silvia Lacorte. "Screening of Perfluorinated Chemicals (PFCs) in Various Aquatic Organisms." Analytical and Bioanalytical Chemistry Anal Bioanal Chem 398.3 (2010): 1447-456.
- Filipovic, Marko, Andreas Woldegiorgis, Karin Norström, Momina Bibi, Maria Lindberg, and Ann-Helen Österås. "Historical Usage of Aqueous Film Forming Foam: A Case Study of the Widespread Distribution of Perfluoroalkyl Acids from a Military Airport to Groundwater, Lakes, Soils and Fish." Chemosphere 129 (2015): 39-45
- Giesy, J., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 35, 1339–1342.
- Haukås, Marianne, Urs Berger, Haakon Hop, Bjørn Gulliksen, and Geir W. Gabrielsen. "Bioaccumulation of Per- and Polyfluorinated Alkyl Substances (PFAS) in Selected Species from the Barents Sea Food Web." Environmental Pollution 148.1 (2007): 360-71
- Higgins, Christopher P., and Richard G. Luthy. "Sorption of Perfluorinated Surfactants on Sediments †." Environmental Science & Technology Environ. Sci. Technol. 40.23 (2006): 7251-256.
- Higgins, Christopher P., Pamela B. Mcleod, Laura A. Macmanus-Spencer, and Richard G. Luthy. "Bioaccumulation of Perfluorochemicals in Sediments by the Aquatic Oligochaete Lumbriculus Variegatus."Environmental Science & Technology Environ. Sci. Technol. 41.13 (2007): 4600-606
- Hoffman, K., Webster, T.F., Weisskopf, M.G., Weinberg, J. and Vieira, V.M. 2010. Exposure to polyfluoroalkyl chemicals and attention deficit/hyperactivity disorder in U.S. children 12–15 years of age. Environmental Health Perspectives 118 (12), 1762–1767

- Kallenborn, Roland, Urs Berger, and Ulf Järnberg. Perfluorinated Alkylated Substances (PFAS) in the Nordic Environment. Kbh.: Nordisk Ministerråd, 2004. Print.
- Hu, W., Jones, P.D., Upham, B.L., Trosko, J.E., Lau, C. and Giesy, J.P. 2002. Inhibition of gap junctional intercellualr communication by perfluorinated compounds in rat liver and dolphin kidney epithelial cell lines *in Vitro* and Sprague–Dawley rats *in Vivo*. Toxicological Sciences 68 (2), 429–436
- Johnson, Ramona L., Amy J. Anschutz, Jean M. Smolen, Matt F. Simcik, and R. Lee Penn. "The Adsorption of Perfluorooctane Sulfonate onto Sand, Clay, and Iron Oxide Surfaces." Journal of Chemical & Engineering Data J. Chem. Eng. Data 52.4 (2007): 1165-170
- Kaŕrman,A.;Elgh-Dalgren,K.Environmentallevelsand distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination. Environ. Chem. 2011, 8, 372−380.
- Kwon, Bum Gun. "Reply to Comment on “Biodegradation of Perfluorooctanesulfonate (PFOS) as an Emerging Contaminant”." *Chemosphere* 138 (2015): 1039-044
- Lee, Youn Ju, Min-Kyun Kim, Jisuk Bae, and Jae-Ho Yang. "Concentrations of Perfluoroalkyl Compounds in Maternal and Umbilical Cord Sera and Birth Outcomes in Korea." Chemosphere 90.5 (2013): 1603-609
- Lemal, David M. "Perspective on Fluorocarbon Chemistry." The Journal of Organic Chemistry 69 (2009): 1-11
- Lin, Hui, Junfeng Niu, Shiyuan Ding, and Lilan Zhang. "Electrochemical Degradation of Perfluorooctanoic Acid (PFOA) by Ti/SnO2–Sb, Ti/SnO2–Sb/PbO2 and Ti/SnO2–Sb/MnO2 Anodes." Water Research 46.7 (2012): 2281-289.
- Lindstrom, Andrew B., Mark J. Strynar, and E. Laurence Libelo. "Polyfluorinated Compounds: Past, Present, and Future." Environmental Science & Technology Environ. Sci. Technol. 45.19 (2011): 7954-961.

- Liu, C.s., C.p. Higgins, F. Wang, and K. Shih. "Effect of Temperature on Oxidative Transformation of Perfluorooctanoic Acid (PFOA) by Persulfate Activation in Water." Separation and Purification Technology 91 (2012): 46-51
- Martin, J.W., Whittle, M., Muir, D.C.G. and Mabury, S.A. 2004b. Perfluoroalkyl contaminants in food web from Lake Ontario. Environmental Science & Technology 38 (20), 5379–5385.
- Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003a. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). Environ. Toxicol. Chem. 22, 196–204.
- Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003b. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss). Environ. Toxicol. Chem. 22, 189–195.
- Moody, Cheryl A., Jonathan W. Martin, Wai Chi Kwan, Derek C. G. Muir, and Scott A. Mabury. "Monitoring Perfluorinated Surfactants in Biota and Surface Water Samples Following an Accidental Release of Fire-Fighting Foam into Etobicoke Creek." Environmental Science & Technology Environ. Sci. Technol. 36.4 (2002): 545-51.
- Moody, C.A., Hebert, G.N., Strauss, S.H. and Field, J.A. 2003. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. Journal of Environmental Monitoring 5, 341–345.
- Post, Gloria B., Perry D. Cohn, and Keith R. Cooper. "Perfluorooctanoic Acid (PFOA), an Emerging Drinking Water Contaminant: A Critical Review of Recent Literature." Environmental Research 116 (2012): 93-117
- Santos, Aurora, Sergio Rodríguez, Fernando Pardo, and Arturo Romero. "Use of Fenton Reagent Combined with Humic Acids for the Removal of PFOA from Contaminated Water." *Science of The Total Environment* (2015)
- Schaefer, Charles E., Christina Andaya, Ana Urtiaga, Erica R. Mckenzie, and Christopher P. Higgins. "Electrochemical Treatment of Perfluorooctanoic Acid

(PFOA) and Perfluorooctane Sulfonic Acid (PFOS) in Groundwater Impacted by Aqueous Film Forming Foams (AFFFs)." *Journal of Hazardous Materials* 295 (2015): 170-75

- Shih, Kaimin, and Fei Wang. "Adsorption Behavior of Perfluorochemicals (PFCs) on Boehmite: Influence of Solution Chemistry." Procedia Environmental Sciences 18 (2013): 106-13
- Suja, F., Pramanik, B.K. and Zain, S.M. 2009. Contamination, bioaccumulation and toxic effects of perfluorinated chemicals (PFCs) in the water environment: A review paper. Water Science and Technology 60 (6), 1533–1544.
- Stock, N.L., Muir, D.C.G. and Mabury, S. 2010. Perfluoroalkyl Compounds. In *Persistent Organic Pollutants*; Harrad, S., (ed), pp. 25–70, Wiley: Chichester, UK
- Tabtong, Wadcharid, Suwanna Kitpati Boontanon, and Narin Boontanon. "Fate and Risk Assessment of Perfluoroalkyl Substances (PFASs) in Water Treatment Plants and Tap Water in Bangkok, Thailand." Procedia Environmental Sciences 28 (2015): 750-57.
- Takagi, S., Adachi, F., Miyano, K., Koizumi, Y., Tanaka, H., Mimura, M., Watanabe, I., Tanabe, S. and Kannan, K. 2008. Perfluorooctanesulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan. Chemosphere 72 (10), 1409–1412.
- Takagi, S., Adachi, F., Miyano, K., Koizumi, Y., Tanaka, H., Watanabe, I., Tanabe, S. and Kannan, K. 2011. Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes. Water Research 45 (13), 3925–3932.
- Thompson, Jack, Geoff Eaglesham, Julien Reungoat, Yvan Poussade, Michael Bartkow, Michael Lawrence, and Jochen F. Mueller. "Removal of PFOS, PFOA and Other Perfluoroalkyl Acids at Water Reclamation Plants in South East Queensland Australia." Chemosphere 82.1 (2011): 9-17
- Urtiaga, Ane, Carolina Fernández-González, Sonia Gómez-Lavín, and Inmaculada Ortiz. "Kinetics of the Electrochemical Mineralization of Perfluorooctanoic Acid on Ultrananocrystalline Boron Doped Conductive Diamond Electrodes." Chemosphere 129 (2015): 20-26

- V. Ochoa-Herrera, R. Sierra-Alvarez, Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge, Chemosphere 72 (2008) 1588–1593
- Urtiaga, Ane, Carolina Fernández-González, Sonia Gómez-Lavín, and Inmaculada Ortiz. "Kinetics of the Electrochemical Mineralization of Perfluorooctanoic Acid on Ultrananocrystalline Boron Doped Conductive Diamond Electrodes." Chemosphere 129 (2015): 20-26
- Vecitis, Chad D., Hyunwoong Park, Jie Cheng, Brian T. Mader, and Michael R. Hoffmann. "Treatment Technologies for Aqueous Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA)." *Front. Environ. Sci. Eng. China Frontiers of Environmental Science & Engineering in China* 3.2 (2009): 129-51
- Wang, Ling, Yu Wang, Yong Liang, Jia Li, Yuchen Liu, Jie Zhang, Aiqian Zhang, Jianjie Fu, and Guibin Jiang. "PFOS Induced Lipid Metabolism Disturbances in BALB/c Mice through Inhibition of Low Density Lipoproteins Excretion." Sci. Rep. Scientific Reports 4 (2014)
- Wilhelm, M., Bergmann, S. and Dieter, H.H. 2010. Occurrence of perfluorinated compounds (PFCs) in drinking water of North Rhine-Westphalia, Germany and new approach to assess drinking water contamination by shorter-chained C4–C7 PFCs. International Journal of Hygiene and Environmental Health 213 (3), 224–232.
- Xiao, Feng, Matt F. Simcik, Thomas R. Halbach, and John S. Gulliver. "Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Soils and Groundwater of a U.S. Metropolitan Area: Migration and Implications for Human Exposure." Water Research 72 (2015): 64-74.
- Xiao, Feng, Matt F. Simcik, and John S. Gulliver. "Mechanisms for Removal of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) from Drinking Water by Conventional and Enhanced Coagulation." Water Research 47.1 (2013): 49-56

- Xiao, Feng, Xiangru Zhang, Lee Penn, John S. Gulliver, and Matt F. Simcik. "Effects of Monovalent Cations on the Competitive Adsorption of Perfluoroalkyl Acids by Kaolinite: Experimental Studies and Modeling."Environmental Science & Technology Environ. Sci. Technol. 45.23 (2011): 10028-0035. Web
- Xioana, Li. "Enhanced Adsorption of PFOA and PFOS on Multiwalled Carbon Nanotubes under Electrochemical Assistance." *ResearchGate*. N.p., n.d.
- Yeung, L.W.Y., Loi, E.I.H., Wong, V.Y.Y., Guruge, K.S., Yamanaka, N., Tanimura, N., Hasegawa, J., Yamashita, N., Miyazaki, S. and Lam, P.K.S. 2009. Biochemical responses and accumulation properties of long-chain perfluorinated compounds (PFOS/PFDA/PFOA) in juvenile chickens (*Gallus gallus*) Archives of Environmental Contamination and Toxicology 57 (2), 377–386.
- Zhang, Chunhui, Yi Peng, Ke Ning, Xiameng Niu, Shuhui Tan, and Peidong Su. "Remediation of Perfluoroalkyl Substances in Landfill Leachates by Electrocoagulation." *Clean Soil Air Water CLEAN - Soil, Air, Water* 42.12 (2014): 1740-743
- Zhang, Kunlun, Jun Huang, Gang Yu, Qiwu Zhang, Shubo Deng, and Bin Wang. "Destruction of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA) by Ball Milling." *Environmental Science & Technology Environ. Sci. Technol.* (2013)

Appendix A

Linear Fits	PFBS	PFHxS	PFOS	PFHpA	PFOA	PFNA
Control	y = 0.0229x - 0.3666 R^2 = 0.99305	y = 0.0295x - 0.3087 R^2 = 0.97587	y = 0.0957x - 1.1824 R^2 = 0.94706	y = 0.0282x - 0.1955 R^2 = 0.92039	y = 0.0218x - 0.0691 R^2 = 0.86866	y = 0.0105x - 0.0812 R^2 = 0.99649
POLYDADMAC	y = 0.0402x - 0.4059 R^2 = 0.96149	y = 0.0513x - 0.5279 R^2 = 0.93557	y = 0.1338x + 1.0062 R^2 = 0.94669	y = 0.0396x + 0.1332 R^2 = 0.94288	y = 0.1064x - 0.4117 R^2 = 0.9307	y = 0.0299x - 0.0491 R^2 = 0.99428
PA	y = 0.0217x - 0.1581 R^2 = 0.95325	y = 0.0335x - 0.0771 R^2 = 0.97888	y = 0.0935x + 0.7495 R^2 = 0.91773	y = 0.0224x - 0.2915 R^2 = 0.91891	y = 0.0439x - 0.1608 R^2 = 0.95603	y = 0.0241x - 0.1677 R^2 = 0.96743
PAlC	y = 0.0178x - 0.173 R^2 = 0.92487	y = 0.0373x + 0.0155 R^2 = 0.95726	y = 0.0929x - 0.7159 R^2 = 0.97098	y = 0.0219x + 0.0425 R^2 = 0.87212	y = 0.0294x - 0.317 R^2 = 0.90466	y = 0.0158x + 0.0365 R^2 = 0.92963

Appendix B

Experiment	K_d (mL/g)
Control	y = 0.0957x - 1.1824 R^2 = 0.94706
PFOS → POLYDADMAC	y = 0.1096x - 0.0198 R^2 = 0.94556
POLYDADMAC → PFOS	y = 0.0563x - 0.2899 R^2 = 0.97603
PFOS + POLYDADMAC	y = 0.1338x + 1.0062 R^2 = 0.94669

Appendix C – Raw Data

PEAK AREA

PFBS – Calibration Standard

299	402	RRF
8632.3	14960.9	1.73313022
11426.7	18965	1.659709277
12292.2	22000.8	1.789817933
11564.1	20590.6	1.780562257
10752.5	19115.1	1.77773541
9427.6	16541.9	1.754624719
12066.6	20801.1	1.72385759
9810.8	16952.2	1.727912097
5156.4	9286.6	1.800985183
	average	**1.749814965**

PFHxS – Calibration standard

399	402	RRF
24463.8	24412.3	0.997894849
20983.2	20739	0.988362118
21725.7	21645.8	0.996322328
19946.8	20939.1	1.049747328
20333.2	20127.7	0.989893376
21102.6	21789.8	1.032564708
20537.5	20879.8	1.016667072
20932.5	20741.7	0.990884987
20640.5	20582.2	0.997175456
	average	**1.006612469**

399	403	RRF
54688	53621.2	0.980492978
56043.2	57292.8	1.022297085
42918.6	51789.1	1.206681951
	average	**1.069824005**

PFOS – Calibration Standard

499	507	RRF
101529.6	52823.8	0.5202798
108179.6	52571.3	0.485963158
102103.9	52384.6	0.513051901
100550.8	53279.2	0.529873457
	average	**0.512292079**

499	503	RRF
62139.4	78158.4	1.257791353
63454.8	78984.7	1.244739563
61408.4	76750.4	1.249835527
	average	**1.250788814**

PFHpA – Calibration Standard

363	367	RRF
32830	34580.3	1.053314042
30134.6	31144.7	1.033519609
32060.9	32780.1	1.022432309
31805.3	37799.1	1.188452868
31092	33445	1.075678631
31166.6	32748.5	1.050756258
31993.8	32980.4	1.030837225
30665.2	34235.9	1.116441439
30480.3	32887.9	1.078988724
	average	**1.072269012**

PFOA – Calibration Standard

413	421	RRF
35136.6	38625.3	1.09928963
59767.3	53828.8	0.900639647
58695.4	51150.7	0.871460114
59332.9	52158.9	0.879089005
63794.3	53850.1	0.84412087
64112.5	54432.2	0.849010723
62682.3	53490.5	0.853358923
61164.6	51817.8	0.847186117
61056.9	52924.9	0.86681276
	average	**0.890107532**

PFNA – Calibration Standard

463	472	RRF
18773.7	18242.7	0.971715751
20600.7	23069	1.119816317
20915.5	21609.4	1.033176352
20981.7	22816.9	1.087466697
20584.4	23220.9	1.128082431
21382.6	22729.4	1.062985792
22362.6	23313.9	1.042539776
20057	20581.6	1.026155457
20399.9	21335.6	1.045867872
	average	**1.05753405**

C_0 (ng/mL)	**m/z**	**m/z (labeled standard**	**mass (ng)**
PFBS – Control	**299**	**402**	
10	1684.7	28310.7	10.41271791
10	1884.7	29879.6	11.03721713
10	1500.2	25872	10.14638398
		average	**10.53210634**
20	3441.5	31292.7	19.24406754

20	3832.5	31231.7	21.47230534
20	2534.2	24704.9	17.9493994
		average	**19.55525743**
40	7213.7	31899.8	39.56965393
40	6515	29758.1	38.3090477
40	5063	23078.3	38.38806734
		average	**38.75558966**
50	8725.6	31818.4	47.98539764
50	8936.9	32400.6	48.26429657
50	6046.9	22016.9	48.05833847
		average	**48.10267756**
75	13579.1	**33410.3**	**71.11852592**
75	15092.4	37284.7	70.83041544
75	14069.9	33557	73.36687448
		average	**71.77193861**
100	17046.9	31270.5	95.38997241
100	18740.2	33838.4	96.90730963
100	15516.5	28818.3	94.21445556
		average	**95.50391254**

PFBS – polyDADMAC

10	1882.9	35349.9	9.320328101
10	1833.4	34371.5	9.333636359
10	1444.5	25371.2	9.962507755
		average	**9.538824072**
20	4235.9	37683.7	19.6690913
20	3250.5	30972.8	18.36376969
20	2595.5	24235.5	18.73963744
		average	**18.92416614**
40	8664.5	38667.7	39.20913855
40	6798.9	30676.2	38.78191303
40	4837.6	23978.7	35.301768
		average	**37.76427319**
50	9566	35611.2	47.0041175
50	9577.4	35984.1	46.57245334
50	5363.1	20313.7	46.19755547
		average	**46.59137544**
75	14256.5	36116.8	69.07100725
75	12424.4	31824.6	68.31319635

75	6883.3	16755.9	71.88215249
		average	**69.75545203**
100	20016.8	37985.5	92.20807122
100	15466.8	30104.3	89.90090665
100	9517.7	18297.4	91.01956685
		average	**91.04284824**

PFBS – polyAmine

10	2141.2	38646.8	9.694732495
10	2174.2	38227	9.952253049
10	1342.6	23925.5	9.819237295
		average	**9.82207428**
20	4634.8	35226.2	23.02275739
20	3294.7	31989.2	18.02206832
20	1705.3	19009.6	15.69711893
		average	**18.91398155**
40	8608.5	36104.7	41.72111229
40	6475.2	34212.7	33.11753264
40	4825.1	20747.1	40.69500006
		average	**38.51121499**
50	9168.9	33028.9	48.57527424
50	9577.4	33824.2	49.54641405
50	8961.6	33773.6	46.43017654
		average	**48.18395494**
75	14817.3	36342.2	71.34277451
75	10497.7	26399.6	69.58072443
75	6009.1	14089	74.63136714
		average	**71.85162203**
100	19363.4	36415.6	93.04355213
100	15896.9	29088.2	95.62858504
100	7507.9	13722.9	95.73367173
		average	**94.8019363**

PFBS – poly-aluminum chloride

10	1723.3	54670.7	8.671445048
10	2331.4	52811.8	12.14425968
10	1811.3	49195.1	10.12870126
		average	**10.314802**

20	3871.9	53894	19.76373113
20	3769.8	52281.4	19.83610161
20	3510.1	48668	19.8408929
		average	**19.81357521**
40	7427.6	55209.6	37.01000381
40	7729.2	54810.5	38.79323562
40	7354.2	52018.9	38.89192997
		average	**38.23172313**
50	10031.2	55466	49.75208261
50	8754.5	51561.5	46.70797368
50	9007	52898.2	46.84082022
		average	**47.76695883**
75	14884.1	55476.8	73.806804
75	13548.6	53606.1	69.52891172
75	13865	51455.1	74.127042
		average	**72.48758591**
100	20747.5	60280.7	94.68315246
100	19464.2	56721.7	94.40011921
100	18820.3	51821	99.90931362
		average	**96.33086176**

PFHxS – Control	**399**	**402/403* (*PAlC)**	
10	4567.3	46512.2	9.884501244
10	4232.1	40540.6	10.50818845
10	4117.6	39070.7	10.60852652
		average	**10.33373874**
20	7824	38372.1	20.52463193
20	7010.1	38303.2	18.42261425
20	7274	38143.8	19.19603104
		average	**19.38109241**
40	14236.9	38287.9	37.42966938
40	14079.9	38002.2	37.29519949
40	14671.6	38148.4	38.71357283
		average	**37.8128139**
50	18309	38985.4	47.27425936
50	18059.3	38414.2	47.32288605
50	18051.8	38869.8	46.74878312
		average	**47.11530951**
75	28387.9	40762.1	70.10335776

75	28047	40483.2	69.73867373
75	28413.1	40611.6	70.42561095
		average	**70.08921415**
100	36227.1	38647	94.35825183
100	35087.8	37792.2	93.45791072
100	35086	37140.8	95.09215911
		average	**94.30277389**

PFHxS – polyDADMAC

10	4546.7	40376	11.33535462
10	4617.4	36878.2	12.60346288
10	3953.6	38687.7	10.28683846
		average	**11.40855199**
20	6406.1	38293.5	16.83956059
20	6846	36418.8	18.92227573
20	6702.8	34558.7	19.52364792
		average	**18.42849474**
40	13613	38664.7	35.44061937
40	14101.5	39085.6	36.31705569
40	13256.2	36939.9	36.12313513
		average	**35.96027006**
50	18654.8	41618.5	45.11970767
50	16253.8	37218.9	43.95957464
50	16066.7	36557.5	44.23971284
		average	**44.43966505**
75	24924.2	35918.9	69.84901768
75	23522.6	35401.8	66.88397604
75	22898.5	34133.5	67.52868848
		average	**68.0872274**
100	32578.4	36632.6	89.52083221
100	30786	34326.4	90.27907684
100	30597.2	33933.9	90.76324468
		average	**90.18771791**

PFHxS – polyAmine

10	3600	38113.8	9.5078507
10	3512.8	36287.9	9.744368326
10	3309	33795.3	9.856042432

		average	**9.702753819**
20	6287	35262.2	17.94717756
20	7246.8	35727.2	20.41782127
20	6308.7	34636.2	18.3346127
		average	**18.89987051**
40	13920.7	38813.4	36.10285022
40	13883.2	37864.9	36.90752047
40	12827.5	34918.4	36.97854263
		average	**36.66297111**
50	16527.3	37218.8	44.69939522
50	17540.1	37800.7	46.70832853
50	14841.2	32344.4	46.18830467
		average	**45.8653428**
75	27573.5	39747.1	69.83104675
75	27055.7	38955.9	69.91134151
75	22039.4	32412.9	68.44535513
		average	**69.39591446**
100	34087.6	37541.8	91.39941934
100	32865	36412.7	90.85374987
100	31007	32520.1	95.97762087
		average	**92.7435967**

PFHxS - poly-aluminum chloride

10	5405.3	55052.9	10.50393288
10	4865.6	52778.8	9.862550218
10	4611.5	51814.1	9.52152672
		average	**9.962669941**
20	8635.4	51316.1	18.00284544
20	8691.1	54100.8	17.18633988
20	8831.2	51714.9	18.26906696
		average	**17.81941743**
40	18072.2	54429.3	35.52144395
40	17927	54089.4	35.45747383
40	18757.4	54325.2	36.93887312
		average	**35.97259696**
50	22581.1	52566.3	45.95682543
50	21405.6	50594.8	45.26201233
50	22356.6	51340.1	46.58663937
		average	**45.93515904**

75	34004.3	52615.1	69.14101892
75	33098.4	52633.8	67.27514008
75	33170.3	51610	68.75873479
		average	**68.39163126**
100	44790	51799.7	92.50520169
100	42436.3	50990.9	89.03426339
100	44382.5	50368.4	94.2683581
		average	**91.93594106**

PFOS – Control 499 507/503* (*PAlC)

10	37348.2	53580.9	10.85187022
10	36379.3	54336.9	14.35924642
10	30824.8	52055.1	7.179568807
		average	**10.79689515**
20	40443.7	56084.9	19.21530314
20	36177.7	52372.3	14.61617926
20	40745.2	55210.2	19.91939001
		average	**17.91695747**
40	46155.1	53703.5	27.85060155
40	46673.5	41907.9	36.59485844
40	51239.4	53085.9	35.18386529
		average	**33.20977509**
50	47716.1	53615.7	30.02694946
50	73315.9	47137	73.90004868
50	47856.4	54113.6	29.94041629
		average	**44.62247148**
75	69660.6	51622.1	62.29725233
75	69183.8	49081	64.81164973
75	68997.2	49497	63.99103657
		average	**63.69997954**
100	82722.9	49925.8	83.56148452
100	79622.8	50185.2	78.60872208
100	83638.8	50373.5	84.14947787
		average	**82.10656149**

PFOS – polyDADMAC

10	24457.8	50967.7	13.36462525
10	22725.8	55863.9	10.63245618
10	23157.8	55832.9	11.02788072

		average	**11.67498739**
20	27012.7	38447.5	21.06204278
20	25091.1	39982.7	17.83385291
20	25138	40036.2	17.86894138
		average	**19.46549208**
40	37927.5	35459.4	38.33306357
40	35290.1	38153.6	32.14616386
40	34155.7	37570	31.12540748
		average	**33.86821164**
50	40904.7	32947.2	45.80495951
50	38358.8	39089.8	35.32838663
50	39947.4	38542.1	37.90537392
		average	**39.67957336**
75	57996.7	35343.4	67.04517437
75	55039.2	38560.2	57.59096583
75	52759.7	37900.3	55.5657643
		average	**60.0673015**
100	81337.4	38222.8	92.73631146
100	71531.2	39952.1	76.36576627
100	66051.7	38194.4	72.65765988
		average	**80.5865792**

PFOS – polyAmine

10	13440.16	39417.6	24.52187341
10	6343.66	39535.3	11.53969273
10	2155.76	35701.2	4.342671522
		average	**7.941182126**
20	26380.96	17641.7	107.5448327
20	7811.96	39471.9	14.23348881
20	8714.96	37787.9	16.58639585
		average	**15.40994233**
40	26118.96	36647.9	51.25617243
40	15650.06	38584.1	29.17071121
40	16080.36	36055.5	32.07477586
		average	**30.62274354**
50	23988.06	48449	35.60817325
50	25663.16	47978.8	38.46804677
50	23491.46	47833	35.32008781
		average	**36.46543595**

75	39584.96	46868.4	60.74205323
75	36567.36	46484.1	56.57552151
75	36124.76	44787.1	58.00847034
		average	**58.44201503**
100	43121.36	40604.58	76.3759829
100	44857.06	39177.2	82.34491728
100	44479.96	37810.5	84.60408892
		average	**81.1083297**

PFOS – poly-aluminum chloride

10	5396.5	70644.4	9.55473164
10	5605.5	75342.5	9.305900042
10	5457.4	73546.7	9.2812538
		average	**9.380628494**
20	10739.7	72418.7	18.5492126
20	10395.1	71769.8	18.11636194
20	10031.4	67470	18.59665744
		average	**18.42074399**
40	20027.3	76653.9	32.67925903
40	20269	76363.8	33.1992937
40	19834.8	71585.8	34.65652358
		average	**33.5116921**
50	24318.9	76241.7	39.8965561
50	25599.6	77854.2	41.12777228
50	26360.4	78188.4	42.16904088
		average	**41.06445642**
75	35838.7	73178.3	61.25675471
75	36443.2	72065.7	63.25166298
75	37795.1	70915.3	66.66219467
		average	**63.72353745**
100	50133.1	79192.4	79.18175231
100	50733.8	75385.4	84.17714699
100	50961.7	77083.7	82.69236399
		average	**82.01708776**

PFHpA – Control 363 367

10	2908.8	33856.9	9.212349823
10	2991.2	33217.7	9.655608404
10	2940.9	33579.8	9.390871602
		average	**9.419609943**
20	5675.3	34906	17.43381727
20	6087.9	34926.8	18.69013607
20	6711.2	36507.1	19.71181418
		average	**18.6119225**
40	13032.9	37128.3	37.63914494
40	13550.6	38602.7	37.63956488
40	14312	37605	40.80923794
		average	**38.69598259**
50	19657.6	43729.3	48.20162933
50	19356.2	43745.7	47.44478479
50	19608	43900.8	47.8921809
		average	**47.84619834**
75	22433.7	33706.3	71.36636494
75	22760.1	34588.6	70.55778397
75	22330.7	34925.4	68.55903542
		average	**70.16106145**
100	40613.2	46382.1	93.8902623
100	41604.2	47118.5	94.67808595
100	40529.8	47185.2	92.10271042
		average	**93.55701956**

PFHpA – polyDADMAC

10	2566.6	35123.7	7.835409184
10	3308	35133.9	10.09585003
10	2596.5	34171	8.147687977
		average	**8.692982395**
20	5321.7	35022.1	16.29340884
20	6425.7	35651.1	19.32641325
20	5506.2	34812.2	16.95993809
		average	**17.52658673**
40	11954.7	34900.8	36.72882631
40	12310	34803.9	37.92572496

40	11399	33902.5	36.05278174
		average	**36.90244434**
50	14038.2	35085.9	42.90249552
50	14835.4	34888.5	45.59536673
50	14464.6	34237.6	45.30090362
		average	**44.59958862**
75	35159	53577.6	70.36505139
75	34382.4	54248.3	67.96006818
75	34068.5	53619.1	68.12982021
		average	**68.81831326**
100	31849.9	39995.1	85.38961129
100	33096.6	37921.5	93.58400429
100	30822.1	36247.8	91.17679513
		average	**90.0501369**

PFHpA – polyAmine

10	3561.5	36697.1	10.40650635
10	3528.6	36409.7	10.39175932
10	3016.1	35348.3	9.149154361
		average	**9.982473345**
20	6611.1	36633.7	19.35070055
20	6574.2	38132	18.48660144
20	6985.2	37110.4	20.18305763
		average	**19.34011987**
40	13492.6	36510	39.62666861
40	12955	36305.3	38.26230577
40	12326.4	34646.4	38.14888878
		average	**38.67928772**
50	15358.6	34127.8	48.2555297
50	14922.3	33279.2	48.08024141
50	15344.6	33768.4	48.7246624
		average	**48.35347783**
75	24261.9	37154.5	70.01919889
75	24960.3	36311.4	73.70730933
75	25363.9	36915.4	73.67365297
		average	**72.4667204**
100	31774.1	35537.7	95.87109586
100	30837.5	35328.6	93.59582686

100	30964.6	35087.2	94.62818543
		average	**94.69836938**

PFHpA – poly-aluminum chloride

10	3481.5	37175.2	9.419235373
10	3719	33329.3	11.22283427
10	3519	38554.5	9.180086114
		average	**9.940718585**
20	6717.3	36678.6	18.41978504
20	6592.3	37800.2	17.54063974
20	6939.8	38645.2	18.06150597
		average	**18.00731025**
40	12542.7	34247.5	36.83534349
40	13567.1	36764	37.11648425
40	13976.3	35548.3	39.54357603
		average	**37.83180126**
50	16719.9	34809.4	48.31029636
50	19075.5	39637.2	48.40336178
50	16808.1	37452.3	45.13803961
		average	**47.28389925**
75	26461.9	38194.9	69.6816154
75	28917.6	39637.2	73.37731931
75	28668.8	39776.3	72.49160177
		average	**71.85017883**
100	35409.4	38329.9	92.91448953
100	38689.6	40594.3	95.85874667
100	36560	39203.8	93.79519394
		average	**94.18947671**

PFOA – Control 413 421

10	7059.9	61338.6	10.24489224
10	6533.1	54862.7	10.59948667
10	6728.4	57631.1	10.39196314
		average	**10.41211402**
	12753.9	57616.4	19.70332826
20	11671	52980.4	19.60810124
20	11387.1	54401.8	18.63127471
20		**average**	**19.31423474**

	24356.8	57099	37.969461
	22819.8	54203.3	37.4738928
40	22421.3	54517.2	36.60748993
40		**average**	**37.35028124**
40	30699	56408.4	48.44212119
	27707.9	53197.4	46.36133242
	28490.5	54844.3	46.23930285
50		**average**	**47.01425216**
50	45872.6	56455.4	72.3253546
50	44695	58901.6	67.54209913
	45956.6	55991.5	73.05812009
		average	**70.97519127**
75	58436.6	54629.9	95.21321685
75	61185.6	55246	98.58051632
75	56638.2	54052.3	93.2691392
		average	**95.68762412**

PFOA – polyDADMAC

10	5626.6	51613.9	9.703358345
10	5253.6	55056.6	8.493570959
10	5771.8	50187	10.23676521
		average	**9.47789817**
20	9549.7	53049.6	16.02323932
20	10091.4	57986.9	15.49045711
20	10856.9	52963.5	18.24617623
		average	**16.58662422**
40	19350.4	50728.8	33.95299286
40	20819.5	55952.6	33.12018299
40	19855.5	51756.2	34.14767582
		average	**33.74028389**
50	20664.8	51771.4	35.52908324
50	26030.8	57785.6	40.0968811
50	22926.1	50472.1	40.43165436
		average	**38.6858729**
75	35941	50002.3	63.97980019
75	33770.8	55308.5	54.34907699
75	32732	52303.1	55.70418399
		average	**58.01102039**
100	48241.1	54595.6	78.65064042

100	55421.9	60052.5	82.14724877
100	53591.8	57212.8	83.37730353
		average	**81.3917309**

PFOA – polyAmine

10	5906.7	52923.2	9.934397247
10	5248.5	56045.1	8.335665095
10	5837.6	54021.3	9.618603145
		average	**9.296221829**
20	10363.4	53994.2	17.08432618
20	11672.7	55566.4	18.69828467
20	11519.4	52933.3	19.37062321
		average	**18.38441135**
40	22552	53615	37.44048422
40	24703.9	54758.3	40.15672331
40	20644.1	52871.6	34.75491296
		average	**37.45070683**
50	29191.1	54189.3	47.94900772
50	30072.6	65681.9	40.75378733
50	27095.1	53927.6	44.72211868
		average	**44.47497124**
75	41209	54553.8	67.23722375
75	41929.9	56728.2	65.79115754
75	41728.4	52969	70.12173661
		average	**67.71670597**
100	56198.5	53582.9	93.35578037
100	56282	55177.9	90.79189033
100	58309.3	59021.6	87.93657645
		average	**90.69474905**

PFOA – poly-aluminum chloride

10	6536.9	60998.7	9.538804901
10	6116.1	55018.6	9.894816551
10	6293.4	57554.1	9.73311317
		average	**9.722244874**
20	11357.4	54983.1	18.38621795
20	10985.8	50986.2	19.17881401
20	11024.5	52123.4	18.82646881

		average	**18.79716692**
40	25653.8	56999	40.06149689
40	23981.8	53205.6	40.12057384
40	24123.1	59715.2	35.95761932
		average	**38.71323002**
50	29996	56234.5	47.47918016
50	29915.6	53987	49.32319796
50	28547.3	55095.3	46.12041337
		average	**47.6409305**
75	45123.9	56345	71.28430984
75	46839	57341.2	72.70822482
75	43973.9	55823.4	70.11668974
		average	**71.36974147**
100	57234.5	54348	93.73829088
100	59437.6	56001	94.47310452
100	55394	54325.4	90.76167419
		average	**92.9910232**

PFNA – control 463 472

10	3617.9	36267.5	10.54953404
10	3082.7	38607.6	8.444088889
10	3628.7	38671.6	9.923234689
		average	**9.63895254**
20	6823.1	37464.6	19.25994201
20	6770.3	36603.3	19.56059273
20	6718	38016.3	18.68807173
		average	**19.16953549**
40	14016.5	38035.2	38.97159818
40	14901.1	39476.5	39.91848286
40	14109.7	39448.6	37.82513823
		average	**38.90507309**
50	18421.3	38518.7	50.575827
50	18254.8	41469.6	46.55234597
50	17611	38832.8	47.96005252
		average	**48.36274183**
75	27448.3	38897.5	74.62564559
75	25715.3	38607.5	70.43917392
75	25354.5	36838.3	72.78632782
		average	**72.61704911**
100	35513	38723.4	96.98581463

100	35562.3	39876.9	94.31109582
100	35575.7	37869	99.34910434
		average	**96.88200493**

PFNA – polyDADMAC 463 472

10	3076.4	33930.4	9.588444574
10	3049.5	36028	8.951232189
10	3059.5	32250	10.03263651
		average	**9.524104423**
20	6087.4	35562.1	18.10250933
20	6335.9	35943	18.64182086
20	6059.9	33870.4	18.92079895
		average	**18.55504305**
40	13500.4	37239.6	38.3385751
40	13260.5	37556.9	37.33915634
40	12352	35263.9	37.04258454
		average	**37.57343866**
50	17909.4	38292.6	49.4607298
50	16605.9	38802.9	45.25770973
50	15316.9	36314.9	44.60467336
		average	**46.44103763**
75	25794.2	39522.1	69.02022793
75	25855.8	40442.7	67.61019318
75	24923	36101.5	73.00782483
		average	**69.87941531**
100	33880.1	38656.3	92.68698161
100	35248.4	40428.1	92.20413882
100	31711	35410.9	94.70377955
		average	**93.1983**

PFNA – polyAmine

10	3466.4	1561.318238	9.568425022
10	4191	2525.045955	9.959294317
10	3530.8	1579.598583	9.226350733
		average	**9.584690024**
20	6774.1	5442.813729	18.90958901
20	7052.6	5557.825074	18.21049772
20	6806.2	5738.728822	19.7999805

		average	**18.97335574**
40	14459.8	15869.42635	41.37708725
40	14264.5	13602.33087	36.03811305
40	13672.2	13765.43674	38.34629688
		average	**38.58716573**
50	17418.8	18448.06389	48.46757222
50	19311.6	20688.78071	48.35680279
50	18103.2	18611.47642	46.79815178
		average	**47.8741756**
75	25235.3	26981.87252	70.31641175
75	29007.2	31931.46519	71.52490107
75	25674.9	28022.30375	71.66273769
		average	**71.16801684**
100	33940.5	37175.93357	93.79560391
100	36176.1	39587.58364	93.31633007
100	36821.5	41544.5105	96.10587984
		average	**94.40593794**

PFNA – poly-aluminum chloride

10	4073.9	45620.9	9.537131446
10	4362.9	45095.4	10.33271065
10	4167.8	42940.4	10.36601988
		average	**10.07862066**
20	8101.3	45274.5	19.11051121
20	7536.2	45179.7	17.81477433
20	8499.3	46024.1	19.72282435
		average	**18.8827033**
40	15247.9	41719.3	39.03410939
40	16699.7	47853.9	37.2702739
40	16635.8	46220.8	38.43947833
		average	**38.24795387**
50	19302	43828	47.0350826
50	20162.9	44355	48.54915387
50	20556.8	46305.1	47.41305472
		average	**47.66576373**
75	29490.1	44231.2	71.20635841
75	30663.8	44624.2	73.38829245
75	29576.8	44197.6	71.46999475
		average	**72.02154854**
100	43541.1	45733.1	101.6810468

100	38644.7	44444.5	92.86309802
100	38862.3	43894	94.55719779
		average	**96.3671142**