REMOVAL OF PERFLUOROOCTANOIC ACID FROM WATER USING PRIMITIVE, CONVENTIONAL AND NOVEL CARBONACEOUS SORBENT MATERIALS

THESIS

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Abstract

Polyfluoroalkyl Substances (PFAS), like perfluorooctanoic acid, have been used for the last 50 years in a wide variety of industrial processes and consumer-based products, including polymer additives, lubricants, fire retardants and suppressants, pesticides, and surfactants (Buck et al. 2015). The Department of Defense (DoD) has used PFAS-based Aqueous Film Forming Foam (AFFF) at fire training facilities and aircraft hangars. AFFF has contaminated approximately 600 sites classified as fire training facilities with PFAS (Huang, 2013).

This study focused on testing the most likely carbonaceous adsorbent compounds to remediate PFAS-contaminated sites on Air Force installations. Batch tests were performed to determine the perfluorooctanoic acid adsorptive characteristics, both in capacity and rate, of conventional granular activated carbon (GAC), primitive carbon materials, and advanced carbon materials. GAC was found to remove PFAS from aqueous solution well. Biochar and CNT materials exhibited less adsorption than GAC but demonstrated some capability. Variability in controls made precise quantitative comparisons difficult. Analysis of the data collected lead to an investigation of sample prep techniques and found that low sample volumes and large dilutions ratios contribute to variability. When preparing large quantities of samples, manually pipetting small volumes can present a challenge for the technician. Automated devices that can repeatedly mix and dilute samples prior to analysis should be considered to reduce variability.

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Christopher K. Brown

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REMOVAL OF PERFLUOROOCTANOIC ACID FROM WATER USING PRIMITIVE, CONVENTIONAL AND NOVEL CARBONACEOUS SORBENT MATERIALS

I. Introduction

1.1 General Issue

Polyfluoroalkyl Substances (PFAS), have been used for the last 50 years in a wide variety of industrial processes and consumer-based products, including polymer additives, lubricants, fire retardants and suppressants, pesticides, and surfactants (Buck et al. 2011). The suite of PFAS contains several chemical formations with varying carbon fluorine bond chain lengths. The two most commonly studied PFAS that have received the most attention from the public and regulatory community are perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS). Toxicology studies continue to increase the awareness of PFAS and its potential role in immunotoxicity, cancer, and other adverse health effects (Grandjean and Clapp 2015). Low levels of PFOA have been detected in humans and animal studies show correlations of exposure to toxicity and human health risks. Drinking water is the most likely exposure route for people who do not work directly with these chemicals. There is currently no regulatory standard for PFAS listed under the Safe Drinking Water Act. However, the US EPA has reviewed several studies and determined a provisional health advisory level for PFOA and PFOS of 0.4 and 0.2 µg/l. The unique properties of PFAS present analytical challenges in accurately detecting their presence. Special care must be taken with analytical equipment such as avoiding the use of Teflon products. PFOA is used in the making of Teflon

products and if used in instrument tubing, pumps, and sample containers can contribute background noise during analysis.

The Department of Defense (DoD) has used PFAS-based Aqueous Film Forming Foam (AFFF) at fire training facilities and aircraft hangars due to its unique properties. Specifically, PFAS has been used in AFFF on Air Force installations since 1970, after demonstrating its capability to meet military specifications to extinguish hydrocarbon based fires. AFFF was needed to improve emergency procedures required to mitigate the risk of handling the vast amounts of petroleum, oil, and lubricants on Air Force installations. The DoD as a whole is the largest consumer of AFFF materials making up 75% of the demand (Moody and Field 2000). The Air Force (AF) has nearly one million gallons of PFOS based AFFF in stock (BRAC Academy, 2014). With growing concerns of PFAS as an emerging contaminant, there is a need for the development of remediation technologies specific to the PFAS contamination.

1.2 Problem Statement

The AF has identified 600 sites with potential PFAS contamination across its inventory. Effective remediation technology selection for PFAS impacted water is a challenge (Rahman, 2014). Identifying the most efficient remediation technology has not been accomplished.

These chemicals have been detected at sites as long as 10 years after use of AFFF (Moody and Field 1999). The sources for this contamination on Air Force installations are firefighting training areas and exercise locations, testing aircraft hangar fire suppression systems, and emergency response and spills. Air Force Instruction 32-2001

Fire and Emergency Services Program and installation level fire and emergency service training plans state that hands-on egress and aircraft live fire training shall be provided to all firefighters as often as necessary to meet certification and proficiency requirements, to perform duties of flight line fire and rescue, but not less than twice each year. A typical firefighting exercise could use between 75-100 L of AFFF concentrate mixed with 1200-3200 L water (Moody and Field 1999). The Air Force Civil Engineer Center (AFCEC) has conducted site surveys at 30 fire training areas and 39 non-fire training area site surveys at installations (AFCEC, 2014). The Emerging Issues and Emerging Contaminants Program under AFCEC has confirmed that PFAS is present at all fire training areas operable since 1970 (Anderson et al. 2016).

PFAS do not break down easily and are resistant to degradation in soil, which can lead to transport to surface water and groundwater. PFAS are also not substantially removed by most common drinking water treatment processes including coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation (chlorination, ozonation, AOPs), UV irradiation, and low-pressure membranes (Rahman et al. 2014), although several attempts have been made and research continues.

One study used hydrogen peroxide (Hori et al. 2004) and UV light to degrade PFOA. Concentrations of 0.34-3.35 mM PFOA solution were completely degraded in 24 hours using a reactor at a pressure of 0.48 MPa and a 200 watt xenon-mercury lamp. This process took advantage of photolysis of hydrogen peroxide causing the creation of OH^- radicals. The OH^- radicals react with PFOA to break it down to a F- ion and CO_2 (Hori et al. 2004). The OH- radicals do not singularly target PFOA, so it is difficult to determine effectiveness in the field versus using organic free laboratory water.

A study of 14 Japanese water treatment plants (Takagi et al. 2008) revealed when granular activated carbon (GAC) was exchanged once or twice a year at water treatment plants, PFAS was effectively removed up to 90 %. Concentrations of PFOA ranged from 5.2-92 ng/L and PFOS ranged from 0.26-22 ng/L in raw water from both ground water and surface water sources. Final tap water concentrations ranged from 0.16-22 ng/l for PFOS and 2.3–84 ng/l for PFOA (Takagi et al. 2008). Other plants using chlorination, ozonation, slow sand filtration, and rapid filtration reported removal rates lower that 50% for PFOS and PFOA (Takagi et al. 2008). The removal efficiency in Takagi's (2008) study was based on the difference between the water treatment plant source water and the treated tap water. Similarly Appleman et al. (2014) found U.S. full-scale water treatment systems ineffective for the removal of PFAS. Full-scale water treatment plants use multiple treatment techniques such as: ozonation, aeration-packed towers, potassium permanganate, ultraviolet (UV) treatment, UV/H_2O_2 advanced oxidation, chlorination, and chlorine dioxide; to treat water prior to distribution into public water supplies. Anion exchange coupled with GAC removed longer-chain PFASs, while reverse osmosis systems were effective for the removal of 23 PFAS considered in the study (Appleman et al. 2014). The effectiveness of reverse osmosis treatment was also observed by Quinones and Snyder (2009), but high-energy requirements make reverse osmosis a costly option for PFAS removal. Nanofiltration has also been shown to be effective. This treatment process resulted in 90-99% removal of PFOS (Tang et al. 2007).

Particularly, for PFOA, the most effective removal technology appears to be adsorption. Several sorbents have been shown to be effective at removing PFOA and PFOS. Powder Activated Carbon (PAC) can reach adsorption equilibrium within 3-5

hours (Du et al. 2014), while some Granular Activated Carbon (GAC) has a slow adsorption of 48 hours to 168 hours for PFOS and PFOA respectively. Deng et al. (2104) tested bamboo derived GAC on PFOS and PFOA and reached equilibrium in 24 hours which is faster than some commercially available coal based GAC. Novel materials such as carbon nanotubes can reach equilibrium in 2 hours and primitive material such as chars reach equilibrium in 384 hours (Chen et al. 2011).

An advantage of activated carbon for PFAS removal is that many water treatment systems use GAC filters. Appleman (2014) studied one particular water utility using Calgon Filtrasorb F600 GAC to remove PFAS from groundwater. The system known as utility 20 in the study consisted of two activated carbon contactors in series with flow rates of 1.4 and 1.5 m^3/minute and empty bed contact times of 13 minutes per contactor. Utility 20 removed more than 92% of PFOA and more than 95% PFOS while many of the 23 PFAS studied were removed below detection limits for a one year period (Appleman et al. 2014)

PAC has also proven effective for the removal of PFAS. Qu et al. (2009) evaluated the adsorption of PFOA in batch experiments and reported 99% removal under experimental conditions. Yu et al. (2009) compared GAC, PAC and anion exchange resin adsorption kinetics and isotherms and considered PAC as the most effective for removing PFOA and PFOS. This is likely due to the PAC higher sorption capacity than GAC and reaching equilibrium in 4 hours, much faster than GAC and anion exchange at 168 hours (Yu et al. 2009).

1.3 Research Objectives/Questions

The objective of this research is to evaluate the effectiveness of various sorbents to remove PFOA. The specific goals of this study included; determining the adsorptive characteristics, both in capacity and rate, of conventional, primitive, and novel carbon materials for PFOA. Additionally, to model capacity and kinetics of PFOA adsorption.

1.4 Scope and Approach

This research effort focused on lab-scale tests conducted with PFOA as the representative PFAS. Three different adsorbent types were used: primitive, conventional and novel. Each of the adsorbents were used in kinetic experiments in triplicate and one isotherm was conducted on the conventional adsorbent.

1.5 Significance

The focus of this thesis was to test sorbents for remediation of PFAS-contaminated groundwater at sites on Air Force installations. Performance characteristics of the adsorbents will lead to estimates of the cost to meet regulatory compliance.

1.6 Preview

This thesis was written in the scholarly format. The manuscript for submission to the Journal of Environmental Engineering, a peer-reviewed scientific journal, is contained in chapter 2. The manuscript includes an abstract, introduction, materials and methods, results, discussion, and conclusions. Chapter 3 offers a final discussion of the conclusions along with pertinent findings and future research not discussed in Chapter 2.

II. Scholarly Article

Written for consideration of submission to the

Journal of Env Engineering

2.1 Abstract

Polyfluoroalkyl Substances (PFAS) have been used for the last 50 years in a wide variety of industrial processes and consumer-based products, including polymer additives, lubricants, fire retardants and suppressants, pesticides, and surfactants (Buck et al. 2015). The Department of Defense (DoD) has used PFAS-based Aqueous Film Forming Foam (AFFF) at fire training facilities and aircraft hangars. Specifically, PFAS has been used in AFFF on Air Force installations since 1970, after demonstrating its capability to effectively extinguish hydrocarbon fires. The AFFF improved emergency procedures and mitigated the risk associated with the storage and use of vast amounts of petroleum, oil, and lubricants (POL) on Air Force installations. The DOD is the largest consumer of AFFF materials, making up 75% of the market demand (Moody & Field, 2000). These AFFFs have potentially contaminated approximately 600 sites classified as fire training facilities with PFAS (Huang, 2013). Data is needed to characterize more potential sites at non-fire training areas, such as emergency response locations, AFFF lagoons, hangar-related AFFF storage tanks and pipelines, and fire station testing and maintenance areas (Anderson et al. 2016).

This study focused on lab-scale tests conducted with PFOA as the selected PFAS. Three different adsorbent types, that could be selected to remediate contaminated

groundwater sites on Air Force installations, were used: primitive, conventional and novel. Each of the adsorbents were used in kinetic experiments in triplicate and one isotherm was conducted on the conventional adsorbent. GAC was found to remove PFAS from aqueous solution well. Biochar and CNT materials exhibited less adsorption than GAC but demonstrated some capability. Variability in controls made precise quantitative comparisons difficult. The capacity and kinetics of PFOA adsorption followed the Langmuir isotherm model. Knowing the characteristics and abilities of these adsorbents will assist those responsible for environmental remediation projects.

2.2 Introduction

The US Environmental Protection Agency (EPA) has listed PFAS as a contaminant of emerging concern due to their wide distribution and prevalence in the environment. PFAS present a toxicological concern due to their persistence in the environment and their biomagnification potential through the food chain (Fromme et al. 2009). An excellent source of data related to PFAS in humans has been the C8 Health project, which contains information on approximately 70,000 Ohio and West Virginia residents. Other published reports are based on rat studies, which eliminates PFAS much more rapidly than humans, and therefore, is not an ideal species (Grandjean & Clapp, 2015). The US EPA issued a provisional drinking water health advisory of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS, which are two of the most common PFAS studied (US EPA, 2009).

Children's exposures to PFAS are greater than adults, when considering the smaller body mass of children (US EPA, 2009). Some potential adverse health effects

are cancer, decreased birth weight in newborns, immunotoxicity, thyroid disease, chronic kidney disease, and decreased sperm count (Rahman et al. 2014). Recent findings suggest that populations with elevated PFOA blood serum levels, such as those working in or living near PFOA production facilities, have an elevated risk of developing testicular and kidney cancers (Barry et al. 2013). Toxicological studies have correlated PFAS to adverse health issues including total cholesterol, glucose metabolism, body mass index, thyroid function, infertility, uric acid, lowered immune response to vaccinations, and attention deficit hyperactivity disorder (Grandjean et al. 2012, Saikat et al. 2013).

The Air Force has large quantities of POLs required to support and fly aircraft. Having large amounts of hydrocarbons poses a potential serious risk to life and property, which requires fast and effective response techniques. This potential fire risk calls for efficient fire-extinguishing agents to prevent damage and re-ignition of the POLs. Aqueous film forming foams (AFFFs) were developed in the 1960s as important tools for extinguishing fires involving flammable liquid fuels (Moody and Field 2000). In 1985, the U.S. market for AFFF products was 6.8 million liters, with the military making up 75% of the market (Moody and Field 2000). The oil refining industry by comparison only made up for 5% of the total market in 1985 (Moody and Field 2000). AFFF is a potential source of PFAS released into the environment. Additionally the AFFF contamination is complicated due to AFFFs contain proprietary fluorinated surfactants, which are typically not clearly listed by the manufacturer (D'Agostino and Mabury 2014).

In 2001, wildlife studies were detecting PFAS in animals (Giesy and Kannan, 2001). Subsequently, there have been numerous studies characterizing the fate and

transport of PFAS. In May 2012, Michigan Department of Community Health issued a "do not eat fish" advisory for Clark's Marsh and the lower Au Sable River after the Michigan Department of Environmental Quality detected PFAS in fish tissue (AFCEC, 2014). The Clark's Marsh and Lower Au Sable River are both down gradient of the Wurtsmith AFB Fire Training Area. In January 2009, EPA's Office of Water developed Provisional Health Advisory values for PFOA and PFOS to mitigate potential risk from exposure to these chemicals through drinking water. The advisories recommend taking action to reduce human exposure when concentrations for PFOA and PFOS are higher than 0.4 µg/L and 0.2 µg/L, respectively (US EPA, 2009).

PFAS does not degrade easily and are persistent in soil, which can lead to transport into groundwater. Plumes of contaminated groundwater are associated with past fire-training sites at several military bases in the United States to include Naval Air Station Fallon, NV; Tyndall Air Force Base, FL; and Wurtsmith Air Force Base, MI. Runoff from AFFF has entered groundwater without prior treatment at these sites (Moody & Field, 2000). The Air Force Civil Engineer Center (AFCEC) investigated fire training areas at Wurtsmith AFB, MI; and Pease AFB, NH; PFAS were found in groundwater at 3-4 orders of magnitude greater than the EPA provisional health advisories (BRAC academy, 2014). The detection of PFOS in the water at Pease AFB caused the city of Portsmouth to shut down one well when level exceeded the provisional health advisory. Since then, four public drinking water wells, and 30 private wells nearby have been sampled biweekly for PFAS. A private well had concentrations above EPA provisional health advisory levels and reports state that steps were taken to ensure access to clean water (Anderson et al 2015). The New Hampshire Division of Public

Health Services offered blood screening for those in the community concerned about being exposed to PFAS from Pease AFB (NH Public Health, 2016).

If AFFF containing post fire runoff is disposed of into the sewer system, the result of large quantities of AFFF reaching waste water treatment plants (WWTP) cause foaming and sludge bulking (Rupert et al. 2001). This excess foam causes operational problems with aeration and sludge handling facilities due to the high oxygen demand and foaming in wastewater treatment plants. PFAS are also not substantially removed by most drinking water treatment processes to include coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation, UV irradiation, and low-pressure membranes (Rahman et al. 2014). PFOA and PFOS can be removed from the aqueous phase using an ion exchange resin, although the process has kinetic limitations (Lampert et al. 2007). The mass transfer kinetics in the ion exchange resin requires 24 hours to reach equilibrium. This equilibrium time would require extended hydraulic residence time that are not typical in water treatment processes. One of the more common methods for removing organic contamination from waters is the use of activated carbon materials in "pump-and-treat" systems; where contaminated water is pumped through activated carbon filters to remove the contaminants and then discharged back into the environment (US EPA, 1996).

Activated carbon works relatively well at adsorbing hydrophobic pollutants (Du et al 2014). The mechanisms of which PFAS are adsorbed onto activated carbon and biochars have been studied (Du et al 2014, Inyang and Dickenson 2015). These studies suggest that pore filling, diffusion, hydrophobic interaction, π–π bonding, electrostatic

interaction, and hydrogen bonding all play a role in adsorption of organic contaminants either singularly or simultaneously. From this group of interactions, Du (2014) suggests the π–π bond does not form during adsorption of perfluoronated compounds on CNTs because of the absence of π electrons in the PFAS molecule, while van der Waals force is also insignificant because of the low polarizabilities and small molecular sizes of PFAS (Du et al 2014). PFAS adsorption is related to activated carbons particle diameter and pore size and those with more mesoporous and macroporous area have faster adsorption of PFOA and PFOS (Du et al 2014). At low concentrations the sorption of organic contaminants is believed to be controlled by pore filling in biochar. Pore filling is a fast process as the contaminant passes through the macropores and mesopores (Inyang and Dickenson 2015). Diffusion of contaminates onto activated carbon is a slow process and happens during the pore filling process. Hydrophobic interactions of PFAS is believed to be the main interaction controlling adsorption (Du et al 2014). The hydrophobic tail of PFAS is responsible for the hydrophobic interaction in solution and the adsorption to activated carbon. The longer the C-F chain, the longer the hydrophobic tail of the molecule, the less water soluble the PFAS molecule becomes and contributes to its effective removal by activated carbon.

Chars made by burning biomass, such as wood in a furnace at temperatures greater than 350°C, are commonly regarded as a strong adsorbent for nonionic organic contaminants but current knowledge on the sorption of PFOS, an anionic contaminant, is scarce (Chen et al. 2011, Kearns et al 2015). Kupryianchyk et al. (2015) studied activated carbon (AC) and biochar made from mixed wood and papermill waste used to

immobilize PFAS in soil. They studied sorption of perfluorooctanesulfonic acid (PFOS), perfluorooctanecarboxylic acid (PFOA), and perfluorohexanesulfonic acid (PFHxS) on AC and biochar made from mixed wood (MW) and paper mill waste (Kupryianchyk et al, 2015). Kupryianchyk examined the possibility of remediating PFAS contaminated soil by adding carbonaceous adsorbents. It was discovered that AC adsorbed PFAS so well that aqueous concentrations in pore water were below the limit of detection. AC had the greatest adsorption capacity compared to paper mill waste biochar and mixed wood biochar. Of the biochars, the mixed wood had greater capacity compared to the papermill waste. The adsorption capacity correlated with the materials surface area and pore size distribution. It was concluded that the addition of AC may be an effective means for in situ remediation of PFAS contaminated soils (Kupryianchyk et al, 2015). Another study by Chen et al. (2011) found that chars made from pyrolysis of maize straw and willow sawdust reached equilibrium in 16 days. This is much slower than equilibrium times for ash (48 hours), and carbon nanotubes (CNT) (2 hours)(Chen et al. 2011).

Several studies of CNT application for the removal of toxic organic pollutants from contaminated water have reviewed adsorption properties, removal efficiencies, and reaction kinetics (Yu et al. 2014). CNT offer great adsorption characteristics, due to their high surface area and hydrophobicity. Yu et al. (2014) studied the adsorption behavior of PFOS with relation to CNTs, PFOS isotherm adsorption data fit the Langmuir model. Chen et al. (2011) reported the sorption kinetics and isotherm of PFOS on three CNTs, and found sorption equilibrium was reached within 2 hours.

Organic compounds favor adsorption to CNTs however, the technology involved in creating and applying CNTs increases the cost more than conventional adsorbents. Sorption increased as the C-F chain length increased according to a study of six PFAS on CNTs (Deng et al. 2012). Deng's study (2012) and another by Bei (2014) stated sorption was controlled by hydrophobic interaction of PFAS on to CNT. However, the amount of PFOA adsorbed on to powder activated carbon (PAC) was greater than on to CNT (Deng et al. 2012). Adsorption and removal of organic contaminants with CNTs is effected by the pH, temperature, adsorbate concentration, amount of adsorbent, adsorbent particle size, and contact time (Yu et al. 2014). CNTs are also difficult to recover from the treatment process for reuse when in their pristine powder form compared to GAC, contributing to their increased cost. In addition, they are not currently readily available in the large quantities that water treatment plants and environmental remediation operations require.

CNTs adsorption properties make them suitable for removing organic pollutants in aqueous environments. However these properties could also contribute toxicity as CNT is spread into the environment along with the pollutants. For this reason, increased production of CNTs along with their toxicity has also become a concern in environmental research (Deng et al. 2012).

Disposal and reuse of activated carbons after PFAS has been adsorbed has its challenges. Regeneration of activated carbon uses another chemical like methanol or ethanol to cause PFAS to desorb from the activated carbon. However this process does not remove 100 percent of the PFAS and bring back the activated carbon's initial

capacity (Du et al 2014). This will reduce the effectiveness and breakthrough time of the filter when put back into use. Another challenge presented from regeneration is disposal and treatment of the concentrated waste. Reactivation of AC uses chemicals, steam and heat to recover its capacity. This process is not used in drinking water treatment systems due to the inability to adequately reactivate carbon for the removal of organics at low concentrations (Clark, 1991). Reactivated carbon adsorption characteristics are also not the same after the reactivation process due to pore size enlargement during the pyrolysis and burning off the sorbed organics (Clark, 1991). Therefore since regeneration or reactivation AC is difficult after PFAS has been adsorbed the most likely safe disposal of spent AC is in a landfill. This may prevent a problem in the future if concentrated levels of PFAS begin to leach from landfills.

The GAC made from bamboo in the Deng et al. (2014) study was regenerated after PFOS adsorption using deionized water, methanol, and ethanol at temperatures ranging from 25°- 45 °C. Methanol and ethanol regeneration at 25°C after 24 hours was at 83% and 96%, respectively. Increasing ethanol solution temperature to 45°C increased regeneration after 4 hours to 94% and to 98% after 24 hours (Deng et al. 2014). The subsequent removal of PFOS decreased 3.9% from the first use to the second use and was stable across the three reuse cycles after regeneration.

CalgonCarbon® Corporation reactivates in furnaces under negative pressure at temperatures greater than 1,700° F. The emissions are passed through a chemical scrubber and baghouse filters to remove any acidic gases and particulate matter (Calgon, 2016a). Calgon estimates 10 % loss in capacity each reactivation for F600. Reactivated carbon from a react pool product costs $1.00 per pound. Custom reactivation cost $2.00

per pound depending on what is being adsorbed and the base material. Normally what drives this price is how much energy it takes to mineralize the contaminants off of the carbon (Calgon, 2016b). Customers using Calgon's custom reactivation can save 30-40% in operational costs in the long term but small pump and treat systems or short term remediation projects may still find landfilling more economical (Calgon, 2016b).

The main objective of this study was to compare conventional, primitive, and novel carbon materials. The capacity and rate of GAC, Biochar, and CNTs was investigated in kinetic and isotherm batch experiments. Of the three carbon materials studied GAC performed better than biochar and CNT. Comparisons between CNT and biochar were difficult distinguish due to analytical challenges. The biochar as a whole demonstrated that some adsorption is possible, and CNT removal trended slightly lower than biochar. Results were difficult to analyze due to variations in analytical instruments, sample storage containers, and dilution ratios for sample prep. The results of this research will provide more information and understanding of adsorbents that could be selected for ground water remediation of PFAS sites.

2.3 Methods

After an initial review of literature (Rahman 2014, Zhao 2011) and considering the worst case scenario of high PFAS concentrations near fire training areas a PFAS concentration of 10 mg/L was chosen. In order to achieve faster equilibrium times the received adsorbents were reduced to 0.18 mm. To prevent complete removal of PFAS in the experimental process various carbon doses were considered. Carbon doses of 10, 20,

40, 80 mg/L were chosen for the isotherm study and an initial 10 mg/L carbon dose was chosen for the kinetic study.

2.3.1 Material

Perfluorooctanoic acid (PFOA) was obtained from Sigma Aldrich in powder form with the properties listed in Table 1. Calgon Filtrasorb 600 granular activated carbon was selected for this study, as it was designed to maximize the density of high-energy sorption sites for organic contaminants. Biochar was made from wood pellets that were prepared in a 55-gallon Top-Lit Up-Draft (TLUD) biomass gasifier at temperatures of 750 to 950 °C that is described by Kearns (2012). Carbon nanotubes (CNT) were grown on fabric material and were created by chemical vapor deposition (CVD) using the process described by Vijwani (2015). The first step of CVD uses plasma enhanced deposition of a nano layer of silicon dioxide followed by CNT growth using floating catalyst CVD technique (Vijwani et al. 2015). Then CNT growth was carried out using a multi-zone CVD furnace reactor maintained at 380°C (Vijwani et al. 2015). The CNTs were provided by Wright State University, Dayton Ohio.

Table 1: Physical and Chemical Properties of PFOA (EPA, 2014)

Property	PFOA (Free Acid)
Chemical Abstracts Service(CAS) Number	335-67-1
Physical Description (physical state at room temperature and atmospheric pressure)	White powder/ waxy white solid
Molecular weight (g/mol)	414
Water solubility at 25°C (mg/L)	9.5 X 10^3(purified)
Melting Point (°C)	45 to 54
Boiling point (°C)	188 to 192
Vapor pressure at 20 °C (mm Hg)	0.0171
Octanol-water partition coefficient (log Kow)	Not measured
Organic-carbon partition coefficient (log Koc)	2.06
Henry's law constant (atm-m3/mol)	Not measured
Half-Life	Atmospheric: 90 days, Water: > 92 years (at 25º C)

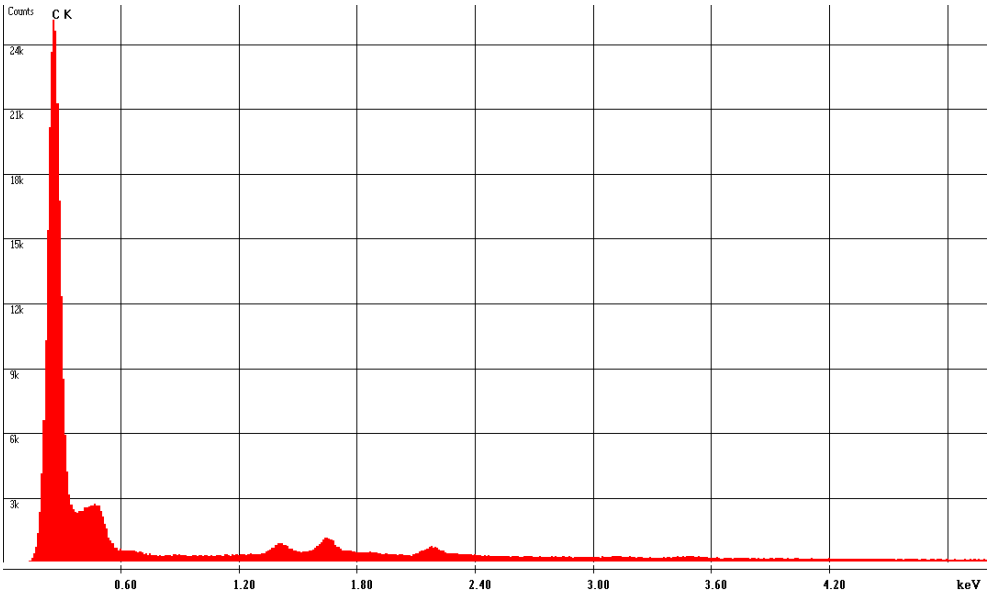

Figure 1. F600 GAC EDS analysis showing the purity of the carbon material

The GAC was analyzed at the University of Dayton using an Energy Dispersive X-ray Spectroscopy system (EDS) and Scanning Electron Microscope to determine the purity of the carbon material. Figure 1 shows the elemental composition of F600 GAC. While the SEM image of F600 GAC shows the heterogeneity of the as received F600 prior to being pulverized in the mortar and pestle, Figure 2A shows multiple granules scaled at 300µm. The SEM image in Figure 2B is a single granule scaled at 100 um shows the macropore structure of F600 GAC.

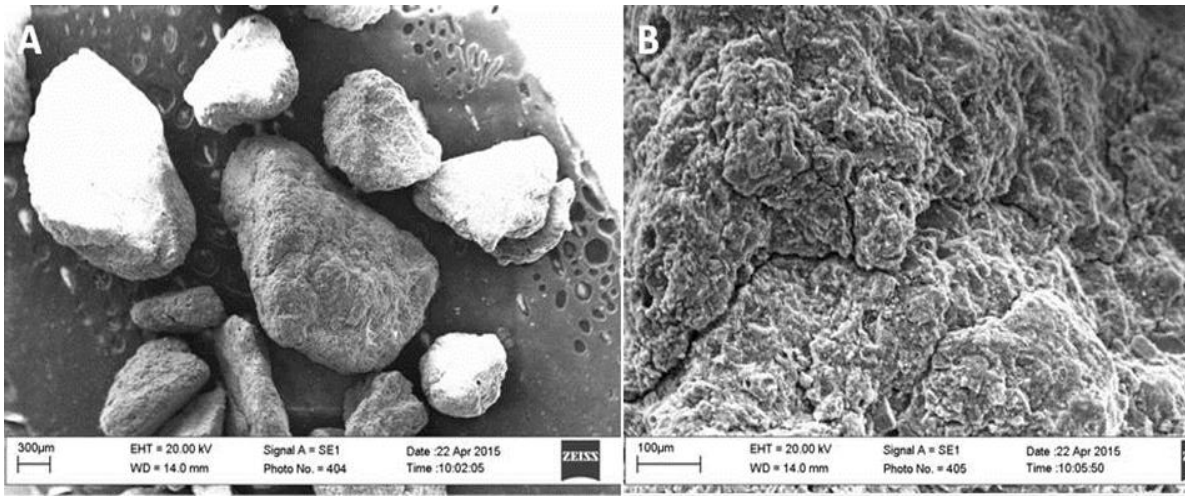

Figure 2. SEM images of GAC granules. a) Multiple GAC granules at 300µm. b) a single GAC granule at 100 µm (Doanne, 2015)

The biochar images were taken by SEM at Air Force Institute of Technology. Figure 3A is scaled to 200 µm and represents multiple pellets, and Figure 3B shows a single pellet scaled to 20 µm, and Figure 3C is scaled to 2 µm. These images show the heterogeneity and macropore structure of the biochar.

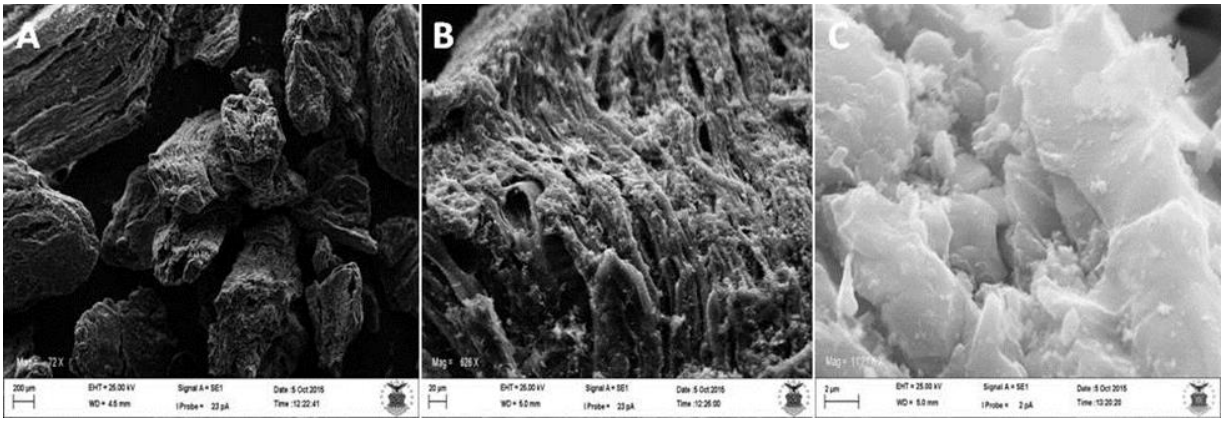

Figure 3: SEM images of Biochar pellets. a) multiple biochar pellets scaled to 200 µm; b) single biochar pellet scaled to 20 µm; c) single biochar pellet scaled to 2 µm (Doanne, 2015)

The SEM images of CNT fabric illustrate the CNT growth onto the fabric from the chemical vapor deposition. Figure 4A shows the fabric before the CVD process and CNT growth. Figure 4B show the homogenous layer of CNT fixed to the fabric.

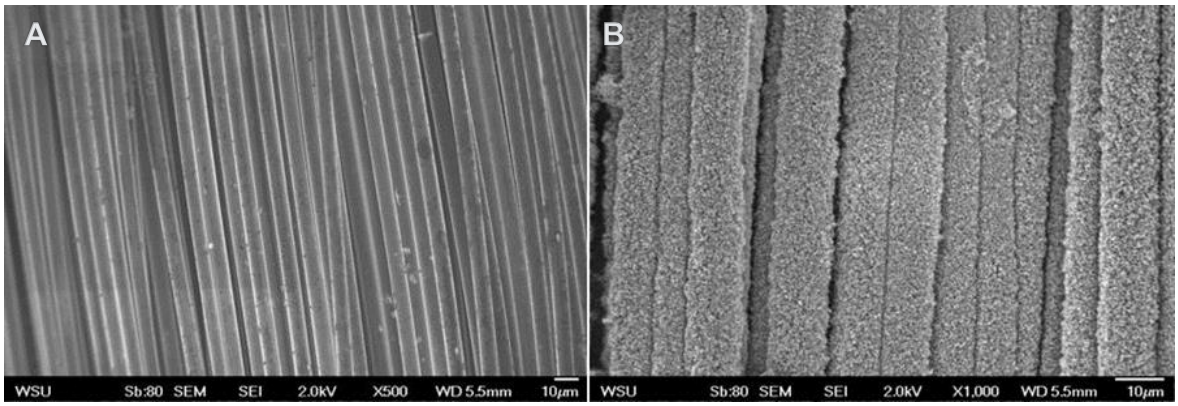

Figure 4. SEM image of CNT. Figure A displays the fabric substrate scaled to 10 µm prior to chemical vapor deposition while Figure B is the CNT-Fabric structure scaled to 10 µm after chemical vapor deposition (Doanne, 2015)

2.3.2 Pretreatment

The GAC and Biochar adsorbents were ground from their stock size using a mortar and pestle and passed through a 0.18 mm sieve size but retained on a 0.074 mm sieve (equivalent of US Standard sieve sizes 80 x 200). Carbonaceous material of this particle size has been demonstrated to have the highest efficiency in sorbing hydrophobic organic contaminants (Kupryianchyk et al. 2015). The material was passed through a sieve to ensure a uniform sample of adsorbent was used and promote faster equilibrium times. The adsorbent was washed repeatedly in a beaker with deionized water until a 30 second settling time provided a visually clear solution with few fines remaining in suspension. During the initial washing stages fines were removed by pouring water (and fines) out of the beaker and retaining the settled material. The adsorbent was then dried in a vacuum oven at 50° C for six hours.

2.3.3 Batch Experiment

A 1,000 mg/L stock solution was created using 100 mg of PFOA powder with 100 ml of deionized water. This stock solution was used to create 10 mg/L PFOA solution used in the sorption studies. Once the solution dispensed into bottles, Teflon-coated stir bars were added, and the solution was mixed at 300 revolutions per minute for 20 minutes prior to adsorbent being applied.

Batch sorption kinetic experiments were performed in 500 ml amber bottles using Teflon coated stir bars on a Fisher multiple-bottle stir plate set to 300 revolutions per minute. A 10 mg/L carbon dose was prepared by weighing out 5 mg of GAC. The GAC was then added to 10 mg/L PFOA solution in 500 ml bottles, 500 µl samples were pulled

from the center of the mixing bottle using a 1000 µl pipette. Samples were taken at 0, 15, 30, 60, 90, 120 minutes, 4, 8, 12, 24, and 48 hours. Biochar samples followed the same schedule and then continued daily until the eighth day and then sampled every third day out to a total of 29 days. Samples were put into a 10 ml syringe with 0.45 µm surfactant free cellulose acetate (SFCA) membrane filter and pushed through filling a polypropylene HPLC vial. This procedure yielded approximately 500 µl in the vial. This process was repeated for all samples using a fresh filter, syringe, pipette, and vial each time.

Batch sorption isotherm experiments were performed in 500 ml amber bottles using Teflon-coated stir bars on a Fisher multiple-bottle stir plate set to 300 revolutions per minute. Carbon doses were varied to determine the isotherm model. For the GAC isotherm, doses of 10, 20, 40, and 80 mg/L were used. Samples were collected in an identical manner to the kinetics experiments described above. The sampling interval was determined from the equilibrium time in the kinetic equilibrium experiment. Equilibrium with GAC was achieved at 12 hours; therefore conservatively samples were taken initially and at 24 hours. All samples were stored at 0° C until ready for analysis.

2.3.3 PFOA Analysis

The samples were diluted 1:100 to bring them into the PFOA methods calibrated range of 0-200 ng/mL. In order for the samples to be analyzed on the instrument, they were diluted with 965 µL of methanol 10 mM formic acid to 10 µL of sample. Finally, 25 µL of internal standard was added to create a 1mL analytical sample.

Analysis of PFOA was performed using Waters Acuity UPLC system and Quattro Premier triple quadrupole mass spectrometer (Waters Corporation, Milford, MA) operated in the multiple reaction monitoring (MRM) mode using negative-ion-spray ionization (ES−). The UPLC system comprised of binary pump, auto sampler, column heater, and other equivalent automated system. To prevent any background contamination from the solvent lines and filters, all solvent lines were replaced with polyether ether ketone (PEEK) tubing and the mobile phase filters were replaced with stainless-steel material. To further differentiate the peaks coming from background, a Perfluorinated Compound (PFC) isolator column (C18 material, 3.0×50 mm, 3.5 µm, Waters PFC Analysis Kit) was installed between the mixing chamber and an analytical column. A 15 µL aliquot of sample was injected onto an Epic FO LB column, 2.1×50 mm, 1.8 µm (straight chain fluorinated phase) (ES Industries, West Berlin, New Jersey) using 10 mM formic acid in Milli-Q water (solvent A) and 10 mM formic acid in methanol (solvent B) as gradient mobile phase. The analytical column was maintained at 50 °C. The flow rate was maintained at 0.35mL/min. The initial gradient started with 30% solvent B and maintained at 1 minutes and increased linearly to 60% at 3 min, 80% at 8 min and then to 100% at 8.01 min. It was held for 0.99 min at 100% solvent B and then reverted to 30% at 9.01 min and re-equilibrated at initial conditions until 11min time point with a total run time of 11 minutes.

The capillary voltage was held at 2.5 kV. Cone and desolvation gas flows were kept at 1 and 802 L/hr, respectively and source and desolvation temperatures were maintained at 120 ºC and 225 ºC. MRM transitions monitored for PFOA are m/z 412.96 > 369.13, 412.96 > 169.18 and the internal standard, ^{13}C PFOA m/z 421.02 > 376.12.

Eight point calibration curves were prepared ranging from 2 - 200 ng/mL. Quantitation was performed using Mass Lynx version 4.1 software (Waters Corporation, Milford, MA) using a linear or quadratic "1/x" weighted regression fit with a coefficient of correlation greater than 0.996, concentration calculations for PFOA are based on the internal standard procedure.

2.4 Results and Discussion

The results of the GAC adsorption kinetics experiment are reported as concentration as a function of time. The concentration of PFOA is reported in ng/mL and time in hours (h). Figure 5A shows GAC D2 which had the best performance of the triplicate GACs tested. Duplicating the results proved challenging as can be seen from the variation in the samples and controls plotted in Figure 5B. The use of error bars representing one standard deviation of all the bottles resulted in overlap all sample points make it difficult to make any distinction between control and adsorbent. The initial concentration of the experiment was 10 mg/L. The samples were diluted 1:100 for analysis in the Waters Acuity UPLC yielding a time zero recovery target of 100 ng/ml.

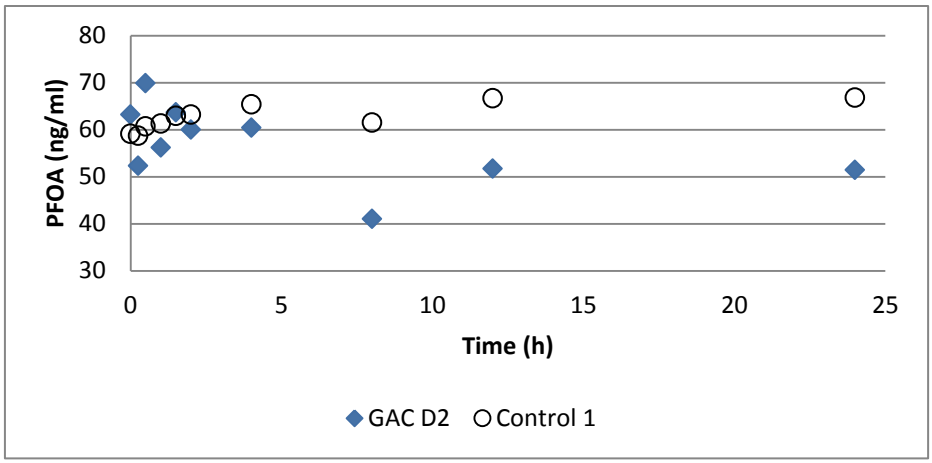

Figure 5A: GAC kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/mL. GAC Type was F600 reduced to 0.18 mm to reduce equilibration time. PFOA concentration was set at 10 mg/L.

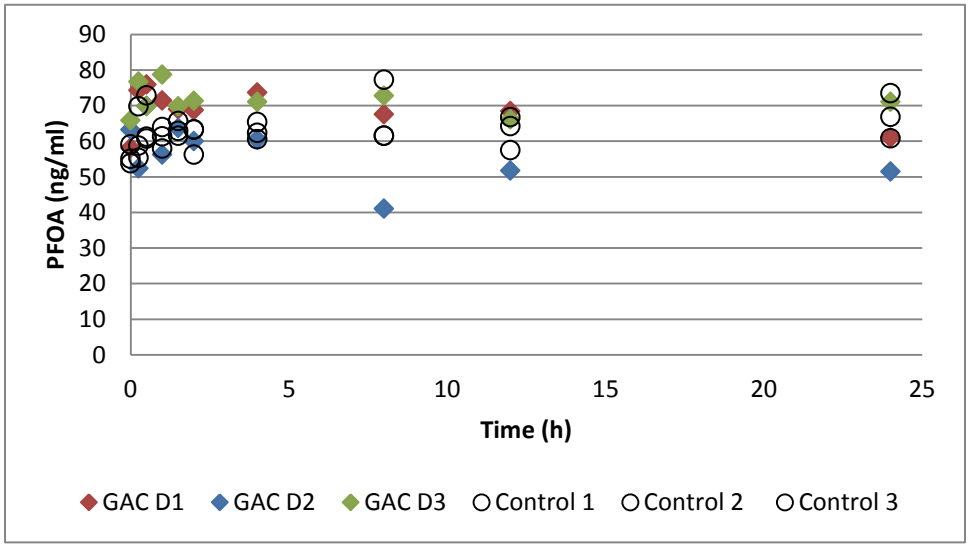

Figure 6B: GAC kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/mL. Samples D1, D2, D3 represent triplicate bottles exposed to 10 mg/L GAC dose. GAC Type was F600 reduced to 0.18 mm to reduce equilibration time. Control 1, 2, 3 represent triplicate bottles with only PFOA at 10 mg/L.

The second kinetic experiment was conducted with 10 mg/L PFOA and 20 mg/L hardwood ground biochar. The biochar as a whole demonstrate that some adsorption is possible. Biochar H was the best performing sample trending just below biochar control 1, Figure 6A. However, similar to the GAC when all the data points are shown it is difficult to determine the difference between the performance of the biochar and that of the controls, Figure 6B. One standard deviation error bars would overlap all curves making it difficult to distinguish the amount of adsorption. Biochar K was a 10 mg/L dose for comparison to other adsorbents of the same mass and was not included in the average.

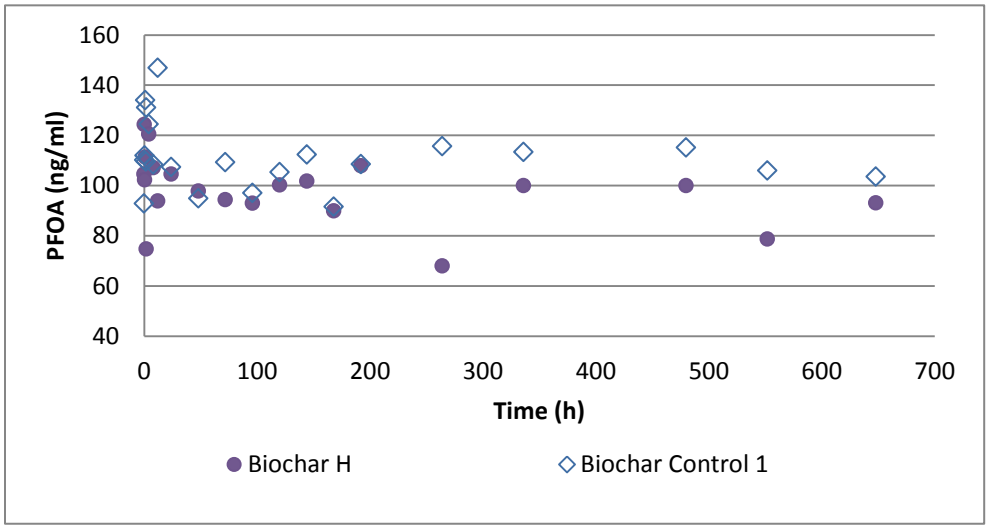

Figure 7A: Biochar kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/ml. Biochar H was exposed to 20 mg/L carbon dose. Biochar was hardwood pellet type reduced 0.18 mm to reduce equilibration time. Control 1 and 2 represent duplicate experimental control bottles with only PFOA at 10 mg/L.

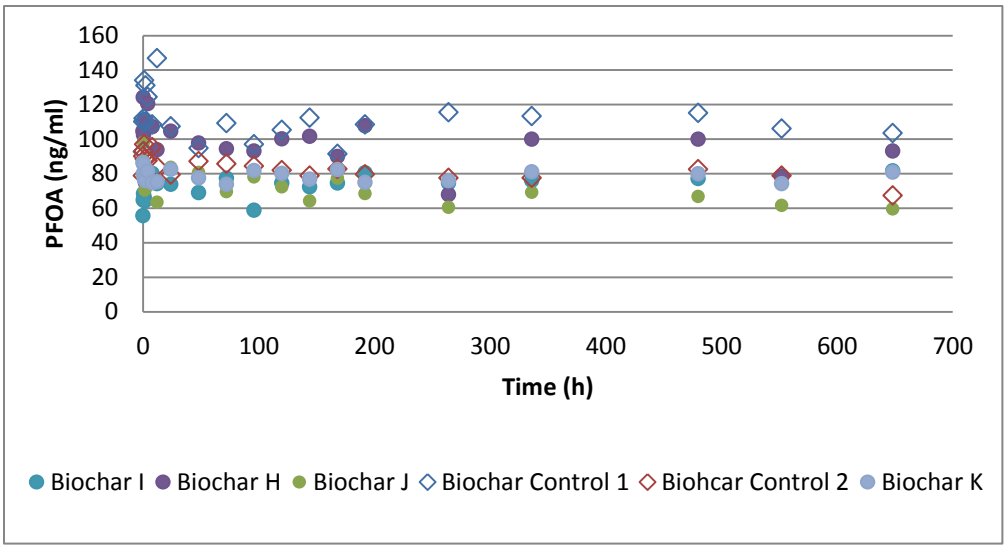

Figure 8B: Biochar kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/ml. Biochar H, I, and J represent triplicate bottles exposed to 20 mg/L carbon dose. Biochar K was a 10 mg/L carbon dose. Biochar was hardwood pellet type reduced 0.18 mm to reduce equilibration time. Control 1 and 2 represent duplicate experimental control bottles with only PFOA at 10 mg/L.

The CNT kinetic experiment was conducted with two different types of CNT materials. CNT A, B, and C where subjected to dry plasma etching after the CVD process creating hydrophilic CNTs; while CNT G, H, I were not subjected to plasma and were hydrophobic. The CNT labeled D, E, and F where control experiments with only 10mg/L PFOA and no adsorbents. CNT C was the best hydrophilic sample and CNT H was the best hydrophobic sample, Figure 7A. The same issue is noted in this experiment as well where variability of the controls and samples points makes it difficult to determine true performance. Looking at all the sample points and controls in Figure 7B, a standard deviation error bar would overlay all the data points as in the other experiments making it difficult to determine the extent of any adsorption.

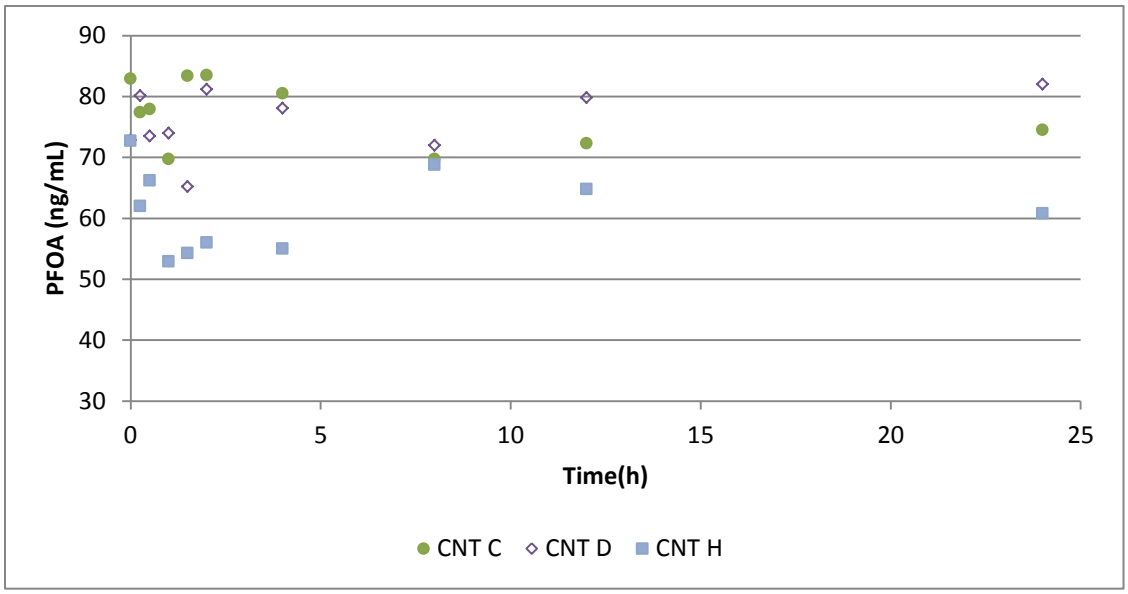

Figure 9A: CNT kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/mL. CNT C 10 mg/L carbon dose of hydrophilic CNT product. CNT H 10 mg/L carbon dose of hydrophobic CNT product. CNT D represents only PFOA at 10 mg/L with no carbon dose applied.

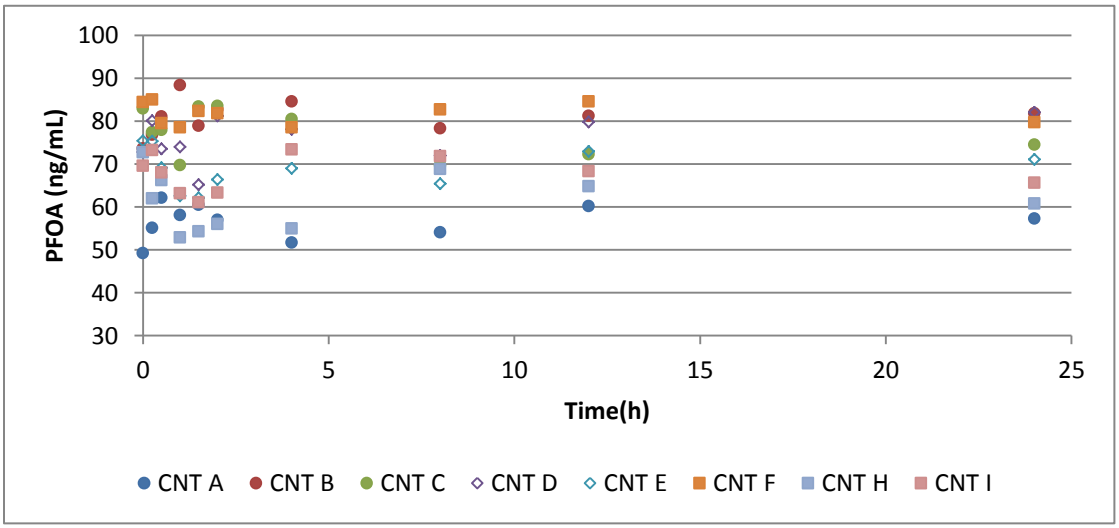

Figure 10B: CNT kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/mL. CNT A, B, and C represent triplicate bottles exposed to 10 mg/L carbon dose of hydrophilic CNT product. CNT G, H, and I represent triplicate samples of 10 mg/L carbon dose of hydrophobic CNT product. CNT D, E, and F represent triplicate bottles with only PFOA at 10 mg/L.

CNT C was the best hydrophilic adsorbent with 10% removal and CNT H was the best hydrophobic adsorbent with 16% removal. If biochar H is an accurate representation of performance 11% removal was achieved. GAC D2 had the best performance of the activated carbons with 19% removal. However, considering all controls and duplicate triplicate samples, it is difficult to make statements about any of the adsorbent's performance. The experimental controls should have remained constant around 100 ng/ml of PFOA, Figure 8.

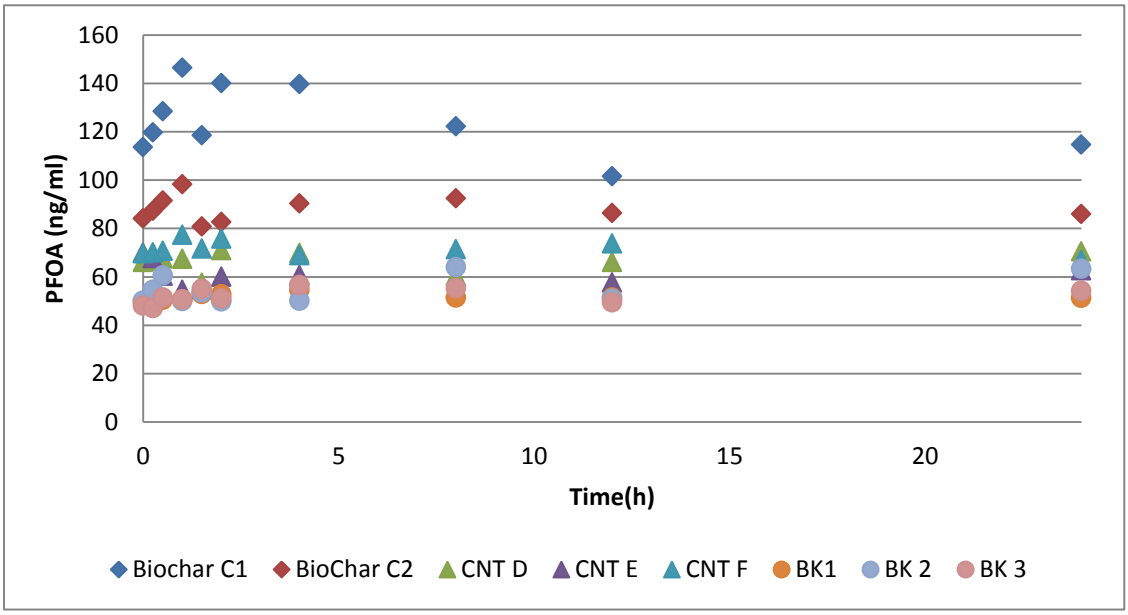

Figure 11: Controls liquid phase concentration of PFOA over time. All points in the figure are experimental control samples at 10 mg/L PFOA

The focus after reviewing all the kinetic experiment data was then changed to more fully understand the root cause of the error witnessed in the results. As part of the troubleshooting a review of the area counts reported for PFOA and the internal standard. It was noted that there was some peculiarities in area counts on both the PFOA and

internal standard. Figure 8 illustrates the variation in the control concentrations across the three kinetic experiments. This error may have been caused by the instrument or by errors in the sample prep. The instrument was checked for sensitivity and determined to be operating within its performance standards. This infers that the error could be associated with pipetting technique and the 1:100 dilution ratio. The pipette used for retrieving the 10 µL of sample and the 25 µL of internal standard was the same 10 uL-100 µL pipette. The internal standard area count variation can be seen in Figure 9. Every sample received 25 µL of internal standard so area counts should not have had this much variation.

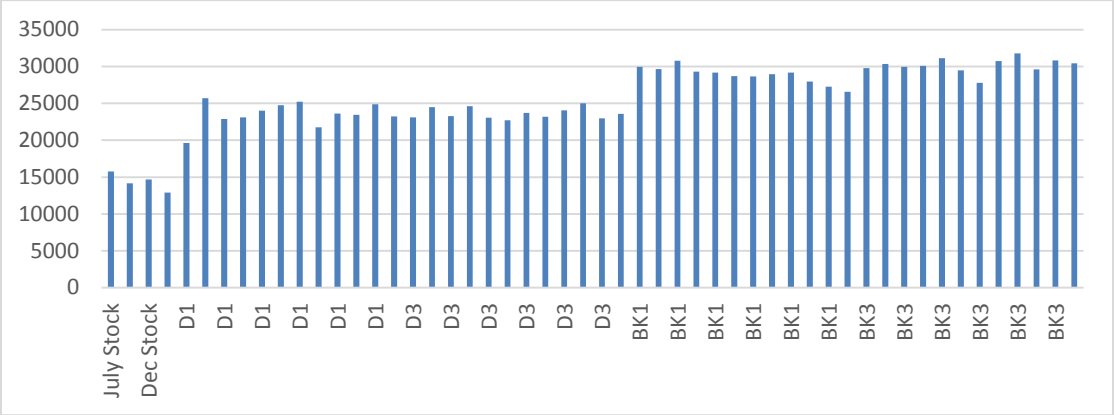

Figure 12: Internal Standard area counts on Waters LC-MS. This figure shows variation in pipetting the internal standard.

Another issue that was investigated was the impact of temperature on sample preparation. The temperature of the stock solution had always been cold since the stock solution was only removed from the lab refrigerator long enough prepare the sample bottles. A control test was conducted to see if allowing the stock solution to come to room temperature would have any effect on the preparation of test solutions. In the

process of analyzing the temperature test two different dilution steps were used. This was done to compare two 1:10 dilutions to achieve the needed 1:100 dilution ratio versus a one step 1:100 dilution ratio. The two step dilution recovery was 10% high for one sample and 50% high for another control sample of 100 ng/mL, Figure 10. The 1:100 dilutions were 35-40% low of the target recovery, Figure 10. This shows how important sample prep technique is for achieving good recoveries at low concentrations. The filters were also tested to see if PFOA was coming from the filter or if the filter contributed to any losses.

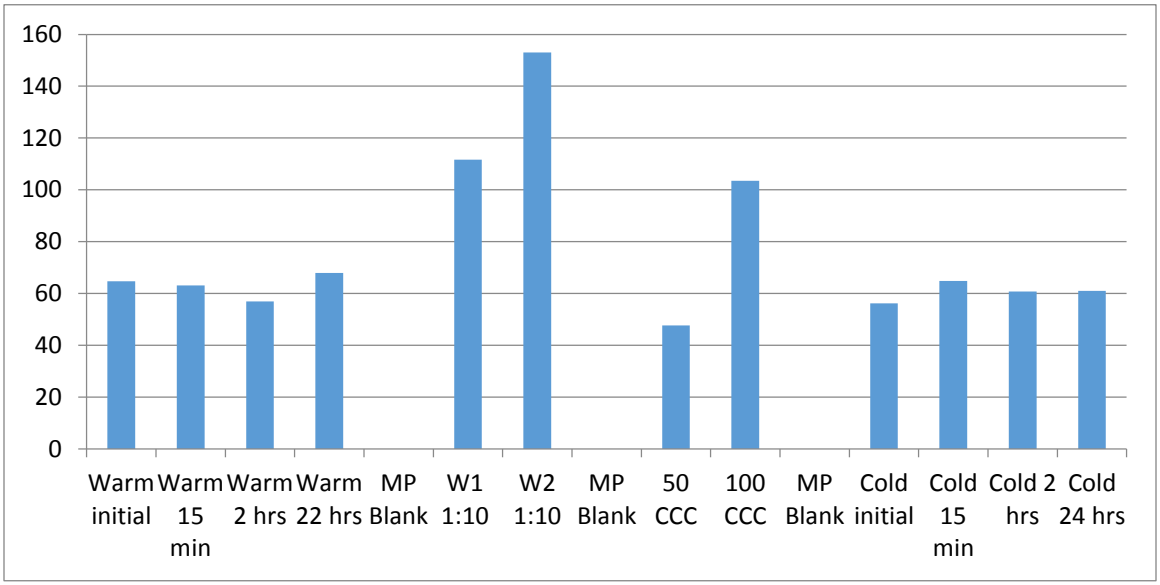

Figure 13: Control temperature test. Warm samples were prepared from stock after it had come to room temperature after 2 hours. W1 and W2 were chosen randomly from the warm samples and prepared using two 1:10 dilutions. 50 CCC and 100 CCC are continuing calibrations checks. Cold sample were prepared with stock solution fresh from the refrigerator.

Triplicate samples of DI water, DI water passed through the filters, stock solution, and stock solution passed through the filters were taken. The difference with and without the filters was not significant enough to be causing the variability observed from the experiments, Figure 11.

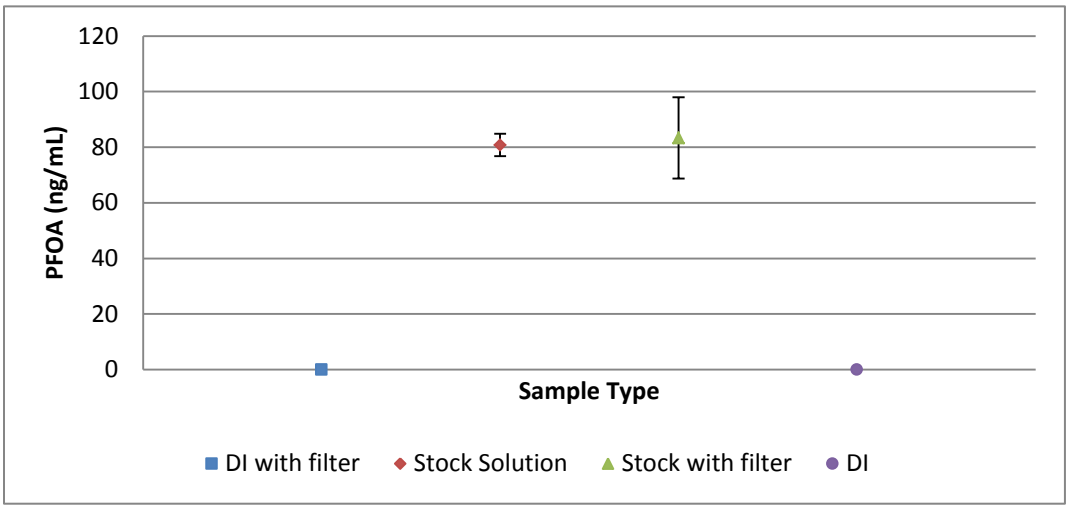

Figure 14: Filter test. Samples of deionized water and deionized water passed through a 0.45 µm SFCA filter. 10 mg/L PFOA stock solution with and without filter. Triplicate samples of each sample type where taken and the error bars represent two standard deviations.

A previous experiment used in the development of the sampling method was analyzed on a ThermoFinnigan, LCQ Classic Liquid Chromatography-Mass Spectrometry system (LCMS) and an EPA developed analytical method were used to determine the concentration of PFOA. Figure 12 shows the concentration of PFOA as a function of time. The PFOA in this experiment was analyzed after a 1:10 dilution ratio. The samples were diluted with 875 µL of 50% deionized water 50% methanol 2 mM ammonium acetate mobile phase and mixed with 25 µL of internal standard and 100 µL of sample. The GAC is Calgon F600 crushed with a mortar and pestle to 0.18 mm. The

carbon dose was 10 mg/L. The initial PFOA concentration was 10 mg/L. This experiment showed a 25% reduction in PFOA concentration and an equilibration time of 24 hours. Figure 12 shows what is typically found among adsorption experiments. Even in the early stages of these experiments it was difficult to get a steady control response.

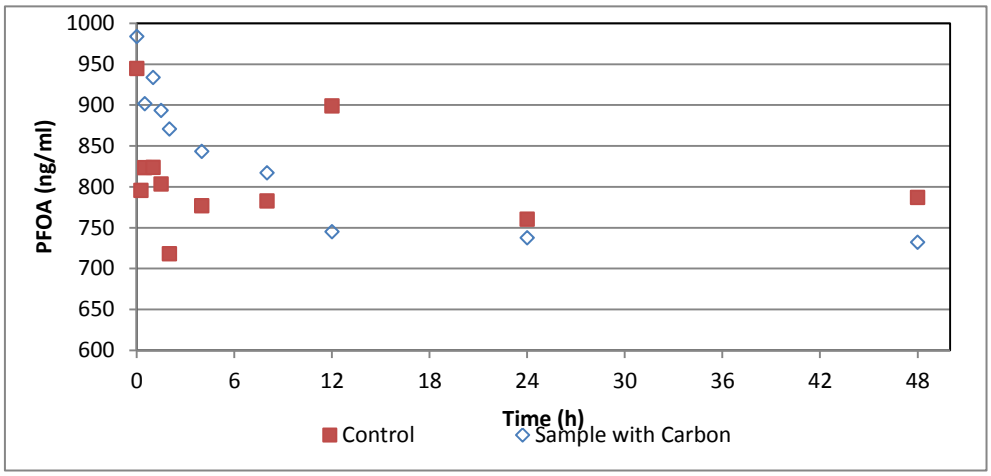

Figure 15: Initial GAC kinetic liquid phase concentration over time. The concentration of PFOA is reported in ng/ml. The samples with carbon line represent duplicate bottles exposed to 10 mg/L GAC dose. GAC Type was F600 reduced 0.18 mm to reduce equilibration time. The control is contained PFOA at 10 mg/L with no adsorbent added.

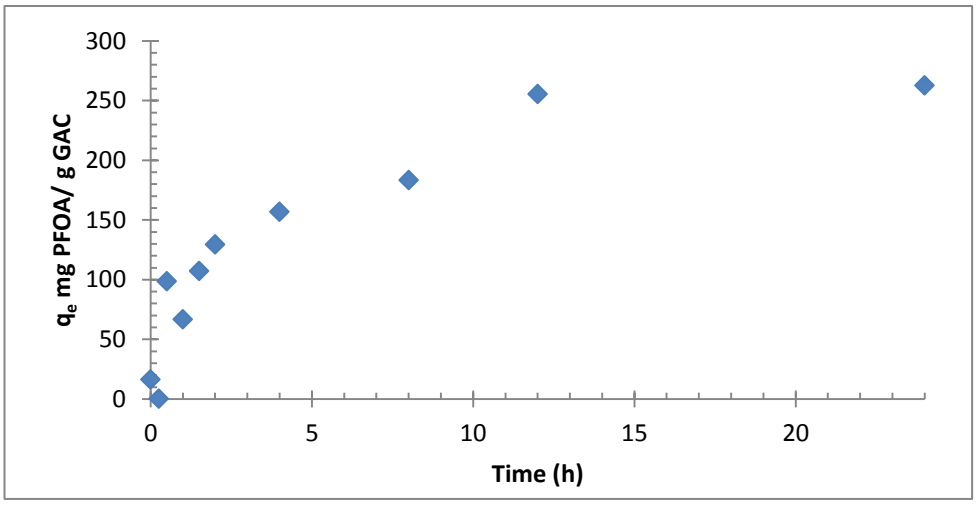

Figure 16: Solid phase concentration q_e as a function of time. The highest qe is 262.7 mg/g at 24 hours.

From the experiment shown in Figure 12 the solid phase concentration (q_e) was calculated. At equilibrium the q_e concentration was 262.7 milligrams PFOA adsorbed per gram of GAC, Figure 13.

The F600 GAC was the only adsorbent where an equilibrium time was found. Therefore it the only adsorbent in the isotherm study. The samples were analyzed in the Waters LC-MS as listed in the data analysis section. The Langmuir model, Figure 14, was a better fit with an R^2 of 0.9925 compared to the Freundlich model with an R^2 of 0.9876, Figure 15.

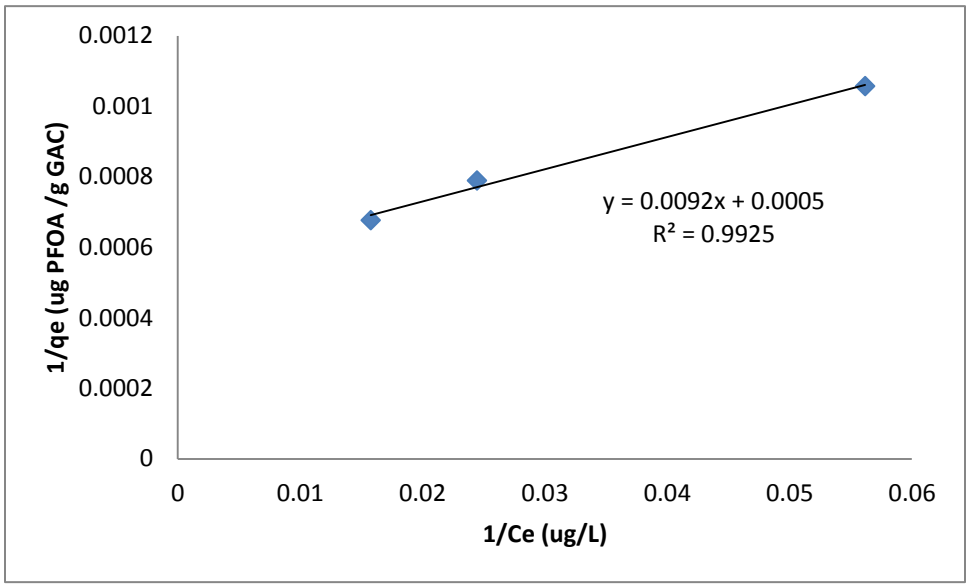

Figure 17: Langmuir Isotherm model for GAC. GAC Type was F600 reduced 0.18 mm to reduce equilibration time. The carbon dose was 20, 40, and 80 mg/L in 10 mg/L PFOA.

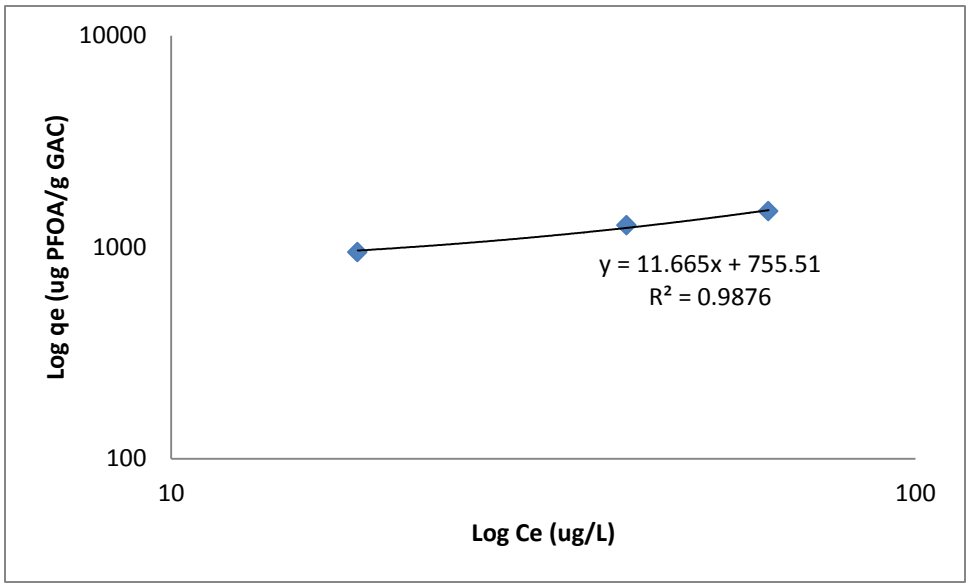

Figure 185: Freundlich Isotherm model for GAC. GAC Type was F600 reduced 0.18 mm to reduce equilibration time. The carbon dose was 20, 40, and 80 mg/L in 10 mg/L PFOA

GAC adsorption is an effective and widely applied in the treatment of organic contaminants from wastewater due to its removal efficacy, robustness, and low-cost. Long-term batch experiments of PFAS adsorption with GAC yielded higher adsorption coefficients for PFOA and PFOS in the range of 100-200 mg of PFAS per 1 g of GAC (Zhao et al. 2011). Another study evaluating the application of GAC to remove PFAS from a waste water treatment plant effluent determined PFOS removal greater than 90% (MN SEC, 2006). Table 2 lists some Langmuir and Freundlich model constants for PFOA and PFOS. Zhao (2011) used the Brunauer-Emmett-Teller (BET) isotherm to fit the data for adsorption with F600 GAC. The maximum adsorption for PFOS and PFOA ranged from 60-110 mg/g (Zhao et al. 2011). The isotherm rate constants for this study are not shown due the subjectivity of the data acquired using the 1:100 dilution on the

Waters LC-MS. The carbon dose was varied at 20, 40, and 80 mg/L. The higher carbon doses did see more adsorption compared to the kinetic tests.

Table 2: Langmuir and Freundlich model constants

Adsorbent	Langmuir q_m (mg/g)	B (L/mg)	R^2	Freundlich K	1/n	R^2	Reference
W400	91.6	0.010	0.988	5.23	0.492	0.992	Chen(2011)
M400	164	0.011	0.994	7.27	0.459	0.986	Chen(2011
MA	811	0.012	0.963	26.8	0.571	0.951	Chen(2011
SWCNT	712	0.044	0.891	122	0.324	0.998	Chen(2011)
MWCNT10	656	0.014	0.975	47.1	0.437	0.991	Chen(2011)
MWCNT50	514	0.008	0.976	14.9	0.569	0.977	Chen(2011)
PAC	16.5	0.606	0.997	24.238	0.450	0.959	Qu(2009)
F400 PFOS	236.4	0.124	0.959	25.9	1.123	0.979	Ochoa(2008)
F400 PFOA	112.1	0.038	0.968	11.8	0.443	0.955	Ochoa(2008)

2.5 Conclusions

The objective of this study was to investigate capacity and rate of primitive, conventional, and novel adsorbents. GAC had the best adsorption of theses adsorbents. Biochar and CNT also showed some adsorption but was difficult to quantify due to experimental control issues. The focus shifted to investigate the low recoveries and variability of controls. There was no significant difference between making solutions with a cold stock solution and allowing the stock solution to warm up to room temperature. The source of variability seems to come from inconsistent area counts on the internal standard and the PFOA. Pipetting technique and the volume of sample used for analysis appears to be the cause of this variability. When preparing a large number of samples using low volumes of sample the use of automated prep benches should be

employed. Keep in mind all equipment must be free of materials that could contaminate or bond with PFOA.

In considering the carbon dosage compared to other studies and seeing the GACs removal performance increase in the isotherm study would suggest that the initial dosage of this study should be considered too low. This dosage may work in PAC or superfine-PAC studies but is too low for GAC. Other studies covering some PFAS concentration were exposed to GAC doses in the range of 200-400 mg/L (Ochoa-Herrera and Sierra-Alvarez 2008, Zhao et al. 2011).

In order to fully understand the performance of adsorbents for PFAS remediation sites the researcher or remediation design engineer will need to perform multiple tests. It will be necessary to know how the other forms of PFAS adsorb to the materials selected. Another thing to consider is testing multiple PFAS together in solution on different adsorbents with organic free water and the contamination site specific water. The matrix of the contamination site water will need to be analyzed to determine what other chemicals and organic matter are competing for sites in the adsorption process along with PFAS.

2.6 References

The references used in this article are provided in the reference section of the thesis. The reference section of the thesis was formatted following the Journal of Environmental Engineering guidelines.

III. Conclusions

3.1 Chapter Overview

Chapter three is the conclusion of the thesis and discusses limitations, significance of the research, and suggestions for future work.

3.2 Review of Findings

The GAC performed the best of the three adsorbents. Biochar and CNT demonstrated some potential for adsorption however, it was hard to quantify due to control issues. The investigation into the control issues found that it is not a best practice to dilute directly 1:100 due to the potential of any error being amplified. Instead the standard practice should be to dilute in two steps of 1:10. This reduces the variability of systematic errors. The large number of samples and time limitations in this study led to the selection of the 1:100 dilution in this experiment

The results of the experiments using the 1:100 dilution were not the typical results expected based on previous studies and one initial experiment. A previous experiment was done in developing the method and run on Finnigan LCQ. The Finnigan LCQ started to have offset voltage to the inlet octapole and would not regulate properly. This interrupted the ability to identify peaks when infusing with the test standard of PFOA. With the Finnigan inoperable all samples collected were analyzed on the Waters LC-MS.

The previous data from the LCQ was acceptable since the quality control standards met their expected values within 7%. Figure 7 showed expected results for the kinetic experiments and is in line with other studies in the literature. The experiment set up was the same for the earlier experiment with 10 mg/L PFOA and 10 mg/L GAC. The

main differences in this experiment were: 1) the samples were diluted 1:10 vs 1:100 for analysis in the Finnigan; 2) the samples were analyzed within 30 days of collection; 3) samples were collected in Agilent glass vials vs the polypropylene vials that were used for the majority of the experiments; 4) the first set of experiments were ran on a Finnigan LCQ vs a Waters LC-MS with a different calibration range.

When setting up kinetic and isotherm experiments it is imperative to know the limits of detection and the optimal calibration curve for the chemical of study. Knowing the operating range of the analysis equipment will assist in developing the parameters for the experiment. This study was conducted at concentrations too high for analysis on the Waters LC-MS but where acceptable for the Finnagin LCQ. There were 384 samples needing to be diluted for analysis. In order to reduce human error involved in the preparation samples a properly equipped auto prep bench should be used. This will ensure dilution of samples into the operating range of the instrument will be done more consistently each time. Also care should be taken when having large dilution ratios.

3.3 Limitations

Limitations included time, available resources, and equipment. Laboratory resources were in a constant state of flux. Experiments were started before all the proper polypropylene pipette tips and vials were available. The biggest limitation was instrument time. In the middle of analyzing the second set of experimental data the Finnigan LCQ had electrical issues and a new instrument, method, and calibration curve had to be created. All the experiments were conducted within the initial parameters for the Finnigan LCQ. The nature of the sensitivity difference between the two instruments

affected data making results difficult to analyze. The dilution ratio of 1:100 was selected in order to complete the analysis with the time allowed for this study. However that decision induced a large error giving the appearance of minimal to no adsorption.

Only one type of GAC was used in this study. However, many different types exist. The CNT from Wright State University represented novel carbon adsorbents but they are a prototype material currently being studied and refined. Many other materials incorporating the use of nanomaterials could have been selected and a larger variety of them should be explored before making a definitive statement about the performance of CNT for PFAS removal. Only one biochar was used in this experiment. The production controls of the biochars can vary widely as they are manufactured in a kiln with potential wide ranges in operating conditions (time in kiln, temperature, uniformity of temperature, stock material, quality of make-up air).

Only PFOA was evaluated. This was done because of availability from a previous study. It should be noted that caution should be exercised when making statements about the suite of PFAS chemicals due to molecular size differences, and variability in chemical characteristics among the different forms of PFAS.

Only laboratory organic free water was used in this effort. When adsorbent materials are applied to environmental applications, dissolved organic matter will be an influential component of the background matrix. This will have to be accounted for in adsorption studies as the organic matter will compete with and reduce the overall capacity of the adsorbent for PFAS.

Only batch studies were conducted in this effort. Environmental applications of these technologies are often used in flow-through systems which behave differently than batch systems. In a flow through system an increasing concentration gradient travels through the adsorber and the adsorbent is exposed to an increasing gradient as time increases. Contrary to this a batch system is exposed initially to the highest concentration of contaminant and the gradient decreases with time.

3.4 Significance of Findings

Activated carbon materials will adsorb PFOA, GAC performs better than biochar followed by CNTs. However there are significant analytical challenges in measuring concentrations. There can be losses to the material in every step of the experiment and PFAS free lab materials need to be available to avoid background contamination. Human error can play a big part in the analytical challenge with large sample sizes. Experience and skill of the lab worker in proper lab techniques in a time constrained environment are an issue. Pipetting is sensitive when using small volumes of sample making it difficult to achieve the expected recoveries.

3.5 Future Research

Some adsorption was seen with each material; but in order to determine if these results are accurate the samples should be retested using smaller dilution ratios. Future research should also consider increasing the mass of CNT fabric and biochar used for adsorption. Studying these materials in a real world groundwater matrix to see how PFAS adsorbs when there is more organic matter competing for sorption sites. Furthermore rapid scale small column tests should be studied to see when PFAS breaks

through these adsorbents when used in a filter. This would be beneficial to pump and treat filter designs.

Appendix A. Waters LC-MS Output

Table A1: Waters LC-MS mass spectrometer output

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
1	1	20160111	MP Blank	MP Blank	Blank						MM-			
2	2	20160111	0 Std	0 Std	Standard	0			32700.8		MM-I			
3	3	20160111	2 ng Std	2 ng Std	Standard	2	7.4	5332.0	46886.4	0.8	bb	2.0	2	12.6
4	4	20160111	5 ng Std	5 ng Std	Standard	5	7.4	10828.0	37890.8	1.8	bb	4.9	-2	10.8
5	5	20160111	10 ng Std	10 ng Std	Standard	10	7.4	23886.1	41373.6	3.6	bb	10.1	1.1	10.8
6	6	20160111	25 ng Std	25 ng Std	Standard	25	7.4	70944.3	50416.0	9.0	bb	25.4	1.8	11.2
7	7	20160111	50 ng Std	50 ng Std	Standard	50	7.4	96623.4	40628.5	16.0	bb	45.3	-9.4	11.2
8	8	20160111	75 ng Std	75 ng Std	Standard	75	7.4	173166.4	40271.9	27.3	bb	77.5	3.4	11.5
9	9	20160111	100 ng Std	100 ng Std	Standard	100	7.4	244897.8	43832.6	36.7	bb	104.5	4.5	12.2
10	10	20160111	200 ng Std	200 ng Std	Standard	200	7.4	554065.5	50832.8	69.2	bb	197.1	-1.4	11.4
11	11	20160111	MP Blank	MP Blank	Blank						MM-			
12	12	20160111	10 ng CCC	10 ng CCC	QC	10			36642.9		MM-I			
13	13	20160111	50 ng CCC	50 ng CCC	QC	50	7.5	104131.2	37585.5	17.4	bb	49.5	-1	11.1
14	14	20160111	100 ng CCC	100 ng CCC	QC	100	7.5	242758.1	43436.1	35.3	bb	100.5	0.5	11.1
15	15	20160111	MP Blank	MP	Blank						MM-			

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Blank										
16	16	20160111	G0	CNT G	Analyte		7.5	112636.1	37312.1	19.2	bb	54.4		11.3
17	17	20160111	G1	CNT	Analyte		7.5	103779.7	36981.7	18.6	MM	52.8		10.9
18	18	20160111	G2	CNT	Analyte		7.5	112199.2	37527.2	19.4	MM	55.1		11.4
19	19	20160111	G3	CNT	Analyte		7.5	110581.1	38768.8	17.8	bb	50.7		11.5
20	20	20160111	G4	CNT	Analyte		7.5	123726.4	39538.6	19.6	MM	55.7		11.1
21	21	20160111	MP Blank	MP Blank	Blank						MM-			
22	22	20160111	G5	CNT	Analyte		7.5	120554.5	39249.3	19.9	MM	56.5		11.4
23	23	20160111	G6	CNT	Analyte		7.5	106106.9	39305.8	17.0	bb	48.2		12.3
24	24	20160111	G7	CNT	Analyte		7.5	122375.9	40304.6	18.6	bb	52.7		11.6
25	25	20160111	G8	CNT	Analyte		7.5	116441.2	41913.0	17.8	MM	50.5		11.9
26	26	20160111	MP Blank	MP Blank	Blank						MM-			
27	27	20160111	10 ng CCC	10 ng CCC	QC	10			36416.3		MM-I			
28	28	20160111	50 ng CCC	50 ng CCC	QC	50	7.4	103955.3	37255.4	17.1	bb	48.4	-3.2	12.4
29	29	20160111	MP Blank	MP Blank	Blank						MM-			
30	30	20160111	G9	CNT	Analyte		7.5	104339.1	39512.2	16.4	bb	46.6		12.6
31	31	20160111	A0	CNT Plasma	Analyte		7.5	108161.0	39421.9	17.3	bb	49.2		12.1
32	32	20160111	A1	CNT Plasma	Analyte		7.5	126579.1	39818.6	19.4	bb	55.1		11.7
33	33	20160111	A2	CNT Plasma	Analyte		7.5	143800.4	41155.5	21.9	MM	62.1		11.3
34	34	20160111	A3	CNT Plasma	Analyte		7.4	136102.9	40202.6	20.5	bb	58.1		12.3

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
35	35	20160111	MP Blank	MP Blank	Blank						MM-			
36	36	20160111	50 ng CCC	50 ng CCC	QC	50	7.5	103319.9	39042.7	16.3	MM	46.4	-7.2	11.4
37	37	20160111	100 ng CCC	100 ng CCC	QC	100	7.4	240762.2	43781.8	33.5	bb	95.2	-4.8	11.7
38	38	20160111	MP Blank	MP Blank	Blank						MM-			
39	39	20160111	A4	CNT Plasma	Analyte		7.5	146385.8	43057.9	21.3	MM	60.5		12.3
40	40	20160111	A5	CNT Plasma	Analyte		7.4	131149.4	41917.3	20.1	MM	57.0		12.1
41	41	20160111	A6	CNT Plasma	Analyte		7.5	126071.2	41157.1	18.2	bb	51.7		12.4
42	42	20160111	A7	CNT Plasma	Analyte		7.4	133507.1	44646.7	19.0	bb	54.1		11.7
43	43	20160111	A8	CNT Plasma	Analyte		7.4	130335.8	38755.6	21.2	MM	60.2		11.3
44	44	20160111	A9	CNT Plasma	Analyte		7.4	136523.4	41136.6	20.2	bb	57.3		11.7
45	45	20160111	MP Blank	MP Blank	Blank		7.4	130473.3	39237.5	20.7	MM	58.7		11.3
46	1	20160112	MP Blank	MP Blank	Blank						MM-			
47	2	20160112	0 Std	0 Std	Standard	0			47158.2		MM-			
48	3	20160112	2 ng Std	2 ng Std	Standard	2	7.4	6813.4	63937.9	0.6	bb	2.0	-0.3	12.8
49	4	20160112	5 ng Std	5 ng Std	Standard	5	7.4	14544.1	52550.5	1.6	bb	5.2	3.1	11.4
50	5	20160112	10 ng Std	10 ng Std	Standard	10	7.4	33891.6	58252.8	3.4	bb	10.6	5.8	12.0
51	6	20160112	25 ng Std	25 ng Std	Standard	25	7.4	89324.0	71486.5	7.6	MM	23.9	-4.6	11.0

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
52	7	20160112	50 ng Std	50 ng Std	Standard	50	7.4	143470.3	56382.0	15.2	bb	47.4	-5.2	12.5
53	8	20160112	75 ng Std	75 ng Std	Standard	75	7.4	236470.7	58734.9	23.7	bb	73.9	-1.5	12.4
54	9	20160112	100 ng Std	100 ng Std	Standard	100	7.4	344171.8	62691.9	32.5	bb	101.2	1.2	11.8
55	10	20160112	200 ng Std	200 ng Std	Standard	200	7.4	759389.9	70547.3	65.1	bb	202.9	1.4	12.3
56	11	20160112	MP Blank	MP Blank	Blank						MM-			
57	12	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	30357.1	64860.8	2.8	bb	8.8	-11.8	12.9
58	13	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	149388.2	53251.1	16.7	bb	51.9	3.9	12.0
59	14	20160112	100 ng CCC	100 ng CCC	QC	100	7.4	341293.9	62751.5	32.7	bb	101.9	1.9	12.7
60	15	20160112	MP Blank	MP Blank	Blank						MM-			
61	16	20160112	J0	Biochar	Analyte		7.4	225404.9	50367.9	27.6	MM	85.9		11.3
62	17	20160112	J1	Biochar	Analyte		7.4	241789.8	53255.8	28.3	bb	88.1		12.1
63	18	20160112	J2	Biochar	Analyte		7.4	215626.3	44008.7	31.5	MM	98.1		11.7
64	19	20160112	J3	Biochar	Analyte		7.4	190005.5	47520.1	25.3	MM	78.9		11.6
65	20	20160112	J4	Biochar	Analyte		7.4	251490.2	66264.3	22.6	bb	70.5		12.3
66	21	20160112	MP Blank	MP Blank	Blank						MM-			
67	22	20160112	J5	Biochar	Analyte		7.4	218874.3	54185.2	24.1	bb	75.0		11.3
68	23	20160112	J6	Biochar	Analyte		7.4	221007.1	56659.8	23.4	bb	73.1		11.9
69	24	20160112	J7	Biochar	Analyte		7.4	208152.6	51246.8	24.6	MM	76.7		11.4
70	25	20160112	J8	Biochar	Analyte		7.4	185413.1	53755.2	20.4	bb	63.5		11.8
71	26	20160112	MP Blank	MP	Blank						MM-			

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Blank										
72	27	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	29800.1	66155.3	2.7	bb	8.3	-16.6	11.5
73	28	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	143689.9	53274.2	15.8	bb	49.4	-1.1	12.4
74	29	20160112	MP Blank	MP Blank	Blank						MM-			
75	30	20160112	J9	Biochar	Analyte		7.4	216143.6	52850.0	26.8	MM	83.6		13.6
76	31	20160112	J10	Biochar	Analyte		7.4	213841.3	51668.8	25.8	MM	80.6		11.8
77	32	20160112	J11	Biochar	Analyte		7.4	189722.9	49085.6	22.3	bb	69.5		12.6
78	33	20160112	J12	Biochar	Analyte		7.4	200153.2	47273.0	25.0	bb	78.0		12.4
79	34	20160112	J13	Biochar	Analyte		7.4	193825.2	50050.6	23.2	bb	72.4		12.1
80	35	20160112	MP Blank	MP Blank	Blank						MM-			
81	36	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	142603.5	51455.1	16.1	bb	50.3	0.5	11.8
82	37	20160112	100 ng CCC	100 ng CCC	QC	100	7.4	327167.4	60104.9	32.0	bb	99.6	-0.4	12.4
83	38	20160112	MP Blank	MP Blank	Blank						MM-			
84	39	20160112	J14	Biochar	Analyte		7.4	170408.2	51368.8	20.6	MM	64.2		11.8
85	40	20160112	J15	Biochar	Analyte		7.4	191685.8	48777.1	24.8	bb	77.4		12.3
86	41	20160112	J16	Biochar	Analyte		7.4	172850.6	49819.5	21.9	bb	68.4		12.0
87	42	20160112	J17	Biochar	Analyte		7.4	169891.8	50796.0	19.4	bb	60.4		12.1
88	43	20160112	J18	Biochar	Analyte		7.4	187734.5	50960.0	22.2	bb	69.1		12.2
89	44	20160112	MP Blank	MP Blank	Analyte									
90	45	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	131675.4	52853.6	16.1	bb	50.2	0.5	12.8

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
91	46	20160112	100ng CCC	100 ng CCC	QC	100	7.4	324801.4	59752.0	32.9	bb	102.5	2.5	12.0
92	47	20160112	MP Blank	MP Blank	Blank									
93	48	20160112	J19	Biochar	Analyte		7.4	181834.8	52634.8	21.4	bb	66.7		11.1
94	49	20160112	J20	Biochar	Analyte		7.4	169490.4	52250.2	19.8	MM	61.6		11.7
95	50	20160112	J21	Biochar	Analyte		7.4	162512.6	53860.4	19.1	MM	59.6		12.4
96	51	20160112	J22	Biochar	Analyte		7.4	204061.7	52052.5	23.2	bb	72.3		12.3
97	52	20160112	MP Blank	MP Blank	Blank									
98	53	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	30120.0	62710.6	2.9	bb	9.1	-8.9	12.5
99	54	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	138837.5	52571.3	16.3	bb	51.0	1.9	13.6
100	55	20160112	MP Blank	MP Blank	Blank									
101	56	20160112	E0	CNT Control	Analyte		7.4	217732.0	52639.3	24.2	MM	75.4		12.4
102	57	20160112	E1	CNT Control	Analyte		7.4	209960.4	49122.4	24.2	bb	75.3		12.3
103	58	20160112	E2	CNT Control	Analyte		7.4	186053.6	48929.7	22.2	bb	69.1		12.4
104	59	20160112	E3	CNT Control	Analyte		7.4	168007.7	47433.5	20.1	bb	62.6		11.7
105	60	20160112	E4	CNT Control	Analyte		7.4	168360.4	49656.7	19.9	MM	62.1		12.7
106	61	20160112	MP Blank	MP Blank	Blank									
107	62	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	28888.1	63839.2	2.7	bb	8.5	-15.5	12.7
108	63	20160112	50ng CCC	50 ng CCC	QC	50	7.4	122929.5	51182.5	15.5	MM	48.4	-3.1	11.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
109	64	20160112	MP Blank	MP Blank	Blank									
110	65	20160112	E5	CNT Control	Analyte		7.4	184537.9	49343.3	21.3	bb	66.4		12.5
111	66	20160112	E6	CNT Control	Analyte		7.4	186935.8	48817.2	22.1	bb	69.0		12.7
112	67	20160112	E7	CNT Control	Analyte		7.4	170277.5	46959.3	21.0	bb	65.4		12.5
113	68	20160112	E8	CNT Control	Analyte		7.4	177096.6	46503.3	23.4	MM	72.9		11.0
114	69	20160112	E9	CNT Control	Analyte		7.4	193036.2	47798.3	22.8	bb	71.1		12.5
115	70	20160112	MP Blank	MP Blank	Blank									
116	71	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	139498.8	50916.5	15.8	bb	49.4	-1.1	12.5
117	72	20160112	100 ng CCC	100 ng CCC	QC	100	7.4	322347.5	58505.9	32.1	bb	100.1	0.1	13.0
118	73	20160112	MP Blank	MP Blank	Blank									
119	74	20160112	20A 0	GAC 20A initial	Analyte		7.4	243426.3	49718.5	29.0	MM	90.4		12.1
120	75	20160112	20A 24	GAC 20A 24 hour	Analyte		7.4	159369.1	49629.9	18.8	MM	58.6		11.8
121	76	20160112	20B 0	GAC 20B initial	Analyte		7.4	219825.8	50769.8	24.7	bb	76.9		13.0
122	77	20160112	20B 24	GAC 20B 24 hour	Analyte		7.4	194476.1	51920.0	21.9	bb	68.3		12.3
123	78	20160112	MP Blank	MP	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Blank										
124	79	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	28993.8	64397.8	2.7	bb	8.5	-14.7	11.9
125	80	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	142021.9	51354.3	15.7	bb	48.9	-2.3	12.2
126	81	20160112	MP Blank	MP Blank	Blank									
127	82	20160112	40A 0	GAC 40A initial	Analyte		7.4	182787.5	50769.7	21.2	MM	66.1		10.9
128	83	20160112	40A 24	GAC 40A 24 hour	Analyte		7.4	120627.0	50616.0	14.0	bb	43.6		12.3
129	84	20160112	40B 0	GAC 40B initial	Analyte		7.4	206343.2	52392.6	22.2	bb	69.2		11.7
130	85	20160112	40B 24	GAC 40B 24 hour	Analyte		7.4	98001.0	50118.9	12.2	MM	38.2		12.1
131	86	20160112	MP Blank	MP Blank	Blank									
132	87	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	121873.2	51832.1	14.5	bb	45.2	-9.7	10.8
133	88	20160112	100 ng CCC	100 ng CCC	QC	100	7.4	323828.6	59894.8	31.7	bb	98.9	-1.1	12.8
134	89	20160112	MP Blank	MP Blank	Blank									
135	90	20160112	80A 0	GAC 80A initial	Analyte		7.4	247473.9	45010.4	32.8	bb	102.2		11.9
136	91	20160112	80A 24	GAC 80A 24 hour	Analyte		7.4	52609.6	47827.8	6.2	bb	19.4		10.2

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
137	92	20160112	80B 0	GAC 80B initial	Analyte		7.4	273160.7	50755.2	30.4	bb	94.8		11.8
138	93	20160112	80B 24	GAC 80B 24 hour	Analyte		7.4	40490.6	46638.5	5.2	bb	16.2		11.5
139	94	20160112	MP Blank	MP Blank	Blank									
140	95	20160112	10 ng CCC	10 ng CCC	QC	10	7.4	29102.3	64611.9	2.7	bb	8.3	-16.6	12.4
141	96	20160112	50 ng CCC	50 ng CCC	QC	50	7.4	143873.0	51831.5	16.1	bb	50.3	0.6	12.2
142	97	20160112	MP Blank	MP Blank	Blank									
143	98	20160112	C1	GAC control initial	Analyte		7.4	233646.0	46501.7	30.3	MM	94.6		12.0
144	99	20160112	C2	GAC control 24 hour	Analyte		7.4	239786.9	46169.5	29.7	MM	92.7		12.1
145	100	20160112	MP Blank	MP Blank	Blank									
146	1	20160113	MP Blank	MP Blank	Blank		8.2	1585.9	24.9	201.2	bb	653.4		
147	2	20160113	0 Std	0 Std	Standard	0			43143.0					
148	3	20160113	2 ng Std	2 ng Std	Standard	2	7.5	5856.8	57340.3	0.6	bb	2.0	2	33.6
149	4	20160113	5 ng Std	5 ng Std	Standard	5	7.5	12738.0	49179.4	1.5	bb	4.9	-1.3	8.1
150	5	20160113	10 ng Std	10 ng Std	Standard	10	7.5	29135.0	53394.4	3.1	bb	10.0	0.5	10.5
151	6	20160113	25 ng Std	25 ng Std	Standard	25	7.5	77540.8	63370.7	7.7	bb	25.1	0.3	11.0

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
152	7	20160113	50 ng Std	50 ng Std	Standard	50	7.5	133264.1	51375.7	15.2	bb	49.5	-1	11.3
153	8	20160113	75 ng Std	75 ng Std	Standard	75	7.5	218732.1	54452.9	23.0	bb	74.6	-0.5	11.5
154	9	20160113	100 ng Std	100 ng Std	Standard	100	7.5	300925.0	56871.5	30.5	bb	99.3	-0.7	10.9
155	10	20160113	200 ng Std	200 ng Std	Standard	200	7.5	681051.4	63468.8	62.0	bb	201.5	0.8	11.6
156	11	20160113	MP Blank	MP Blank	Blank									
157	12	20160113	10 ng CCC	10 ng CCC	QC	10	7.5	27679.2	60462.2	2.5	bb	8.1	-19	12.4
158	13	20160113	50 ng CCC	50 ng CCC	QC	50	7.5	134226.0	48233.2	16.3	bb	52.9	5.9	12.0
159	14	20160113	100 ng CCC	100 ng CCC	QC	100	7.5	299320.8	54824.5	31.8	bb	103.3	3.3	12.4
160	15	20160113	MP Blank	MP Blank	Blank									
161	16	20160113	D2_Initial	GAC	Analyte		7.5	190419.8	49081.2	23.1	bb	75.1		12.7
162	17	20160113	D2_0	GAC	Analyte		7.5	161560.9	49773.4	19.4	bb	63.2		11.5
163	18	20160113	D2_1	GAC	Analyte		7.5	123998.1	49506.5	16.1	bb	52.3		10.7
164	19	20160113	D2_2	GAC	Analyte		7.5	169628.4	47109.3	21.5	bb	69.9		11.9
165	20	20160113	D2_3	GAC	Analyte		7.5	136199.6	48037.5	17.3	bb	56.2		11.0
166	21	20160113	MP Blank	MP Blank	Blank									
167	22	20160113	D2_4	GAC	Analyte		7.5	150938.9	46745.5	19.6	bb	63.7		11.2
168	23	20160113	D2_5	GAC	Analyte		7.5	145390.5	44939.9	18.4	bb	60.0		12.3
169	24	20160113	D2_6	GAC	Analyte		7.5	152545.4	47051.3	18.6	bb	60.4		12.5
170	25	20160113	D2_7	GAC	Analyte		7.5	97745.8	49487.7	12.6	bb	41.0		11.0
171	26	20160113	MP Blank	MP	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Blank										
172	27	20160113	10 ng CCC	10 ng CCC	QC	10	7.5	27062.3	58234.1	2.8	bb	9.0	-9.5	12.1
173	28	20160113	50 ng CCC	50 ng CCC	QC	50	7.5	125849.4	47769.9	15.2	bb	49.3	-1.3	12.0
174	29	20160113	MP Blank	MP Blank	Blank									
175	30	20160113	D2_8	GAC	Analyte		7.5	138072.0	49953.9	15.9	bb	51.7		13.0
176	31	20160113	D2_9	GAC	Analyte		7.5	138970.1	48992.9	15.8	bb	51.4		11.9
177	32	20160113	D2_10	GAC	Analyte		7.5	120422.7			bb			11.7
178	33	20160113	BK2_Initial	Control	Analyte		7.5	136205.3	45453.1	17.7	bb	57.5		12.3
179	34	20160113	BK2_0	Control	Analyte		7.5	130316.5	45525.0	16.9	bb	55.0		12.9
180	35	20160113	MP Blank	MP Blank	Blank									
181	36	20160113	50 ng CCC	50 ng CCC	QC	50	7.5	106621.3	46809.3	14.5	bb	47.2	-5.7	11.1
182	37	20160113	100 ng CCC	100 ng CCC	QC	100	7.5	289587.4	52874.7	31.2	bb	101.3	1.3	12.9
183	38	20160113	MP Blank	MP Blank	Blank									
184	39	20160113	BK2_1	Control	Analyte		7.5	141867.8	40355.5	21.5	bb	69.8		11.5
185	40	20160113	BK2_2	Control	Analyte		7.5	157295.4	40257.8	22.4	bb	72.8		11.8
186	41	20160113	BK2_3	Control	Analyte		7.5	129947.3	41456.5	19.7	bb	63.9		10.7
187	42	20160113	BK2_4	Control	Analyte		7.5	138843.1	44270.8	18.9	bb	61.5		11.4
188	43	20160113	BK2_5	Control	Analyte		7.5	129699.9	46380.8	17.3	bb	56.2		11.8
189	44	20160113	MP Blank	MP Blank	Analyte									
190	45	20160113	50 ng CCC	50 ng CCC	QC	50	7.5	127284.8	47445.2	15.0	bb	48.9	-2.3	11.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
191	46	20160113	100ng CCC	100 ng CCC	QC	100	7.5	288594.2	54268.8	30.6	bb	99.4	-0.6	11.6
192	47	20160113	MP Blank	MP Blank	Blank									
193	48	20160113	BK2_6	Control	Analyte		7.5	130165.7	41498.5	18.6	bb	60.5		11.2
194	49	20160113	BK2_7	Control	Analyte		7.5	166494.5	41481.6	23.7	bb	77.2		11.9
195	50	20160113	BK2_8	Control	Analyte		7.5	132286.0	43367.1	19.8	bb	64.2		11.3
196	51	20160113	BK2_9	Control	Analyte		7.5	164811.4	41726.2	22.6	bb	73.5		11.5
197	52	20160113	BK2_10	Control	Analyte				40177.2					
198	53	20160113	MP Blank	MP Blank	Blank									
199	54	20160113	10 ng CCC	10 ng CCC	QC	10	7.5	26180.2	57692.0	2.6	bb	8.4	-16.3	12.2
200	55	20160113	50 ng CCC	50 ng CCC	QC	50	7.5	126233.3	46020.7	15.6	bb	50.7	1.4	11.1
201	56	20160113	MP Blank	MP Blank	Blank									
202	1	20160121	MP Blank	MP Blank	Blank		7.7	24713.4	28253.8	3.6	bb	13.8		24.9
203	2	20160121	0 Std	0 Std	Standard	0	7.5	596.4	30950.9	0.2	bb	0.4		
204	3	20160121	2 ng Std	2 ng Std	Standard	2	6.6	4223.5	40663.6	0.5	bb	1.6	-19.4	
205	4	20160121	5 ng Std	5 ng Std	Standard	5	6.6	8666.8	33828.6	1.3	bb	4.8	-4.7	12.4
206	5	20160121	10 ng Std	10 ng Std	Standard	10	6.6	21256.0	37593.5	2.7	bb	10.3	3	12.9
207	6	20160121	25 ng Std	25 ng Std	Standard	25	6.6	62497.2	44541.6	6.6	bb	25.5	2	11.6
208	7	20160121	50 ng Std	50 ng Std	Standard	50	6.6	94456.5	36103.4	12.2	bb	47.9	-4.1	10.9
209	8	20160121	75 ng Std	75 ng	Standard	75	6.6	155574.5	37185.7	19.7	bb	77.3	3	11.9

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Std										
210	9	20160121	100 ng Std	100 ng Std	Standard	100	6.6	232112.1	41939.0	25.4	bb	99.9	-0.1	12.6
211	10	20160121	200 ng Std	200 ng Std	Standard	200	6.6	518296.8	46654.7	50.7	bb	199.8	-0.1	12.1
212	11	20160121	MP Blank	MP Blank	Blank									
213	12	20160121	10 ng CCC	10 ng CCC	QC	10	6.6	20161.6	44069.6	2.2	bb	8.1	-18.7	13.5
214	13	20160121	50 ng CCC	50 ng CCC	QC	50	6.6	96292.9	35937.5	12.6	bb	49.5	-1	11.8
215	14	20160121	100 ng CCC	100 ng CCC	QC	100	6.6	229277.3	41111.2	26.9	bb	105.9	5.9	12.5
216	15	20160121	MP Blank	MP Blank	Blank		7.5	200.0			bb			
217	16	20160121	0	C1	Analyte		6.6	189641.0	37981.9	23.6	bb	92.8		11.5
218	17	20160121	1	C1	Analyte		6.6	201673.2	33742.8	28.0	bb	110.1		12.2
219	18	20160121	2	C1	Analyte		6.6	219891.3	36055.1	28.5	bb	111.9		12.2
220	19	20160121	3	C1	Analyte		6.6	263017.9	35943.9	34.0	bb	134.0		12.3
221	20	20160121	4	C1	Analyte		6.6	199232.4	33876.4	27.8	bb	109.5		11.7
222	21	20160121	MP Blank	MP Blank	Blank									
223	22	20160121	5	C1	Analyte		6.6	246767.6	33837.9	33.3	bb	131.1		11.4
224	23	20160121	6	C1	Analyte		6.6	245749.7	36324.5	31.6	bb	124.4		12.6
225	24	20160121	7	C1	Analyte		6.6	206560.6	34739.3	27.6	bb	108.4		11.8
226	25	20160121	8	C1	Analyte		6.6	167371.7	20928.2	37.3	bb	146.9		13.0
227	26	20160121	MP Blank	MP Blank	Blank									
228	27	20160121	10 ng CCC	10 ng CCC	QC	10	6.6	21718.5	47900.0	2.2	bb	8.2	-17.9	12.7

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
229	28	20160121	50 ng CCC	50 ng CCC	QC	50	6.6	98101.2	36562.0	12.4	bb	48.3	-3.3	12.3
230	29	20160121	MP Blank	MP Blank	Blank									
231	30	20160121	9	C1	Analyte		6.6	191765.0	33235.9	27.3	bb	107.3		12.6
232	31	20160121	10	C1	Analyte		6.6	174440.3	33793.4	24.1	bb	94.8		12.6
233	32	20160121	11	C1	Analyte		6.6	190089.6	31893.9	27.8	bb	109.3		12.1
234	33	20160121	12	C1	Analyte		6.6	173410.2	35398.2	24.7	bb	97.0		12.3
235	34	20160121	13	C1	Analyte		6.6	191758.3	33568.3	26.8	bb	105.3		11.4
236	35	20160121	MP Blank	MP Blank	Blank									
237	36	20160121	50 ng CCC	50 ng CCC	QC	50	6.6	100512.6	36768.7	13.2	bb	51.6	3.2	11.5
238	37	20160121	100 ng CCC	100 ng CCC	QC	100	6.6	233935.8	43833.7	24.8	bb	97.4	-2.6	11.1
239	38	20160121	MP Blank	MP Blank	Blank									
240	39	20160121	14	C1	Analyte		6.6	198521.5	33323.6	28.5	bb	112.3		11.9
241	40	20160121	15	C1	Analyte		6.6	187440.1	37032.0	23.3	bb	91.5		10.6
242	41	20160121	16	C1	Analyte		6.6	188451.6	32372.8	27.6	bb	108.5		11.2
243	42	20160121	17	C1	Analyte		6.6	201353.4	32882.3	29.4	bb	115.6		11.8
244	43	20160121	18	C1	Analyte		6.6	198555.8	33456.4	28.8	bb	113.3		11.5
245	44	20160121	MP Blank	MP Blank	Analyte									
246	45	20160121	50 ng CCC	50 ng CCC	QC	50	6.6	102642.9	39502.1	12.3	bb	48.1	-3.7	10.8
247	46	20160121	100ng CCC	100 ng CCC	QC	100	6.6	249993.5	45247.2	26.1	bb	102.5	2.5	10.8
248	47	20160121	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
249	48	20160121	19	C1	Analyte		6.6	207427.6	33213.3	29.3	bb	115.1		11.0
250	49	20160121	20	C1	Analyte		6.6	176997.1	34227.7	26.9	bb	106.0		10.7
251	50	20160121	21	C1	Analyte		6.6	193998.8	33731.5	26.3	bb	103.5		10.8
252	51	20160121	22	C1	Analyte		6.6	205349.1	33454.5	28.6	bb	112.7		11.5
253	52	20160121	MP Blank	MP Blank	Blank									
254	53	20160121	10 ng CCC	10 ng CCC	QC	10	6.6	22497.7	49229.4	2.2	bb	8.2	-17.5	9.6
255	54	20160121	50 ng CCC	50 ng CCC	QC	50	6.6	102804.0	38742.9	12.8	bb	50.0	0	11.2
256	55	20160121	MP Blank	MP Blank	Blank									
257	56	20160121	0	H	Analyte		6.6	194064.6	33546.8	26.6	bb	104.6		11.3
258	57	20160121	1	H	Analyte		6.6	223831.0	33599.4	31.6	bb	124.3		12.1
259	58	20160121	2	H	Analyte		6.6	174488.8	30933.0	26.0	bb	102.3		11.3
260	59	20160121	3	H	Analyte		6.6	185604.5	30492.4	28.3	bb	111.3		12.2
261	60	20160121	4	H	Analyte		6.6	138163.4	32827.5	19.0	bb	74.7		12.4
262	61	20160121	MP Blank	MP Blank	Blank									
263	62	20160121	10 ng CCC	10 ng CCC	QC	0	6.6	21049.9	46273.0	2.2	bb	8.2		11.7
264	63	20160121	50 ng CCC	50 ng CCC	QC	0	6.6	102814.9	36718.4	13.1	bb	51.3		11.0
265	64	20160121	MP Blank10	MP Blank	Blank									
266	65	20160121	6	H	Analyte		6.6	200366.2	30151.4	30.6	bb	120.5		12.7
267	66	20160121	7	H	Analyte		6.6	188142.3	31811.2	27.2	bb	107.1		11.4
268	67	20160121	8	H	Analyte		6.6	172184.2	32693.0	23.9	bb	93.9		11.4
269	68	20160121	9	H	Analyte		6.6	189980.8	32737.3	26.6	bb	104.6		12.1

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
270	69	20160121	10	H	Analyte		6.6	168429.8	31070.2	24.9	bb	97.8		12.7
271	70	20160121	MP Blank	MP Blank	Blank									
272	71	20160121	50 ng CCC	50 ng CCC	QC	0	6.6	98402.7	35882.9	12.7	bb	49.6		11.2
273	72	20160121	100 ng CCC	100 ng CCC	QC	0	6.6	222636.6	41380.4	25.0	bb	98.3		12.5
274	73	20160121	MP Blank	MP Blank	Blank									
275	74	20160121	11	H	Analyte		6.6	170386.8	33425.1	24.0	bb	94.3		12.4
276	75	20160121	12	H	Analyte		6.6	164888.6	32407.5	23.7	bb	93.0		12.6
277	76	20160121	13	H	Analyte		6.6	173295.0	31841.6	25.5	bb	100.2		13.1
278	77	20160121	14	H	Analyte		6.6	177564.6	31474.9	25.9	bb	101.7		12.0
279	78	20160121	15	H	Analyte		6.6	140795.2	30031.6	22.9	bb	89.9		11.7
280	79	20160121	MP Blank	MP Blank	Blank									
281	80	20160121	10 ng CCC	10 ng CCC	QC	0	6.6	20791.8	45072.9	2.2	bb	8.4		12.5
282	81	20160121	50 ng CCC	50 ng CCC	QC	0	6.6	98460.2	35631.3	12.8	bb	50.3		12.4
283	82	20160121	MP Blank	MP Blank	Blank									
284	83	20160121	16	H	Analyte		6.6	190568.7	32904.8	27.4	bb	107.8		11.8
285	84	20160121	17	H	Analyte		6.6	123363.0	32255.3	17.3	bb	67.9		11.7
286	85	20160121	18	H	Analyte		6.6	173213.9	31418.0	25.4	bb	100.0		12.0
287	86	20160121	19	H	Analyte		6.6	170089.5	32272.4	25.4	bb	99.9		11.7
288	87	20160121	20	H	Analyte		6.6	157688.2	35642.5	20.0	bb	78.7		12.0
289	88	20160121	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
290	89	20160121	50 ng CCC	50 ng CCC	QC	0	6.6	100299.2	35994.4	12.5	bb	49.0		12.0
291	90	20160121	100 ng CCC	100 ng CCC	QC	0	6.6	225036.4	41370.5	25.6	bb	100.8		11.6
292	91	20160121	MP Blank	MP Blank	Blank									
293	92	20160121	21	H	Analyte		6.6	161664.6	32773.5	23.7	bb	93.1		10.9
294	93	20160121	22	H	Analyte		6.6	171238.9	29409.2	27.9	bb	109.8		12.2
295	94	20160121	23	H	Analyte				29547.6					
296	95	20160121	MP Blank	MP Blank	Blank									
297	96	20160121	MP Blank36	MP Blank	Blank									
298	1	20160122	MP Blank	MP Blank	Blank									
299	2	20160122	0 Std	0 Std	Standard	0			28645.9					
300	3	20160122	2 ng Std	2 ng Std	Standard	2	6.7	4378.7	39683.8	0.5	bb	2.0	-0.7	
301	4	20160122	5 ng Std	5 ng Std	Standard	5	6.7	8906.6	33458.2	1.3	bb	5.0	-0.4	11.6
302	5	20160122	10 ng Std	10 ng Std	Standard	10	6.7	20495.6	36491.3	2.7	bb	10.1	1.5	14.4
303	6	20160122	25 ng Std	25 ng Std	Standard	25	6.7	60764.2	43681.2	6.8	bb	26.0	3.9	12.4
304	7	20160122	50 ng Std	50 ng Std	Standard	50	6.7	91235.8	35920.9	12.1	bb	46.3	-7.5	12.5
305	8	20160122	75 ng Std	75 ng Std	Standard	75	6.7	152550.6	36421.8	20.1	bb	76.7	2.2	12.7
306	9	20160122	100 ng Std	100 ng Std	Standard	100	6.7	217308.5	38290.2	26.5	bb	100.9	0.9	12.4
307	10	20160122	200 ng Std	200 ng Std	Standard	200	6.7	460321.9	42718.1	52.5	bb	200.1	0	11.8

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
308	11	20160122	MP Blank	MP Blank	Blank									
309	12	20160122	10 ng CCC	10 ng CCC	QC	10	6.7	18084.7	40816.1	2.2	bb	8.2	-17.6	12.5
310	13	20160122	50 ng CCC	50 ng CCC	QC	50	6.7	91535.5	36610.5	11.8	bb	45.0	-10	11.1
311	14	20160122	100 ng CCC	100 ng CCC	QC	100	6.7	218476.5	38083.2	26.9	bb	102.4	2.4	12.7
312	15	20160122	MP Blank	MP Blank	Blank									
313	16	20160122	1	July Stock	Analyte		6.7	109488.1	15741.3	33.2	bb	126.4		13.0
314	17	20160122	2	July Stock	Analyte		6.7	113297.9	14169.9	37.0	bb	140.9		11.8
315	18	20160122	1	Dec Stock	Analyte		6.7	129376.7	14659.7	41.5	bb	158.1		12.5
316	19	20160122	2	Dec Stock	Analyte		6.7	97477.7	12920.5	35.8	bb	136.5		11.2
317	20	20160122	Initial	D1	Analyte				19624.3					
318	21	20160122	MP Blank	MP Blank	Blank									
319	22	20160122	0	D1	Analyte		6.7	81568.9	25702.6	15.3	bb	58.1		13.8
320	23	20160122	1	D1	Analyte		6.7	93530.4	22869.0	19.5	bb	74.3		13.2
321	24	20160122	2	D1	Analyte		6.7	95848.2	23091.5	19.9	bb	75.9		12.7
322	25	20160122	3	D1	Analyte		6.7	96583.4	24018.5	18.7	bb	71.4		12.2
323	26	20160122	MP Blank	MP Blank	Blank									
324	27	20160122	10 ng CCC	10 ng CCC	QC	10	6.7	19025.9	41144.7	2.2	bb	8.5	-15.1	13.3
325	28	20160122	50 ng CCC	50 ng CCC	QC	50	6.7	89700.0	36130.1	11.6	bb	44.3	-11.3	12.9

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
326	29	20160122	MP Blank	MP Blank	Blank									
327	30	20160122	4	D1	Analyte		6.7	95059.0	24738.4	18.1	bb	69.0		12.2
328	31	20160122	5	D1	Analyte		6.7	93560.0	25230.1	18.0	bb	68.7		12.0
329	32	20160122	6	D1	Analyte		6.7	91438.9	21759.1	19.3	bb	73.6		12.0
330	33	20160122	7	D1	Analyte		6.7	89511.0	23616.9	17.7	bb	67.5		11.9
331	34	20160122	8	D1	Analyte		6.7	87651.0	23464.7	18.0	bb	68.4		12.4
332	35	20160122	MP Blank	MP Blank	Blank									
333	36	20160122	50 ng CCC	50 ng CCC	QC	50	6.7	89130.7	36128.4	11.9	bb	45.2	-9.6	13.3
334	37	20160122	100 ng CCC	100 ng CCC	QC	100	6.7	195721.1	35778.5	25.3	bb	96.6	-3.4	11.8
335	38	20160122	MP Blank	MP Blank	Blank									
336	39	20160122	9	D1	Analyte		6.7	85147.9	24860.2	16.0	bb	61.0		12.7
337	40	20160122	10	D1	Analyte		6.7	86705.9	23217.8	18.4	bb	70.0		13.1
338	41	20160122	Initial	D3	Analyte		6.6	93120.8	23074.6	18.9	bb	72.1		12.0
339	42	20160122	0	D3	Analyte		6.7	94137.2	24504.1	17.3	bb	65.8		12.4
340	43	20160122	1	D3	Analyte		6.7	101541.3	23270.3	20.1	bb	76.7		12.6
341	44	20160122	MP Blank	MP Blank	Analyte									
342	45	20160122	50 ng CCC	50 ng CCC	QC	50	6.7	85082.3	34891.0	11.5	bb	44.0	-12.1	11.8
343	46	20160122	100ng CCC	100 ng CCC	QC	100	6.7	202341.0	33503.0	28.2	bb	107.7	7.7	12.2
344	47	20160122	MP Blank	MP Blank	Blank									
345	48	20160122	2	D3	Analyte		6.6	95728.4	24634.3	18.3	bb	69.8		12.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
346	49	20160122	3	D3	Analyte		6.7	97213.4	23043.3	20.6	bb	78.7		12.2
347	50	20160122	4	D3	Analyte		6.7	88742.7	22710.7	18.3	bb	69.8		12.4
348	51	20160122	5	D3	Analyte		6.6	95222.7	23683.4	18.7	bb	71.3		12.3
349	52	20160122	MP Blank	MP Blank	Blank									
350	53	20160122	10 ng CCC	10 ng CCC	QC	10	6.7	17231.2	38831.4	2.1	bb	8.2	-18.4	13.3
351	54	20160122	50 ng CCC	50 ng CCC	QC	50	6.7	85904.9	34154.1	11.7	bb	44.4	-11.2	11.9
352	55	20160122	MP Blank	MP Blank	Blank									
353	56	20160122	6	D3	Analyte		6.6	91341.4	23197.9	18.6	bb	71.0		12.3
354	57	20160122	7	D3	Analyte		6.7	94999.5	24045.3	19.1	bb	72.7		11.6
355	58	20160122	8	D3	Analyte		6.6	94274.1	25002.3	17.3	bb	66.1		10.8
356	59	20160122	9	D3	Analyte		6.7	90602.5	22973.6	18.6	bb	71.0		13.1
357	60	20160122	10	D3	Analyte		6.7	82949.4	23567.4	17.3	bb	65.8		13.3
358	61	20160122	MP Blank	MP Blank	Blank									
359	62	20160122	10 ng CCC	10 ng CCC	QC	0	6.7	17939.3	39542.0	2.2	bb	8.2		12.8
360	63	20160122	50 ng CCC	50 ng CCC	QC	0	6.6	84554.2	33605.9	12.2	bb	46.5		12.0
361	64	20160122	MP Blank10	MP Blank	Blank									
362	65	20160122	Initial	BK1	Analyte		6.6	94142.3	29956.0	14.9	bb	56.6		12.6
363	66	20160122	0	BK1	Analyte		6.7	97733.9	29660.2	15.5	bb	59.1		11.6
364	67	20160122	1	BK1	Analyte		6.7	101310.1	30761.5	15.4	bb	58.7		11.9
365	68	20160122	2	BK1	Analyte		6.6	98859.1	29320.1	15.9	bb	60.7		12.1
366	69	20160122	3	BK1	Analyte		6.6	99014.6	29150.8	16.1	bb	61.3		11.7

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
367	70	20160122	MP Blank	MP Blank	Blank									
368	71	20160122	50 ng CCC	50 ng CCC	QC	0	6.7	84262.1	32750.1	12.4	bb	47.2		12.0
369	72	20160122	100 ng CCC	100 ng CCC	QC	0	6.6	165161.7	33514.1	25.6	bb	97.5		12.1
370	73	20160122	MP Blank	MP Blank	Blank									
371	74	20160122	4	BK1	Analyte		6.6	102990.6	28678.2	16.5	bb	62.9		12.1
372	75	20160122	5	BK1	Analyte		6.6	102596.1	28651.1	16.6	bb	63.2		12.1
373	76	20160122	6	BK1	Analyte		6.6	105685.8	28957.2	17.2	bb	65.4		12.8
374	77	20160122	7	BK1	Analyte		6.7	100429.6	29174.5	16.1	bb	61.5		12.4
375	78	20160122	8	BK1	Analyte		6.6	100523.3	27974.1	17.5	bb	66.7		12.0
376	79	20160122	MP Blank	MP Blank	Blank									
377	80	20160122	10 ng CCC	10 ng CCC	QC	0	6.6	17276.6	36307.0	2.3	bb	8.7		11.2
378	81	20160122	50 ng CCC	50 ng CCC	QC	0	6.6	82338.2	33337.3	11.8	bb	45.1		11.5
379	82	20160122	MP Blank	MP Blank	Blank									
380	83	20160122	9	BK1	Analyte		6.6	100228.1	27267.9	17.5	bb	66.8		13.4
381	84	20160122	10	BK1	Analyte		6.6	99483.6	26545.8	17.8	bb	67.9		12.0
382	85	20160122	Initial	BK3	Analyte		6.6	101806.5	29780.8	16.0	bb	61.1		12.3
383	86	20160122	0	BK3	Analyte		6.7	95009.6	30342.3	14.1	bb	53.8		11.6
384	87	20160122	1	BK3	Analyte		6.6	93194.8	29973.5	14.5	bb	55.3		12.1
385	88	20160122	MP Blank	MP Blank	Blank									
386	89	20160122	50 ng CCC	50 ng CCC	QC	0	6.6	82874.2	32851.8	12.0	bb	45.7		12.0

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
387	90	20160122	100 ng CCC	100 ng CCC	QC	0	6.6	182886.5	33347.9	26.1	bb	99.4		11.7
388	91	20160122	MP Blank	MP Blank	Blank									
389	92	20160122	2	BK3	Analyte		6.6	100376.7	30093.2	16.0	bb	61.2		12.1
390	93	20160122	3	BK3	Analyte		6.6	99070.3	31136.0	15.2	bb	57.9		12.6
391	94	20160122	4	BK3	Analyte		6.6	106397.0	29460.7	17.2	bb	65.6		13.0
392	95	20160122	5	BK3	Blank		6.6	99684.2	27783.1	16.6	bb	63.3		11.9
393	96	20160122	6	BK3	Blank		6.6	109131.9	30750.6	16.4	bb	62.3		12.6
394	97	20160122	MP Blank	MP Blank	Blank									
395	98	20160122	50 ng CCC	50 ng CCC	QC	0	6.6	83157.1	33320.3	11.8	bb	44.9		13.1
396	99	20160122	100 ng CCC	100 ng CCC	QC	0	6.6	191922.6	33839.0	26.0	bb	99.0		13.4
397	100	20160122	MP Blank	MP Blank	Blank									
398	101	20160122	7	BK3	Analyte		6.6	106909.6	31784.3	16.1	bb	61.5		12.4
399	102	20160122	8	BK3	Analyte		6.6	97174.3	29616.6	15.1	bb	57.5		11.8
400	103	20160122	9	BK3	Analyte		6.6	105005.1	30817.1	16.0	bb	60.8		11.7
401	104	20160122	10	BK3	Analyte		6.6	93268.4	30425.9	14.6	bb	55.6		11.2
402	105	20160122	MP Blank	MP Blank	Blank									
403	1	20160126	MP Blank	MP Blank	Blank		6.6	114397.3	64242.9	27.9	bd	105.2		21.7
404	2	20160126	0 Std	0 Std	Standard	0	7.5	2512.2	32621.8	0.4	bb	1.0		
405	3	20160126	2 ng Std	2 ng Std	Standard	2	6.5	5139.5	44672.2	0.6	bb	1.5	-27	
406	4	20160126	5 ng Std	5 ng Std	Standard	5	6.6	10079.9	37470.4	1.2	bb	3.8	-23.4	9.7

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
407	5	20160126	10 ng Std	10 ng Std	Standard	10	6.6	23511.0	40305.1	2.8	bb	10.0	0.4	9.0
408	6	20160126	25 ng Std	25 ng Std	Standard	25	6.5	72952.0	49876.8	7.1	bb	26.2	4.8	11.6
409	7	20160126	50 ng Std	50 ng Std	Standard	50	6.6	102526.9	39947.3	12.4	bb	46.3	-7.4	9.3
410	8	20160126	75 ng Std	75 ng Std	Standard	75	6.5	175684.3	42730.3	19.4	bb	72.7	-3	9.7
411	9	20160126	100 ng Std	100 ng Std	Standard	100	6.5	263970.5	44687.5	27.4	bb	103.4	3.4	10.4
412	10	20160126	200 ng Std	200 ng Std	Standard	200	6.5	563493.8	50518.4	53.7	bb	203.1	1.5	9.7
413	11	20160126	MP Blank	MP Blank	Blank		7.5	845.1			bb			
414	12	20160126	10 ng CCC	10 ng CCC	QC	10	6.5	9544.6	12958.5	3.3	bb	11.8	17.9	8.7
415	13	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	107609.8	41771.8	12.0	bb	44.8	-10.4	9.7
416	14	20160126	100 ng CCC	100 ng CCC	QC	100	6.6	99334.3	10746.8	43.8	bb	165.3	65.3	10.2
417	15	20160126	MP Blank	MP Blank	Blank									
418	16	20160126	9	CNT B	Analyte		6.6	148922.4	32791.2	21.7	bb	81.8		10.2
419	17	20160126	8	CNT B	Analyte		6.6	144742.4	31526.4	21.6	bb	81.2		9.7
420	18	20160126	7	CNT B	Analyte		6.6	149681.8	33295.4	20.8	bb	78.3		10.6
421	19	20160126	6	CNT B	Analyte		6.6	150521.7	31566.6	22.5	bb	84.6		10.4
422	20	20160126	5	CNT B	Analyte		6.6	147712.4	31586.7	22.0	bb	82.7		10.2
423	21	20160126	MP Blank	MP Blank	Blank									
424	22	20160126	4	CNT B	Analyte		6.6	139562.1	31611.1	21.0	bb	78.9		10.3
425	23	20160126	3	CNT B	Analyte		6.6	154841.7	30968.8	23.5	bb	88.4		10.0

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
426	24	20160126	2	CNT B	Analyte		6.6	149982.0	32528.6	21.6	bb	81.1		10.5
427	25	20160126	1	CNT B	Analyte		6.6	147618.6	33695.7	20.4	bb	76.8		9.8
428	26	20160126	MP Blank	MP Blank	Blank									
429	27	20160126	10 ng CCC	10 ng CCC	QC	10	6.6	9500.5	12746.8	3.6	bb	13.0	29.6	13.0
430	28	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	103961.5	39140.0	13.1	bb	48.9	-2.1	10.1
431	29	20160126	MP Blank	MP Blank	Blank									
432	30	20160126	0	CNT B	Analyte		6.6	146344.8	34984.5	19.6	bb	73.6		11.2
433	31	20160126	9	CNT C	Analyte		6.6	135720.1	32081.0	19.8	bb	74.5		10.4
434	32	20160126	8	CNT C	Analyte		6.6	120858.4	32194.0	19.2	bb	72.3		10.1
435	33	20160126	7	CNT C	Analyte		6.6	141240.9	34409.9	18.6	bb	69.7		10.6
436	34	20160126	6	CNT C	Analyte		6.6	144115.7	31100.8	21.4	bb	80.5		10.9
437	35	20160126	MP Blank	MP Blank	Blank									
438	36	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	102887.2	38260.0	12.9	bb	48.2	-3.6	10.7
439	37	20160126	100 ng CCC	100 ng CCC	QC	100	6.6	93186.4	9003.1	48.9	bb	184.6	84.6	11.3
440	38	20160126	MP Blank	MP Blank	Blank									
441	39	20160126	5	CNT C	Analyte		6.6	144408.7	30590.9	22.2	bb	83.5		9.9
442	40	20160126	4	CNT C	Analyte		6.6	145268.2	29976.1	22.2	bb	83.4		10.6
443	41	20160126	3	CNT C	Analyte		6.6	133217.5	35284.3	18.6	bb	69.7		11.2
444	42	20160126	2	CNT C	Analyte		6.6	137294.2	30728.9	20.7	bb	77.9		10.0
445	43	20160126	1	CNT C	Analyte		6.6	137109.1	29977.1	20.6	bb	77.4		10.2
446	44	20160126	MP Blank	MP	Analyte									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
				Blank										
447	45	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	99634.1	37089.4	12.4	bb	46.2	-7.6	10.7
448	46	20160126	100ng CCC	100 ng CCC	QC	100	6.6	87874.2	8836.9	45.9	bb	173.5	73.5	10.7
449	47	20160126	MP Blank	MP Blank	Blank									
450	48	20160126	0	CNT C	Analyte		6.6	140543.1	30112.5	22.0	bb	82.9		10.1
451	49	20160126	9	CNT D	Analyte		6.6	142214.8	31304.9	21.8	bb	82.0		10.3
452	50	20160126	8	CNT D	Analyte		6.6	133986.1	28726.0	21.2	bb	79.8		10.1
453	51	20160126	7	CNTD	Analyte		6.6	123571.1	29333.9	19.2	bb	72.0		10.5
454	52	20160126	MP Blank	MP Blank	Blank									
455	53	20160126	10 ng CCC	10 ng CCC	QC	10	6.6	9080.0	11456.3	3.6	bb	12.8	28.2	8.0
456	54	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	97783.7	37226.6	12.1	bb	45.2	-9.6	10.0
457	55	20160126	MP Blank	MP Blank	Blank									
458	56	20160126	6	CNT D	Analyte		6.6	140994.3	31669.5	20.8	bb	78.1		10.6
459	57	20160126	5	CNT D	Analyte		6.6	143430.8	30682.9	21.6	bb	81.2		10.1
460	58	20160126	4	CNT D	Analyte		6.5	118251.4	30826.0	17.4	bb	65.2		10.4
461	59	20160126	3	CNT D	Analyte		6.6	136483.0	31537.4	19.7	bb	74.0		10.6
462	60	20160126	2	CNT D	Analyte		6.6	136609.1	32205.8	19.6	bb	73.5		10.3
463	61	20160126	MP Blank	MP Blank	Blank									
464	62	20160126	10 ng CCC	10 ng CCC	QC	10	6.6	8864.2	11892.3	3.4	bb	12.4	24	76.2
465	63	20160126	50 ng CCC	50 ng CCC	QC	50	6.6	97426.9	37000.9	12.0	bb	44.7	-10.6	9.9

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
466	64	20160126	MP Blank10	MP Blank	Blank									
467	65	20160126	1	CNT D	Analyte		6.5	134987.2	29627.1	21.3	bb	80.1		10.7
468	66	20160126	0	CNT D	Analyte		6.6	133898.1	31470.5	19.4	bb	72.8		10.6
469	67	20160126	9	CNT F	Analyte		6.6	135389.4	30699.2	21.2	bb	79.7		10.5
470	68	20160126	8	CNT F	Analyte		6.5	148876.4	30498.5	22.5	bb	84.6		10.8
471	69	20160126	7	CNT F	Analyte		6.5	144178.2	30335.4	22.0	bb	82.7		10.4
472	70	20160126	MP Blank	MP Blank	Blank									
473	71	20160126	50 ng CCC	50 ng CCC	QC	50	6.5	97312.7	36963.3	12.3	bb	46.1	-7.8	10.6
474	72	20160126	100 ng CCC	100 ng CCC	QC	100	6.6	88023.2	8692.5	47.6	bb	179.8	79.8	10.8
475	73	20160126	MP Blank	MP Blank	Blank									
476	74	20160126	6	CNT F	Analyte		6.5	139288.5	29822.1	20.9	bb	78.5		9.8
477	75	20160126	5	CNT F	Analyte		6.5	152712.4	32109.0	21.7	bb	81.8		9.7
478	76	20160126	4	CNT F	Analyte		6.6	144582.6	30670.6	21.9	bb	82.3		10.4
479	77	20160126	3	CNT F	Analyte		6.5	156037.0	33560.5	20.9	bb	78.5		10.4
480	78	20160126	2	CNT F	Analyte		6.6	142898.2	31191.9	21.1	bb	79.5		10.0
481	79	20160126	MP Blank	MP Blank	Blank									
482	80	20160126	10 ng CCC	10 ng CCC	QC	10	6.6	8523.9	11125.2	3.7	bb	13.5	35.4	10.2
483	81	20160126	50 ng CCC	50 ng CCC	QC	50	6.5	95243.7	36189.4	12.5	bb	46.6	-6.9	11.2
484	82	20160126	MP Blank	MP Blank	Blank									
485	83	20160126	1	CNT F	Analyte		6.6	141588.5	29056.3	22.6	bb	85.0		9.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
486	84	20160126	0	CNT F	Analyte		6.5	140684.3	28655.0	22.4	bb	84.4		10.6
487	85	20160126	9	CNT H	Analyte		6.5	119689.6	34350.3	16.2	bb	60.8		10.6
488	86	20160126	8	CNT H	Analyte		6.5	136618.6	35945.0	17.3	bb	64.8		10.6
489	87	20160126	7	CNT H	Analyte		6.5	137109.0	34639.4	18.3	bb	68.8		10.3
490	88	20160126	MP Blank	MP Blank	Blank									
491	89	20160126	50 ng CCC	50 ng CCC	QC	50	6.5	94021.2	36599.8	12.3	bb	46.0	-8.1	11.6
492	90	20160126	100 ng CCC	100 ng CCC	QC	100	6.6	84556.1	8622.2	44.7	bb	168.8	68.8	9.3
493	91	20160126	MP Blank	MP Blank	Blank									
494	92	20160126	6	CNT H	Analyte		6.5	113117.5	34761.0	14.7	bb	55.0		10.0
495	93	20160126	5	CNT H	Analyte		6.6	118631.9	36392.7	15.0	bb	56.0		9.6
496	94	20160126	4	CNT H	Analyte		6.5	116871.1	35190.5	14.5	bb	54.3		10.4
497	95	20160126	3	CNT H	Blank		6.6	110507.0	35690.9	14.1	bb	52.9		9.6
498	96	20160126	2	CNT H	Blank		6.5	127372.9	32488.2	17.6	bb	66.2		10.2
499	97	20160126	MP Blank	MP Blank	Blank									
500	98	20160126	50 ng CCC	50 ng CCC	QC	50	6.5	99295.0	36260.6	12.3	bb	45.8	-8.4	10.6
501	99	20160126	100 ng CCC	100 ng CCC	QC	100	6.6	88065.7	9032.4	43.7	bb	165.0	65	10.1
502	100	20160126	MP Blank	MP Blank	Blank									
503	101	20160126	1	CNT H	Analyte		6.5	118070.2	32360.6	16.5	bb	62.0		10.8
504	102	20160126	0	CNT H	Analyte		6.6	138227.8	32520.5	19.3	bb	72.7		10.6
505	103	20160126	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
506	1	20160127	MP Blank	MP Blank	Blank		7.4	36.1			bb			
507	2	20160127	0 Std	0 Std	Standard	0			23501.9					
508	3	20160127	2 ng Std	2 ng Std	Standard	2	6.6	4188.9	36688.5	0.5	bb	1.8	-7.6	
509	4	20160127	5 ng Std	5 ng Std	Standard	5	6.6	8283.8	29784.4	1.3	bb	4.6	-7.4	9.5
510	5	20160127	10 ng Std	10 ng Std	Standard	10	6.6	21177.3	31104.3	3.1	bb	11.4	14.3	12.7
511	6	20160127	25 ng Std	25 ng Std	Standard	25	6.6	62045.6	39040.7	7.4	bb	27.8	11.3	10.3
512	7	20160127	50 ng Std	50 ng Std	Standard	50	6.6	88502.1	32942.4	12.5	bb	47.0	-6	11.3
513	8	20160127	75 ng Std	75 ng Std	Standard	75	6.6	139927.2	35596.3	18.2	bb	68.2	-9.1	10.0
514	9	20160127	100 ng Std	100 ng Std	Standard	100	6.6	216032.8	36028.5	27.4	bb	103.0	3	10.4
515	10	20160127	200 ng Std	200 ng Std	Standard	200	6.5	480549.2	40801.2	54.1	bb	203.1	1.5	10.0
516	11	20160127	MP Blank	MP Blank	Blank									
517	12	20160127	10 ng CCC	10 ng CCC	QC	10	6.6	21142.2	32114.6	3.0	bb	11.1	11.3	10.0
518	13	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	89411.7	33641.6	12.3	bb	45.9	-8.1	10.5
519	14	20160127	100 ng CCC	100 ng CCC	QC	100	6.5	207087.2	36083.5	25.3	bb	94.9	-5.1	9.5
520	15	20160127	MP Blank	MP Blank	Blank									
521	16	20160127	0	I	Analyte		6.5	123325.6	37066.1	14.8	bb	55.6		9.8
522	17	20160127	1	I	Analyte		6.5	139330.0	36396.3	17.3	bb	64.7		9.8
523	18	20160127	2	I	Analyte		6.5	153417.6	38512.0	18.2	bb	68.4		10.3

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
524	19	20160127	3	I	Analyte		6.5	142365.7	36566.8	17.7	bb	66.3		9.7
525	20	20160127	4	I	Analyte		6.5	129217.7	37564.3	17.1	bb	64.1		8.8
526	21	20160127	MP Blank	MP Blank	Blank									
527	22	20160127	5	I	Analyte		6.5	165583.0	38385.2	20.1	bb	75.3		10.4
528	23	20160127	6	I	Analyte		6.5	165049.4	36362.9	20.0	bb	75.0		10.1
529	24	20160127	7	I	Analyte		6.5	165093.5	35962.6	21.4	bb	80.2		10.3
530	25	20160127	8	I	Analyte		6.5	157285.3	35993.4	19.8	bb	74.2		9.8
531	26	20160127	MP Blank	MP Blank	Blank									
532	27	20160127	10 ng CCC	10 ng CCC	QC	10	6.5	21727.8	33865.4	2.9	bb	10.7	7.3	9.5
533	28	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	90542.0	33257.2	12.6	bb	47.2	-5.7	10.2
534	29	20160127	MP Blank	MP Blank	Blank									
535	30	20160127	9	I	Analyte		6.5	165108.4	37019.6	19.7	bb	73.8		9.4
536	31	20160127	10	I	Analyte		6.5	152377.4	37389.7	18.4	bb	69.0		9.9
537	32	20160127	11	I	Analyte		6.5	161724.6	35757.7	20.6	bb	77.4		10.7
538	33	20160127	12	I	Analyte		6.5	120132.1	34355.8	15.7	bb	58.7		10.2
539	34	20160127	13	I	Analyte		6.5	150777.4	34809.3	19.9	bb	74.5		10.6
540	35	20160127	MP Blank	MP Blank	Blank									
541	36	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	95763.8	35231.2	12.5	bb	46.7	-6.6	12.2
542	37	20160127	100 ng CCC	100 ng CCC	QC	100	6.5	213594.0	36363.7	25.7	bb	96.6	-3.4	10.3
543	38	20160127	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
544	39	20160127	14	I	Analyte		6.5	145586.4	33827.8	19.3	bb	72.3		10.3
545	40	20160127	15	I	Analyte		6.5	155448.0	34957.4	19.9	bb	74.6		10.5
546	41	20160127	16	I	Analyte		6.5	159200.5	33976.6	21.5	bb	80.5		10.7
547	42	20160127	17	I	Analyte		6.5	151908.6	35062.8	19.9	bb	74.5		10.8
548	43	20160127	18	I	Analyte		6.5	152256.5	33886.7	20.3	bb	76.0		10.6
549	44	20160127	MP Blank	MP Blank	Analyte									
550	45	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	91819.4	33537.6	12.4	bb	46.4	-7.3	11.1
551	46	20160127	100ng CCC	100 ng CCC	QC	100	6.5	214388.6	38099.4	24.5	bb	91.9	-8.1	10.5
552	47	20160127	MP Blank	MP Blank	Blank									
553	48	20160127	19	I	Analyte		6.5	151665.5	33300.8	20.5	bb	77.1		11.5
554	49	20160127	20	I	Analyte		6.5	151977.0	33599.7	20.8	bb	78.0		11.0
555	50	20160127	21	I	Analyte		6.5	146677.4	30312.9	21.7	bb	81.5		10.1
556	51	20160127	22	I	Analyte		6.5	152450.5	30667.2	22.5	bb	84.4		9.9
557	52	20160127	MP Blank	MP Blank	Blank									
558	53	20160127	10 ng CCC	10 ng CCC	QC	10	6.5	21860.4	33503.5	3.1	bb	11.5	15.2	8.9
559	54	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	87563.9	34731.1	11.8	bb	44.2	-11.7	9.3
560	55	20160127	MP Blank	MP Blank	Blank									
561	56	20160127	0	K	Analyte		6.5	185486.5	36017.6	23.0	bb	86.4		9.5
562	57	20160127	1	K	Analyte		6.5	160858.8	34059.9	21.3	bb	80.0		9.5
563	58	20160127	2	K	Analyte		6.5	183117.0	36793.2	22.8	bb	85.5		9.7
564	59	20160127	3	K	Analyte		6.5	169122.2	37506.6	20.6	bb	77.4		9.1

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
565	60	20160127	4	K	Analyte		6.5	169159.6	37945.5	20.3	bb	76.2		9.4
566	61	20160127	MP Blank	MP Blank	Blank									
567	62	20160127	10 ng CCC	10 ng CCC	QC	10	6.5	21058.8	32677.7	2.9	bb	10.9	8.7	8.8
568	63	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	92889.2	35081.0	11.9	bb	44.6	-10.9	9.6
569	64	20160127	MP Blank	MP Blank	Blank									
570	65	20160127	5	K	Analyte		6.5	169815.9	37879.7	20.3	bb	76.2		10.1
571	66	20160127	6	K	Analyte		6.5	184325.2	37828.2	21.7	bb	81.4		9.9
572	67	20160127	7	K	Analyte		6.5	166604.1	37987.1	19.9	bb	74.7		9.6
573	68	20160127	8	K	Analyte		6.5	166425.0	37895.6	20.1	bb	75.3		9.4
574	69	20160127	9	K	Analyte		6.5	179293.0	36429.3	22.0	bb	82.6		9.5
575	70	20160127	MP Blank	MP Blank	Blank									
576	71	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	93196.9	34385.2	12.1	bb	45.5	-9.1	10.8
577	72	20160127	100 ng CCC	100 ng CCC	QC	100	6.5	215499.5	37595.5	25.3	bb	95.0	-5	9.6
578	73	20160127	MP Blank	MP Blank	Blank									
579	74	20160127	10	K	Analyte		6.5	164461.8	36083.2	20.7	bb	77.6		9.1
580	75	20160127	11	K	Analyte		6.5	158071.0	35635.3	19.7	bb	73.8		9.6
581	76	20160127	12	K	Analyte		6.5	177079.5	37692.1	21.8	bb	81.7		9.7
582	77	20160127	13	K	Analyte		6.5	172283.3	36412.3	21.4	bb	80.2		9.7
583	78	20160127	14	K	Analyte		6.5	166944.9	38335.7	20.5	bb	76.8		9.3
584	79	20160127	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
585	80	20160127	10 ng CCC	10 ng CCC	QC	10	6.5	20287.7	31793.2	2.8	bb	10.5	5	8.8
586	81	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	90544.2	33652.2	11.6	bb	43.4	-13.2	10.0
587	82	20160127	MP Blank	MP Blank	Blank									
588	83	20160127	15	K	Analyte		6.5	176325.8	36337.2	21.9	bb	82.3		10.2
589	84	20160127	16	K	Analyte		6.5	163225.5	37386.6	20.0	bb	75.0		10.5
590	85	20160127	17	K	Analyte		6.5	163427.2	37669.8	20.2	bb	75.8		10.2
591	86	20160127	18	K	Analyte		6.5	169384.0	35894.2	21.6	bb	81.1		9.9
592	87	20160127	19	K	Analyte		6.5	167614.6	35445.6	21.3	bb	79.9		8.8
593	88	20160127	MP Blank	MP Blank	Blank									
594	89	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	79254.1	31895.1	11.7	bb	43.9	-12.1	9.4
595	90	20160127	100 ng CCC	100 ng CCC	QC	100	6.5	210402.3	37514.9	25.4	bb	95.2	-4.8	9.8
596	91	20160127	MP Blank	MP Blank	Blank									
597	92	20160127	20	K	Analyte		6.5	156522.9	35446.4	19.8	bb	74.2		10.8
598	93	20160127	21	K	Analyte		6.5	162864.7	33924.2	21.5	bb	80.8		9.8
599	94	20160127	22	K	Analyte		6.5	168298.4	35785.6	21.0	bb	79.0		10.4
600	95	20160127	MP Blank	MP Blank	Blank									
601	96	20160127	50 ng CCC	50 ng CCC	QC	50	6.5	85474.8	32726.9	11.7	bb	43.9	-12.2	9.7
602	97	20160127	100 ng CCC	100 ng CCC	QC	100	6.5	206386.6	36037.0	25.5	bb	95.8	-4.2	10.9
603	98	20160127	MP Blank	MP Blank	Blank									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
604	99	20160127	0	CNT I	Analyte		6.5	137058.7	32968.1	18.6	bb	69.6		10.1
605	100	20160127	1	CNT I	Analyte		6.5	141959.5	32359.7	19.5	bb	73.2		10.1
606	101	20160127	2	CNT I	Analyte		6.5	130794.2	33401.6	18.1	bb	68.0		10.2
607	102	20160127	3	CNT I	Analyte		6.5	125565.4	32908.8	16.8	bb	63.2		9.8
608	103	20160127	4	CNT I	Analyte		6.5	124588.7	34236.8	16.3	bb	61.1		9.3
609	104	20160127	MP Blank	MP Blank	Analyte									
610	105	20160127	10 ng CCC	10 ng CCC	Blank		6.5	21073.7	32640.9	2.8	bb	10.3		8.7
611	106	20160127	50 ng CCC	50 ng CCC	QC	10	6.5	86228.5	34241.2	11.6	bb	43.5	335	9.5
612	107	20160127	MP Blank	MP Blank	QC	50								
613	108	20160127	5	CNT I	Analyte		6.5	125516.9	32650.8	16.9	bb	63.3		9.6
614	109	20160127	6	CNT I	Analyte		6.5	136627.9	31044.4	19.6	bb	73.4		9.4
615	110	20160127	7	CNT I	Analyte		6.5	140159.8	32891.7	19.2	bb	71.8		10.0
616	111	20160127	8	CNT I	Analyte		6.5	137816.4	34103.4	18.2	bb	68.3		10.4
617	112	20160127	9	CNT I	Analyte		6.5	121424.1	32111.5	17.5	bb	65.6		9.6
618	113	20160127	MP Blank	MP Blank	Blank									
619	1	20160129	MP Blank	MP Blank	Blank		8.0	108.7			bb			
620	2	20160129	0 Std	0 Std	Standard	0	7.5	439.9	23606.4	0.2	bb	0.3		
621	3	20160129	2 ng Std	2 ng Std	Standard	2	6.6	4374.0	38391.4	0.6	bb	1.9	-3.7	
622	4	20160129	5 ng Std	5 ng Std	Standard	5	6.6	8729.5	32776.6	1.3	bb	4.5	-9.3	11.6
623	5	20160129	10 ng Std	10 ng Std	Standard	10	6.6	21462.3	32729.9	2.9	bb	11.0	10	12.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
624	6	20160129	25 ng Std	25 ng Std	Standard	25	6.6	60997.5	39172.3	7.0	bb	26.9	7.8	10.0
625	7	20160129	50 ng Std	50 ng Std	Standard	50	6.6	87938.0	34040.2	11.6	bb	44.8	-10.4	10.3
626	8	20160129	75 ng Std	75 ng Std	Standard	75	6.6	144223.6	37419.1	16.6	bb	64.2	-14.5	10.2
627	9	20160129	100 ng Std	100 ng Std	Standard	100	6.6	222696.4	37743.1	26.0	bb	100.7	0.7	10.4
628	10	20160129	200 ng Std	200 ng Std	Standard	200	6.6	501372.3	40294.7	54.9	bb	213.0	6.5	10.4
629	11	20160129	MP Blank	MP Blank	Blank									
630	12	20160129	10 ng CCC	10 ng CCC	QC	10	6.6	20421.4	31844.1	2.9	bb	11.1	10.8	10.5
631	13	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	90200.1	33063.8	11.8	bb	45.6	-8.8	10.8
632	14	20160129	100 ng CCC	100 ng CCC	QC	100	6.6	207821.2	37358.8	25.0	bb	96.6	-3.4	10.4
633	15	20160129	MP Blank	MP Blank	Blank									
634	16	20160129	0	C2	Analyte		6.6	165342.1	36273.3	20.4	bb	78.9		9.9
635	17	20160129	1	C2	Analyte		6.6	175423.1	33687.4	23.3	bb	90.2		10.4
636	18	20160129	2	C2	Analyte		6.6	191044.6	35387.2	24.0	bb	93.0		10.1
637	19	20160129	3	C2	Analyte		6.4	260815.7	48485.8	25.1	bb	97.0		11.2
638	20	20160129	4	C2	Analyte		6.6	156199.3	31769.1	22.8	bb	88.4		11.2
639	21	20160129	MP Blank	MP Blank	Blank									
640	22	20160129	5	C2	Analyte		6.6	161042.9	35603.9	20.6	bb	79.7		9.6
641	23	20160129	6	C2	Analyte		6.6	186429.3	37652.2	22.6	bb	87.5		9.9
642	24	20160129	7	C2	Analyte		6.6	195315.6	36512.5	24.6	bb	95.3		10.1

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
643	25	20160129	8	C2	Analyte		6.6	172348.5	36616.5	21.7	bb	84.0		10.8
644	26	20160129	MP Blank	MP Blank	Blank									
645	27	20160129	10 ng CCC	10 ng CCC	QC	10	6.6	19861.5	31581.9	2.9	bb	10.8	7.5	9.5
646	28	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	86588.4	32217.2	11.8	bb	45.6	-8.8	9.1
647	29	20160129	MP Blank	MP Blank	Blank									
648	30	20160129	9	C2	Analyte		6.6	170927.3	36925.6	20.5	bb	79.3		10.1
649	31	20160129	10	C2	Analyte		6.6	181490.4	35401.0	22.5	bb	87.2		9.8
650	32	20160129	11	C2	Analyte		6.6	180475.5	35485.9	22.1	bb	85.7		10.2
651	33	20160129	12	C2	Analyte		6.6	170121.2	34716.3	21.8	bb	84.3		10.1
652	34	20160129	13	C2	Analyte		6.6	170957.9	36300.2	21.2	bb	82.0		10.7
653	35	20160129	MP Blank	MP Blank	Blank									
654	36	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	85199.9	32170.9	11.5	bb	44.5	-11	9.1
655	37	20160129	100 ng CCC	100 ng CCC	QC	100	6.6	204350.0	35710.5	24.8	bb	96.2	-3.8	10.2
656	38	20160129	MP Blank	MP Blank	Blank									
657	39	20160129	14	C2	Analyte		6.6	171296.3	37083.8	20.4	bb	78.8		10.6
658	40	20160129	15	C2	Analyte		6.6	166960.2	34498.0	21.4	bb	82.7		10.0
659	41	20160129	16	C2	Analyte		6.6	157777.5	34999.0	20.6	bb	79.6		10.4
660	42	20160129	17	C2	Analyte		6.6	162212.4	36571.6	20.0	bb	77.5		10.2
661	43	20160129	18	C2	Analyte		6.6	163331.2	35447.9	20.0	bb	77.5		9.6
662	44	20160129	MP Blank	MP Blank	Analyte									

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
663	45	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	82044.8	31027.7	11.5	bb	44.3	-11.4	10.7
664	46	20160129	100ng CCC	100 ng CCC	QC	100	6.6	192897.1	35714.9	24.2	bb	93.8	-6.2	9.7
665	47	20160129	MP Blank	MP Blank	Blank									
666	48	20160129	19	C2	Analyte		6.6	171058.2	35406.0	21.3	bb	82.5		10.5
667	49	20160129	20	C2	Analyte		6.6	164365.4	35510.1	20.4	bb	78.8		9.9
668	50	20160129	21	C2	Analyte		6.6	137807.6	34357.6	17.4	bb	67.4		9.9
669	51	20160129	22	C2	Analyte		6.6	162395.6	33364.0	21.7	bb	83.9		10.2
670	52	20160129	MP Blank	MP Blank	Blank									
671	53	20160129	10 ng CCC	10 ng CCC	QC	10	6.6	18561.3	29477.0	2.8	bb	10.7	6.6	8.6
672	54	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	80901.4	31557.0	11.7	bb	45.1	-9.8	10.5
673	55	20160129	MP Blank	MP Blank	Blank									
674	56	20160129	1	DI/F	Analyte				30122.8					
675	57	20160129	2	DI/F	Analyte				29971.5					
676	58	20160129	3	DI/F	Analyte				29852.5					
677	59	20160129	1	S	Analyte		6.6	150952.0	31928.0	21.4	bb	83.0		9.9
678	60	20160129	2	S	Analyte		6.6	139288.4	31223.7	20.4	bb	79.0		10.8
679	61	20160129	3	S	Analyte		6.6	142514.5	29812.2	20.8	bb	80.4		9.6
680	62	20160129	MP Blank	MP Blank	Blank									
681	63	20160129	10 ng CCC	10 ng CCC	QC	10	6.6	19455.1	29168.0	3.0	bb	11.2	11.6	11.1
682	64	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	81186.0	29661.9	12.4	bb	47.7	-4.7	11.6

Master #	Sample sequence #	Sample Run Date	Sample ID	Sample Text	Sample Type	Std. Conc	Retention Time	Area	IS Area	Response	Detection Flags	Conc.	%Dev	Ion Ratio
683	65	20160129	MP Blank	MP Blank	Blank									
684	66	20160129	1	S/F	Analyte		6.6	131736.2	29786.7	19.6	bb	75.9		9.7
685	67	20160129	2	S/F	Analyte		6.6	144341.6	29367.5	23.4	bb	90.5		10.9
686	68	20160129	3	S/F	Analyte		6.6	135444.3	28510.5	21.6	bb	83.6		11.1
687	69	20160129	MP Blank	MP Blank	Blank									
688	70	20160129	50 ng CCC	50 ng CCC	QC	50	6.6	79653.3	30374.5	11.7	bb	45.1	-9.8	10.7
689	71	20160129	100 ng CCC	100 ng CCC	QC	100	6.6	188227.1	33699.8	24.5	bb	95.0	-5	11.1
690	72	20160129	MP Blank	MP Blank	Blank									
691	73	20160129	1	DI	Analyte				29377.3					
692	74	20160129	2	DI	Analyte				27860.4					
693	75	20160129	3	DI	Analyte				28872.6					
694	76	20160129	MP Blank	MP Blank	Blank									

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14. ABSTRACT
Polyfluoroalkyl Substances (PFAS), like perfluorooctanoic acid, have been used for the last 50 years in a wide variety of industrial processes and consumer-based products, including polymer additives, lubricants, fire retardants and suppressants, pesticides, and surfactants (Buck et al. 2015). The Department of Defense (DoD) has used PFAS-based Aqueous Film Forming Foam (AFFF) at fire training facilities and aircraft hangars. These AFFFs have contaminated approximately 600 sites classified as fire training facilities with PFAS (Huang, 2013). This study focused on testing the most likely adsorbent compounds that would be selected to remediate contaminated sites on Air Force installations. Batch tests were performed to determine the adsorptive characteristics, both in capacity and rate, of conventional granular activated carbon GAC, primitive carbon materials, and advanced carbon materials for PFOA. Analysis of the data collected lead to an investigation of sample prep techniques and found that low sample volumes and large dilutions ratios contribute to variability. When preparing large quantities of samples the manual method can present a challenge for the technician. Automated devices that can repeatedly mix and dilutes samples prior to analysis should be considered to reduce variability.

15. SUBJECT TERMS
Polyfluoroalkyl Substances, carbon nanotubes, biochar, activated carbon

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