

FINAL REPORT

Plasma Based Treatment Processes for PFAS Investigation Derived Waste

SERDP Project ER18-1624

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14. ABSTRACT Removal of PFASs from field site investigation derived waste (IDW) by soil washing coupled with destruction of PFASs in the wash solutions by plasma treatment was investigated. A wash solution of 50% water and 50% methanol with 1% NaCl was found to be most effective, however water alone was somewhat effective. Removal was fast, taking minutes, however kinetic limitations were largely eliminated in the experimental design. Plasma treatment of distilled wash solution resulted in > 99.6% destruction of precursors qualified by the total oxidizable precursor (TOP) assay, > 99% destruction of long and short-chain PFAA's (except PFBA) and of identifiable precursors, with a 10-fold dilution of the concentrated still bottoms.						
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Acronyms

10:2 FTS	10:2 Fluorotelomere sulfonate
4:2 FTS	4:2 Fluorotelomere sulfonate
6:2 FTS	6:2 Fluorotelomere sulfonate
8:2 FTS	8:2 Fluorotelomere sulfonate
AEC	anion exchange capacity
AFFF	aqueous film forming foam
ASTM	American Society for Testing and Materials
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
C	Celsius
C-F	carbon-fluorine
Cm	centimeter
CTAB	cetrimonium bromide
DoD	Department of Defense
DI	distilled water
EC	enhanced contact
FOSA-1	perfluorooctane sulfonamide
FOSAA	perfluorooctane sulfonamide acetate
EtFOSA	N-ethylperfluorooctane sulfonamide
EtFOSAA	N-ethyl perfluorooctane sulfonamido acetic acid
MeFOSA	N-methylperfluorooctane sulfonamide
MeFOSAA	N-methyl perfluorooctane sulfonamido acetic acid
PFCAs	perfluoroalkyl carboxylic acids
PFSAs	perfluoroalkyl sulfonic acids
G	gram
HV	high voltage
IDW	investigation derived waste
IX	ion exchange
IXRS	ion exchange regenerate solution
JBSA	Joint Base San Antonio
JV	Jacksonville
LCMS	liquid chromatogram mass spectrophotometer
MeOH	methanol
Min	minute
mL	milliliter
mM	millimolar
NaCl	sodium chloride
PFBA	perfluorobutanoic acid
PFPeA	perfluoropentanoic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFHpS	perfluoroheptane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFNA	perfluorononanoic acid
PFDA	perfluorodecanoic acid
PFUnA	perfluoroundecanoic acid

PFDoA	perfluorododecanoic acid
PFAS	Per- and Polyfluoroalkyl Substance
PP	polypropylene
pH	- log [H ⁺]
pKa	- log equilibrium constant
SB	still bottoms
TOC	total organic carbon
TOP	total oxidizable precursors
W	Wurtsmith
WG	Willow Grove
wt	weight

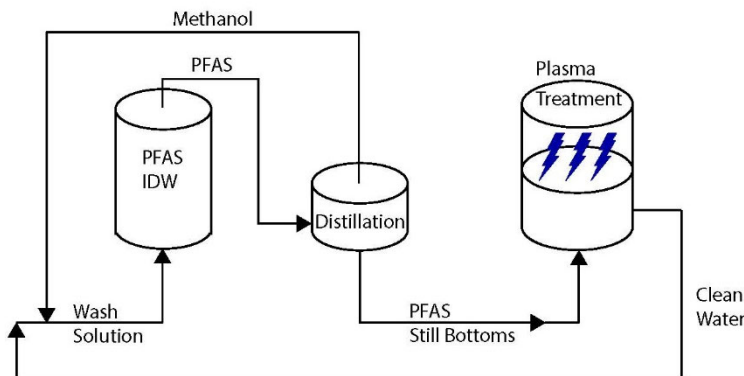
Abstract

Introduction and Objectives. This project's objectives were to investigate the use of an integrated approach of soil washing and destructive treatment using plasma for treatment of PFAS-contaminated investigation derived waste (IDW). The combination of systems could permit unrestricted disposal and/or discharge of IDW onsite. Information from this study and ongoing PFAS research efforts will serve as a foundation for the development of fully developed field-scale systems for the treatment of PFAS-impacted IDW. These systems would be mobile and easily deployable, minimizing the spatial footprint and mobilization time and effort and allow cost effective treatment compared to current disposal methods

Technical Approach. Field site IDW was obtained from several DoD sites. Removal of PFASs from the IDW by soil washing was evaluated using a variety of solutions including water alone, water plus solvent, and water plus solvent and salt. Destruction of PFASs in these concentrated soil washing solutions using the enhanced contact electrical discharge plasma reactor was then verified.

Results. An optimized wash solution of 50% water and 50% methanol with 1% NaCl was found to be the most effective wash, however for soils with low organic carbon content and for short-chain PFAS, water alone was somewhat effective. Single washes removed the vast majority of compounds from the IDW samples. Removal was fast, taking minutes, however the soil was pulverized in these experiments and vessels were completely mixed thus kinetic limitations were largely eliminated. Plasma treatment of distilled (to recover methanol) solution (i.e., brine still bottoms) resulted in > 99.6% destruction of precursors qualified by the total oxidizable precursor (TOP) assay, > 99% destruction of long and short-chain PFAA's (except PFBA) and of identifiable precursors, with a 10-fold dilution of the concentrated still bottoms. Two sequenced reactors for high concentration followed by low concentration treatment were required for effective treatment. The addition of cationic surfactant (CTAB) resulted in greater removal of short-chain compounds, treating all except PFBA (260 ng/L) to below detection.

Benefits. A significant amount of PFAS containing IDW will be generated in the coming years - an on-site desorption method combined with a destructive treatment technology would decrease IDW disposal costs and limit DoD future liability associated with PFAS going off-site.



Executive Summary

1.0 Introduction

Per- and Poly- fluoroalkyl substances (PFAS) are a class of surfactants characterized by a carbon-fluorine (C-F) alkyl chain attached to a functional head group (Buck et al., 2011). PFAS have been used for a variety of industrial and commercial applications since the 1950's including metal plating, fluoropolymer processing aids, textiles, and aqueous film-forming foam (AFFF) for hydrocarbon firefighting (Ahrens & Bundschuh, 2014). Recently PFAS have received international public attention because of their persistence in the environment, potential for bioaccumulation, and possible adverse health effects such as carcinogenesis, and endocrine disruption (Giesy & Kannan, 2001; Kannan, 2011; H. Zhang et al., 2011). The presence of PFAS is ubiquitous across a diverse set of environmental matrices, including water, soils, sediments and sewage sludge (Ahrens et al., 2009; Pan & You, 2010; Taniyasu et al., 2003; P. Wang et al., 2013). Biomonitoring studies have identified significant global distribution of PFAS in humans, wildlife and the environment, they have even been identified in remote areas such as the arctic (John P. Giesy, 2002; Kannan et al., 2002; Smithwick et al., 2006). Between 1992 and 2012 perfluorooctane sulfonic acid (PFOS) was detected in blood serum in up to 99% of the US population, however levels have been decreasing since the phase out of production. In 2016 EPA issued a lifetime drinking water health advisory for PFOS and perfluorooctanoic acid (PFOA) at a combined concentration of 0.07 µg/L based on a reference dose derived from toxicity studies in rats which indicated adverse developmental effects, adverse liver effects, impaired immune system function or cancer (United States Environmental Protection Agency, 2016).

The Department of Defense has identified 401 active and former military installations with at least one area of known or suspected release of PFOS or PFOS in a Report to Congress in July 2019. The DoD is currently investigating the sites following the CERCLA process to assess the risks to drinking water and prioritize future actions. This review is expected to be concluded at the end of 2020 and the DoD will initiate remedial investigations accordingly (DoD, 2019). Current and future PFAS investigations at DoD sites have focused on fire-fighting training areas where a variety of PFAS and co-contaminants are present in the subsurface soils and groundwater. As part of these investigations large quantities of investigation-derived waste (IDW) in the form of soil cuttings are generated from boring advancement and well installation. The DoD requires generated IDW to remain on site in many cases as a measure to minimize potential for future environmental liability. The volumes of IDW generated and stored at DoD sites continues to grow as investigations continue. Decontaminating the IDW soil on site would forego the need for specialized containment areas for holding the soil and allow the soil to be returned to the environment.

Soil Washing. Soil washing, the ex-situ treatment of contaminated soil with an aqueous solution to remove sorbed contaminants, has been shown to be effective in removing hydrophobic organic compounds such as polyaromatic hydrocarbons, polychlorinated biphenyls, herbicides and pesticides (Chu & Chan, 2003; Chu & Kwan, 2003; Peng et al., 2011; Trellu et al., 2016). Although, to date, the authors are not aware of soil washing being evaluated for PFAS in any peer reviewed journals, there is literature on an analogous scenario that is applicable: ion exchange (IX) resin regeneration. Ion exchange resins are composed of organic polymers that

form a matrix of hydrocarbons embedded with functional groups that, depending on composition, serve as either cation or anion exchange sites (Deng et al., 2010a; Du et al., 2015; Zaggia et al., 2016). Previous work using IX resins to remove PFAS from water have reported observations of the following sorption behaviors: hydrophobic, anion exchange, electrostatic (Chularueangaksorn et al., 2013; Yu et al., 2009); hydrophobic and anion exchange (Deng et al., 2010a; Nickelsen & Woodard, 2017; Zaggia et al., 2016); hydrophobic and electrostatic (Xiao et al., 2012).

PFAS's sorb to soils in a similar manner as they do to IX resin; by a combination of hydrophobic and charge interactions. This hypothesis is supported by Higgins and Luthy 2006, who are among the first to have measured the sorption of PFAS on sediments and found organic content of the soil the most important property controlling sorption; with an increase in total organic carbon (TOC) content resulting in increased sorption, subsequently supported by (Milinovic et al., 2015; Xiao et al., 2017; Zhao et al., 2014b; Zhi & Liu, 2018). It was also observed that sorption capacity increased with increasing PFAS C-F chain length, each additional C-F moiety incrementally increases the compounds hydrophobicity; also supported by (Krippner et al., 2014; Mejia-Avendaño et al., 2020; Milinovic et al., 2015). In addition, Higgins and Luthy 2006 observed that sorption increases with Ca^{2+} ions and decreasing pH, indicating that electrostatic interactions play a role in sorption. At standard environmental pH values PFAS usually exist as anionic species due to their low pK_a values (Burns et al., 2008; Vierke et al., 2013). It was later found that PFAS can bond to sorbent surfaces through electrostatic interactions (Jeon et al., 2011; Johnson et al., 2007; Uwayezu et al., 2019; Xiao et al., 2011; R. Zhang et al., 2014; Zhao et al., 2014a) or via divalent cation bridging and that changes in pH affect electrostatic interactions and changes in cation availability affects the bridge bonding (Campos Pereira et al., 2018; Eberle et al., 2019; Pan et al., 2009). Another sorption pathway for anionic compounds is through anion exchange to iron oxides and clays (Li et al., 2019; Wei et al., 2017).

IX resins sorbed with PFAS have successfully been regenerated utilizing process analogous to ex-situ soil washing (Deng et al. 2010; Senevirathna et al. 2010; Xiao et al. 2012; Yu et al. 2009; Chularueangaksorn et al. 2013; Du et al. 2015; Zaggia et al. 2016; W. Wang et al. 2019; Woodard, Berry, and Newman 2017; Gagliano et al. 2020). The IX regeneration solution can be adapted to be utilized as a soil washing solution to remove PFAS. Previous work on IX resin regeneration has identified solutions of methanol (MeOH) with sodium chloride (NaCl) and/or ammonium hydroxide (NH_4OH) as effective at removing sorbed PFAS (Du et al., 2015; Gagliano et al., 2020; Woodard et al., 2017; Zaggia et al., 2016). Woodard, Berry and Newman (2017) determined that brine solutions can be used to effectively desorb the anionic head group, which is involved in electrostatic interactions, but the hydrophobic tail, which is involved with hydrophobic adsorption to organic matter, remains adsorbed to the resin. They found that an organic solvent like methanol (MeOH) was effective to desorb the hydrophobic portion of the PFAS, but would leave the anionic head of the PFAS attached to the ion exchange site on the resin (Woodard et al., 2017). These results were supported by others (Chularueangaksorn et al., 2013; Deng et al., 2010b) who found that regeneration solutions consisting of organic solvents (MeOH) and sodium chloride (NaCl) are the most effective at desorbing PFAS.

Chularueangaksorn et al., (2013) determined that a methanol to deionized water ratio (v/v) of 70:30 with 5% NaCl was the most effective at regenerating a polystyrene-divinylbenzene anion exchange resin, which exhibits both hydrophobic and anion sorption mechanisms.

Plasma Treatment. Our recent studies have shown that an enhanced contact (EC) plasma reactor is extremely effective at degrading PFAS in groundwater (Stratton et al., 2017; Singh et al., 2019). In this reactor, PFAS compounds are transported to the gas-liquid interphase, using argon gas bubbles, where they are effectively degraded by plasma. Plasma produces numerous oxidative (e.g., $\cdot\text{OH}$, O , $\text{HO}_2\cdot$, $\text{O}_2\cdot^-$, O_2 , H_2O_2) and reductive species (e.g., free and aqueous electrons e_{aq}^- , $\text{H}^\cdot$) the latter of which play a key role in degrading PFAAs (Mededovic et al. 2016; Stratton et al., 2017). Comparisons with other technologies show that the effectiveness of the EC reactor for PFAS destruction is greater than other leading water treatment technologies (Nzeribe et al., 2019).

Preliminary results revealed that the bench-scale EC plasma reactor designed to treat groundwater is significantly less effective in degrading PFOA and PFOS in high conductivity solutions like those that will be found in this project in terms of treatment time and energy requirements. This result was attributed to: (1) the changes in fundamental physical and chemical processes occurring in the plasma and in the bulk liquid due to high ionic strength compared to low ionic strength solutions (Wang et al., 2018), which affect production rates and types of reactive species formed, chemical degradation pathways and final byproducts, (2) high solution electrical conductivity (i.e., ionic strength) which lowers the area of the plasma in contact with the treated water and, (3) low solution surface tension due to high PFAS concentration which interferes with the formation of plasma through the formation of a thick layer of foam at the plasma-liquid interface (caused by argon gas bubbling).

For this study, the EC plasma reactor and the plasma-generating network previously developed for the treatment of low conductivity groundwater were modified and used to treat soil washing solutions after methanol recovery. For these experiments since we did not have much soil washing solution available, and in practice the methanol would likely be recovered through distillation, we used lab prepared solutions and still bottoms from IX regenerant solutions to simulate soil washing solutions after MeOH recovery.

2.0 Objectives

This project's objectives were to investigate the use of an integrated approach of soil washing and destructive treatment using plasma for treatment of PFAS-contaminated investigation derived waste (IDW). The combination of systems could permit unrestricted disposal and/or discharge of IDW onsite. Information from this study and ongoing PFAS research efforts will serve as a foundation for the development of fully developed field-scale systems for the treatment of PFAS-impacted IDW. These systems would be mobile and easily deployable, minimizing the spatial footprint and mobilization time and effort and allow cost effective treatment compared to current disposal methods

3.0 Technical Approach

Experiment Materials. Soil samples were obtained from DoD sites with active PFAS investigations into the fate of AFFF discharges and have measured PFAS in the groundwater. LCMS grade methanol and LCMS grade deionized water stock solutions, used for wash solutions, soil extraction solution, and LCMS vial preparation, were purchased from Sigma Aldrich. Sodium chloride was purchased from Sigma Aldrich. The 600 mL polypropylene jars, 50 mL and 15 mL polypropylene centrifuge tubes, and 200 μ L and 1000 μ L polypropylene pipette tips were purchased from VWR. Agilent 1 mL amber glass LCMS vials with polypropylene caps were used for the LCMS analyses.

IDW Soil Samples. Soil samples were dried in an oven at 104° C for 8 hours, then ground using a mortar and pestle, passed through a 2mm mesh sieve, homogenized and placed into a new polypropylene jar with an airtight lid for storage. Total organic carbon (TOC) was measured by using a Shimadzu TOC-Vcpn analyzer (Shimadzu, Tokyo, Japan) with solid sample module (SSM-5000A). The pH was measure using a pH meter calibrated with pH 4, 7 and 10 buffer solutions. Soil was added to water with a soil to water ratio of 1:5. The soil and water solution was mixed for 5 minutes then left to sit for 1 hour before the pH was measured. The anion exchange capacity (AEC) was measured by Alfa Chemistry. The results of the soil analysis are shown below in **Table 1**. The soil samples are organized according to decreasing TOC, AEC and pH.

Table 1. IDW soil samples arranged according to descending value for the soil property: (a.) TOC, (b.) AEC, (c.) pH

a. Decreasing TOC				b. Decreasing AEC				c. Decreasing pH			
IDW Soil	pH	AEC (cmol _c kg ⁻¹)	TOC	IDW Soil	pH	AEC (cmol _c kg ⁻¹)	TOC	IDW Soil	pH	AEC (cmol _c kg ⁻¹)	TOC
Willow Grove	7.93	0.28	0.88%	Wurtsmith	9.1	0.94	0.08%	JBSA	11.07	0.63	0.004%
Jacksonville	6.22	0.9	0.54%	Jacksonville	6.22	0.9	0.54%	Wurtsmith	9.1	0.94	0.08%
Wurtsmith	9.1	0.94	0.08%	JBSA	11.07	0.63	0.004%	Willow Grove	7.93	0.28	0.88%
JBSA	11.07	0.63	0.004%	Willow Grove	7.93	0.28	0.88%	Jacksonville	6.22	0.9	0.54%

Soil Washing. Soil washing experimental procedures were based on previously published sorption/desorption procedures (Higgins & Luthy, 2006; Milinovic et al., 2015; OECD 106, 2000). The experiments used 50 mL polypropylene (PP) centrifuge tubes containing 2 g of soil and 40 mL of wash solution and tumbled for 1 week. All experiments were run in triplicate and accompanied by blanks and triplicate deionized water (DI) run as a control. Previous work with PFAS sorption experiments cite 48 hours as the time to equilibrium conditions (Shih & Wang, 2013; F. Wang et al., 2012; Wei et al., 2017). However preliminary desorption experimental times were increased given previous observations of: 1) sorption irreversibility increasing with increasing C-F chain length, 2) PFASs displaying higher irreversibility than analog PFCAs, with PFOS displaying the highest irreversibility (Chen et al., 2016; Miao et al., 2017; Milinovic et al., 2015), and 3) some soil properties increasing irreversibility due to pore deformation (Zhao et al., 2014a), and soil organic matter being positively correlated with increase irreversibility (Miao et al., 2017). Miao et al., (2017) found that PFOA exhibited high sorption irreversibility in certain

soils with high organic content, which contradicts other work that observed PFOA to exhibit low irreversibility (Chen et al., 2016).

The compositions of the soil wash solutions evaluated in this investigation are shown in **Table 2**. The wash type lists compositions as follows: [deionized water: methanol] by volume: volume (v/v), the subsequent columns detail the relative amount of each wash component: deionized water, methanol, and sodium chloride by weight percent (NaCl wt %) with a (-) indicating that particular component was not part of wash.

Table 2. Wash Type column list wash solutions in format of [DI: Methanol]: NaCl wt/%

Wash Type	Deionized Water (%)	Methanol (%)	NaCl (wt%)
DI	100	-	-
[75:25]	75	25	-
[50:50]	50	50	-
[25:75]	25	75	-
[75:25]:1%	75	25	1
[50:50]:1%	50	50	1
[25:75]:1%	25	75	1
[75:25]:3%	75	25	3
[50:50]:3%	50	50	3
[25:75]:3%	25	75	3
[75:25]:5%	75	25	5
[50:50]:5%	50	50	5
[25:75]:5%	25	75	5

Batch Equilibrium Experiments. The washes in Table 2 were evaluated in batch equilibrium soil washing experiments. The tubes were vortexed for 30 seconds, then tumbled end over end for a week before they were centrifuged at 9000g for 30 min to ensure all suspended sediment is removed from the supernatant without having to rely on using a filter to prevent the transfer of residual particulate matter to LCMS vials. The lack of a filter avoided potential PFAS losses due to sorption on filter media (Chandramouli et al., 2015; Lath et al., 2019). Batch equilibrium experimental results were compared with a soil extraction procedure based on ASTM D7968-14, Standard Test Method for Determination of Perfluorinated Compounds in Soil. The soil extraction was a 3-phase exhaustive extraction that involved the complete replacement of the wash solution at the start of each subsequent phase. The experiments were carried out in triplicate with blanks. The extraction experiments used 2 g soil with 10 mL of 99% methanol, 1% ammonium hydroxide in a 15 mL PP centrifuge tube which were vortexed for 30 seconds or until complete soil mobilization is achieved. The samples were sonicated at 30 ° C for 60 minutes, then tumbled end over end for 2 hours before they were centrifuged at 9000g for 30 minutes. The supernatant was decanted and stored in 15 mL PP centrifuge tube until LCMS vial preparation. Extractions 2 and 3 repeated the steps for phase 1,

each time fully decanting and replacing the wash solution. The supernatants are stored separately for individual analysis.

Wash Solution Optimization. Kinetic experiments followed the batch equilibrium procedures although only select washes are used: [50:50]:1% and [25:75]:3%, and DI as a control. The samples are vortexed until complete soil mobilization and set on the tumbler for the desired sampling interval. At the sampling interval the samples were centrifuged for 5 minutes and then a 200 μ L sample was taken using a pipette and placed in a 1.5 mL PP vial with 800 μ L of methanol, each time interval sample was placed in a new 1.5 mL PP vial. The 50 mL PP centrifuge tube was then vortexed and put back on the tumbler, the whole sampling process and preparation took about 15 minutes. At the end of the experiment the vials were centrifuged again at 9000g for 20 minutes to remove residual suspended solids.

Plasma Treatment. Each wash solution was processed through two plasma reactors (acrylic rectangular tank, 34.5 cm $\times$ 7.6 cm $\times$ 7.6 cm; total liquid volume ($\sim$ 750 mL)), connected in series, each containing six high voltage (HV) tungsten saw tooth blade electrodes (each 6 cm in length), for the generation of plasma. These electrodes were arranged parallel to each other (3 cm apart) and perpendicular to the long side of reactor (Figure 1). The HV electrodes were suspended 1.2 cm above the surface of the water (the thickness of the treated water layer was 2.9 cm). A coarse iron mesh screen, submerged 3 cm into the liquid, served as the ground electrode. A single gas diffuser (61.0 cm $\times$ 6.35 cm $\times$ 2.00 cm, 0.4 μ m pore size and 50 psi maximum pressure; Pentair, USA) was placed on the bottom of the reactor immediately below the ground electrode. Due to the excessive foaming observed in each SB solution which interfered with plasma formation, the flowrate of argon was gradually increased from 1 L/min to 4 L/min over the course of the experiment. Argon gas was recirculated immediately upon leaving the reactor.¹³ To generate plasma, -30 kV was applied using a custom-built HV electrical circuit to charge three dedicated capacitor banks (4 nF each) each connected to a pair of HV electrodes. Charged capacitors were simultaneously discharged via three dedicating rotating spark gaps at the discharge frequency of 60 Hz. The treated liquid was continuously recirculated through a heat exchanger set at 10°C. Power drawn by the high voltage supply, peristaltic pump, chiller and spark gap was measured by a digital power meter (Kill A, P3 P4400).

Initial tests of undiluted solutions exhibited excessive foaming for extended periods (>3 hr), at all argon flow rates tested. Since excessive foaming is detrimental to the plasma process, a 10-fold dilution, of as received still bottoms (SB) solutions, was performed. Thus, the high concentration reactor was used as the first treatment unit, where 10-fold diluted SBs were treated to lower the concentration of long-chain PFAAs to <1 μ g/L. Treated SBs were then introduced and treated in the second low concentration reactor to further decrease PFAA concentrations. To enhance the removal of short-chain PFAS (primarily PFBA and PFBS), in the low concentration reactor, a cationic surfactant, cetrimonium bromide (CTAB) was added at 30-minute intervals to achieve initial concentrations of 0.2 mM in the reactor. CTAB was added to assist in the short-chain foam production. Frequent dosing of CTAB was required due to its rapid degradation by plasma.

PFAS Analyses. Quantification of PFAS and their precursors. Seventeen PFAAs and their 10 precursor concentrations were measured in negative ionization mode using a UPLC-MS-MS (Thermo Scientific, Vanquish-TSQ ALTIS) equipped with Phenomenex Luna Omega PS C18 column (2.1 mm $\times$ 100 mm, 1.6

µm). A detailed description of the analytical methods, QA procedures and individual detection limits is provided in Tables 3 to 5.

4.0 Results and Discussion

Soil washing results. The 50:50_1% NaCl wash solution was found to be the most effective wash, although for low TOC soils and shorter chain PFAS DI water alone was somewhat effective. Longer chain sulfonated compounds were the most difficult to remove. Single washes generally removed the vast majority of the compounds present. Removal was generally fast, taking minutes to remove the vast majority of the compounds. However in these experiments the soil was pulverized and the solutions were tumbled end-over-end so kinetic limitations were largely eliminated.

Plasma treatment results. To the best of our knowledge, this is the first study reporting the treatment of high concentration PFAS-containing IX brine solution. In this study, destruction of TOP was > 99.6% (99.8±0.1%) for all six SB solutions. Long-chain PFAAs, short-chain PFAAs (except PFBA) and PFAS precursors were removed >99% in all 10-fold diluted 1.5 L samples in six hours of treatment. Two different reactors: one for treatment of high-concentration solutions followed by a second reactor for treatment of the lower concentration SB solutions were required for effective treatment. In the optimized plasma reactor, periodic addition of cationic surfactant (CTAB) resulted in even short-chain PFAS being degraded below detection limits, except for PFBA (260 ng/L). Considering the extremely high concentrations of PFAAs and precursors in SBs, the plasma treatment process appears to be a promising and efficient technology for the removal of PFAS from high-conductivity waters such as IX brine regenerant solutions. Combining regenerable IX with plasma treatment would result in a treatment train with near zero PFAS waste.

Overall Conclusions. Key project findings include:

- Soil washing with MeOH + NaCl is effective at removing PFAS from soil although water alone is fairly effective, especially for short chain PFAS in low organic carbon content soils.
- PFAS are removed from soil quickly (minutes in these experiments).
- Plasma treatment to destroy PFAS in high concentration salt solutions is effective.
- Precursor concentrations are an important determinant of required plasma treatment times. Precursor oxidation before plasma treatment would decrease treatment times and may be economically beneficial.

5.0 Implications for Future Research and Benefits

A significant amount of PFAS containing IDW will be generated in the coming years - an on-site desorption method combined with a destructive treatment technology would decrease IDW disposal costs and limit DoD future liability associated with PFAS going off-site. Future research should test the efficacy of an integrated, field-scale soil washing – plasma treatment system for IDW management.

1.0 Objective

This project's objectives were to investigate the use of an integrated approach of soil washing and destructive treatment using plasma for treatment of PFAS-contaminated investigation derived waste (IDW). The combination of systems could permit unrestricted disposal and/or discharge of IDW onsite. Information from this study and ongoing PFAS research efforts will serve as a foundation for the development of fully developed field-scale systems for the treatment of PFAS-impacted IDW. These systems would be mobile and easily deployable, minimizing the spatial footprint and mobilization time and effort and allow cost effective treatment compared to current disposal methods

2.0 Background

Per- and poly- fluoroalkyl substances (PFAS) are a class of surfactants characterized by a carbon-fluorine (C-F) alkyl chain attached to a functional head group (Buck et al., 2011). PFAS have been used for a variety of industrial and commercial applications since the 1950's including metal plating, fluoropolymer processing aids, textiles, and aqueous film-forming foam (AFFF) for hydrocarbon firefighting (Ahrens & Bundschuh, 2014). Recently PFAS have received international public attention because of their persistence in the environment, potential for bioaccumulation, and possible adverse health effects such as carcinogenesis, and endocrine disruption (Giesy & Kannan, 2001; Kannan, 2011; H. Zhang et al., 2011). The presence of PFAS is ubiquitous across a diverse set of environmental matrices, including water, soils, sediments and sewage sludge (Ahrens et al., 2009; Pan & You, 2010; Taniyasu et al., 2003; P. Wang et al., 2013). Biomonitoring studies have identified significant global distribution of PFAS in humans, wildlife and the environment, they have even been identified in remote areas such as the arctic (John P. Giesy, 2002; Kannan et al., 2002; Smithwick et al., 2006). Between 1992 and 2012 Perfluorooctane sulfonic acid (PFOS) was detected in blood serum in up to 99% of the US population, however levels have been decreasing since the phase out of production. In 2016 EPA issued a lifetime drinking water health advisory for PFOS and perfluorooctanoic acid (PFOA) at a combined concentration of 0.07 µg/L based on a reference dose derived from toxicity studies in rats which indicated adverse developmental effects, adverse liver effects, impaired immune system function or cancer (United States Environmental Protection Agency, 2016).

Sites impacted with AFFF display the highest PFAS concentrations in surface water, groundwater and soil (Baduel et al., 2015; Cheryl A. Moody & Field, 1999). Over 240 unique PFAS related compounds have been identified in AFFF formulations and impacted waters (Backe et al., 2013; Barzen-Hanson et al., 2017). The PFAS components of AFFF lower the surface tension of the extinguishing fluid allowing a film to form over the hydrocarbon fuel, preventing reignition (C. A. Moody & Field, 2000). The USEPA's 2010/2015 PFOA Stewardship Program, which requires sites where AFFF is used, to comply with federal regulations has identified: 16 industrial sites, 664 military fire training sites on bases and 533 civilian airports with the potential to release AFFF into the environment (USEPA, 2006). As a consequence of frequent training, these sites have become major point sources of AFFF discharge resulting in widespread groundwater contamination (Das et al., 2015; Guelfo & Higgins, 2013; Place & Field, 2012). Hu et al (2016) positively correlated PFAS concentrations in drinking water to proximity of known potential PFAS discharge point source locations and discovered 6 million residents had PFOA and PFOS levels higher than the USEPA's lifetime health advisory limit of (70ng/L) (Hu et al., 2016).

The Department of Defense has identified 401 active and former military installations with at least one area of known or suspected release of PFOS or PFOA in a Report to Congress in July 2019. The DoD is currently investigating the sites following the CERCLA process to assess the risks to drinking water and prioritize future actions. This review is expected to be concluded at the end of 2020 and the DoD will initiate remedial investigations accordingly (DoD, 2019). Current and future PFAS investigations at DoD sites have focused on fire-fighting training areas where a variety of PFAS and co-contaminants are present in the subsurface soils and

groundwater. As part of these investigations large quantities of investigation-derived waste (IDW) in the form of soil cuttings are generated from boring advancement and well installation. The DoD requires generated IDW to remain on site in many cases as a measure to minimize potential for future environmental liability. The volumes of IDW generated and stored at DoD sites continues to grow as investigations continue. Decontaminating the IDW soil on site would forego the need for specialized containment areas for holding the soil and allow the soil to be returned to the environment.

Soil Washing. Soil washing, the ex-situ treatment of contaminated soil with an aqueous solution to remove sorbed contaminants, has been shown to be effective in removing hydrophobic organic compounds such as polyaromatic hydrocarbons, polychlorinated biphenyls, herbicides and pesticides (Chu & Chan, 2003; Chu & Kwan, 2003; Peng et al., 2011; Trellu et al., 2016). Although, to date, the authors are not aware of soil washing being evaluated for PFAS in any peer reviewed journals, there is literature on an analogous scenario that is applicable: ion exchange (IX) resin regeneration. Ion exchange resins are composed of organic polymers that form a matrix of hydrocarbons embedded with functional groups that, depending on composition, serve as either cation or anion exchange sites (Deng et al., 2010a; Du et al., 2015; Zaggia et al., 2016). Previous work using IX resins to remove PFAS from water have reported observations of the following sorption behaviors: hydrophobic, anion exchange, electrostatic (Chularueangaksorn et al., 2013; Yu et al., 2009); hydrophobic and anion exchange (Deng et al., 2010a; Nickelsen & Woodard, 2017; Zaggia et al., 2016); hydrophobic and electrostatic (Xiao et al., 2012).

PFAS's sorb to soils in a similar manner as they do to IX resin; by a combination of hydrophobic and charge interactions. This hypothesis is supported by Higgins and Luthy 2006, who are among the first to have measured the sorption of PFAS on sediments and found organic content of the soil the most important property controlling sorption; with an increase in total organic carbon (TOC) content resulting in increased sorption, subsequently supported by (Milinovic et al., 2015; Xiao et al., 2017; Zhao et al., 2014b; Zhi & Liu, 2018). It was also observed that sorption capacity increased with increasing PFAS C-F chain length, each additional C-F moiety incrementally increases the compounds hydrophobicity; also supported by (Krippner et al., 2014; Mejia-Avendaño et al., 2020; Milinovic et al., 2015). In addition, Higgins and Luthy 2006 observed that sorption increases with Ca^{2+} ions and decreasing pH, indicating that electrostatic interactions play a role in sorption. At standard environmental pH values PFAS usually exist as anionic species due to their low pK_a values (Burns et al., 2008; Vierke et al., 2013). It was later found that PFAS can bond to sorbent surfaces through electrostatic interactions (Jeon et al., 2011; Johnson et al., 2007; Uwayezu et al., 2019; Xiao et al., 2011; R. Zhang et al., 2014; Zhao et al., 2014a) or via divalent cation bridging and that changes in pH affect electrostatic interactions and changes in cation availability affects the bridge bonding (Campos Pereira et al., 2018; Eberle et al., 2019; Pan et al., 2009). Another sorption pathway for anionic compounds is through anion exchange to iron oxides and clays (Li et al., 2019; Wei et al., 2017).

IX resins sorbed with PFAS have successfully been regenerated utilizing process analogous to ex-situ soil washing (Deng et al. 2010; Senevirathna et al. 2010; Xiao et al. 2012; Yu et al. 2009; Chularueangaksorn et al. 2013; Du et al. 2015; Zaggia et al. 2016; W. Wang et al. 2019; Woodard, Berry, and Newman 2017; Gagliano et al. 2020). The IX regeneration solution can be

adapted to be utilized as a soil washing solution to remove PFAS. Previous work on IX resin regeneration has identified solutions of methanol (MeOH) with sodium chloride (NaCl) and/or ammonium hydroxide (NH₄OH) as effective at removing sorbed PFAS (Du et al., 2015; Gagliano et al., 2020; Woodard et al., 2017; Zaggia et al., 2016). Woodard, Berry and Newman (2017) determined that brine solutions can be used to effectively desorb the anionic head group, which is involved in electrostatic interactions, but the hydrophobic tail, which is involved with hydrophobic adsorption to organic matter, remains adsorbed to the resin. They found that an organic solvent like methanol (MeOH) was effective to desorb the hydrophobic portion of the PFAS, but would leave the anionic head of the PFAS attached to the ion exchange site on the resin (Woodard et al., 2017). These results were supported by others (Chularueangaksorn et al., 2013; Deng et al., 2010b) who found that regeneration solutions consisting of organic solvents (MeOH) and sodium chloride (NaCl) are the most effective at desorbing PFAS. Chularueangaksorn et al., (2013) determined that a methanol to deionized water ratio (v/v) of 70:30 with 5% NaCl was the most effective at regenerating a polystyrene-divinylbenzene anion exchange resin, which exhibits both hydrophobic and anion sorption mechanisms.

Plasma Treatment. Our recent studies have shown that an enhanced contact (EC) plasma reactor is extremely effective at degrading PFAS in groundwater (Stratton et al., 2017; Singh et al., 2019). In this reactor, PFAS compounds are transported to the gas-liquid interphase, using argon gas bubbles, where they are effectively degraded by plasma. Plasma produces numerous oxidative (e.g., $\cdot\text{OH}$, O , $\text{HO}_2\cdot$, $\text{O}_2\cdot^-$, O_2 , H_2O_2) and reductive species (e.g., free and aqueous electrons e_{aq}^- , $\text{H}\cdot$) the latter of which play a key role in degrading PFAAs (Mededovic et al. 2016; Stratton et al., 2017). Comparisons with other technologies show that the effectiveness of the EC reactor for PFAS destruction is greater than other leading water treatment technologies (Nzeribe et al., 2019).

Preliminary results revealed that the bench-scale EC plasma reactor designed to treat groundwater is significantly less effective in degrading PFOA and PFOS in high conductivity solutions like those that will be found in this project in terms of treatment time and energy requirements. This result was attributed to: (1) the changes in fundamental physical and chemical processes occurring in the plasma and in the bulk liquid due to high ionic strength compared to low ionic strength solutions (Wang et al., 2018), which affect production rates and types of reactive species formed, chemical degradation pathways and final byproducts, (2) high solution electrical conductivity (i.e., ionic strength) which lowers the area of the plasma in contact with the treated water and, (3) low solution surface tension due to high PFAS concentration which interferes with the formation of plasma through the formation of a thick layer of foam at the plasma-liquid interface (caused by argon gas bubbling).

For this study, the EC plasma reactor and the plasma-generating network previously developed for the treatment of low conductivity groundwater were modified and used to treat soil washing solutions after methanol recovery. For these experiments since we did not have much soil washing solution available, and in practice the methanol would likely be recovered through distillation, we used lab prepared solutions and still bottoms from IX regenerant solutions to simulate soil washing solutions after MeOH recovery.

3.0 Materials and Methods

3.1 Experiment Materials

Soil samples were obtained from DoD sites with active PFAS investigations into the fate of AFFF discharges and have measured PFAS in the groundwater. LCMS grade methanol and LCMS grade deionized water stock solutions, used for wash solutions, soil extraction solution, and LCMS vial preparation, were purchased from Sigma Aldrich. Sodium chloride was purchased from Sigma Aldrich. The 600 mL polypropylene jars, 50 mL and 15 mL polypropylene centrifuge tubes, and 200 μ L and 1000 μ L polypropylene pipette tips were purchased from VWR. Agilent 1 mL amber glass LCMS vials with polypropylene caps were used for the LCMS analyses.

3.2 IDW Soil Samples

Soil samples were dried in an oven at 104°C for 8 hours, then ground using a mortar and pestle, passed through a 2mm mesh sieve, homogenized and placed into a new polypropylene jar with an airtight lid for storage. Total organic carbon (TOC) was measured by using a Shimadzu TOC-Vcpn analyzer (Shimadzu, Tokyo, Japan) with solid sample module (SSM-5000A). The pH was measure using a pH meter calibrated with pH 4, 7 and 10 buffer solutions. Soil was added to water with a soil to water ratio of 1:5. The soil and water solution was mixed for 5 minutes then left to sit for 1 hour before the pH was measured. The anion exchange capacity (AEC) was measured by Alfa Chemistry. The results of the soil analysis are shown below in **Table 1**. The soil samples are organized according to decreasing TOC, AEC and pH.

Table 1. IDW soil samples arranged according to descending value for the soil property: (a.) TOC, (b.) AEC, (c.) pH

<i>a. Decreasing TOC</i>				<i>b. Decreasing AEC</i>				<i>c. Decreasing pH</i>			
IDW Soil	pH	AEC ($\text{cmol}_c \text{ kg}^{-1}$)	TOC	IDW Soil	pH	AEC ($\text{cmol}_c \text{ kg}^{-1}$)	TOC	IDW Soil	pH	AEC ($\text{cmol}_c \text{ kg}^{-1}$)	TOC
Willow Grove	7.93	0.28	0.88%	Wurtsmith	9.1	0.94	0.08%	JBSA	11.07	0.63	0.004%
Jacksonville	6.22	0.9	0.54%	Jacksonville	6.22	0.9	0.54%	Wurtsmith	9.1	0.94	0.08%
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3.3 Soil Wash

Soil washing experimental procedures were based on previously published sorption/desorption procedures (Higgins & Luthy, 2006; Milinovic et al., 2015; OECD 106, 2000). The experiments used 50 mL polypropylene (PP) centrifuge tubes containing 2 g of soil and 40 mL of wash solution and tumbled for 1 week. All experiments were run in triplicate and accompanied by blanks and triplicate deionized water (DI) run as a control. Previous work with PFAS sorption experiments cite 48 hours as the time to equilibrium conditions (Shih & Wang, 2013; F. Wang et al., 2012; Wei et al., 2017). However preliminary desorption experimental times were increased given previous observations of: 1) sorption irreversibility increasing with increasing C-

F chain length, 2) PFSAAs displaying higher irreversibility than analog PFCAs, with PFOS displaying the highest irreversibility (Chen et al., 2016; Miao et al., 2017; Milinovic et al., 2015), and 3) some soil properties increasing irreversibility due to pore deformation (Zhao et al., 2014a), and soil organic matter being positively correlated with increase irreversibility (Miao et al., 2017). Miao et al., (2017) found that PFOA exhibited high sorption irreversibility in certain soils with high organic content, which contradicts other work that observed PFOA to exhibit low irreversibility (Chen et al., 2016).

The compositions of the soil wash solutions evaluated in this investigation are shown in **Table 2**. The wash type lists compositions as follows: [deionized water: methanol] by volume: volume (v/v), the subsequent columns detail the relative amount of each wash component: deionized water, methanol, and sodium chloride by weight percent (NaCl wt %) with a (-) indicating that particular component was not part of wash.

Table 2. Wash Type column list wash solutions in format of [DI: Methanol]: NaCl wt/%

Wash Type	Deionized Water (%)	Methanol (%)	NaCl (wt%)
DI	100	-	-
[75:25]	75	25	-
[50:50]	50	50	-
[25:75]	25	75	-
[75:25]:1%	75	25	1
[50:50]:1%	50	50	1
[25:75]:1%	25	75	1
[75:25]:3%	75	25	3
[50:50]:3%	50	50	3
[25:75]:3%	25	75	3
[75:25]:5%	75	25	5
[50:50]:5%	50	50	5
[25:75]:5%	25	75	5

3.4 Batch Equilibrium Experiments

Batch Equilibrium. The batch equilibrium soil washing experiments evaluated the washes in Table 2. The tubes were vortexed for 30 seconds, then tumbled end over end for a week before they were centrifuged at 9000g for 30 min to ensure all suspended sediment is removed from the supernatant without having to rely on using a filter to prevent the transfer of residual particulate matter to LCMS vials. The lack of a filter avoided potential PFAS losses due to sorption on filter media (Chandramouli et al., 2015; Lath et al., 2019).

Soil Extraction. The batch equilibrium experimental results were compared with a soil extraction procedure based on ASTM D7968-14, Standard Test Method for Determination of Perfluorinated Compounds in Soil. The soil extraction was a 3-phase exhaustive extraction that

involved the complete replacement of the wash solution at the start of each subsequent phase. The experiments were carried out in triplicate with blanks. The extraction experiments used 2 g soil with 10 mL of 99% methanol, 1% ammonium hydroxide in a 15 mL PP centrifuge tube which were vortexed for 30 seconds or until complete soil mobilization is achieved. The samples were sonicated at 30 ° C for 60 minutes, then tumbled end over end for 2 hours before they were centrifuged at 9000g for 30 minutes. The supernatant was decanted and stored in 15 mL PP centrifuge tube until LCMS vial preparation. Extractions 2 and 3 repeated the steps for phase 1, each time fully decanting and replacing the wash solution. The supernatants are stored separately for individual analysis.

3.5 Wash Solution Optimization

Kinetics. The kinetic experiments followed the batch equilibrium procedures although only select washes are used: [50:50]:1% and [25:75]:3%, and DI as a control. The samples are vortexed until complete soil mobilization and set on the tumbler for the desired sampling interval. At the sampling interval the samples were centrifuged for 5 minutes and then a 200 μ L sample was taken using a pipette and placed in a 1.5 mL PP vial with 800 μ L of methanol, each time interval sample was placed in a new 1.5 mL PP vial. The 50 mL PP centrifuge tube was then vortexed and put back on the tumbler, the whole sampling process and preparation took about 15 minutes. At the end of the experiment the vials were centrifuged again at 9000g for 20 minutes to remove residual suspended solids.

3.6 Plasma Treatment

Plasma reactor. Each wash solution was processed through two plasma reactors (acrylic rectangular tank, 34.5 cm $\times$ 7.6 cm $\times$ 7.6 cm; total liquid volume ($\sim$ 750 mL)), connected in series, each containing six high voltage (HV) tungsten saw tooth blade electrodes (each 6 cm in length), for the generation of plasma. These electrodes were arranged parallel to each other (3 cm apart) and perpendicular to the long side of reactor (Figure 1). The HV electrodes were suspended 1.2 cm above the surface of the water (the thickness of the treated water layer was 2.9 cm). A coarse iron mesh screen, submerged 3 cm into the liquid, served as the ground electrode. A single gas diffuser (61.0 cm $\times$ 6.35 cm $\times$ 2.00 cm, 0.4 μ m pore size and 50 psi maximum pressure; Pentair, USA) was placed on the bottom of the reactor immediately below the ground electrode. Due to the excessive foaming observed in each SB solution which interfered with plasma formation, the flowrate of argon was gradually increased from 1 L/min to 4 L/min over the course of the experiment. Argon gas was recirculated immediately upon leaving the reactor.¹³ To generate plasma, -30 kV was applied using a custom-built HV electrical circuit to charge three dedicated capacitor banks (4 nF each) each connected to a pair of HV electrodes (Figure 1). Charged capacitors were simultaneously discharged via three dedicating rotating spark gaps at the discharge frequency of 60 Hz. The treated liquid was continuously recirculated through a heat exchanger set at 10°C. Power drawn by the high voltage supply, peristaltic pump, chiller and spark gap was measured by a digital power meter (Kill A, P3 P4400).

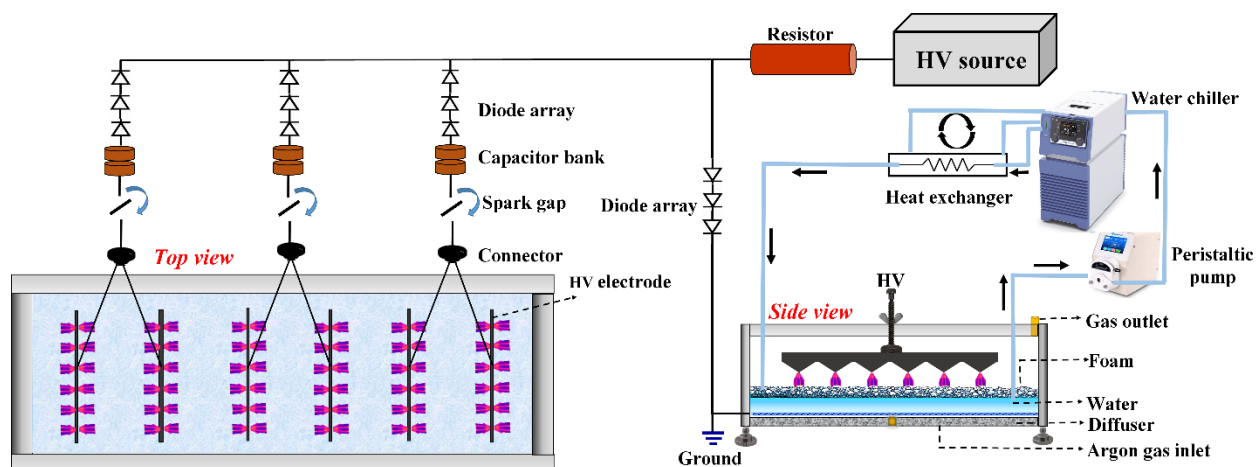


Figure 1. Schematic of the experimental setup.

Plasma Treatment Experimental Procedure. Solutions were treated in two identical plasma reactors, connected in series (Figure 1): (a) a “high concentration” reactor intended for the treatment of high initial PFAA concentrations ($C_0 > 100$ mg/L), and (b) a “low concentration” reactor for the treatment of the “high concentration” reactor’s effluent (PFAA $C_0 < 1$ $\mu\text{g/L}$). Previous work by this group¹³, found that PFAAs readily adsorb onto reactor components which desorb during the treatment as their bulk liquid concentration decreases. This desorption process makes treatment in a single reactor impractical as it would require long treatment times to decrease the initial PFAS concentration by several orders of magnitude. Sorption to reactor components proceeds until the components and solution are in equilibrium. Once equilibrium is reached, there is no further removal from solution unless the solution concentrations change. In the batch experiments used in this project PFAS concentrations were initially extremely high and continually decreased during treatment. As concentrations decreased, any initially sorbed PFAS molecules desorbed back into solution. This desorption continuously fortifies solution concentrations necessitating the need for high and low concentration reactors. In previous PFAS plasma experiments in which we performed mass balances on fluorine we found minimal irreversible sorption to reactor components indicating this sorption–desorption process did not influence the removal results seen.

Initial tests of undiluted solutions exhibited excessive foaming for extended periods (> 3 hr), at all argon flow rates tested. Since excessive foaming is detrimental to the plasma process, a 10-fold dilution, of as received still bottoms (SB) solutions, was performed. Thus, the high concentration reactor was used as the first treatment unit, where 10-fold diluted SBs were treated to lower the concentration of long-chain PFAAs to < 1 $\mu\text{g/L}$. Treated SBs were then introduced and treated in the second low concentration reactor to further decrease PFAA concentrations. To enhance the removal of short-chain PFAS (primarily PFBA and PFBS), in the low concentration reactor, a cationic surfactant, cetrimonium bromide (CTAB) was added at 30-minute intervals to achieve initial concentrations of 0.2 mM in the reactor. CTAB was added to assist in the short-chain foam production. Frequent dosing of CTAB was required due to its rapid degradation by plasma.

3.7 PFAS Analytical Methods

Linear perfluoroalkyl carboxylic acids, sulfonates and labeled internal standards consisting of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA) and perfluorododecanoic acid (PFDoA) were purchased from Wellington Laboratories (Guelph, ON). Individual calibration and labeled internal standards for precursor fluorotelomer sulfonates (10:2 FTS, 8:2 FTS, 6:2 FTS and 4:2 FTS), perfluorooctane sulfonamide (FOSA-1), perfluorooctane sulfonamide acetate (FOSAA), N-ethylperfluorooctane sulfonamide (EtFOSA), N-ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA), N-methylperfluorooctane sulfonamide (MeFOSA) and N-methyl perfluorooctane sulfonamido acetic acid (MeFOSAA) were also purchased from Wellington Laboratories (Guelph, ON). Analytical grade PFOA (purity >95%) and sodium chloride salt (purity >99%) used for preparing synthetic water samples were procured from Sigma-Aldrich (St. Louis, MO). Methanol and acetonitrile (LC-MS grade) were purchased from Thermo Fisher Scientific (Waltham, MA).

Quantification of PFAS and their precursors. Seventeen PFAAs and their 10 precursor concentrations were measured in negative ionization mode using a UPLC-MS-MS (Thermo Scientific, Vanquish-TSQ ALTIS) equipped with Phenomenex Luna Omega PS C18 column (2.1 mm x 100 mm, 1.6 μ m). A detailed description of the analytical methods, QA procedures and individual detection limits is provided in Tables 3 to 5.

Instrumental Method. A UPLC-MS-MS (Thermo Scientific, Vanquish-TSQ ALTIS) was used for the analysis of PFAS and their precursors. Separation was performed with a Phenomenex Luna Omega PS C18 column (2.1 mm x 100 mm, 1.6 μ m) and samples were analyzed by electrospray in negative ion mode. Samples were diluted with methanol (1:3 ratio), sonicated and centrifuged prior to injection (10 μ L). A gradient solvent program was operated with 5mM ammonium acetate in LCMS grade water (solution A) and a LCMS grade acetonitrile (solution B). The details of the gradient method are provided in Table S1. Mass range was set at 50 to 950 Da with a scan rate of 0.055/sec.

Quality Assurance. For quality assurance and control, all samples were spiked with 2 ng of ^{13}C or ^2D labeled internal standards. Based on the analysis of method blanks, the nominal limit of detection (LOD) was determined to be 3 ng/L. Six-point calibration in the range of 9 and 2000 ng/L was used for the quantification of samples using internal standard methods. Quantification was carried out using TraceFinder software from Thermo Scientific using regression fit of $r^2 > 0.99$ and deviation $< 30\%$. Calibration verifications standards were included in each sample batch (1 per every 20 samples) to validate the time-dependent response from the instruments. Resultant raw data were quantified if surrogate recovery was between 70 and 120 %.

Table 3. Gradient solvent program for the UPLC

Time (min)	Flowrate (mL/min)	%A	%B
0.00	0.5	70	30
0.50	0.5	70	30
3.00	0.5	10	90
3.10	0.5	0	100
4.50	0.5	0	100
4.60	0.5	70	30
6.50	0.5	70	30

Table 4. List of calibration standards, surrogate standards and minimum detection limit (MDL) used for perfluorinated alkyl acids (PFAAs)

Analyte abbreviation	Analyte name	Surrogate standard	Surrogate name	MDL (ng/L)
PFBA	Perfluorobutanoic acid	[¹³ C ₄]PFBA	perfluoro-n-[¹³ C ₄] butanoic acid	25
PFPeA	Perfluoropentanoic acid	[¹³ C ₂]PFHxA	perfluoro-n-[1,2- ¹³ C ₂] hexanoic acid	10
PFBS	Perfluorobutane sulfonate	[¹⁸ O ₂]PFHxS	perfluoro-n-hexane[¹⁸ O ₂] sulfonate	15
PFHxA	Perfluorohexanoic acid	[¹³ C ₂]PFHxA	perfluoro-n-[1,2- ¹³ C ₂] hexanoic acid	20
PFPeS	Perfluoropentane sulfonate	[¹⁸ O ₂]PFHxS	perfluoro-n-hexane[¹⁸ O ₂] sulfonate	15
PFHpA	Perfluoroheptanoic acid	[¹³ C ₄]PFOA	perfluoro-n-[1,2,3,4- ¹³ C ₄] octanoic acid	20
PFHxS	Perfluorohexane sulfonate	[¹⁸ O ₂]PFHxS	perfluoro-n-hexane[¹⁸ O ₂] sulfonate	20
PFOA	Perfluorooctanoic acid	[¹³ C ₄]PFOA	perfluoro-n-[1,2,3,4- ¹³ C ₄] octanoic acid	15
PFHpS	Perfluoroheptane sulfonate	[¹³ C ₄]PFOS	perfluoro-n-[1,2,3,4- ¹³ C ₄] octane sulfonates	35
PFNA	Perfluoronanoic acid	[¹³ C ₅]PFNA	perfluoro-n-[1,2,3,4,5- ¹³ C ₅] nonanoic acid	15
PFOS	Perfluorooctane sulfonate	[¹³ C ₄]PFOS	perfluoro-n-[1,2,3,4- ¹³ C ₄] octane sulfonates	35
PFDA	Perfluorodecanoic acid	[¹³ C ₂]PFDA	perfluoro-n-[1,2- ¹³ C ₂] decanoic acid	15
PFNS	Perfluoronanone sulfonate	[¹³ C ₄]PFOS	perfluoro-n-[1,2,3,4- ¹³ C ₄] octane sulfonates	40
PFDS	Perfluorodecane sulfonate	[¹³ C ₂]PFOS	perfluoro-n-[1,2,3,4- ¹³ C ₄] octane sulfonates	45
PFUnA	Perfluoroundecanoic acid	[¹³ C ₂]PFUnA	perfluoro-n-[1,2- ¹³ C ₂] undecanoic acids	80
PFDoA	Perfluorododecanoic acid	[¹³ C ₂]PFDoA	perfluoro-n-[1,2- ¹³ C ₂] dodecanoic acid	25
PFTrA	Perfluorotridecanoic acid	[¹³ C ₂]PFDoA	perfluoro-n-[1,2- ¹³ C ₂] dodecanoic acid	20
PFTeA	Perfluorotetradecanoic acid	[¹³ C ₂]PFTeA	perfluoro-n-[1,2- ¹³ C ₂] tetradecanoic acid	35

Note: MDL are reported in 4 times diluted samples

Table 5. List of calibration standards used for PFAAs precursors, surrogate standards and MDL

Analyte abbreviation	Analyte name	Surrogate standard	Surrogate name	MDL (ng/L)
10:2 FTS	10:2 Fluorotelomere sulfonate	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	25
4:2 FTS	4:2 Fluorotelomere sulfonate	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	15
6:2 FTS	6:2 Fluorotelomere sulfonate	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	35
8:2 FTS	8:2 Fluorotelomere sulfonate	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	30
EtFOSA	N-Ethyl perfluorooctane sulfonamide	d-N-EtFOSA-M	N-ethyl-d3-perfluoro-1-octanesulfonamide	25
EtFOSAA	N-Ethyl perfluorooctane sulfonamide acetic acid	d3-N-EtFOSAA	N-ethyl-d3-perfluoro-1-octanesulfonamidoacetic acid	65
FOSA-1	Perfluoro-1-octane sulfonamide	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	20
FOSAA	Perfluorooctane sulfonamide acetic acid	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	30
MeFOSA	N-Methyl perfluorooctane sulfonamide	d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	35
MeFOSAA	N-Methyl perfluorooctane sulfonamide acetic acid	d3-N-MeFOSAA	N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid	55

Note: MDL are reported in 4 times diluted samples

4.0 Results and Discussions

4.1 Soil Washing Results

4.1.1 PFAS Compounds Observed in IDW Soils

In order to observe trends in PFAS desorption across the different soil types compounds that were found across all IDW soils were chosen for reporting and analysis. The chosen compounds have varying carbon-fluorine (C-F) chain lengths from the two major classes of PFAS; perfluorinated carboxylate acids (PFCAs) and perfluorinated sulfonic acids (PFSAs). A precursor compound, perfluorooctane sulfonamide (FOSA_1) was also included (**Table 6**). The compounds are organized by each major classification and are listed in decreasing (C-F) chain lengths. Higgins and Luthy found that chain length was the dominant compound structure contributing to sorption. They determined that each additional C-F₂ added 0.5-0.6 log units to measured partition coefficients (k_d). The organic carbon/water partition coefficient was calculated using the sediment/ water distribution coefficient(k_d) and fraction of organic carbon in the soil (f_{oc}) in the formula: $k_{oc} = k_d / f_{oc}$ (Higgins & Luthy, 2006).

Table 6. List of compounds used to assess soil washing effectiveness

Compound	Acronym	Chemical Formul (dissociated)	MW [g mol ⁻¹]	log S_w [mol L ⁻¹]	log K_{ow}	log K_{oc} [mL g ⁻¹]	log pK_a^i [25°]
<i>Perfluoroalkyl Sulfonamides (FASAs)</i>							
Perfluorooctane sulfonamide	FOSA-1	C ₈ F ₁₇ SO ₂ NH ₂	499.18	-5.05 ^a , -4.65 ^b	4.33 ^b	4.2 - 4.5 ^{e,f}	-
<i>Perfluorinated Carboxylate acids (PFCAs)</i>							
Perfluorooctanoic acid	PFOA	C ₈ F ₁₅ COO ⁻	413.09	-2.73 ^a , -3.38 ^b	3.55 ^b	1.89 - 3.5 ^{d,e,f,g,h}	-0.2
Perfluorohexanoic acid	PFHxA	C ₆ F ₁₁ COO ⁻	313.06	-1.16 ^a , -1.76 ^b	2.15 ^b	1.31 ^h , 2.1 ^c	-0.16
Perfluoropentanoic acid	PFPeA	C ₄ F ₉ COO ⁻	263.05	-0.37 ^a , -0.95 ^b	1.45 ^b	1.37 ^h	-
<i>Perfluorinated Sulfonic acids (PFSAs)</i>							
Perfluorooctane sulfonic acid	PFOS	C ₈ F ₁₇ SO ₃ ⁻	500.16	-3.92 ^a , -4.56 ^b	4.30 ^b	2.6 - 3.8 ^{c,d,e,f,g,h}	-3.27
Perfluorohexane sulfonic acid	PFHxS	C ₆ F ₁₃ SO ₃ ⁻	400.14	-2.24 ^a , -0.84 ^b	2.91 ^b	2.05 - 3.7 ^{c,f,h}	0.14
Perfluorobutane sulfonic acid	PFBS	C ₄ F ₉ SO ₃ ⁻	300.12	-1.00 ^a , -1.32 ^b	1.15 ^b	1.22 ^g , 1.79 ^h	0.14

^aWang et al., 2011

^bKim et al., 2014

^cLabadie and Chevreuil, 2011

^dHiggins and Luthy, 2006

^eAhrens et al., 2011

^fAhrens et al., 2010

^gMilunovic et al., 2015

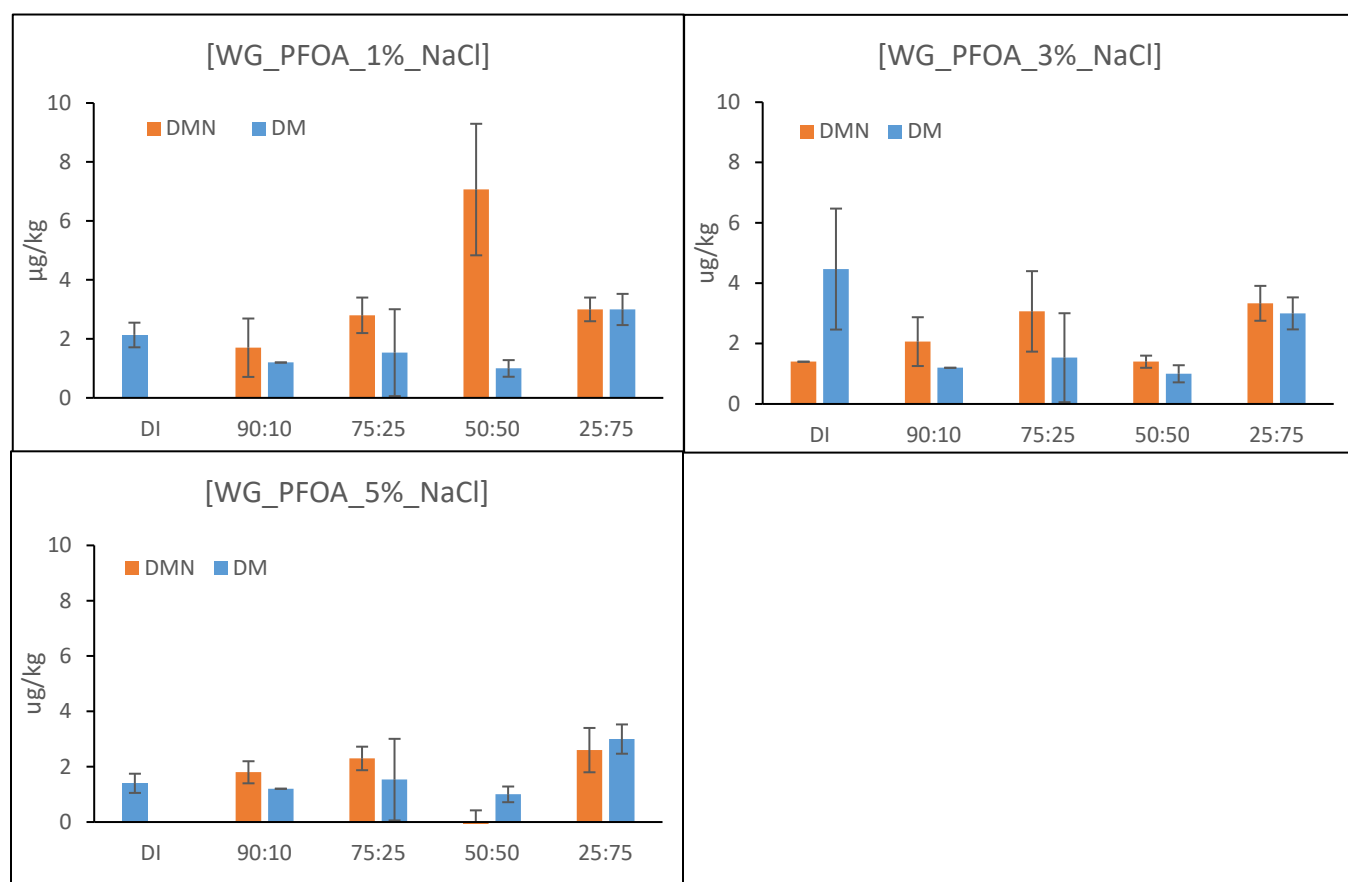
^hGuelfo and Higgins, 2013

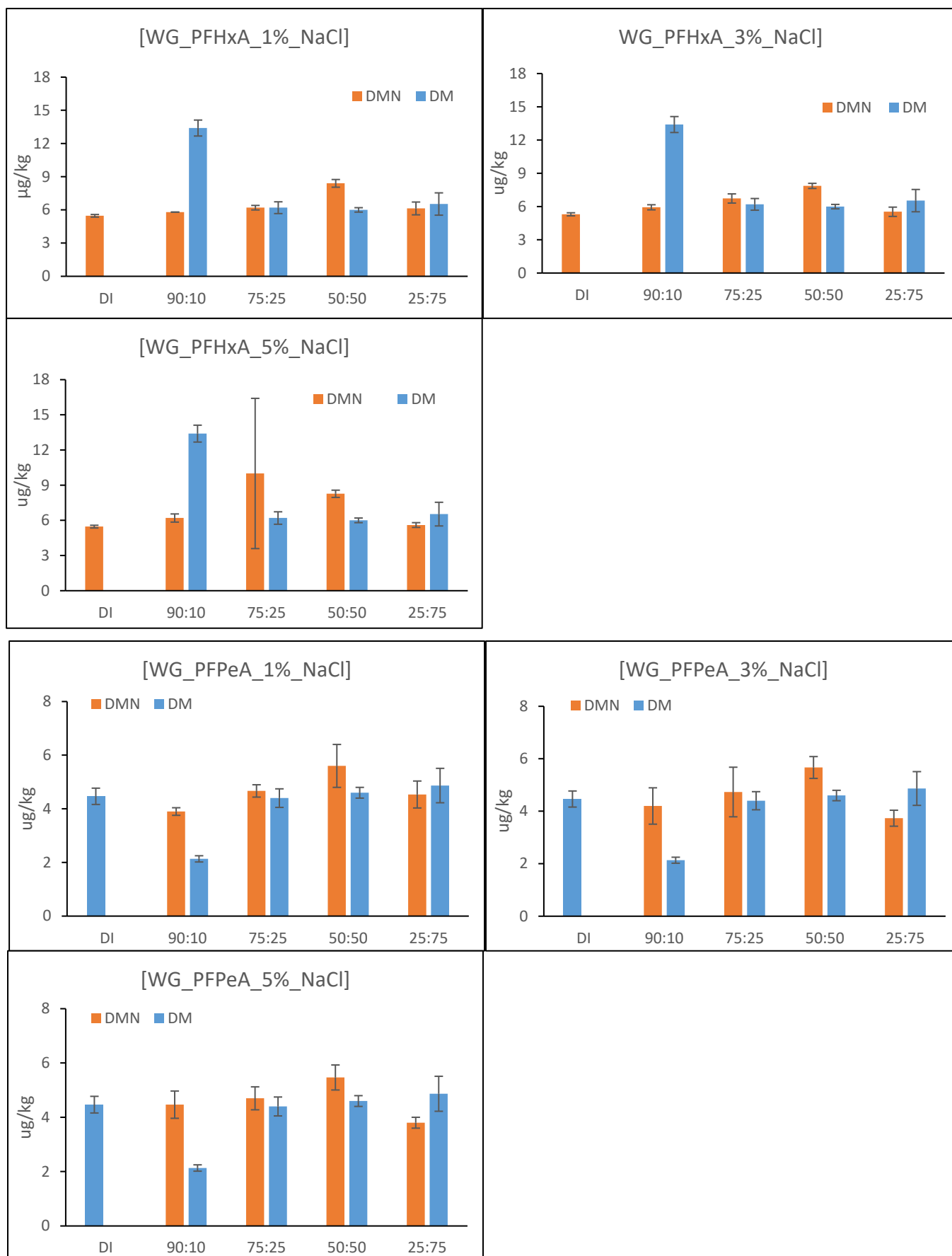
ⁱDu et al., 2004

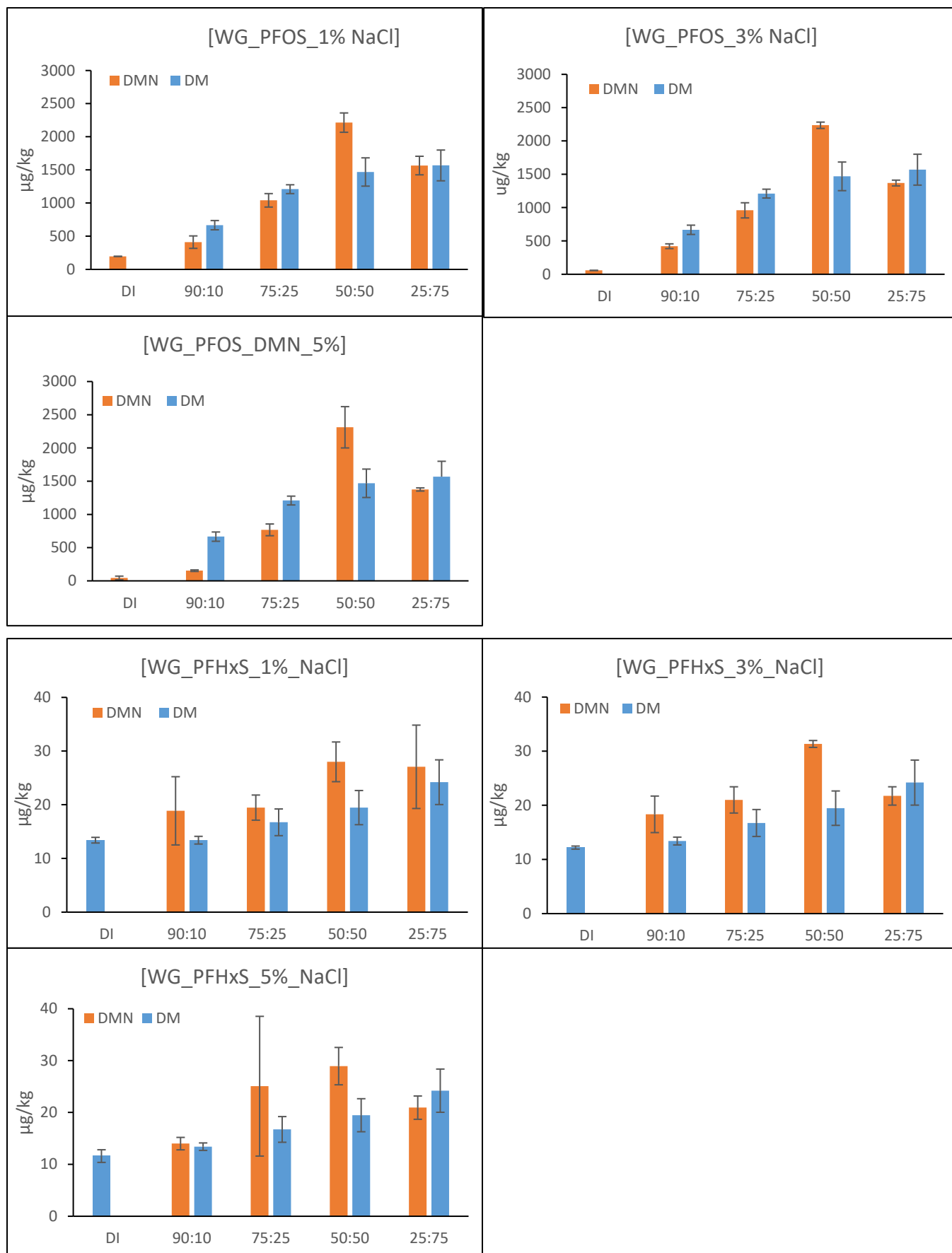
The initial PFAS concentrations and composition are unknown for the IDW samples. To assess the efficacy of the various soil washes the PFAS concentrations in the washes after experiment completion were compared against each other and against deionized water, which was used as a control for the experiments. Each soil wash composition evaluated was run in triplicate. Wash results from WG are shown throughout the report to provide a visual overview of the type of removals measured. All of the results are then analyzed with a Two Factor ANOVA Test, followed up by a Tukey Honest Significant Difference (TukeyHSD) Test to determine which soil wash solutions were the most effective.

4.1.2 Willow Grove Wash Results

The WG results wash results are shown below (**Figure 2**). The graphs display the average of the triplicate run soil washes, reported in ($\mu\text{g}/\text{kg}$). The DI: MeOH ratio is displayed on the x-axis. The blue bars represent DI: MeOH (DM) wash compositions and the orange bars represent DI: MeOH and NaCl wt. % (DMN) wash compositions. The three graphs represent three different NaCl weight percentages evaluated; 1%, 3%, 5%. The title of the graphs lists the NaCl wt. % the data represent.







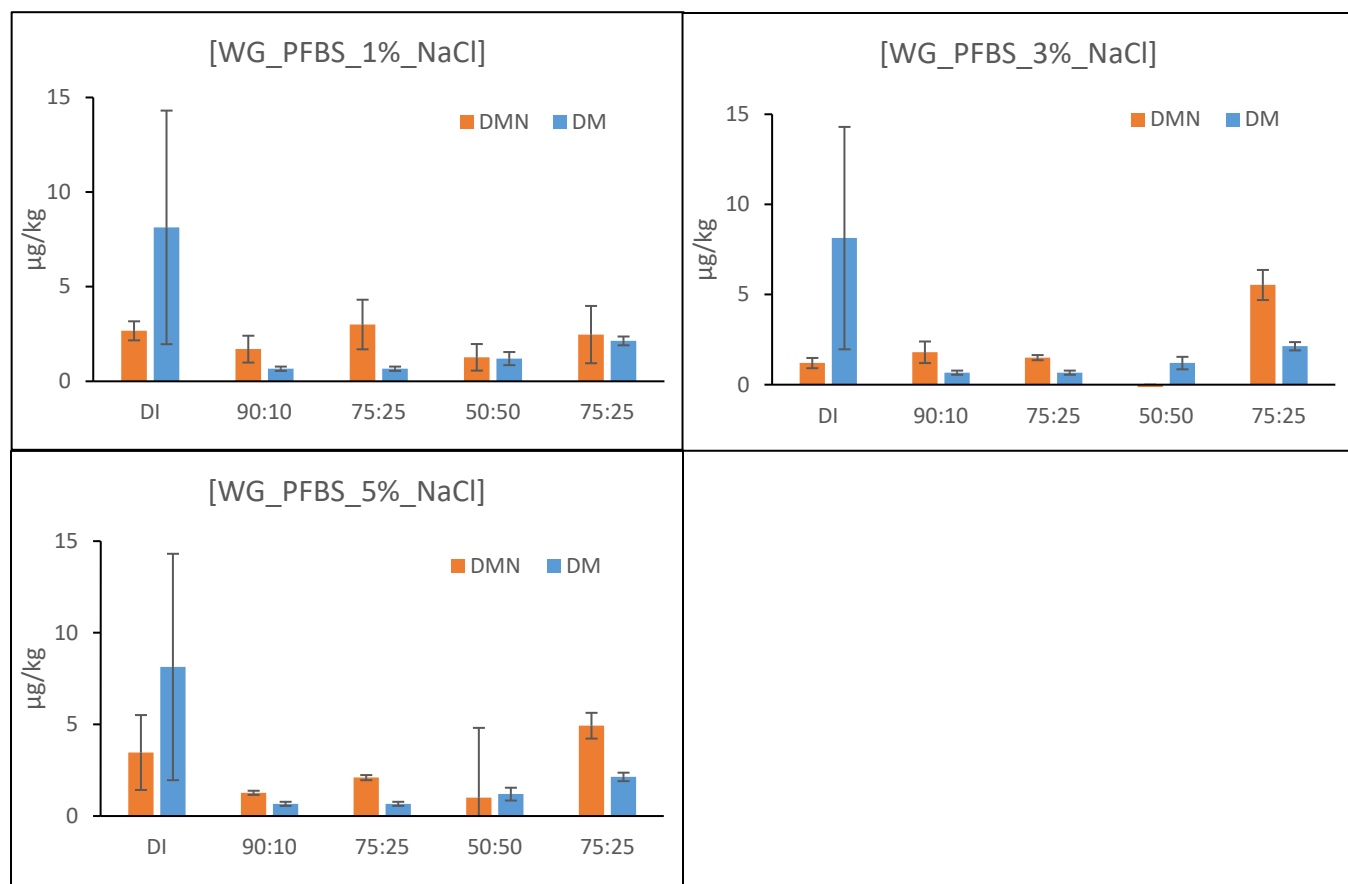


Figure 2. Wash results for Willow Grove. The DI: MeOH ratio is displayed on the x-axis. The blue bars represent DI: MeOH (DM) wash compositions and the orange bars represent DI: MeOH and NaCl wt. % (DMN) wash compositions. The three graphs represent three different NaCl weight percentages evaluated; 1%, 3%, 5%. The title of the graphs lists the NaCl wt. % the data represent.

The most effective washes with and without salt are at DI: MeOH ratios of 25:75, 50:50, and 25:75. The wash composition of 90:10 with or without NaCl was less effective than the other DI: MeOH washes with or without NaCl, except for 90:10 DI: MeOH for PFHxA. Overall it appears that the wash composition of 25:75 with 1, 3, or 5% NaCl were only marginally different in effectiveness. For the carboxylic acid group most of the washes are comparable to DI and there is no apparent trend as methanol and/or NaCl composition increase. For the sulfonic acid group, the higher methanol composition washes with and without NaCl were more effective than the lower methanol composition washes. The wash composition of 50:50 with 1, 3, or 5% NaCl had the highest instance of being the most effective. PFBS, the shortest C-F chain sulfonic acid is the exception to this trend, with DI displaying the highest removal.

Results for the other three sites, Jacksonville (JV), Joint Base San Antonio (JBSA), and Wurtsmith (WS) are presented in Appendix A for reference.

4.1.3 Two Factor ANOVA Results

To assess the efficacy of the various soil washes the PFAS concentrations in the washes were compared against each other and against the deionized water control. The results were analyzed with a Two Factor ANOVA Test, followed up by a Tukey Honest Significant Difference (TukeyHSD) Test. The results of the Two Factor ANOVA Test were tabulated in the heat map shown in **Figure 3**. The composition of the wash solution and amount of NaCl added are shown in the left most column of the map. A 0.05 (95% confidence interval) was the cutoff to determine statistical significance. The degree of significance for each compound is indicated by the darkening shades of red and is detailed in the legend at the bottom of the table. Dark red indicates the strongest statistical significance above the 0.05 threshold is $Pr < E^{-10}$.

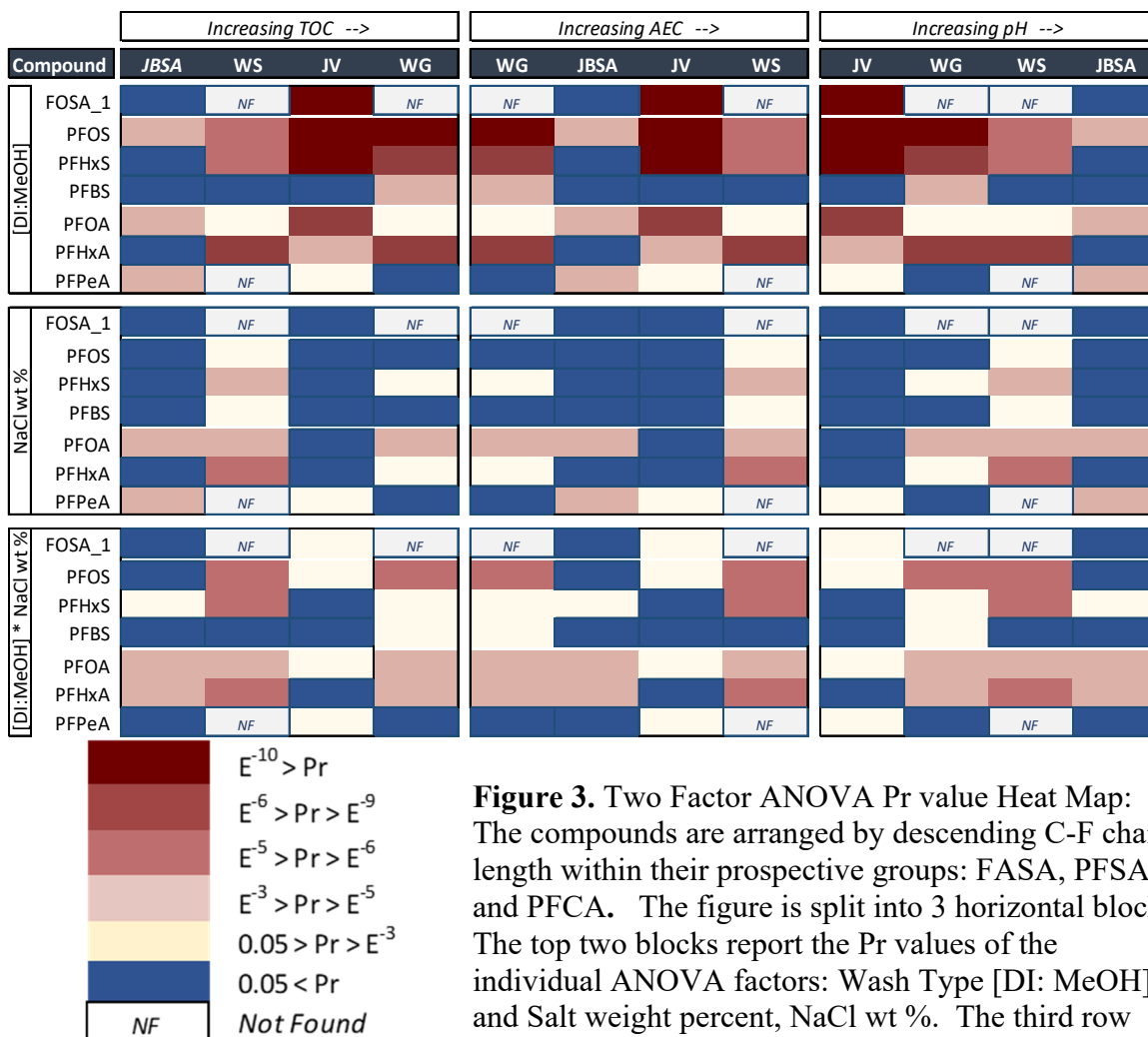


Figure 3. Two Factor ANOVA Pr value Heat Map: The compounds are arranged by descending C-F chain length within their prospective groups: FASA, PFSA and PFCA. The figure is split into 3 horizontal blocks. The top two blocks report the Pr values of the individual ANOVA factors: Wash Type [DI: MeOH], and Salt weight percent, NaCl wt %. The third row reports the Pr values from the combinational analysis of the factors, [DI: MeOH] * NaCl wt %. The same data of Pr values is displayed in each, column block, with the IDW Soil columns arranged to increasing value of TOC, AEC, pH.

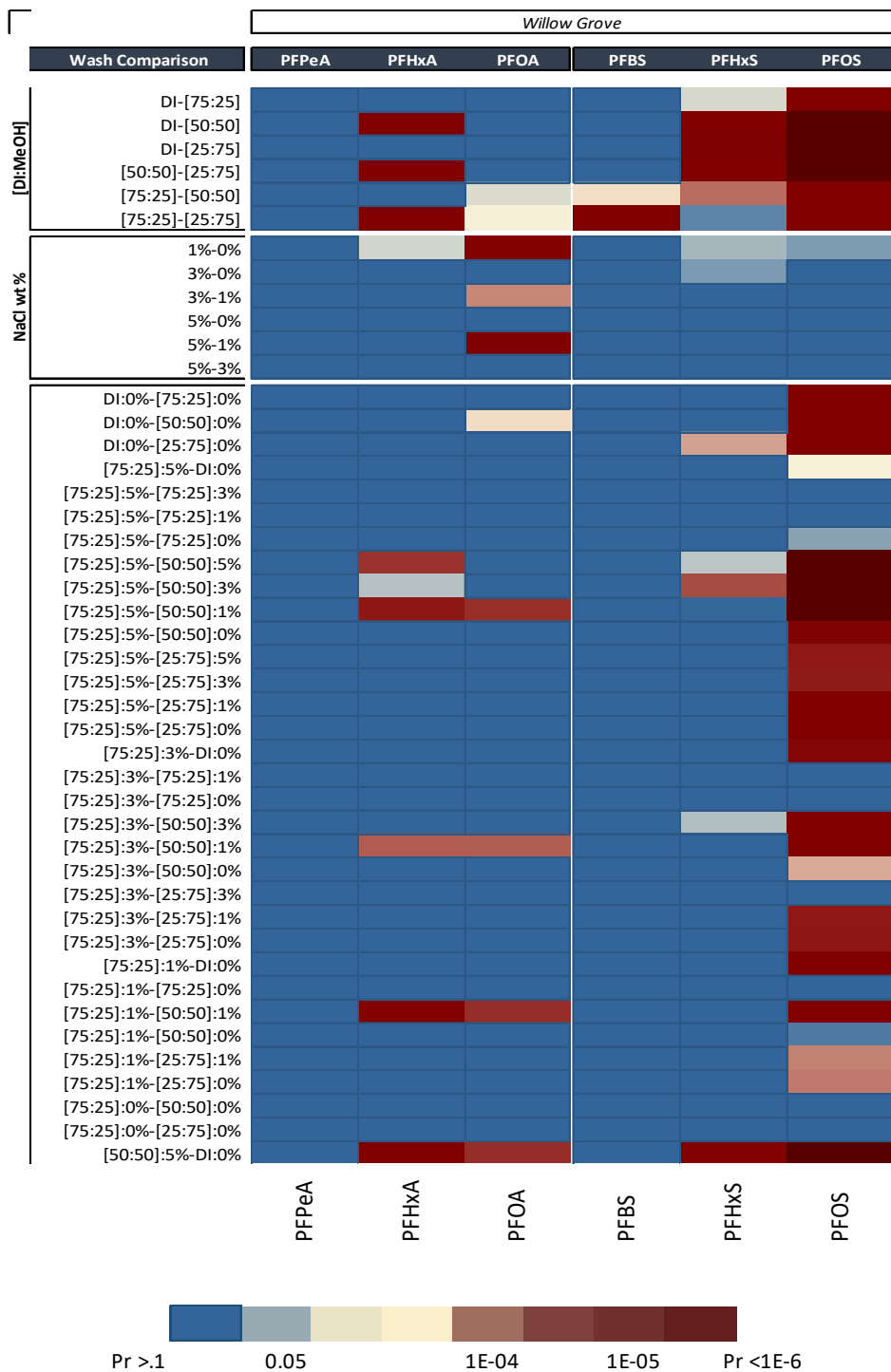
The wash type row had the highest number of statistically significant occurrences. The combination column, had the second highest number of occurrences. The salt row had the lowest number of statistically significant occurrences. These trends indicate that varying the wash type (deionized water: methanol composition) had the greatest impact in PFAS desorption while varying the salt (NaCl) concentration had the smallest effect. The combination of wash type and salt fell somewhere between the two in terms of effectiveness. However, the large number of statistically significant occurrences across the compounds for each soil type indicated that the combination of MeOH solution with NaCl exhibit a synergistic effect (Woodard et al., 2017), making them effective across a range of different soil physiochemical properties.

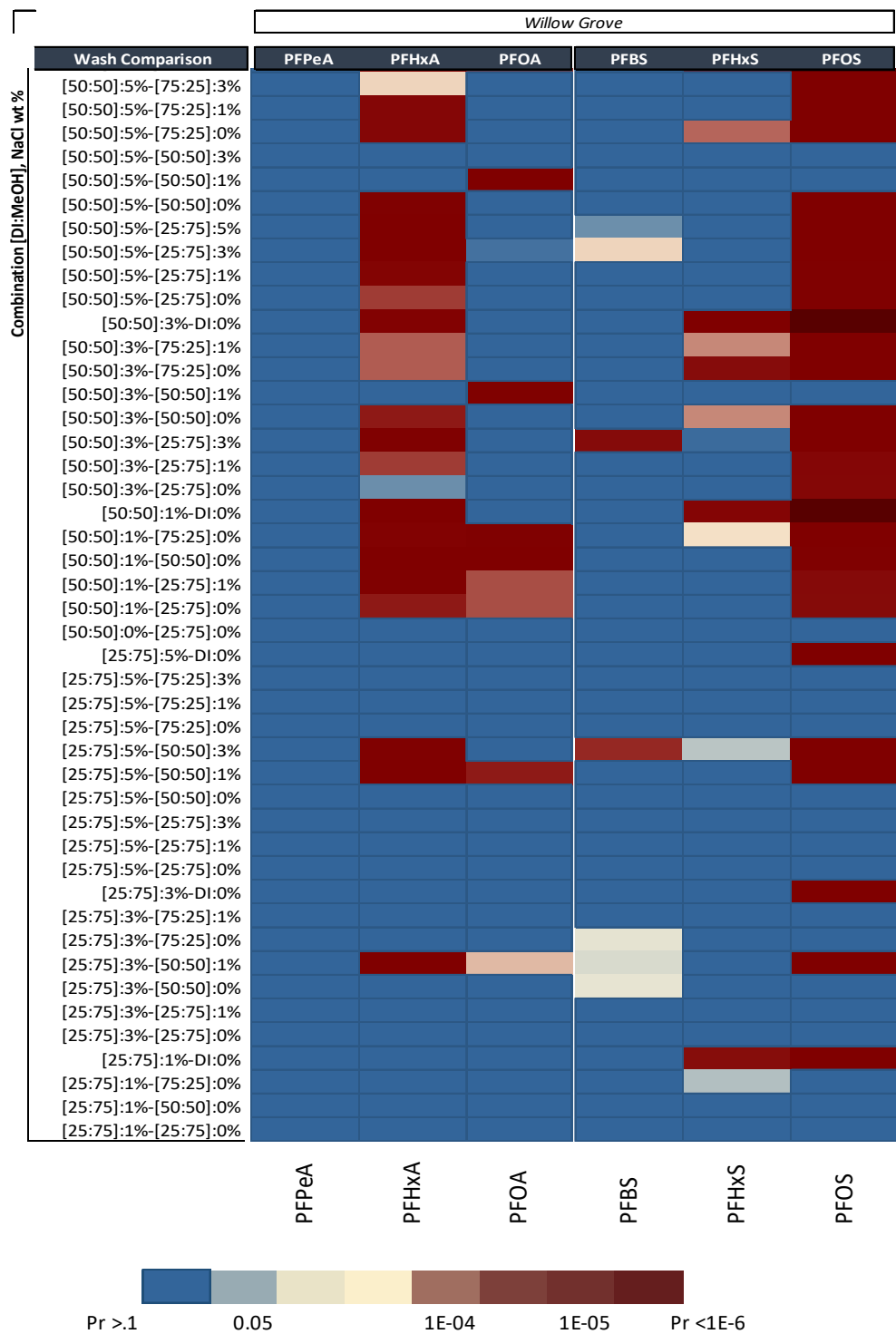
The strongest statistical significance for each IDW soil correlated with longer C-F chain PFAS, although PFSA_s (sulfonic acid) and FOSA_1 exhibit slightly stronger statistical significance than PFCA_s (carboxylate acid). In the wash type column JV, which had the second highest AEC and TOC and lowest pH, had the strongest instance of statistical significance across all the compounds followed by WG, which had the highest TOC and second lowest pH. PFOS, PFOA, and FOSA had the strongest occurrence of statistical significance in JV followed by WG, with the occurrences concentrating in the wash type block, [DI:MeOH]. The IDW soil, JBSA, with the highest pH with the lowest AEC and TOC, had the lowest number of statistically significant occurrences for all compounds in both wash type and the combination column ([DI: MeOH] * NaCl wt %) and the second lowest number of occurrences in salt column. WS which had the second lowest TOC but had the highest AEC exhibited more occurrences of statistical significance than JBSA.

4.1.4 TukeyHSD Results

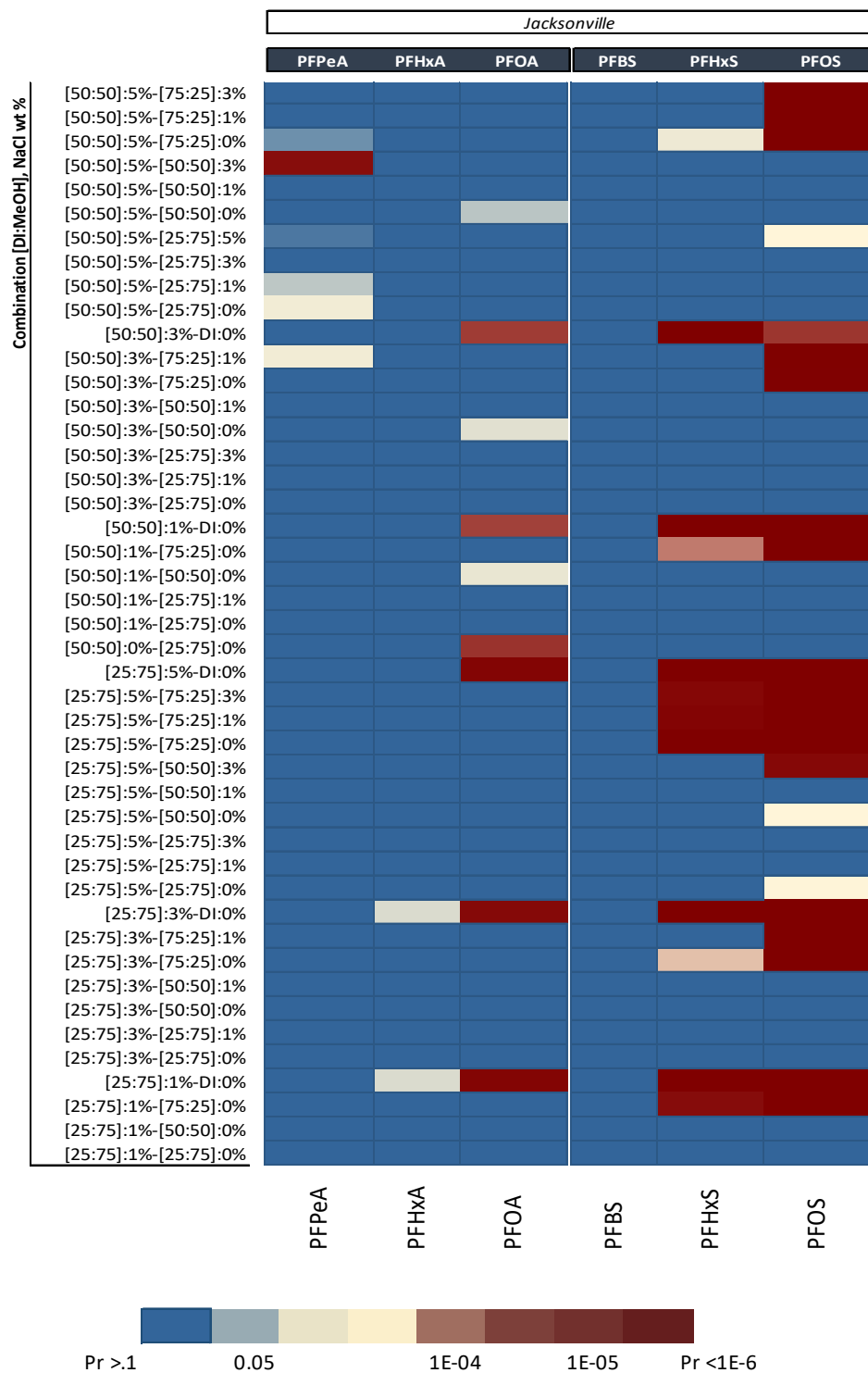
The Tukey Honest Significant Difference Test (TukeyHSD), a post hoc test, was performed on the ANOVA results to identify specific comparisons that contributed to the statistical significances the ANOVA observed. The difference in average PFAS wash concentration (µg/kg), was calculated between all possible factor combinations used in the Two Factor ANOVA. There are three TukeyHSD Test comparison sets; one for each of the ANOVA considerations: wash type [DI: MeOH], salt weight percent, NaCl wt %, and the combinational analysis of the factors, [DI: MeOH] * NaCl wt %. The 95th percentile confidence interval, $Pr < 0.05$, was used to determine statistical significances.

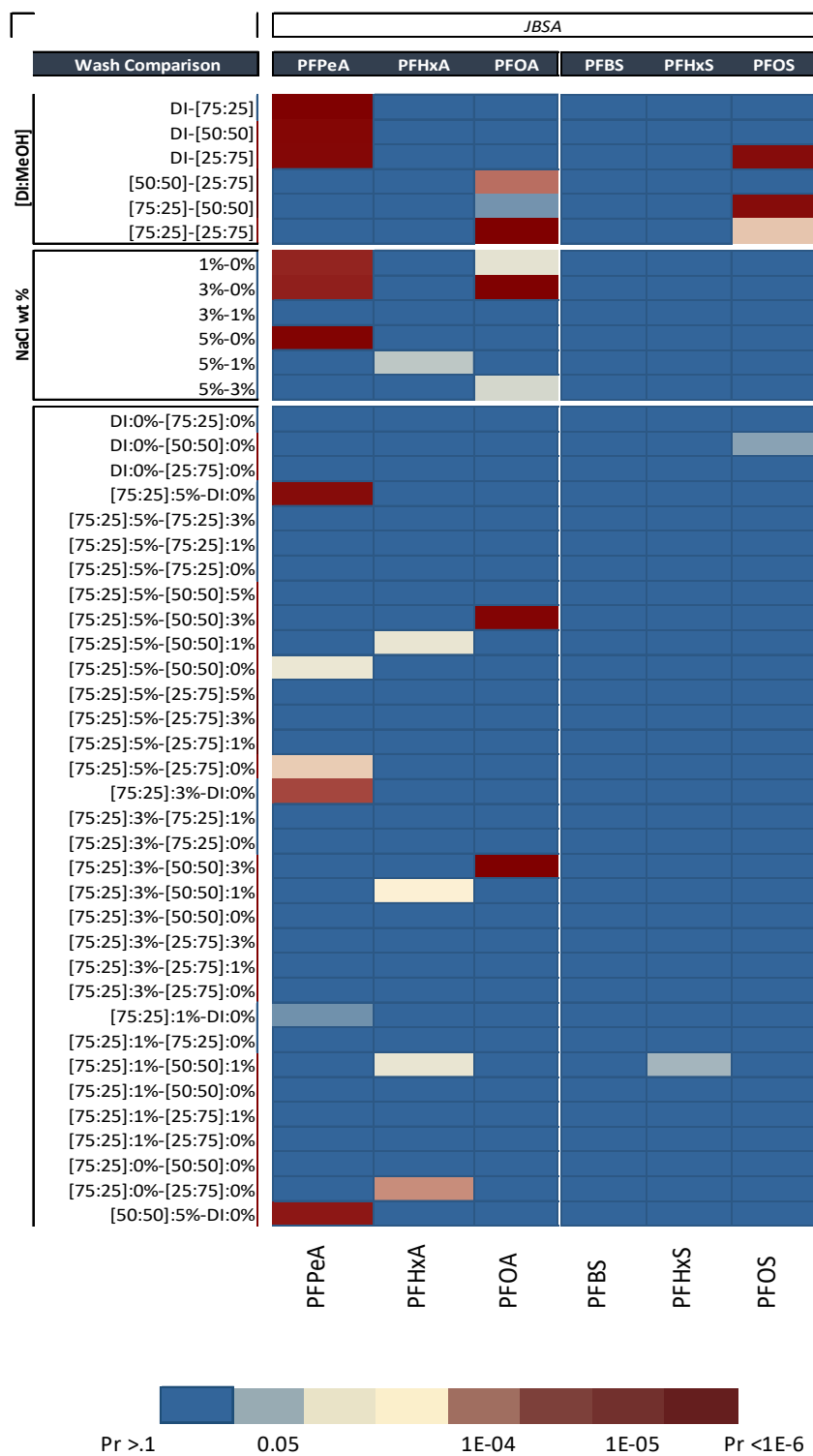
A qualitative comparison of Pr values from the TukeyHSD results was conducted using heat maps to visualize trends of statistically significant occurrences. The figures were divided into column blocks, by soil type with PFCA, and PFSA further split into two sub columns. The comparisons analyzed for honest significant difference are listed along the left side of the map and are split into three horizontal sections by the ANOVA factor type: wash type [DI: MeOH], salt (NaCl wt. %), and combination: [DI: MeOH] * NaCl wt. %. The scale below the figure denotes the color gradient between Pr values in the range of 1 (blue, not significant) and 0 (red, statically significant), where dark red is the highest statistical significance. The Pr values for IDW soils WG, JV and JBSA are shown in **Figure 4**.





		Jacksonville					
Wash Comparison		PFPeA	PFHxA	PFOA	PFBS	PFHxS	PFOS
[DI:MeOH]	DI-[75:25]						
	DI-[50:50]						
	DI-[25:75]						
	[50:50]-[25:75]						
	[75:25]-[50:50]						
	[75:25]-[25:75]						
NaCl wt %	1%-0%						
	3%-0%						
	3%-1%						
	5%-0%						
	5%-1%						
	5%-3%						
	DI:0%-[75:25]:0%						
	DI:0%-[50:50]:0%						
	DI:0%-[25:75]:0%						
	[75:25]:5%-DI:0%						
	[75:25]:5%-[75:25]:3%						
	[75:25]:5%-[75:25]:1%						
	[75:25]:5%-[75:25]:0%						
	[75:25]:5%-[50:50]:5%						
	[75:25]:5%-[50:50]:3%						
	[75:25]:5%-[50:50]:1%						
	[75:25]:5%-[50:50]:0%						
	[75:25]:5%-[25:75]:5%						
	[75:25]:5%-[25:75]:3%						
	[75:25]:5%-[25:75]:1%						
	[75:25]:5%-[25:75]:0%						
	[75:25]:3%-DI:0%						
	[75:25]:3%-[75:25]:1%						
	[75:25]:3%-[75:25]:0%						
	[75:25]:3%-[50:50]:3%						
	[75:25]:3%-[50:50]:1%						
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	[75:25]:3%-[25:75]:0%						
	[75:25]:1%-DI:0%						
	[75:25]:1%-[75:25]:0%						
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	[75:25]:1%-[25:75]:1%						
	[75:25]:1%-[25:75]:0%						
	[75:25]:0%-[50:50]:0%						
	[75:25]:0%-[25:75]:0%						
	[50:50]:5%-DI:0%						
		PFPeA	PFHxA	PFOA	PFBS	PFHxS	PFOS





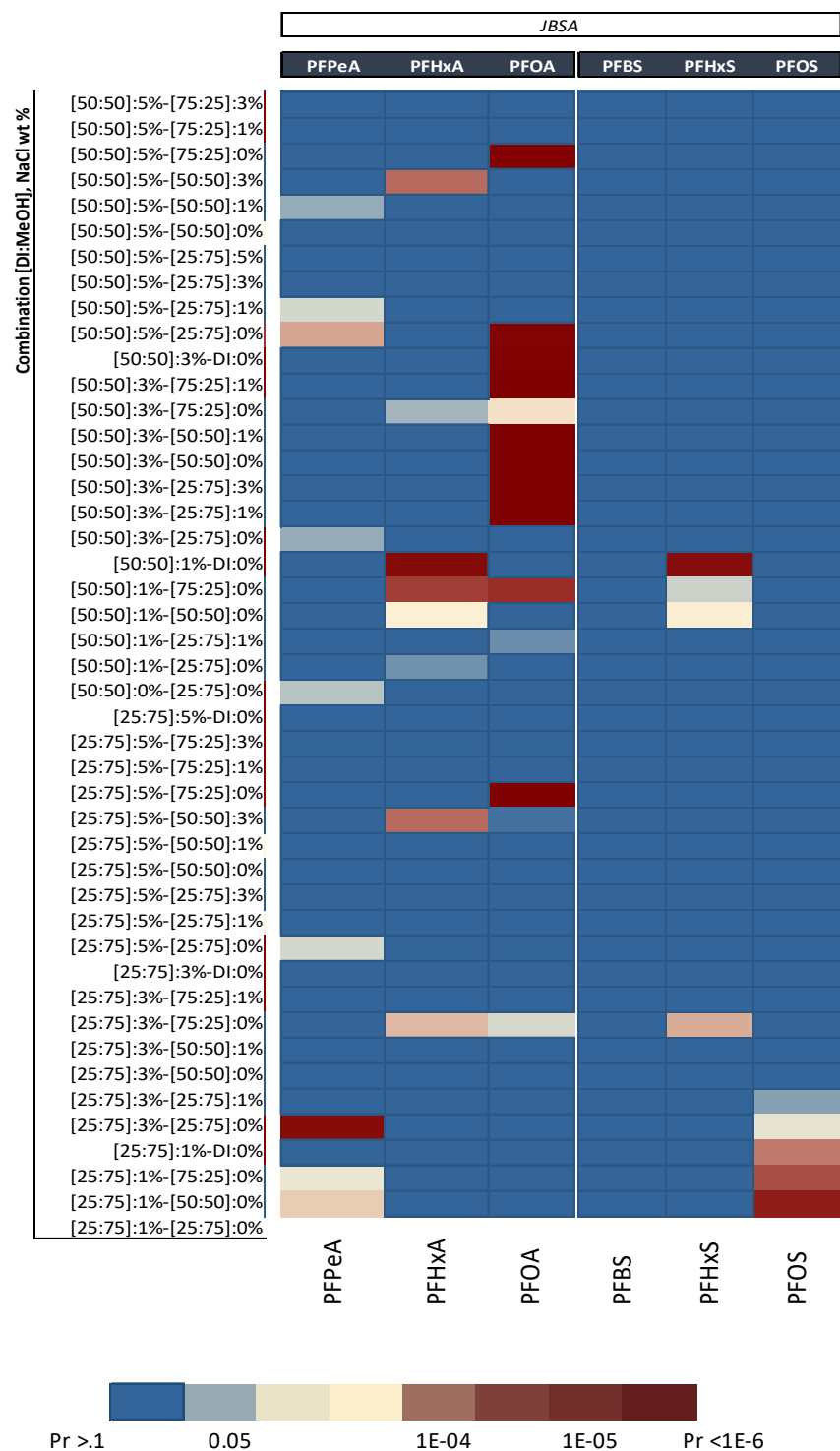


Figure 4. The Tukey Honest Significant Difference Test results. Red shaded cells indicated that the factors or soil wash components in comparison contributed to statistically significant differences in PFAS removal capacity for the soil wash.

The occurrence of statistically significant differences were most common for the longer chained compounds for JV and WG. The number of statistically significant occurrences in the salt comparison category (NaCl wt. %) are higher for PFCAs than for PFSA for all three soil types. The soils, WG and JBSA, displayed slightly more significance for PFSA in the NaCl wt. % section than JV. The highest number of statistically significant differences were for PFOS and PFHxS, in the combination, [DI: MeOH] * NaCl wt. %, and wash type, [DI: MeOH], sections for both WG and JV.

The highest number of statistically significant occurrences were observed for PFOS, and, they are observed for the vast majority of TukeyHSD comparisons in WG and JV, indicating PFOS removal is highly sensitive to wash composition in soils that have high TOC. WG displayed the highest number of statistically significant differences, followed by JV, and then JBSA, which correlated with the TOC trend of the IDW samples: WG > JV > JBSA.

The concentration of statistically significant occurrences, was also found to concentrate in the lower pH samples, but not correlate exactly with the pH trend: JV < WG < JBSA. The pH values of WG and JV are both within 1 unit of neutral, pH 7.93 and 6.22, respectively while JBSA had a basic pH of 11.0. A possible interpretation of the discrepancy between the trend of observed statistical significance and the TOC and pH trend is that the combination of TOC and pH is a stronger correlating factor of sorption than TOC and pH considered separately (Y. Li et al., 2018; Mejia-Avendaño et al., 2020).

The TukeyHSD comparisons with DI were examined to highlight the difference in PFAS removing capacity of a particular soil wash in comparison to DI. Both of the shortest chained compounds PFBS and PFPeA had the most removal using DI for all IDW soil types suggesting their sorption has a low irreversibility when compared to longer chained compounds. Both JV and WG, the IDW soils with high TOC and low pH, consistently had the highest percent changes from DI. WS and JBSA, the two soils with the lowest TOC and basic pH values, had the lowest percent changes and the highest instances of the DI control as the most effective wash for all compounds, indicating that sorption irreversibility was low in these soils when compared to soils with higher TOC and lower pH. The high AEC capacity of WS alone did not yield more sorption capacity, as evident by low percent changes from DI and the high number of instances where the DI control produced the highest PFAS removal. Although the observation of higher percent changes in JV than WG for PFHxS and PFOA could indicate that the higher AEC in JV could be influencing sorption, however more experimentation would be needed to examine this in more detail.

Figures 5 and 6 display all the compounds grouped by soil type WG and JV, respectively. The higher percent changes were associated with the longer chained compounds in both PFSA and PFCA classes for both WG (Figure 8) and JV (Figure 9). The PFSA compounds exhibited the largest percent changes, with PFOS displaying the highest percent change. Compounds that had more PFAS removal with a proposed wash solution than with DI indicated that they were more likely to have been sorbed, and that their sorption displayed higher irreversibility, than the compounds removed with the DI control. The compounds PFHxS and PFOS, which have been documented to have higher sorption capacity than carboxylates of the same chain length (Higgins & Luthy, 2006b; Mejia-Avendaño et al., 2020; Zhou et al., 2010), displayed some sorption irreversibility in the low TOC soils, WS and JBSA as evidenced by exhibiting more removal in wash solutions with MeOH/MeOH + NaCl as components than with the DI control. PFOS which has been observed to

have the highest sorption irreversibility when compared to PFCA and shorter chained compounds (Milinovic et al., 2015; Zhao et al., 2014b) displayed higher percent changes from DI than PFHxS. The concentration of high percent change in compounds with longer C-F chains in soils with higher TOC indicate that hydrophobic interactions played a major role in sorption.

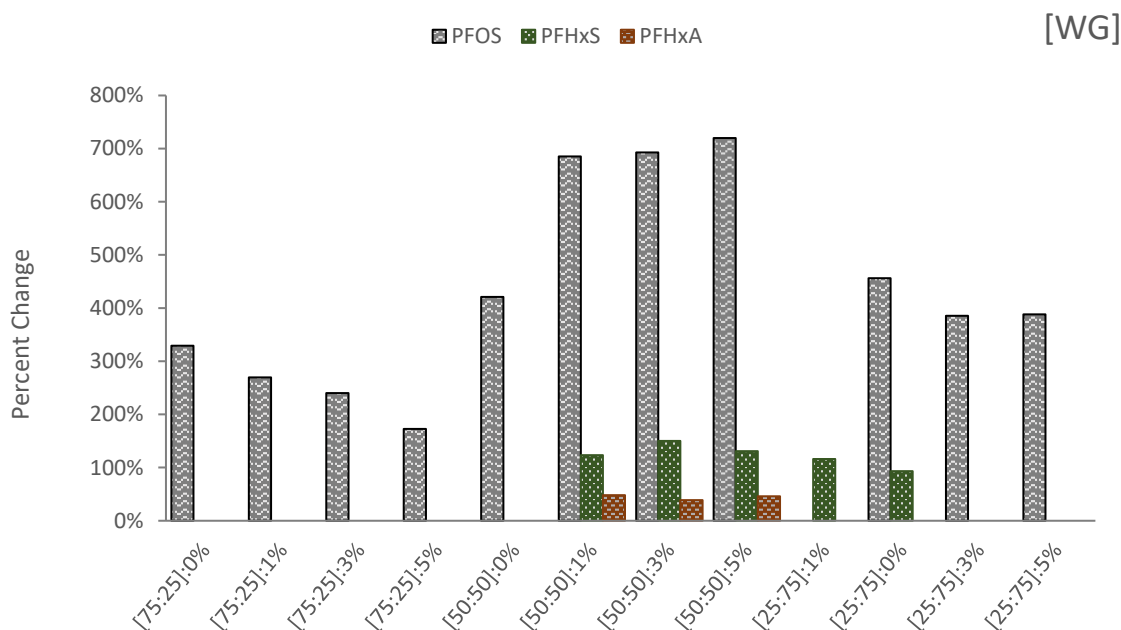


Figure 5. Percent change from DI for PFOS, PFHxS and PFHxA for Willow Grove (WG).

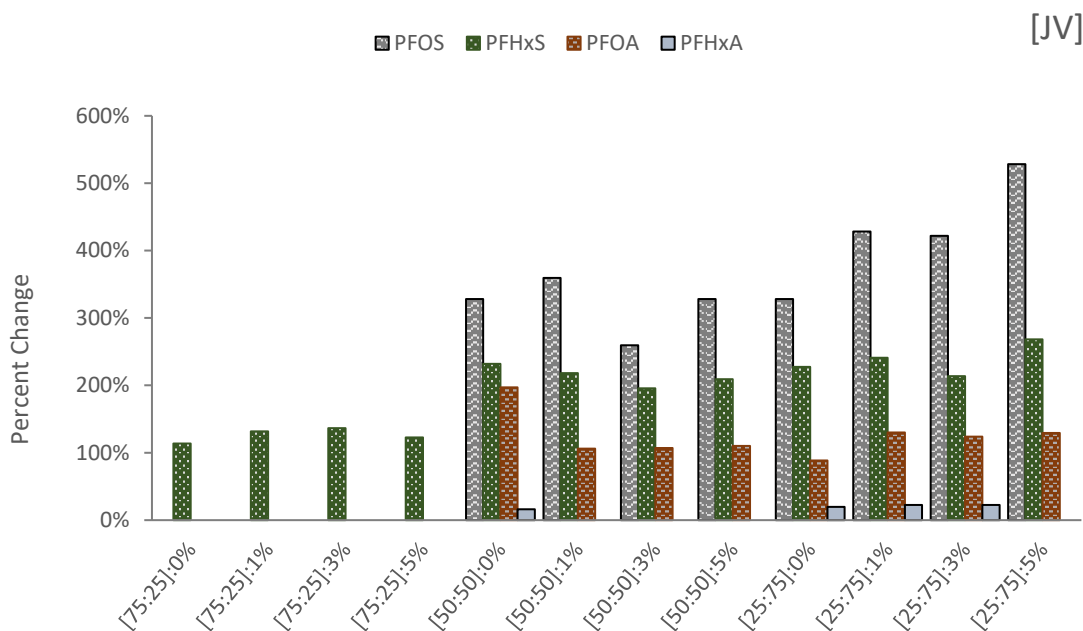


Figure 6. Percent change from DI for PFOS, PFHxS, PFOA, and PFHxA for Jacksonville (JV).

Table 7 displays the most effective wash for each compound and soil type, the wash that displayed the highest percent change from DI. WS has an asterisk to signify only 1 wt. % NaCl was evaluated for the washes that included salt. The IDW soils are organized left to right in descending order of the number of optimum washes other than DI. JV which had the second highest TOC and AEC, and lowest pH had the highest instance of optimum washes other than DI. WG had the highest TOC/lowest AEC/second lowest pH is tied with WS, which has the highest AEC/lowest TOC/mid-level pH. JBSA, the soil with the highest pH along with the lowest TOC and second lowest AEC, has the highest instance of DI being the most efficient wash. PFOS was the only compound in JBSA to have a wash other than DI, [25:75]:5%. The JV IDW soil favored [25:75]:5%, while WG favored [50:50]:1,3,5%, and WS favored [50:50]:1%.

Trends were also observed when examined on a compound basis across the soil types. The shortest C-F chained compounds, PFBS, and PFPeA, had DI as the optimum wash across the soil types. This indicates that both PFBS and PFPeA have high mobility. When PFOA is in a soil with high AEC, DI is no longer the optimum; 50:50 was the most effective wash for JV and [50:50]:1% NaCl was the most effective wash for WS. Over all soil wash types [50:50]:1%, 3%, or 5% NaCl had the highest instance of occurrence for the most effective wash and there are negligible differences between PFAS removal capacity from the [50:50] series and the [25:75] series.

Table 7. The optimum wash composition by soil type for each compound

Compound	JV	WG	WS*	JBSA
FOSA_1	[25:75]:5%	nf	DI	DI
PFOA	[50:50]	DI	[50:50]:1%	DI
PFHxA	[25:75]:5%	[50:50]:1%	DI	DI
PFPeA	DI	DI	nf	DI
PFOS	[25:75]:5%	[50:50]:5%	[50:50]:1%	[25:75]:5%
PFHxS	[25:75]:5%	[50:50]:3%	[50:50]:1%	DI
PFBS	DI	DI	DI	DI

Key:

Wash Composition	Deionized Water (%)	Methanol (%)	NaCl (wt%)
DI	100	-	-
[50:50]	50	50	-
[50:50]:1%	50	50	1
[50:50]:3%	50	50	3
[50:50]:5%	50	50	5
[25:75]:5%	25	75	5

4.1.5 Number of Soil Extraction Cycles

For all compounds across all soil types 80-90% of the PFAS was removed in the first extraction, 8 – 13% in the second extraction and 0 – 3 % in the third extraction. Illustrative graphs for FOSA_1 and PFOS results are displayed below (**Figure 7**) as PFOS has been documented as highly irreversible (Milinovic et al., 2015). FOSA_1 is included because it is longer chained than PFOS, indicating it has increased sorption capacity (Gagliano et al., 2020; Higgins & Luthy, 2006b; Krippner et al., 2014) and is a precursor to PFASs, so it is reasonable to assume it has high sorption irreversibility as well. PFAS concentration in ($\mu\text{g}/\text{kg}$) is displayed on the y-axis and the soil extraction number on the x-axis.

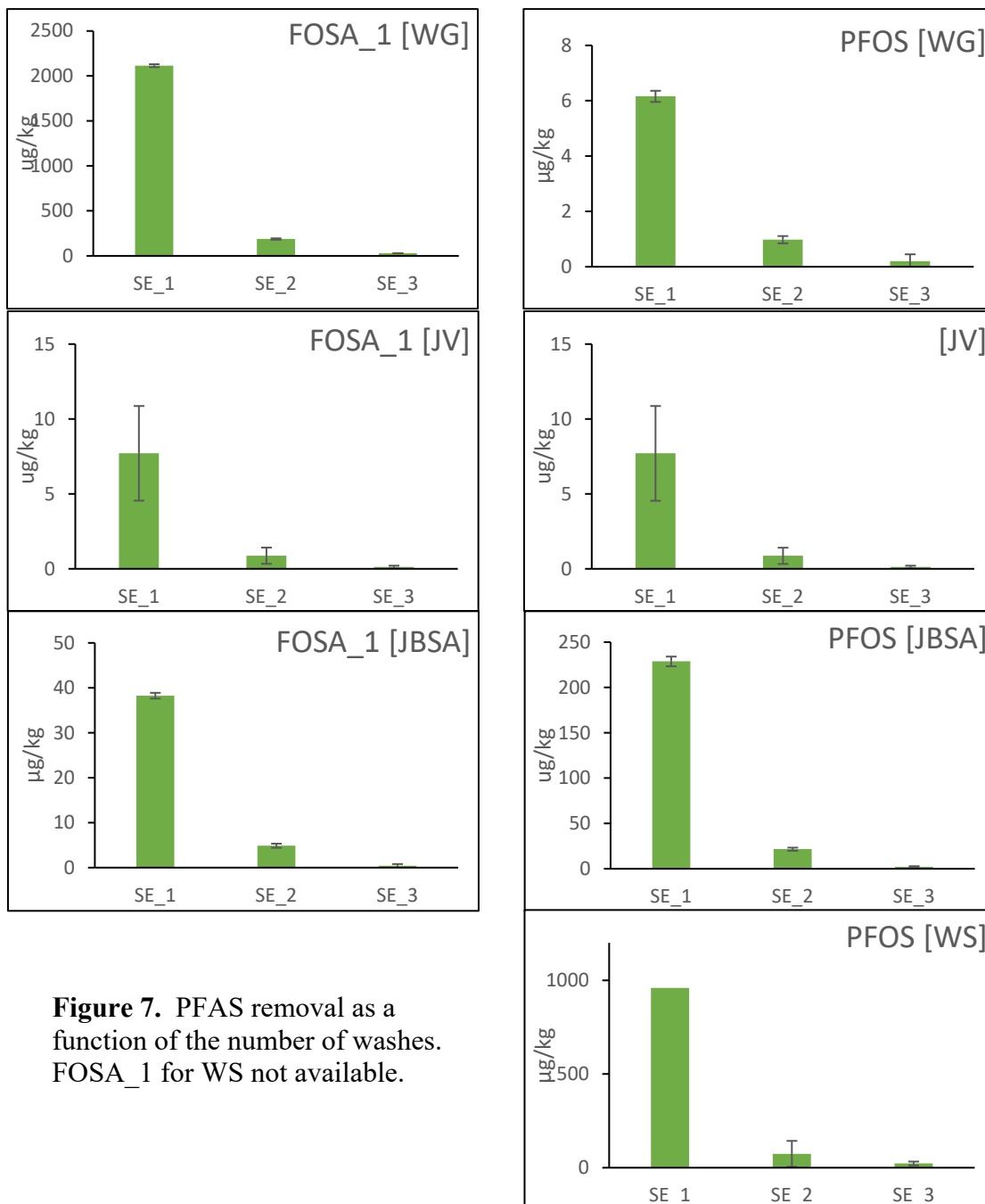


Figure 7. PFAS removal as a function of the number of washes. FOSA_1 for WS not available.

4.1.6 Kinetic Experiments

The kinetic portion of this investigation determined how the wash time period was related to the amount of PFAS removed. This study focused on characterizing the first two hours of the soil wash as preliminary experiments showed little additional removal between two hours and one week (**Figure 8 top panel**). For all of the compounds and all of the washes the vast majority of the mass was removed in the first wash suggesting that short wash times are needed to remove the PFAS (**Figure 8 bottom panel**).

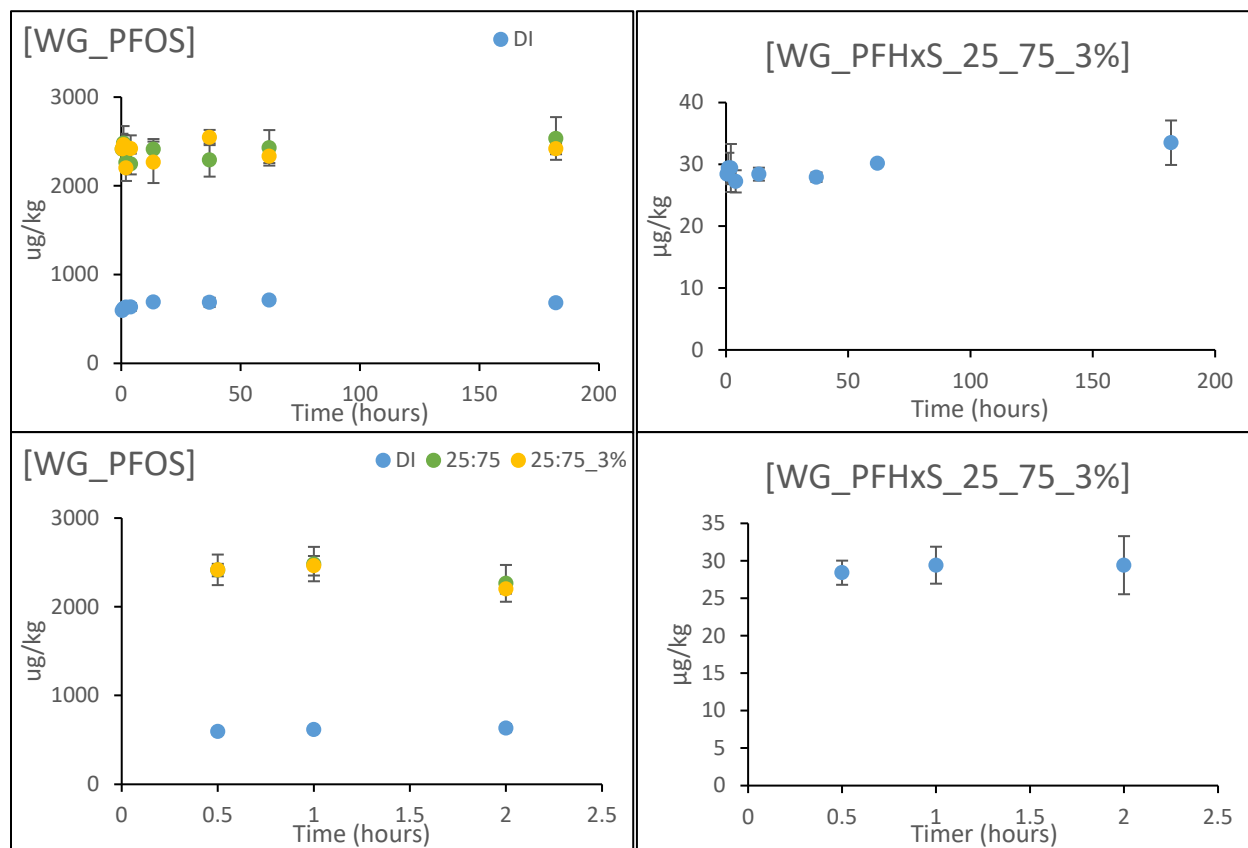


Figure 8. Evaluation of the amount removed as a function of contact time.

4.1.7 Leach Test

The leach test determined how much PFAS was left in the soil after a wash with the optimum conditions of 0.5 hour wash with a solution of 50:50_1% NaCl and with DI by extracting the remaining soil with the conventional method of sonication with 99% methanol and 1% ammonium hydroxide (**Figure 9**).

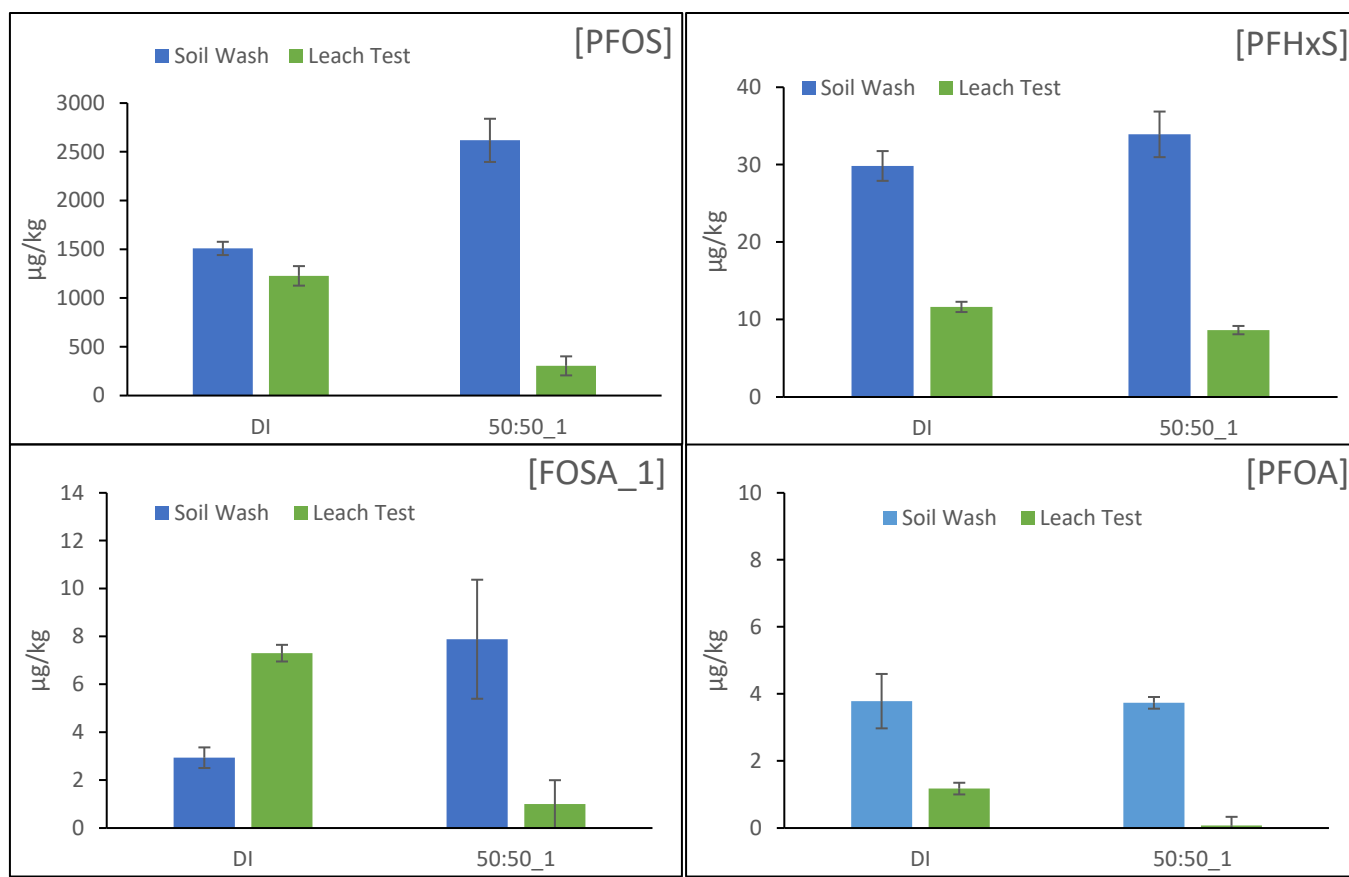


Figure 9. Determination of how much PFAS was left in the soil after extraction as determined by a subsequent extraction with sonication with 99% methanol and 1% ammonium hydroxide

As expected the 50:50_1% NaCl wash extracted significantly more PFAS than DI for FOSA_1, and the sulfonic acids; PFOS, and PFHxS. The 50:50_1% NaCl and DI performed similarly for PFBS and the carboxylic acids; PFOA, PFHxA, and PFPeA. DI performed least efficiently for FOSA_1, PFOS, and PFBS. The soil extraction leach test extracted small amounts of PFAS after the the 50:50_1% NaCl and significant amounts after the DI soil wash. Note that some residual wash and DI solutions remained in the soil pores prior to the more vigorous extraction which likely accounted for some of the PFAS seen in the vigorous wash solution.

4.1.8 Summary Tables

The summary tables (**Tables 8 to 11**) list the total amount of PFAS removed by the optimum soil wash (50:50_1%), DI water alone and the vigorous extraction leach test. The total amount of PFAS removed from the sample after the optimum soil wash and leach test is listed. The OW % removed represents the amount of PFAS removed by the optimum wash relative to that removed by the vigorous extraction. The variance coefficients (CV) for the majority of the compounds analyzed are less than 10% indicating good reproducibility.

Table 8. Willow Grove Summary Results. The wash % removed represents the amount of PFAS removed by the wash relative to that removed by the vigorous extraction.

Compound	Wash Type	Optimum Wash			Exhaustive Extraction			Total	
		µg/kg	STDEV	CV (%)	µg/kg	STDEV	CV (%)	µg/kg	Wash % removed
FOSA_1	DI	2.93	0.43	15	7.30	0.35	5	10.2	29
	50:50_1%	7.88	2.48	31	1.00	1.00	100	8.88	89
PFOA	DI	3.78	0.81	21	1.18	0.17	15	4.96	76
	50:50_1%	3.73	0.25	7	0.08	0.26	350	3.81	98
PFHxA	DI	7.82	0.73	9	1.90	0.17	9	9.72	80
	50:50_1%	8.00	0.43	5	1.60	0.09	5	9.60	83
PFPeA	DI	5.37	0.39	7	.025	0.43	170	5.62	96
	50:50_1%	4.58	0.36	8	0.00	0.00	0	4.58	100
PFOS	DI	1500	67.8	4	1200	20.1	2	2700	55
	50:50_1%	2600	220	8	304	15.0	5	2900	90
PFHxS	DI	29.8	1.92	6	11.6	0.65	6	41.5	72
	50:50_1%	33.9	2.94	9	8.63	0.54	6	42.5	80

Table 9. Jacksonville Summary Results. The wash % removed represents the amount of PFAS removed by the wash relative to that removed by the vigorous extraction.

Compound	Wash Type	Optimum Wash			Exhaustive Extraction			Total	
		µg/kg	STDEV	CV (%)	µg/kg	STDEV	CV (%)	µg/kg	Wash % removed
PFOA	DI	2.78	0.15	5	14.5	0.63	17.4	17.4	16
	50:50_1%	14.5	0.29	2	4.55	0.57	19.0	19.0	76
PFHxA	DI	1.77	0.03	2	0.28	0.29	2.05	2.05	86
	50:50_1%	2.53	0.06	2	0.00	0.03	2.53	2053	100
PFOS	DI	0.07	0.03	43	7.02	0.53	7.08	7.08	1
	50:50_1%	4.10	0.10	2	2.22	0.15	6.32	6.32	65
PFHxS	DI	0.55	0.15	27	4.52	0.38	5.07	5.07	11
	50:50_1%	4.60	0.15	3	1.17	0.13	5.77	5.77	80
PFBS	DI	0.75	0.05	7	0.70	0.15	1.45	1.45	52
	50:50_1%	1.23	0.06	5	0.25	0.05	1.48	1.48	83

Table 10. JBSA Summary Results. The wash% removed represents the amount of PFAS removed by the wash relative to that removed by the vigorous extraction.

Compound	Wash Type	Optimum Wash			Exhaustive Extraction			Total	
		µg/kg	STDEV	CV (%)	µg/kg	STDEV	CV (%)	µg/kg	Wash % removed
FOSA_1	DI	677	9.02	1	264	9.02	3	942	72
	50:50_1%	671	10.7	2	234	27.0	12	906	74
PFOA	DI	18.8	0.03	0	3.12	0.03	1	21.9	86
	50:50_1%	26.3	2.93	11	3.15	0.48	15	29.5	89
PFHxA	DI	19.7	0.03	0	1.92	0.03	2	21.7	91
	50:50_1%	20.8	0.76	4	2.38	0.88	37	21.2	90
PFOS	DI	1240	9.78	1	241	9.78	4	1480	84
	50:50_1%	1580	42.2	3	146	6.92	5	1720	91
PFHxS	DI	15.2	0.12	3	3.83	0.12	3	19.0	80
	50:50_1%	20.3	1.04	5	3.87	0.53	14	21.2	84

Table 11. Wurtsmith Summary Results. The wash % removed represents the amount of PFAS removed by the wash relative to that removed by the vigorous extraction.

Compound	Wash Type	Optimum Wash			Exhaustive Extraction			Total	
		µg/kg	STDEV	CV (%)	µg/kg	STDEV	CV (%)	µg/kg	Wash % removed
FOSA_1	DI	47.2	8.41	18	21.2	0.38	2	68.4	69
	50:50_1%	66.8	14.1	21	23.2	33.5	145	90.0	74
PFOA	DI	11.8	1.24	11	1.53	0.09	6	13.3	89
	50:50_1%	12.9	0.33	3	1.13	0.15	13	14.0	92
PFHxA	DI	9.37	0.37	4	1.60	0.09	5	11.0	85
	50:50_1%	10.0	0.30	3	1.55	0.09	6	11.6	87
PFOS	DI	200	8.16	4	122	0.61	0	322	62
	50:50_1%	344	4.33	1	31.1	1.35	4	376	91
PFHxS	DI	27.3	1.34	5	3.23	0.30	9	30.5	89
	50:50_1%	29.6	0.43	1	2.43	0.43	18	30.0	92
PFBS	DI	1.13	0.16	14	1.08	0.23	21	2.21	21
	50:50_1%	1.28	0.08	6	1.28	0.15	12	2.56	50

For WG the 50:50_1% NaCl wash removed greater than 80% of each individual PFAS and consistently removed more PFAS than the DI wash. The greatest differences were for PFOS, FOSA_1 and PFOA. For the rest of the compound 50:50_1% NaCl exhibited only a marginal improvement over DI. Relative to the vigorous wash 50:50_1% NaCl removed between 80 and 100% of each compound.

For JV 50:50_1% NaCl significantly outperformed the DI wash for every compound evaluated. The removal percentage for 50:50_1% NaCl was between 80 and 100% for all compounds except for PFOA and PFOS which had removal percentages of 76% and 65%, respectively. DI had a removal percentage between 1% and 16% for all compounds except for PFHxA and PFBS which 86% and 52% removed, respectively. DI and 50:50_1% NaCl had a similar removal performance for PFHxA with 86% and 100% removal, respectively. The 50:50_1% NaCl optimum wash had the lowest removal percentage for PFOS with 65%.

For JBSA FOSA_1, PFOA, PFHxA, PFHxS, and PFBS had only marginal differences in PFAS removal between 50:50_1% NaCl and DI. The removal percentages between 85% -92% for all the compounds except FOSA_1 which 50:50_1% NaCl removed 74% and DI removed 69%. The 50:50_1% NaCl wash significantly outperformed DI in PFOS removal with 50:50_1% NaCl removing 91% while DI removed 62%. PFBS exhibited poor removal with both 50:50_1% NaCl and DI only removing 50% and 51%, respectively. This could be due to the fact that the PFBS concentration is near the detection limit of 1 µg/kg.

For Wurtsmith both the optimum washes, DI and 50:50_1% NaCl, removed between 80% and 91% of PFAS for all compounds except for FOSA_1 in which 50:50_1% NaCl and DI removed 74% and 72% respectively. The 50:50_1% NaCl was performed marginally better than DI for all compounds except

4.2 Plasma treatment of wash solutions

For these experiments since only small volumes of soil washing solution were available after the soil washing experiments were completed and in practice the methanol would likely be recovered through distillation, we used still bottoms (SB) from IX regenerant solutions to simulate soil washing solutions after MeOH recovery. The results below have been submitted for publication to Environmental Science and Technology.

4.2.1 Characterization of still bottoms

Of the 27 PFAS analyzed for, seven long-chain ($C \geq 6$ for PFSA and $C \geq 8$ for PFCA) PFAAs (PFHxS, PFOA, PFHpS, PFNA, PFOS, PFDA and PFNS), six short-chain ($C < 6$ for PFSA and $C < 8$ for PFCA) PFAAs (PFBA, PFPeA, PFBS, PFHxA, PFPeS and PFHpA) and four precursors (4:2 FTS, 6:2 FTS, 8:2 FTS and FOSA-1) were found in all the SB samples in very high concentrations: Σ PFAAs concentrations ranged from 180 to 770 mg/L; Σ short-chain PFAAs ranged from 20 to 60 mg/L; Σ long-chain PFAAs ranged from 160 to 770 mg/L; Σ PFCAAs ranged from 110 to 190 mg/L and Σ PFASAs ranged from 80 to 640 mg/L (**Figure 10**). Total identified precursors ranged from 20 to 50 mg/L. Among the long-chain PFAAs, the mean concentration was the highest for PFHxS (all in mg/L) (140 ± 190) followed by PFOA (100 ± 20), PFOS (90 ± 40), PFHpS (2.3 ± 1.9), PFNA (0.3 ± 0.1), PFNS (0.07 ± 0.04) and PFDA (0.01 ± 0.01). For the short-chain PFAAs, concentrations decreased in the order of PFHxA (16 ± 7.8), PFHpA (7.5 ± 6.1), PFPeS (7.4 ± 1.3), PFPeA (5.9 ± 0.6), PFBS (5.0 ± 1.6) and PFBA (2 ± 0.5). Of the four precursors analyzed for 6:2 FTS had the highest mean concentration (28 ± 13) followed by 8:2 FTS (0.9 ± 0.6), 4:2 FTS (0.13 ± 0.04) and FOSA-1 (0.04 ± 0.01).

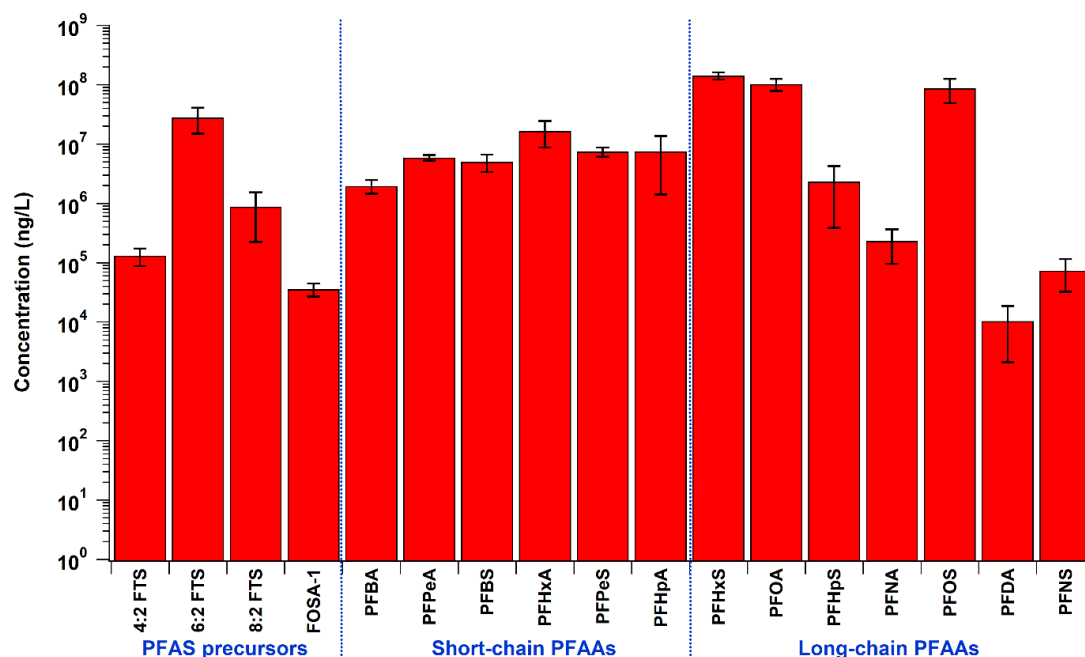


Figure 10. Concentrations of PFAS precursors, short-chain and long-chain PFAAs in six different IX brine regenerant still bottom samples. Concentrations are represented as average $\pm$ SD of six SB samples.

TOP concentrations ranged between 3800 to 9400 mg/L, approximately 10 times higher than the total PFAAs concentration (Table S4). Total fluorine concentration measured by CIC was 99 mg F/L, 3.3 times higher than organic fluorine measured in the TOP assay indicating that many F-containing compounds were not identified by TOP. TOP concentrations were on average 2000 times higher than the total directly measured precursor concentrations indicating the presence of numerous unidentified precursors. Similarly, total fluorine concentrations were on average 50 times higher than the total directly-measured organic fluorine associated with precursors.

4.2.2 High Concentration Reactor Results.

In all the SBs, plasma degradation efficiencies were higher for long-chain PFAAs than short-chain PFAAs, which is consistent with what was found for the treatment of contaminated groundwater (**Figure 11**).⁹ For long-chain PFAAs (PFNS, PFDA, PFOS, PFNA, PFHpS, PFOA and PFHxS), plasma treatment resulted in >99% degradation within 120 minutes and the extent of removal was independent of the PFAA chain length (representative concentration profiles of long-chained PFAAs are shown for the HC1(B) (**Figure 12a**). For short-chain PFAAs (PFHpA, PFPeS, PFHxA, and PFBS)), removal efficiencies were >99% after 6 hours of treatment except for PFPeA ($96.7 \pm 5.4\%$) and PFBA ($23 \pm 42\%$) (**Figure 11**). For the four identified precursors, 8:2 FTS and FOSA-1 were removed to below detection limits (BDL) of approximately 30 ng/L and removal efficiencies for 6:2 FTS and 4:2 FTS were $99.9 \pm .07\%$, and $90 \pm 25\%$, respectively (**Figure 11**). These removal efficiencies were comparable to those measured for TOP ($99.8 \pm 0.1\%$) (Table S5). Inorganic fluoride concentrations increased by 1 to 3 orders of magnitude post-treatment (Table S6) indicating significant defluorination of PFAS molecules.

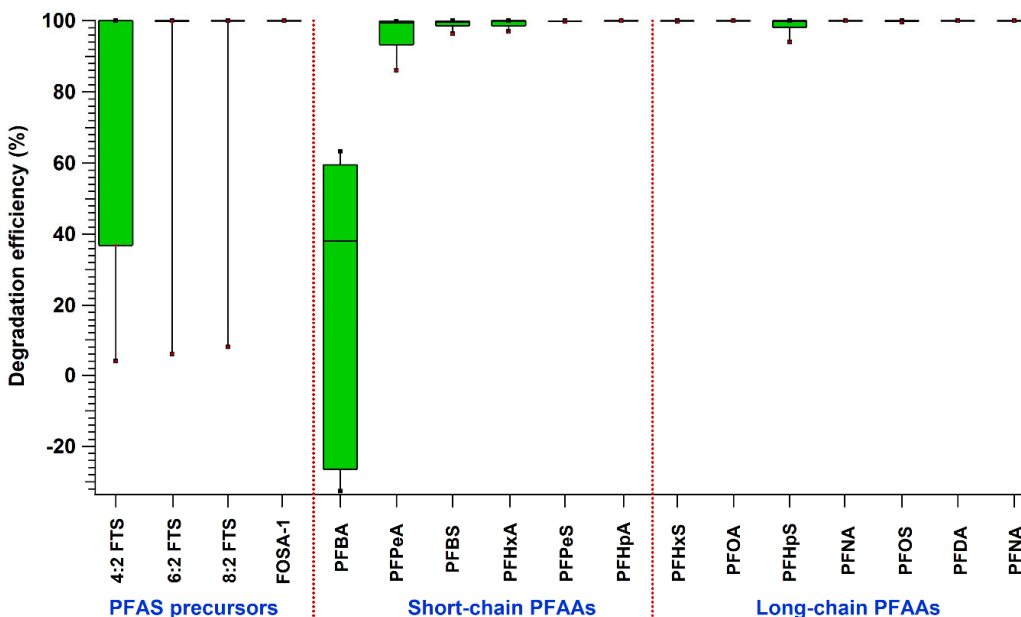


Figure 11. Box and whisker plot showing the plasma degradation efficiency (average $\pm$ SD %) for PFAS precursors, short-chain PFAAs, and long-chain PFAAs in six different SB samples in the high concentration reactor. Removal efficiencies were calculated from initial and final samples after six hours of treatment time (3 hours for HC1(C) SB sample) from 750 mL treatment volume.

Overall the high concentration reactor decreased the initial concentrations of Σ PFAAs by approximately $93.5 \pm 3.1\%$ and removed the vast majority of the long-chain PFAAs ($99.1 \pm 0.7\%$), TOP ($99.8 \pm 0.1\%$), precursors ($97.4 \pm 6.4\%$) and short-chain PFAAs ($86.4 \pm 6.9\%$). The greater removal of long-chained compared to short-chained PFAAs can be explained by the decrease in surface activity of PFAAs molecules with decreasing chain length, which limits their transport to the plasma-liquid interface where PFAS molecules are rapidly degraded by plasma-generated species.⁹ The slower removal of short-chain PFAAs is augmented by the fact that short-chain PFAAs can be generated as byproducts of degradation of long-chain PFAAs and/or precursors (Singh et al., 2019b). The substantial removal of TOP is due to the oxidative transformation/degradation of precursors to PFCAs by plasma-generated hydroxyl radicals.

The time-dependent degradation profiles of long-chain PFAAs, short-chain PFAAs and precursors are shown for HC1(B) in **Figure 12**, which is typical for all SB samples. In general, precursors were removed to BDL, long-chain PFAAs were removed 2-3 log-orders and short-chain PFAAs were removed 1-3 log-order (**Figure 12**). Pseudo-first order removal rate constants for PFOA and PFOS ($k_{PFOA+PFOS}$) degradation calculated for the first 30 min of treatment ranged between 0.13 and 0.22 min^{-1} . These values are, on average, an order of magnitude lower than the PFOA and PFOS removal rate constants previously measured in contaminated groundwater (Singh et al., 2019a). The lower removal rates in SBs could be attributed to the very high concentrations of PFAS, changes in the chemistry and physics of the plasma at high solution electrical conductivity, the presence of numerous degradation byproducts and/or complex chemistry between the bulk liquid constituents and plasma-generated reactive species.

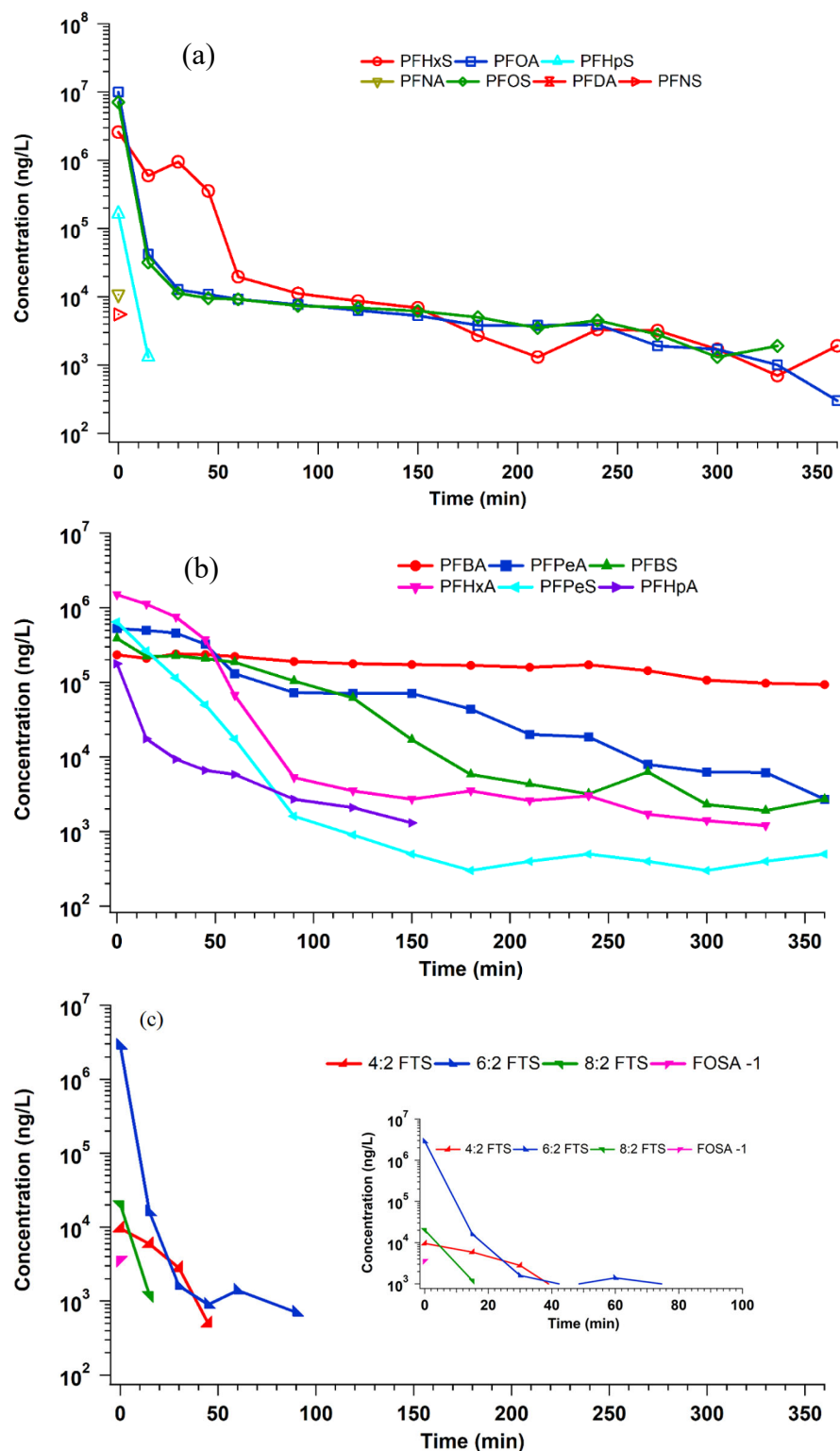


Figure 12. Representative concentration profiles of (a) long-chain PFAAs, (b) short-chain PFAAs, and (c) PFAS precursors from the HC1(B) sample (10-fold dilution) treated in the high concentration plasma reactor. The missing data points in the figures represent the concentration below the detection limit (9 ng/L).

To develop a better understanding of the effect of dilution on the plasma treatment efficiency for PFAAs, treated HC1(B) sample (six hours in high concentration plasma reactor) was further diluted by five times and treated for an additional five hours in the high concentration plasma reactor. This additional treatment resulted in no significant removal for most PFAAs, other than PFPeA and PFBA which were removed by 90 and 67%, respectively. This overall poor removal is likely due to desorption of PFAAs from the reactor components which continually fortify their concentration as they are removed from the solution. Our previous study showed that many PFAAs readily sorb to reactor components and desorb during treatment as concentrations decrease, contributing to bulk liquid PFAAs concentrations (Singh et al., 2019b). PFPeA and PFBA are the least surfactant-like PFAAs and least likely to adsorb onto reactor components, and therefore are not fortified by desorption which allows them to slowly degrade.

4.2.3 Low Concentration Reactor Results

To further reduce PFAAs concentrations in the HC1(B) SB sample treated in the high concentration reactor, treatment continued in the low concentration reactor which had not been exposed to the high concentration solution. All the long-chain PFAAs were removed to BDL after 30 minutes of additional treatment, except for short-chain PFAAs (**Figure 13a**). To remove short-chain PFAAs, an additional experiment was performed in which CTAB was added initially and after every 30 minutes of treatment (**Figure 13b**, dotted black arrows) for another 210 minutes of treatment. Dosing every 30 minutes was needed to maintain a CTAB concentration of 0.2 mM since it is readily degraded by the plasma. In this experiment all the short-chain PFAAs were removed to BDL in 90 minutes of treatment time (dotted red line), except PFBA whose concentration decreased from 6000 to 260 ng/L (**Figure 13b**).

CTAB is a quaternary ammonium surfactant that contains a positively charged hydrophilic group and a hydrophobic aliphatic (C19) chain. Electrostatic interaction between the positively charged trimethyl ammonium group of CTAB and negatively charged carboxylate group of PFAAs transports PFAAs molecules to the plasma-liquid interface where short-chain compounds are rapidly degraded by the reactive species. The lower removal of PFBA is likely due to competition between long-chain and other short-chain PFAAs and PFBA for binding with CTAB since PFBA association with CTAB is likely the weakest since it is the least hydrophobic of the PFAAs, resulting in less accumulation of PFBA at the plasma-liquid interface.

Because there is a high salt (NaCl) concentrations in SB samples, formation of perchlorate was investigated. Perchlorate concentrations in all untreated and treated still bottoms were below detection limits of 0.2 mg/L. Recovery of perchlorate in a standard addition experiment performed by adding 3.3 mg/L to a treated sample was 102%, indicating there were no matrix effects that interfered with perchlorate analysis.

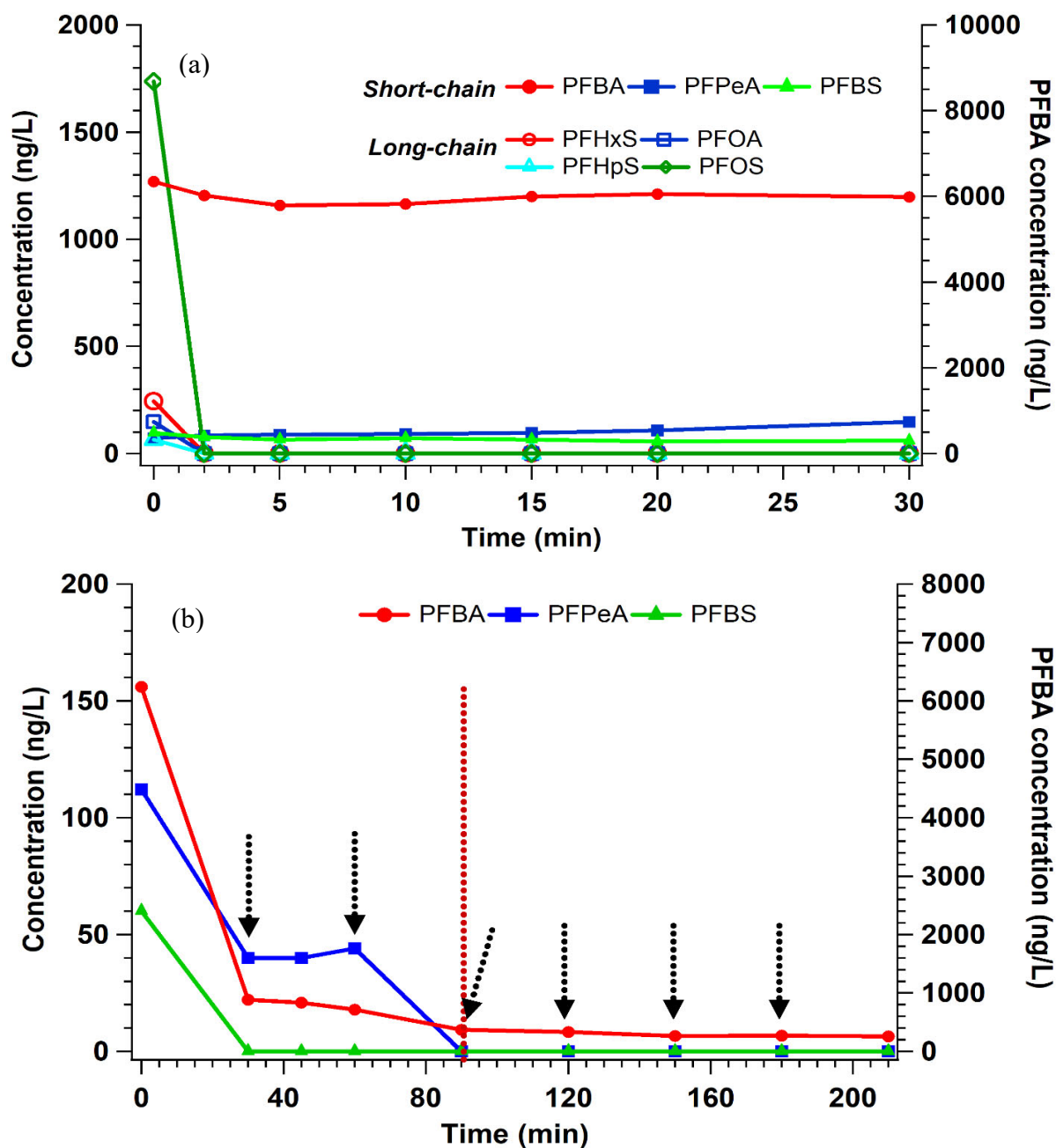


Figure 13. PFAAs concentration profiles during additional plasma treatment of the HC1(B) sample in the low concentration reactor in the (a) absence of CTAB, and (b) presence of CTAB (cationic surfactant); CTAB concentration was increased to 0.2 mM at every 30 minutes (black arrows). The vertical red dotted line at 90 min mark indicates the time that all short-chain PFAAs reached to BDL except PFBA.

Energy requirements for the treatment of SBs samples were calculated using electrical energy per order (EE/O) parameter as discussed in our previous study (in Eq. 1).¹¹

$$EE / O = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i / C_f)} \quad (1)$$

In Eq. (1), P (kW) is total power consumed by the high voltage supply, peristaltic pump, chiller and spark gap, t (min) is the time required to achieve 90% degradation of contaminant ($= 2.303/k$ where k is the pseudo-first order reaction rate constant (min^{-1})), V is the treatment volume in the reactor (0.75 L), and C_i and C_f are the initial and final concentrations of PFOA+PFOS (in $\mu\text{g/L}$). EE/O for the treatment of PFOA and PFOS from SBs ranged from 380 to 830 kWh/m^3 and energy requirement for the treatment of all PFAS compounds (long-chain PFAAs, short-chain PFAAs and precursors) ranged between 1560 to 2370 kWh/m^3 . These EE/O values are 1 to 2 orders of magnitude higher than the EE/O required for the treatment of IDW samples (1.7 to 56 kWh/m^3) in our pilot-scale plasma reactor due to the 3 to 4 order higher PFAS concentrations in SBs than those present in IDW samples (Singh et al., 2019a).

5.0 Conclusions and Implications for Future Research

5.1 Soil washing results

The 50:50_1% NaCl wash solution was found to be the most effective wash, although for low TOC soils and shorter chain PFAS DI water alone was somewhat effective. Longer chain sulfonated compounds were the most difficult to remove. Single washes generally removed the vast majority of the compounds present. Removal was generally fast, taking minutes to remove the vast majority of the compounds. However in these experiments the soil was pulverized and the solutions were tumbled end-over-end so kinetic limitations were largely eliminated. Follow-on work is suggested to evaluate impacts of potential mass transfer limitations under more field-like flow-through conditions.

5.2 Plasma treatment results

To the best of our knowledge, this is the first study reporting the treatment of high concentration PFAS-containing IX brine solution. In this study, destruction of TOP was $> 99.6\%$ ($99.8 \pm 0.1\%$) for all six SB solutions. Long-chain PFAAs, short-chain PFAAs (except PFBA) and PFAS precursors were removed $>99\%$ in all 10-fold diluted 1.5 L samples in six hours of treatment. Two different reactors: one for treatment of high-concentration solutions followed by a second reactor for treatment of the lower concentration SB solutions were required for effective treatment. In the optimized plasma reactor, periodic addition of cationic surfactant (CTAB) resulted in even short-chain PFAS being degraded below detection limits, except for PFBA (260 ng/L). Considering the extremely high concentrations of PFAAs and precursors in SBs, the plasma treatment process appears to be a promising and efficient technology for the removal of PFAS from high-conductivity waters such as IX brine regenerant solutions. Combining regenerable IX with plasma treatment would result in a treatment train with near zero PFAS waste.

5.3 Overall Conclusions

Soil washing with MeOH + NaCl is effective at removing PFAS from soil although water alone is fairly effective, especially for short chain PFAS in low organic carbon content soils.

PFAS are removed from soil quickly (minutes in these experiments).

Plasma treatment to destroy PFAS in high concentration salt solutions is effective.

Precursor concentrations are an important determinant of required plasma treatment times. Precursor oxidation before plasma treatment would decrease treatment times and may be economically beneficial.

5.4 Implications for Future Research and Development

A significant amount of PFAS containing IDW will be generated in the coming years - an on-site desorption method combined with a destructive treatment technology would decrease IDW disposal costs and limit DoD future liability associated with PFAS going off-site. Future research

should test the efficacy of an integrated, field-scale soil washing – plasma treatment system for IDW management.

We propose the following follow-on work:

- Comparatively evaluate alternative wash solutions, including isopropyl and ethyl alcohols, organic acids (e.g., acetic acid, oxalic acid, stearic acid), safe surfactants (e.g., CTAB, SDBS), and other “green” surfactants, in batch systems - applied individually, mixed and sequentially. Selected wash solutions will be based on results of Pan et al., 2009; Gellrich et al., 2012; Tang et al., 2017; Bolan et al., 2021 (and references therein) and will account for their varied effectiveness as a function of PFAS chain length and functional group(s).
 - The ideal wash solution(s) will (1) remove a broad suite of PFASs, (2) be non-toxic and have minimal to no health and safety concerns or related logistical implications, and (3) not require separation prior to plasma treatment.
- Evaluate effectiveness as a function of IDW properties: test at least three different field site IDW samples with a broad range of natural organic matter, anion exchange capacity, particle size/size distribution.
- Perform IDW washing tests under more realistic field conditions.
 - Conduct upflow column testing of top performing wash solution(s) (including combinations of solutions).
 - Evaluate impact of soil properties on solids mobilization under flow conditions.
 - Develop solids management plan, as needed/appropriate based on mobilization results (i.e., filtration, settling steps)
- Expand analyses to determine impact of washing on fate of cationic, zwitterionic, and unknown PFAS compounds
- Plasma treatment
 - Perform plasma destruction experiments on direct IDW wash solutions

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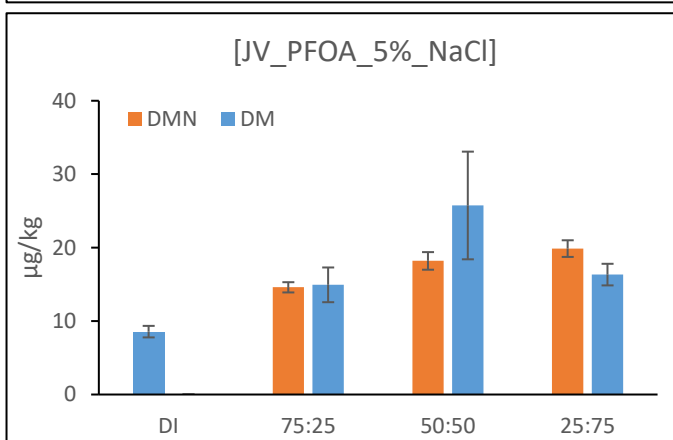
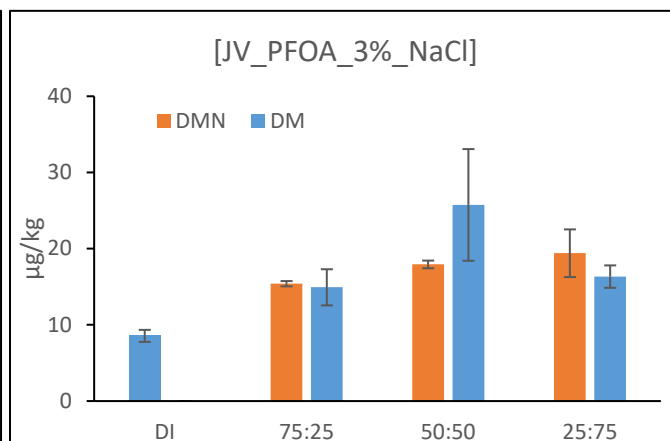
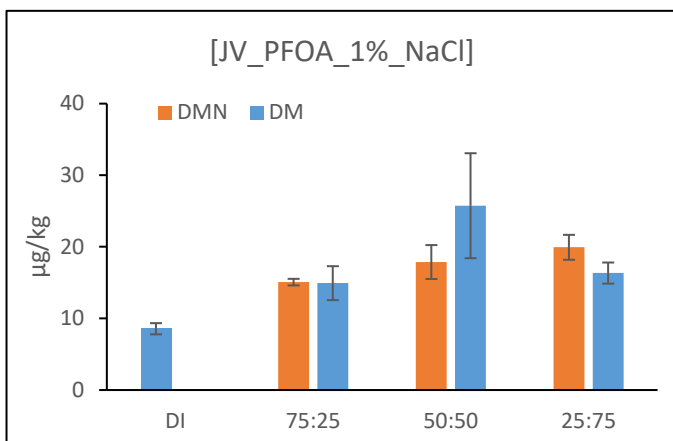
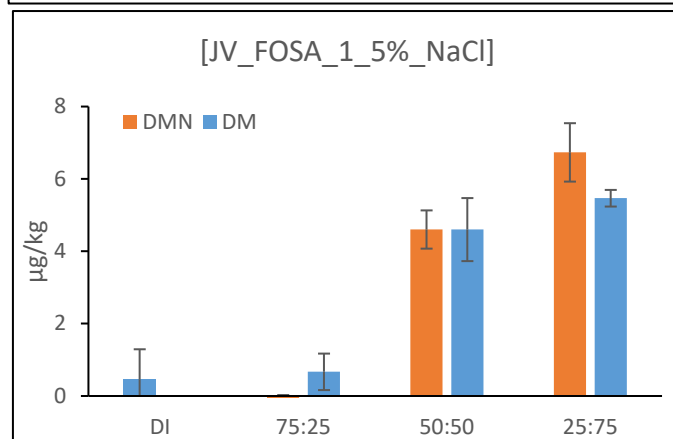
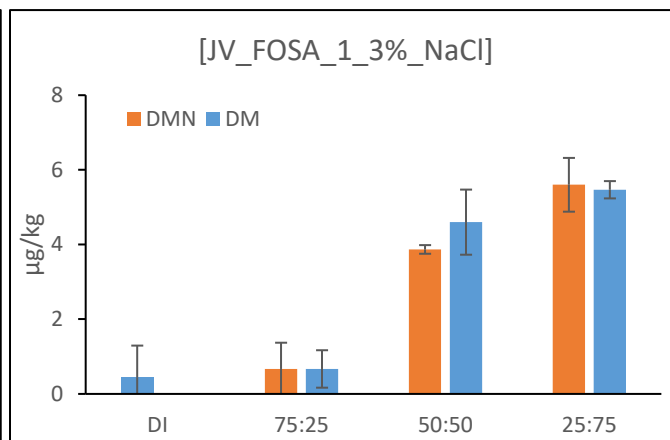
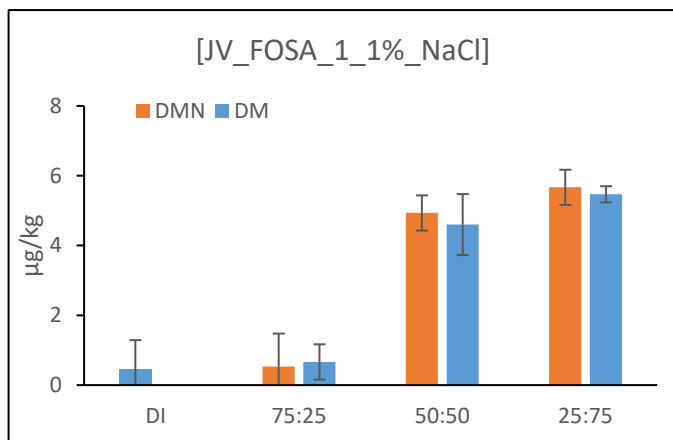
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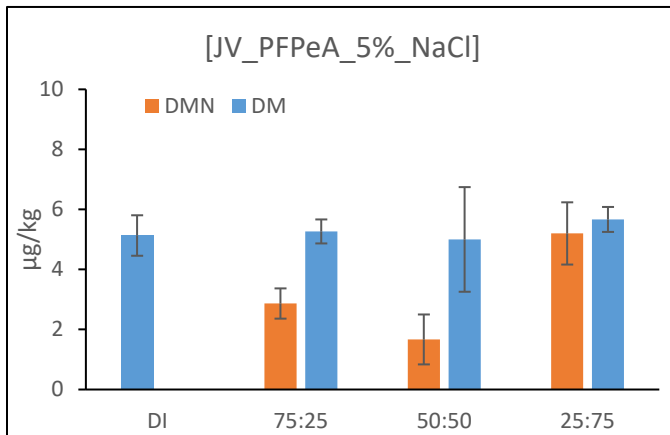
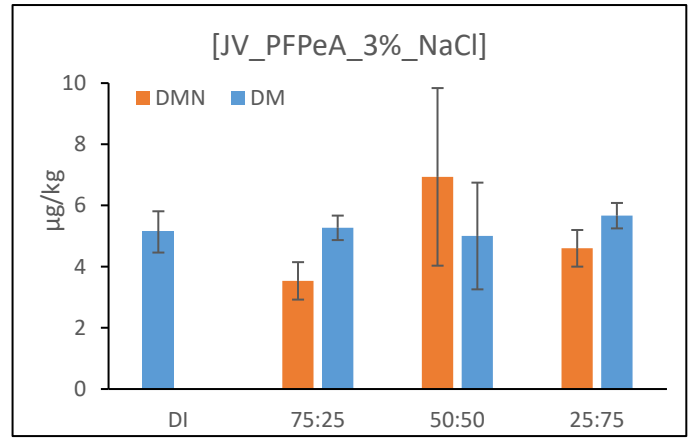
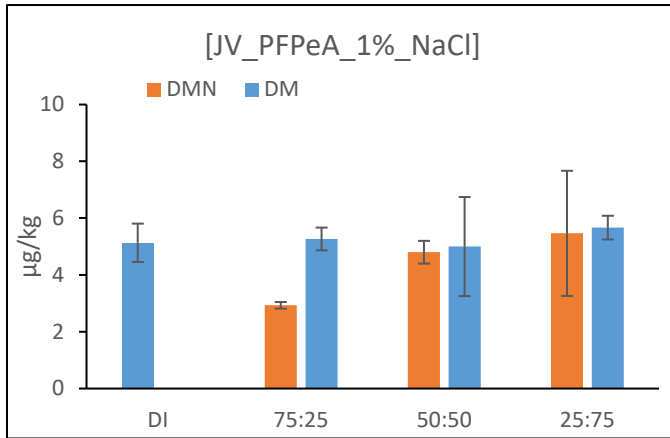
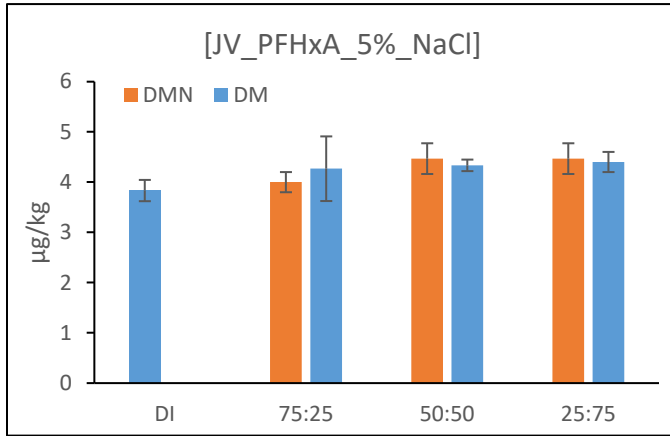
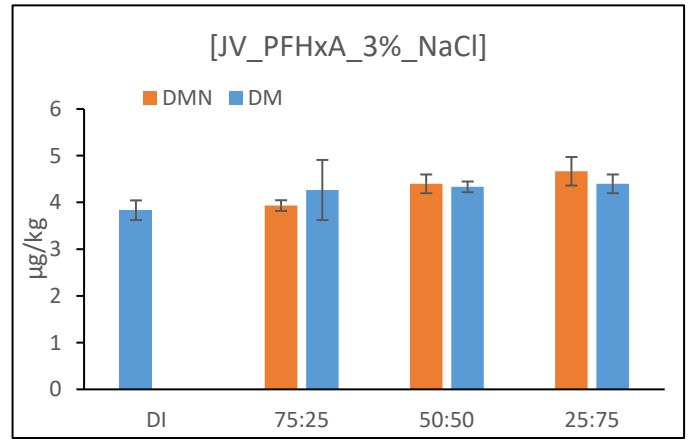
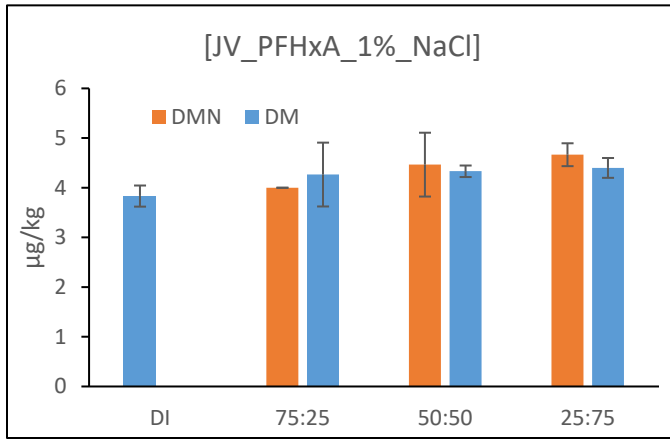
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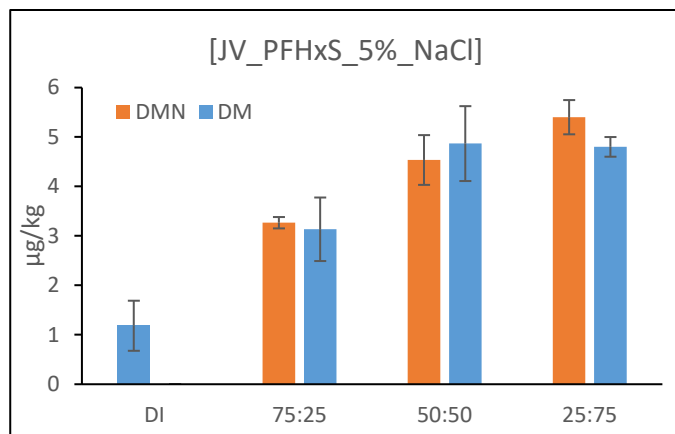
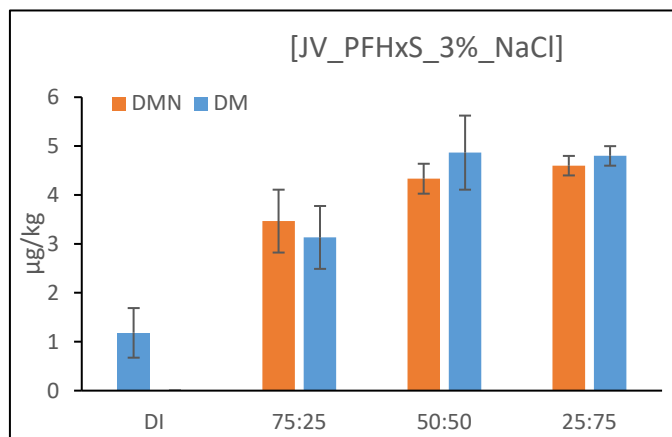
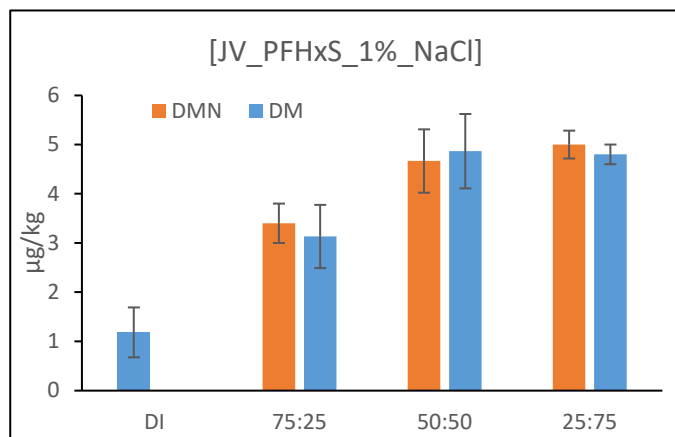
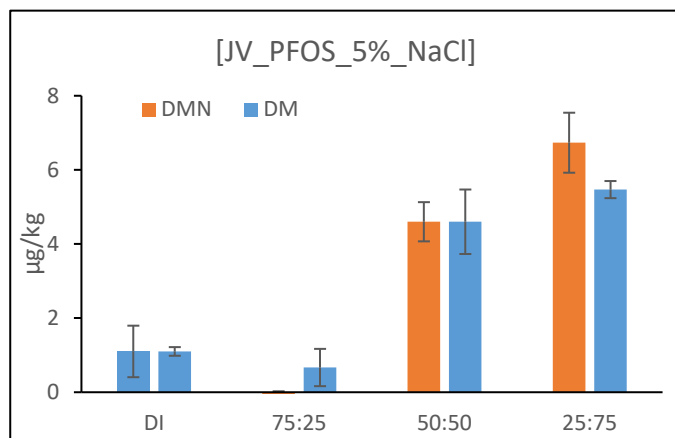
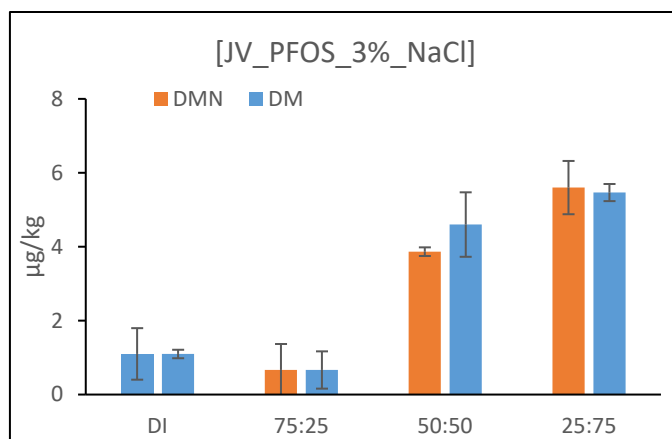
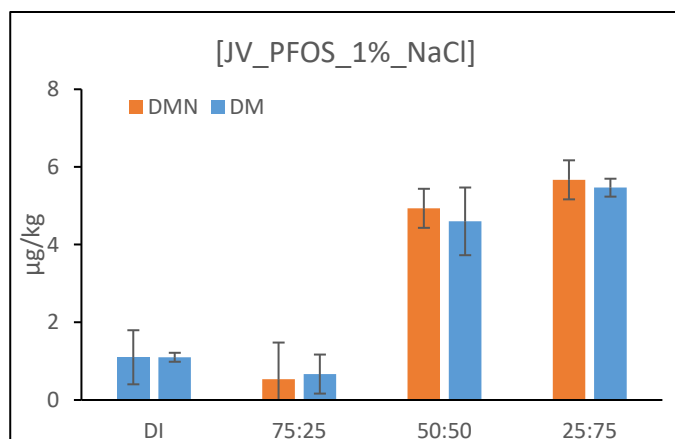
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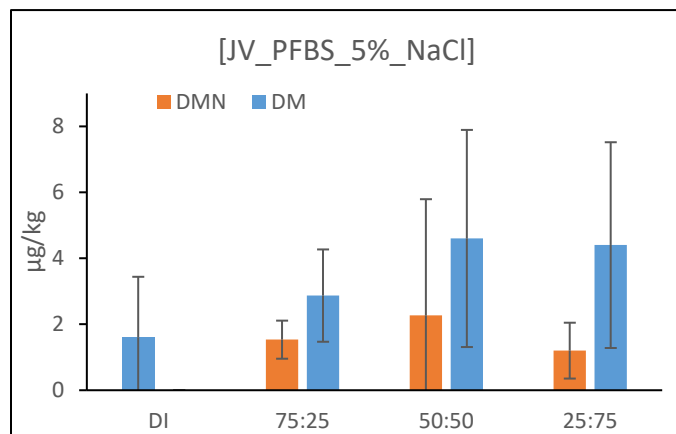
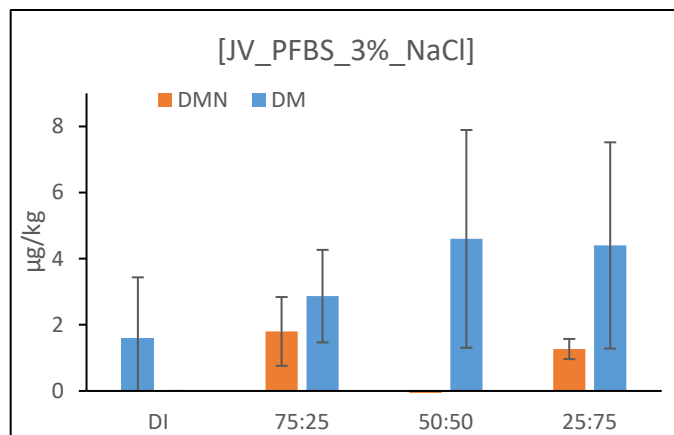
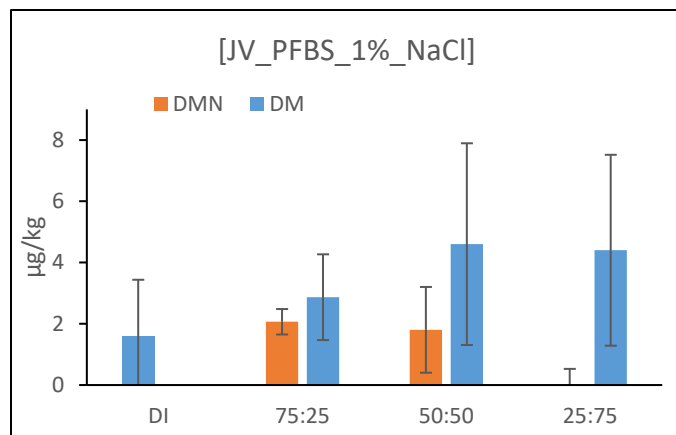
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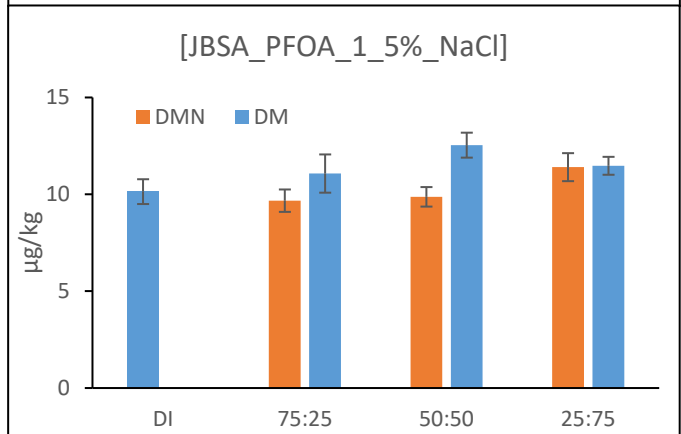
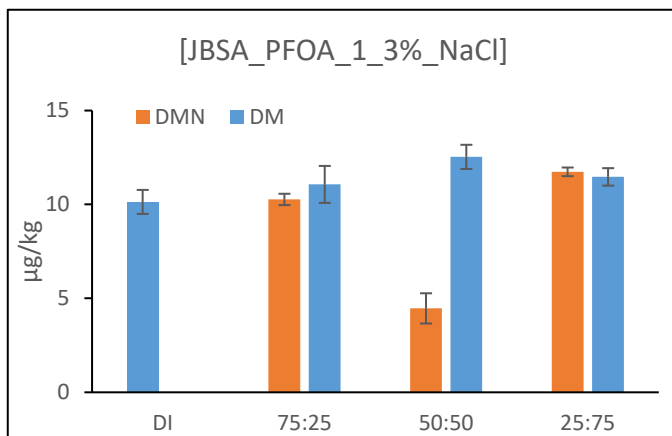
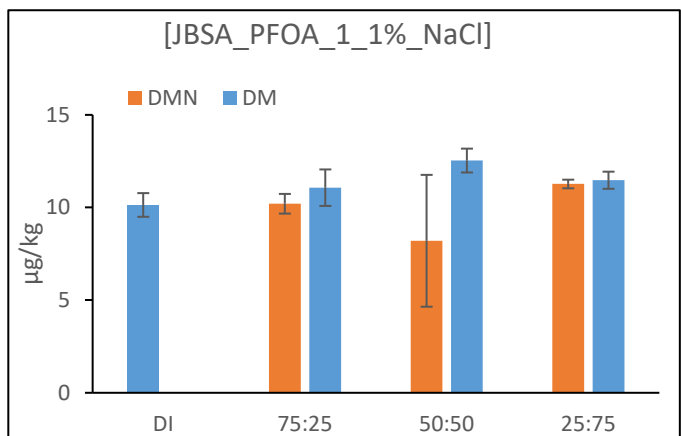
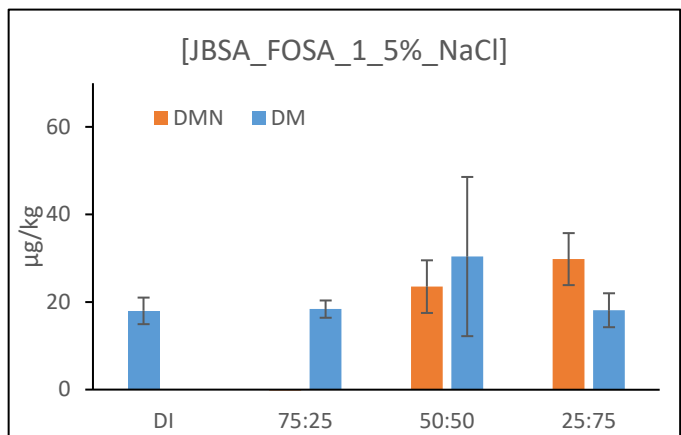
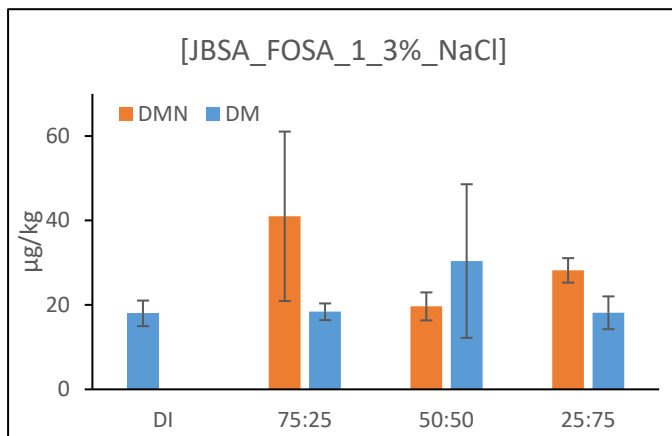
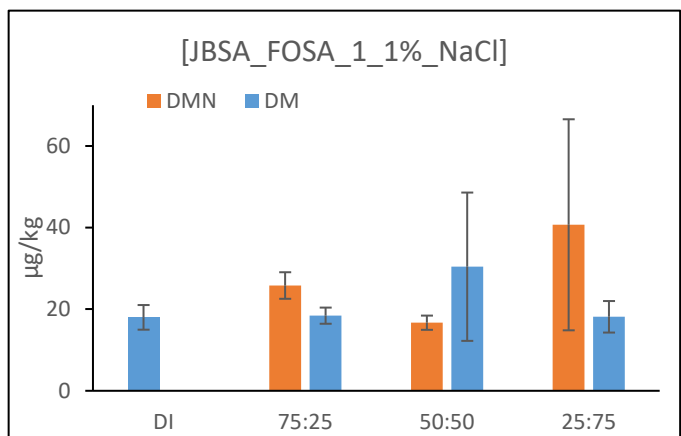
Appendix A. Wash Results for Jacksonville (JV), Joint Base San Antonio (JBSA), and Wurtsmith (WS)

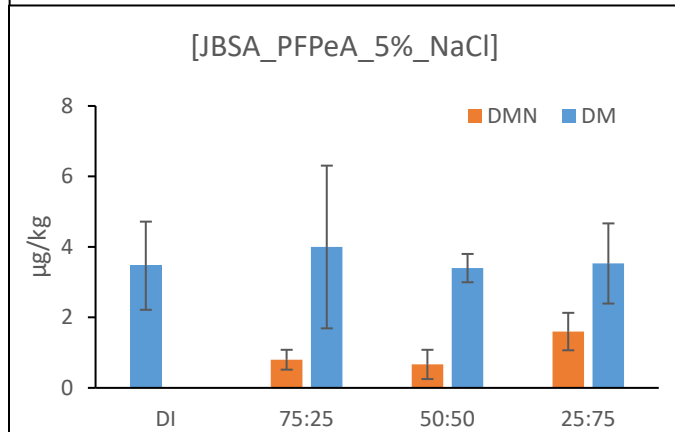
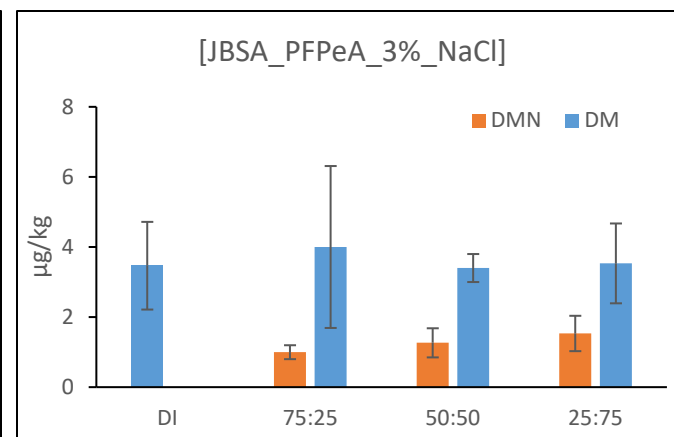
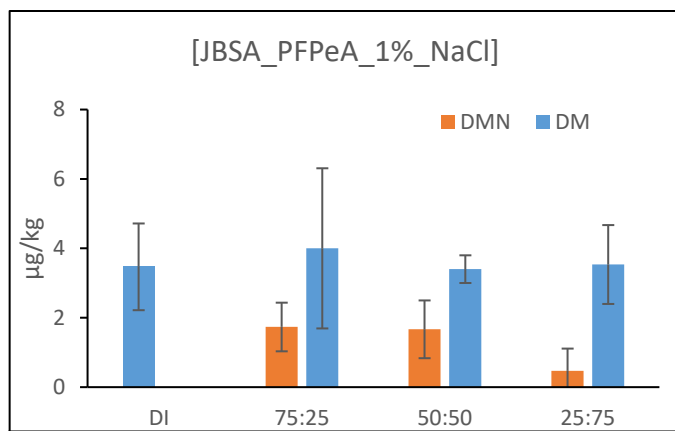
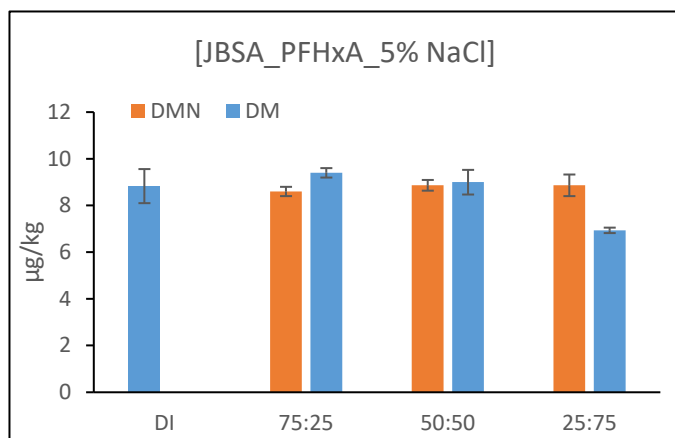
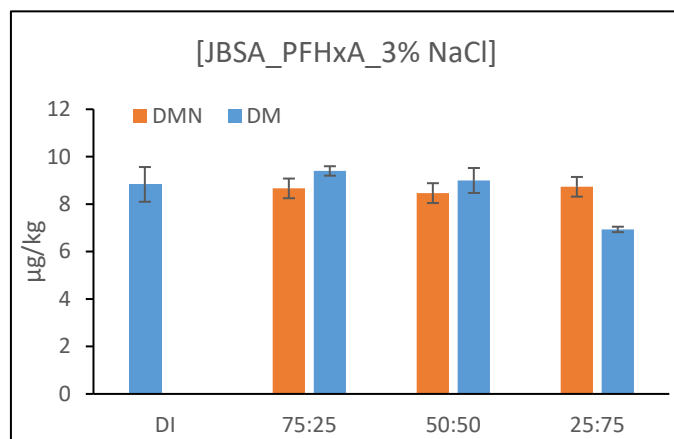
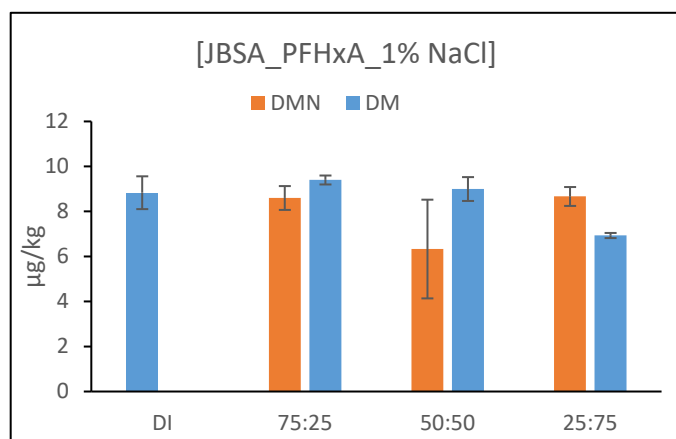


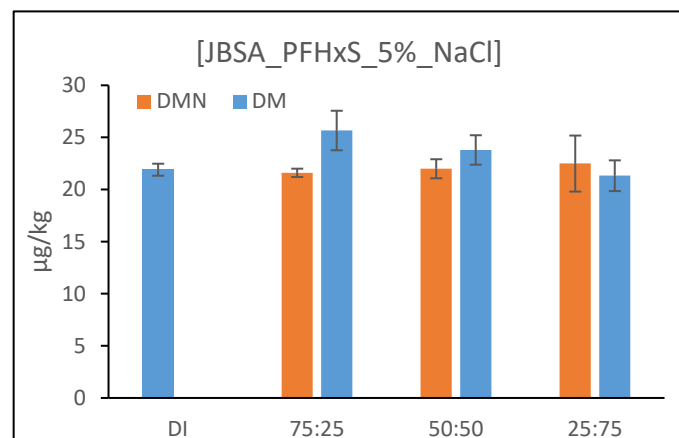
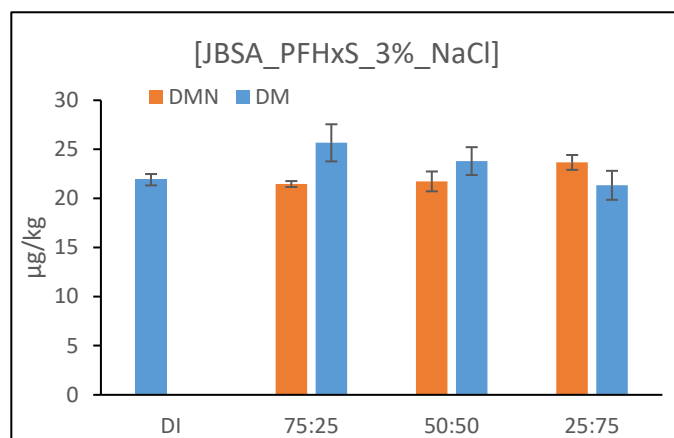
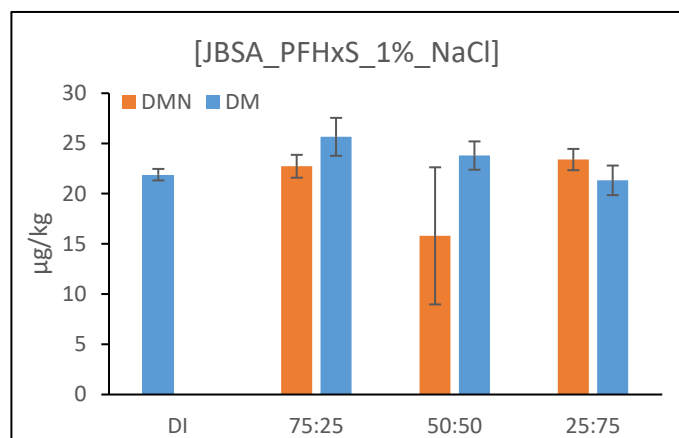
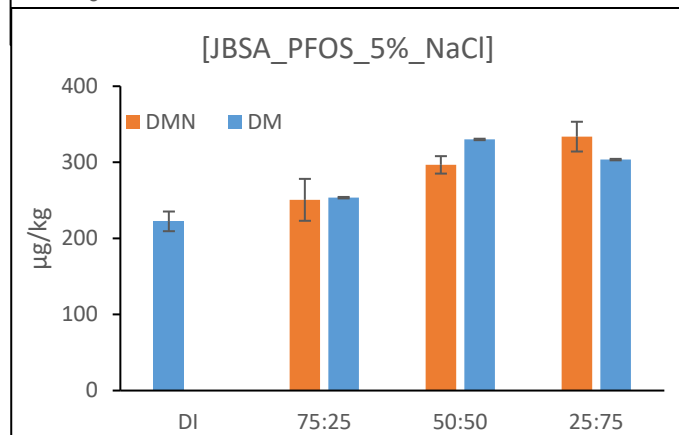
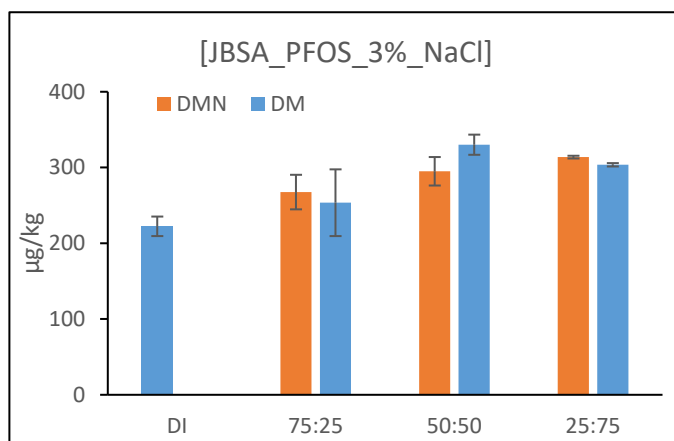
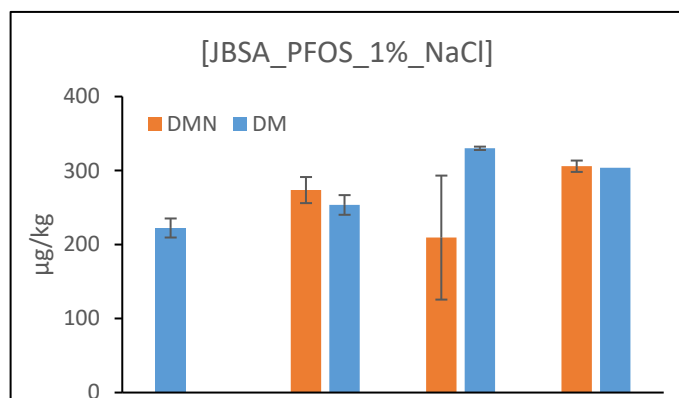


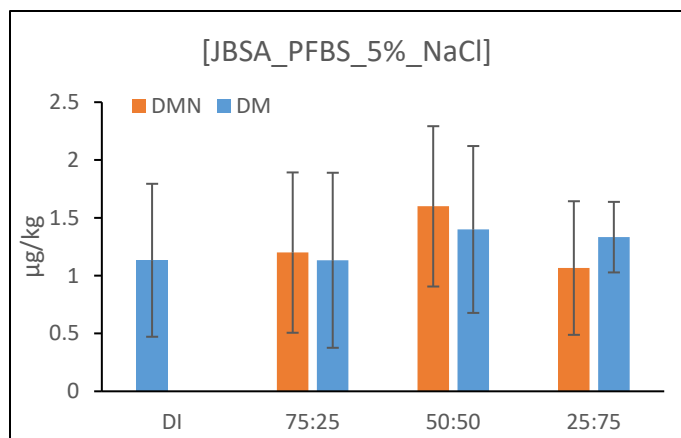
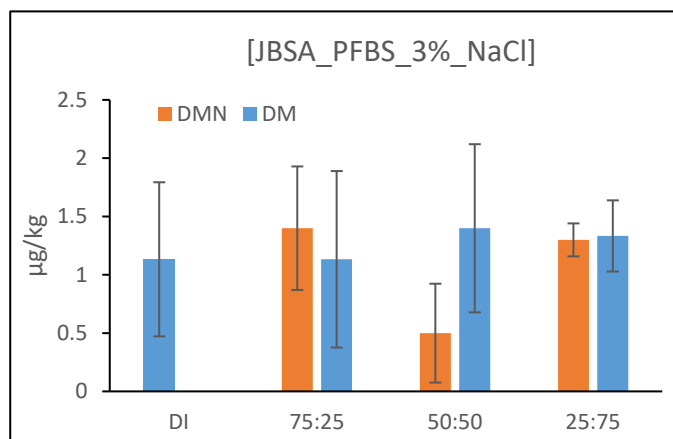
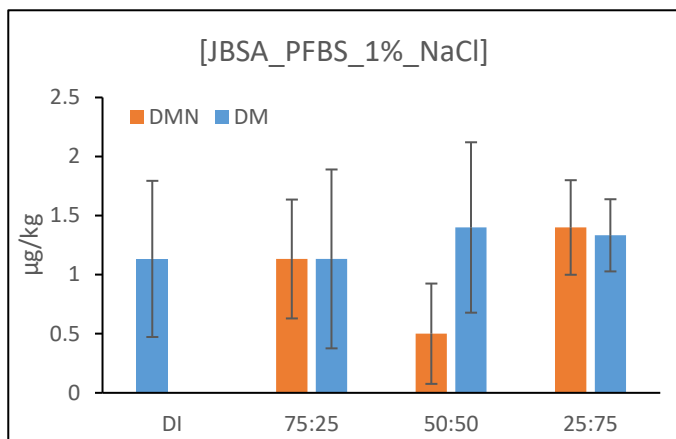


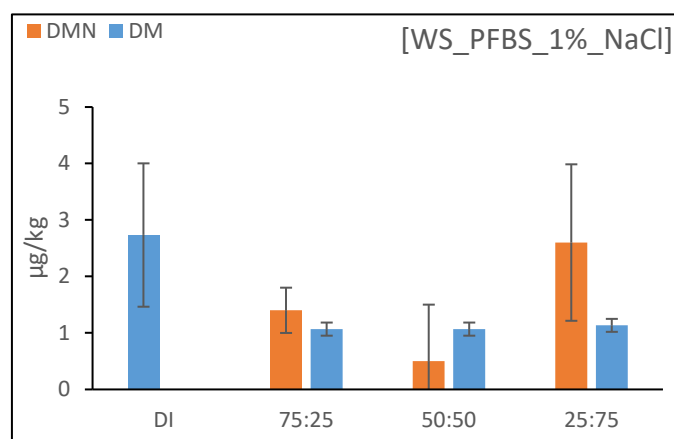
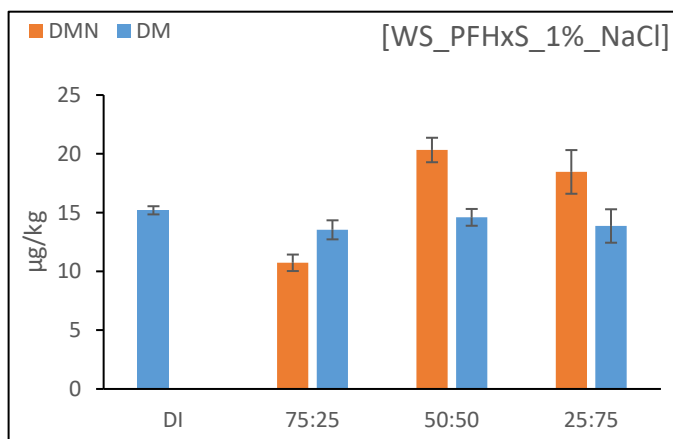
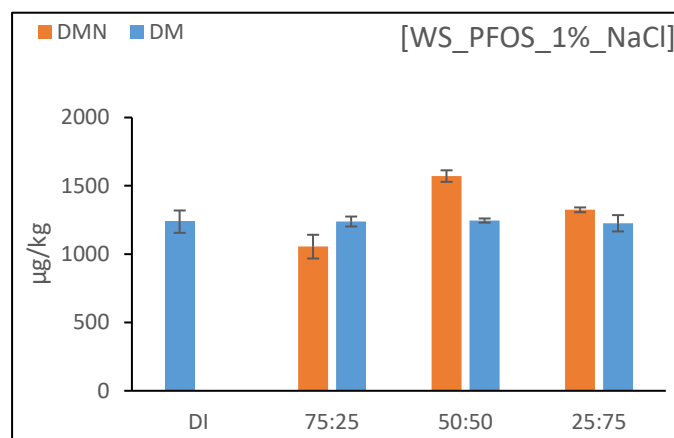
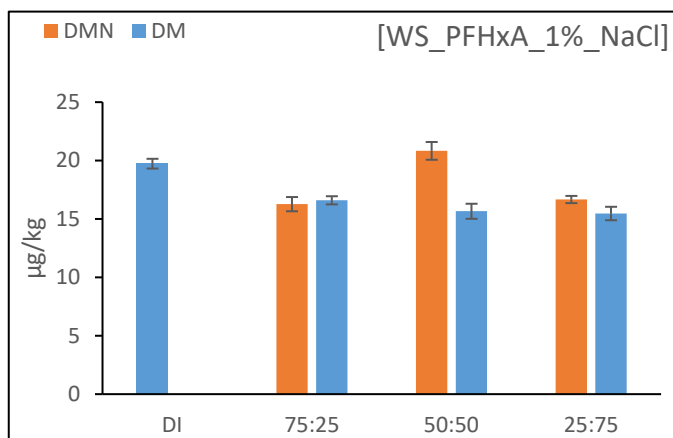
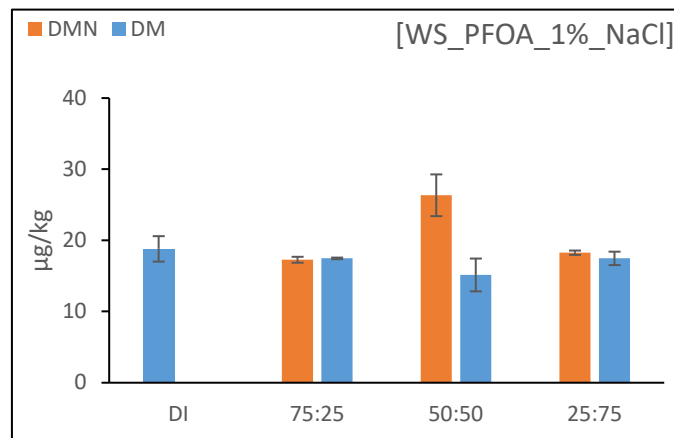
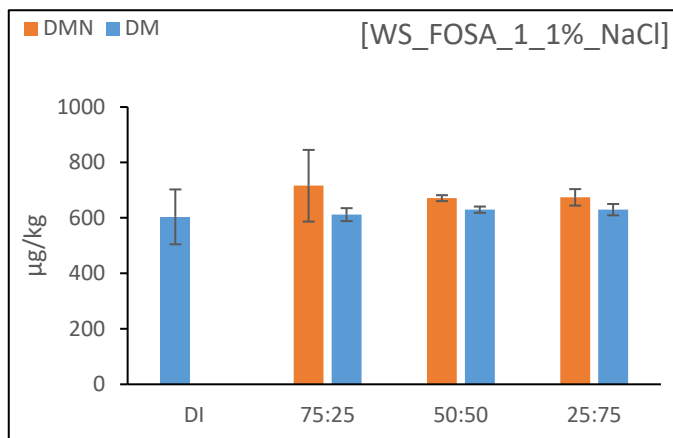












*Wurtsmith arrived at the lab at the end of the project period, thus experimentation and analyses were limited to 1% NaCl.