

FINAL REPORT

High-Performance Treatment of PFAS from Investigation-derived
Waste: Integrating Advanced Oxidation-Reduction and
Membrane Concentration

SERDP Project ER18-1497

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List of Acronyms

AFFF: **a**queous **f**ilm-**f**orming **f**oam
AOP: **a**dvanced **o**xidation **p**rocess
ARP: **a**dvanced **r**eduction **p**rocess
D₂O: **d**euterated water
DI: **d**eionized
ESTCP: **E**nvironmental **S**ecurity **T**echnology **C**ertification **P**rogram
FTS(A): **f**luorot**e**lomer **s**ulfonic **a**cid
GPM: **g**allon **p**er **m**inute
GW: **g**round**w**ater
IC: **i**on **c**hromatography
IDW: **i**nvestigation-**d**erived **w**aste
ISE: **i**on-selective **e**lectrode
LC/MS/MS: **l**iquid **c**hromatography/ **m**ass **s**pectrometry/ **m**ass **s**pectrometry
LMH: **l**iter per square **m**eter per **h**our (flux unit)
LOQ: **l**imit **o**f **q**uantitation
LPM: **l**iter **p**er **m**inute
MeOD: **d**euterated **m**ethanol
NF: **n**anofiltration
NFX/NFW: (the name of two nanofiltration membranes)
NMR: **n**uclear **m**agnetic **r**esonance
PFAS: **p**er- and poly**f**luoro**a**lky**l** **s**ubstance
PFBS: **p**erfluoro**b**utane **s**ulfonic acid
PFCA: **p**erfluoro **c**arboxylic **a**cid
PFHpA: **p**erfluoro**h**eptanoic acid
PFHpS: **p**erfluoro**h**eptane **s**ulfonic acid
PFHxA: **p**erfluoro**h**exanoic acid
PFHxS: **p**erfluoro**h**exane **s**ulfonic acid
PFNA: **p**erfluoro**n**onanoic acid
PFSA: **p**erfluoro **s**ulfonic acid
PFOA: **p**erfluoro**o**ctanoic acid
PFOS: **p**erfluoro**o**ctane **s**ulfonic acid
PI: **p**rincipal **i**nvestigator
RO: **r**everse **o**smosis
SERDP: **S**trategic **E**nvironmental **R**esearch and **D**evelopment **P**rogram
TFC: **t**hin-**f**ilm **c**omposite
TOP: **t**otal **o**xidizable **p**recursor
UCR: **U**niversity of **C**alifornia, **R**iverside
UF: **u**ltrafiltration
UNCC: **U**niversity of **N**orth **C**arolina at **C**harlotte
UV: **u**ltra-**v**iolet

Keywords

Investigation-derived waste (IDW); aqueous film-forming foam (AFFF); advanced oxidation process (AOP); advanced reduction process (ARP); groundwater; per- and polyfluoroalkyl substance (PFAS); nanofiltration; ultra-violet; hydrated electron; hydroxyl radical; defluorination

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Abstract

Introduction and Objectives

This Limited Scope project aims at developing a cost-effective and practical treatment train for the decontamination of investigation-derived waste (IDW). The main target of treatment is the aqueous wastes that contain per- and polyfluoroalkyl substances (PFAS) from the use of aqueous film-forming foam (AFFF). The destruction of PFAS is achieved by the application of the advanced reduction process (ARP) using hydrated electrons and the advanced oxidation process (AOP) using hydroxyl radicals. To ensure the efficient use of chemicals and energies, we combine nanofiltration (NF) to reduce the volume of IDW. The main objective of this project was to evaluate individual treatment modules and the combined treatment train.

Technical Approach

In the one-year time window, we have optimized the operation parameters for the three treatment modules, NF, AOP, and ARP, and evaluated the treatment train of combined processes on two IDW samples- fresh groundwater and AFFF-added groundwater. The AFFF was diluted for 100x to 100,000x for both NF separation and defluorination treatment with UV/sulfite (ARP) and persulfate/hydroxide digestion (AOP). The effect of dilution factor, pH, and the concentration of sulfite and persulfate were systematically investigated. ^{19}F NMR was used to probe the dominant PFAS species in AFFF. Fluoride ion and PFAS compounds on and beyond the EPA Method 537.1 analyte list were quantified to evaluate the degradation treatment and the NF separation.

Results

NF membranes can purify both the original and AFFF-added groundwater. The concentrations for all C4 and longer PFAS are below 50 ng/L in the NF permeate. AOP and ARP have been optimized for the treatment of AFFF solutions. The combination of ARP and AOP can effectively degrade PFAS compounds on the EPA Method 537.1 analyte list in the presence of groundwater matrix and organic additives in AFFF. Unexpectedly, after the ARP-AOP treatment, small amounts of perfluorocarboxylates were detected in the treated NF permeate, suggesting that some neutral PFAS precursors may be present in IDWs and penetrate the NF membrane. With adequate dilution (e.g., 10,000x), at least 8.6 g/L (0.45 M) of organic fluorine can be defluorinated as F^- ion from the original AFFF product. We have identified the dominant PFAS component in the AFFF as a C_6F_{13} based telomeric structure. We have also observed different types of PFAS pollution and transformation in the fresh groundwater versus AFFF-added groundwater. Upon further optimization of the NF and ARP/AOP modules, most PFAS species in the fresh and AFFF-added groundwater are expected to be deeply or completely destructed.

Benefits

PFAS degradation by UV-generated hydrated electron is one of the few competitive methods for practical IDW treatment. To further save the capital cost and the consumption of both chemicals and electricity, NF separation can significantly minimize the volume of IDW. We have shown that the use of UV, sulfite, and persulfate could effectively treat the real groundwater and adequately diluted AFFF. To meet various remediation needs by SERDP and ESTCP, we aim at further improving the efficacy and efficiency for the destruction of concentrated PFAS solutions. We also aim at preventing the membrane penetration by specific PFAS precursors. Future works on the structure-selectivity relationship by the membrane interception, as well as further improvement and integration of the ARP/AOP modules for complex water matrices are proposed.

Executive Summary

Introduction

AFFF-contaminated groundwater contains a complicated mixture of PFASs, including carboxylic acids, sulfonic acids, sulfonamides, fluorotelomers, and many other structures with variable terminal groups and variable chain lengths. For a safe treatment, reuse, and disposal of aqueous IDW samples, the prior technical focus is on the effective and efficient destruction of most PFAS structures. The contaminated groundwater also contains other organic ingredients (e.g., ethylene glycol, propanol, and hydrocarbon surfactants), and possibly petroleum compounds and chlorinated solvents as the co-contaminants. Compared to groundwater, IDW may contain more organic species introduced from the processes of soil extraction, chemical reaction, drilling equipment cleaning, etc. The presence of these co-contaminants complicates the processes for PFAS destruction. The remediation effort requires a destructive treatment of PFASs in IDW. However, current incineration or landfilling treatment of PFAS in liquid wastes requires very high energy consumption and cost in transportation. Recent findings suggest that incomplete PFAS destruction during the incineration of soil and surface water samples may further spread PFAS pollutants through the air. Since IDW treatment needs comprehensive contaminant destruction, direct chemical degradation of a wide variety of PFAS in aqueous IDW at ambient temperature is highly desirable.

The PI has been conducting a regular SERDP project (ER18-1289), which focuses on (1) elucidating the fundamental structure-reactivity mechanisms for PFAS destruction and (2) developing a sorption-destruction treatment train for groundwater remediation. The treatment of IDW in this Limited Scope project (ER18-1497) has very different emphases. First, the volume of IDW is much smaller than a large area of groundwater for remediation. Second, higher concentrations of PFAS may be present in IDW than in groundwater, such as relatively concentrated AFFF diluted in groundwater. Third, IDW may contain a more complicated water matrix than the sorbent regeneration wastes that mainly contain inorganic ions (e.g., chloride, sulfate, nitrate, etc.) and residual methanol.^{10, 11} Hence, it is reasonable to use more aggressive methods to treat IDW at a reasonably higher cost per volume of water than groundwater remediation. Accordingly, we used relatively intense operation conditions for IDW treatment, including (1) elevated dose of chemicals for ARP and AOP and (2) use NF separation to pre-treat IDW by concentrating the PFAS and removing neutral organics. These measures could minimize the spatial footprint, treatment time, energy input, and chemical dosing for IDW decontamination.

Objectives

This SERDP Limited Scope project aims at developing a cost-effective and practical treatment train for the decontamination of IDW. The main target of treatment is the aqueous wastes that contain PFAS from the use of AFFF. The destruction of PFAS is achieved by the application of the advanced reduction process (ARP) using hydrated electrons (e_{aq}^-) and the advanced oxidation process (AOP) using hydroxyl radicals ($HO\bullet$). To ensure the efficient use of chemicals and energies, we combine nanofiltration (NF) membrane to reduce the volume of IDW.

The project has three central technical hypotheses. First, NF can significantly reduce the IDW volume for PFAS destruction. Concentrated PFAS in the NF reject (or retentate) can be treated with minimal amounts of chemical and energy in the following ARP and AOP. Second, the ARP utilizing e_{aq}^- generated from UV/sulfite system is the core of the treatment train for PFAS

destruction. Third, AOP can convert PFAS precursors into perfluorocarboxylates (PFCAs) that are more susceptible to defluorination by ARP. Specific objectives and the associated technical questions we have answered include: (1) optimize the effectiveness of each treatment module on PFAS removal and degradation and (2) investigate the effectiveness of the integrated treatment train on IDW treatment. The full development of this treatment train will meet the criteria of decontaminating IDW for unrestricted disposal and water reuse with reduced space, energy, and chemicals.

Technical Approach

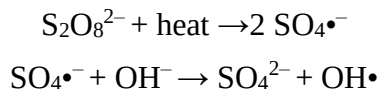
In this Limited Scope project, we have focused on examining the above hypotheses in treating three typical IDW samples: (i) groundwater with historical PFAS pollution, (ii) groundwater after immediate exposure to AFFF, and (iii) relatively concentrated AFFF solutions for harmless disposal. To verify the hypotheses and provide a set of proof-of-concept data for the proposed treatment strategy, the research team has constructed an integrated treatment process that combines chemical treatment and membrane concentration, and used instrumental analysis to evaluate and optimize the treatment. In the one-year time window, we have optimized the operation parameters for the three treatment modules (NF, ARP, and AOP) and evaluated the treatment train of combined processes on the IDW samples. The results obtained to date have shown multiple advantages over a single treatment step and other competing technologies.

Advanced reduction with hydrated electrons. A 600-mL aqueous sample (e.g., original groundwater, AFFF-spiked groundwater, NF concentrates, and NF permeates) was added with Na_2SO_3 (in varying concentrations) and 5 mM NaHCO_3 (only added in non-groundwater samples). The pH was adjusted by 1 M NaOH solution. For a typical sulfite loading at 10 mM in the 600-mL solution, the powder of Na_2SO_3 (756 mg) was directly added without on-shelf storage as a stock solution. The closed-system cylindrical photochemical reactor (**Figure E1**) consisted of a borosilicate glass shell and a quartz immersion well, both of which are double-layered for cooling with circulated water (20 °C) in the jacket. The space between the glass shell and immersion well (~1 cm thickness ring column) was loaded with the 600-mL reaction solution. A magnetic stir bar was placed at the bottom of the reactor, and the stirring speed was set at 360 rpm. An 18 W low-pressure mercury lamp (GPH212T5L/4P/HO) in the immersion well delivered 254 nm UV irradiation to the surrounding solution. The reactor assembly was wrapped in heavy-duty aluminum foil to prevent UV irradiation leaking. After the UV lamp was turned on, aliquots of solution (5 mL each) were taken at time intervals through a 16-gauge stainless steel needle that penetrated the rubber-sealed sampling port. The samples were stored in 7-mL glass scintillation vials at 4 °C prior to analysis.



Figure E1. The UV reactors at UC Riverside.

Advanced oxidation with hydroxyl radicals. A 30-mL aqueous sample was added with varying concentration of K₂S₂O₈ and KOH (2.5 molar equivalent of persulfate). The mixture was loaded in a pressure tube, which was then put into an autoclave at 120 °C for 40 min. Samples were cooled to room temperature naturally prior to analysis. The molar ratio between K₂S₂O₈ and KOH ensures that most sulfate radical is converted to hydroxyl radical:



AFFF and Groundwater Collection and Handling The 3% MS-AFFF (Buckeye 50285) was purchased by the PI and distributed to the labs of the two co-PIs at Vanderbilt and UNCC. The 10 gallons of groundwater sample from NAS JRB Willow Grove was collected by Geosyntec and shipped to Vanderbilt, where the NF separation experiment was conducted. The feed, NF permeate, and NF concentrate were shipped from Vanderbilt to UCR and UNCC, where the AOP-ARP degradation and LC/MS/MS characterization were conducted, respectively.

LC/MS/MS quantification. Standard mix stock solutions were purchased from Wellington Laboratories. Analytes were extracted using Oasis WAX Plus 225 mg, 60 µm extraction cartridge. The concentration of each PFAS was analyzed by an Agilent 1100 liquid chromatography (LC) coupled with an Agilent 6410 triple quadrupole tandem mass spectrometry (MS/MS). The optimized MRM parameters for each PFAS analyte, such as the precursor and product ions, and the limit of quantification (LOQ) are summarized in the full report. Calibration was made based on isotopic dilution.

Nanofiltration separation. Two commercial spiral-wound polyamide-TFC NF membranes, NFX and NFW (manufactured by Synder Filtration), were used in this project. Other membrane element specifications reported by the manufacturer are summarized in [Table E1](#). The NF performance was tested using a stainless steel cross-flow filtration system (Sterlitech™ 1812, [Figure E2](#)). 100 mL permeate and 100 mL retentate of the stabilized system were collected for quality control. The following operating conditions were used: the cross-flow rate was 6 LPM and the applied pressure was 10 bar. Retentate stream was recycled to the feed tank and permeate was collected until target water recovery was reached. In the Willow Grove Groundwater nanofiltration experiment, the NFX membrane was used, and the target recovery was 90%, equivalent to a concentration factor (CF) of 10. After each filtration experiment, the membrane element was flushed with DI water for at least one hour for cleaning.

Table E1. Membrane specifications provided by the manufacturer.^a

Membrane	MWCO (Da)	Flux (LMH/bar)	Rejection MgSO ₄ (NaCl)	pH Range (25 °C)	Cl Tolerance (ppm.hrs)	Max. Temp. (°C)	Spacer
NFX	150-300	34-43/7.6	99% (40%)	3-9.5	500	50	31 mil
NFW	300-500	77-85/7.6	97% (20%)	4-9	500	50	31 mil

^aMore details can be found:

<https://synderfiltration.com/2014/wp-content/uploads/2018/11/NFX-TFC-150-300Da-Sanitary-Specsheet.pdf>
<https://synderfiltration.com/2014/wp-content/uploads/2018/11/NFW-TFC-300-500Da-Sanitary-Specsheet.pdf>

LMH: liter per square meter per hour (flux unit).

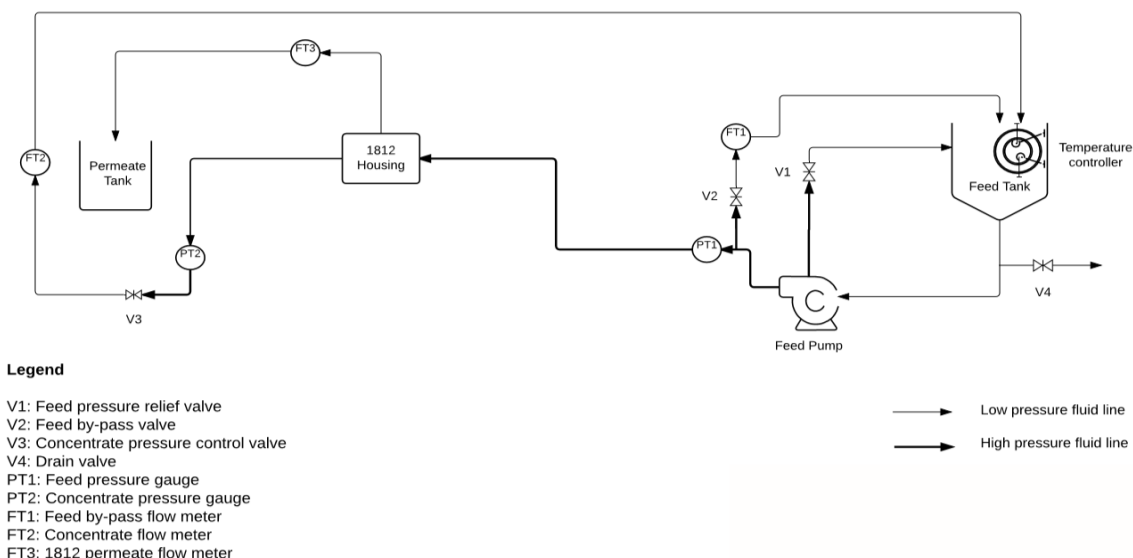


Figure E2. Sterlitech™ 1812 cross-flow filtration system.

Results and Discussion

PFAS removal from groundwater. The LC/MS/MS analyte list contained C4 to C10 perfluorosulfonates, C4 to C14 perfluorocarboxylates, 4:2, 6:2, and 8:2 fluorotelomer sulfonates, and three perfluorooctane sulfonamides with $-\text{NH}_2$, $-\text{NHMe}$ and $-\text{NHEt}$ end groups. **Table E2** shows the quantification of all these PFAS compounds in the feed, permeate, and reject from NF treated fresh groundwater (Fresh GW). In the contaminated groundwater, PFOS and PFHxS are the two dominating species, followed by PFOA and PFHxA. C4, C5, and C7 PFCAs and PFSAs also take significant portions of the total quantifiable PFAS. In this project, the limit of quantification (LOQ) of the LC/MS/MS analysis is 50 ng/L (or 50 ppt) for each compound. Structures longer than C9 either had concentrations lower than 50 ng/L (<LOQ) or not detected (ND). With a few exceptions (see the footnotes in tables), most individual compounds had a concentration factor of 3 to 7. **Most importantly, all compounds in the NF permeate went below 50 ng/L, showing the promise of using nanofiltration to remove the listed PFAS compounds from groundwater IDW.** At the USEPA's current health advisory level for PFOA and PFOS, **the NF-treated permeate may be allowed for disposal.** We note that DI water flushing of the membrane system contained 6:2 FTS so that this structure may also come from certain parts of the membrane system. We also note that if a total concentration of 70 ppt for all PFAS compounds is the treatment goal, the LC/MS/MS analysis will need to further lower the LOQ to quantify the ΣPFAS . At this low concentration, total fluorine analysis does not apply because the detection of < 70 ppt fluoride ion is very difficult.

Table E2. LC/MS/MS analysis results for groundwater samples (unit: ng/L).

<i>Fresh GW</i>	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
Feed	233.3	278.6	1062.1	101.3	1110.6	<LOQ ^a	ND ^b
Permeate	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
Reject	1101.8	1496.1	7516.9	338.4	1022.0 ^c	<LOQ	ND

<i>Fresh GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA ^d
Feed	133.9	136.9	506.9	99.2	408.8	<LOQ	<LOQ	<LOQ	<LOQ
Permeate	<LOQ	ND	<LOQ	ND	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Reject	605.3	799.1	2567.1	531.5	1788.5	<LOQ	<LOQ	<LOQ	<LOQ

<i>Fresh GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
Feed	ND	306.9	<LOQ	<LOQ	ND	<LOQ
Permeate	ND	181.6 ^e	<LOQ	<LOQ	ND	<LOQ
Reject	ND	1564.4	397.6	92.6	ND	<LOQ

^aLOQ = limit of quantitation (50 ng/L for each compound), <LOQ indicates the detection of peaks with a calculated concentration below 50 ng/L.

^bND = not detected.

^cDubious result that does not follow the concentration factor suggested by other data.

^dPFDoA (C12), PFTrDA (C13), and PFTeDA (C14) were not detected in all samples.

^eThe detection of 6:2 FTS in this sample might be from the NF system as the flushing using DI water also observed this compound.

PFAS removal from AFFF-added groundwater. For AFFF-added groundwater, a majority of PFAS compounds are still <LOQ in the NF permeate (**Table E3**), with the exceptions of PFHxS, PFHxA, PFOA, and 8:2 FTS. Nanofiltration is supposed to remove long-chain charged PFAS. The detection of those C6, C8, and even C10 structures is thus attributed to the presence of some neutral PFAS structures that can penetrate NF membrane. As the 3% AFFF is a highly viscous mixture of multiple organics, even after 1000x dilution the organics might also be able to interfere with the normal PFAS interception by NF membrane. We point this out because we later realized that some PFAS compounds were also observed after the fresh groundwater permeate was treated by ARP-AOP (see the section of “*Treatment of NF separation streams*”). Nevertheless, comparing with the concentrations in the feed and reject, **the NF treatment is highly effective in rejecting most PFAS from entering the permeate.**

Table E3. LC/MS/MS analysis results for AFFF-added groundwater samples (unit: ng/L).^a

<i>AFFF+GW</i>	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
Feed	181.7	206.2	781.0	<LOQ ^b	488.8 ^b	<LOQ	ND
Permeate	<LOQ	<LOQ	75.5	<LOQ	<LOQ	<LOQ	ND
Reject	939.9	1042.4	4166.9	<LOQ ^b	3610.4	92.2	ND

<i>AFFF+GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA
Feed	489.2	378.0	5109.4	479.8	6490.5	<LOQ	<LOQ	<LOQ	<LOQ
Permeate	<LOQ	ND	132.9	ND	95.6	<LOQ	<LOQ	<LOQ	<LOQ
Reject	4368.0	1123.8	14786.0 ^c	526.6 ^d	663.6 ^d	<LOQ	88.4	<LOQ	<LOQ

<i>AFFF+GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
Feed	308.4	4044.2	2840.7	<LOQ	ND	<LOQ
Permeate	<LOQ	1234.6 ^e	133.3	<LOQ	ND	<LOQ
Reject	1454.2	8097.7	2559.0	63.7	ND	<LOQ

^aLC-MS/MS analysis in the samples with diluted AFFF matrix is more challenging than the original groundwater.

^bDubious results that are lower than in the original groundwater.

^cDubious result that does not follow the concentration factor suggested by other data, probably due to the deviation from the calibration curve at a high concentration.

^dDubious result that does not follow the concentration factor suggested by other data by unknown reasons.

^eThe detection of 6:2 FTS in this sample might be from the NF system as the flushing using DI water also observed this compound.

Comparison between ARP-AOP and AOP-ARP sequential treatment strategies. Both the ARP and AOP were systematically optimized in this project. Both processes can be used as the first treatment step of the combined reduction/oxidation treatment chain for the specific AFFF that mainly contained an n=6 telomeric structure. Because the telomeric structure was oxidized into a series of PFCAs¹ that are inert to further oxidation with HO•, ARP was used to treat the PFCA products. On the other hand, if ARP was used first, the remaining ~40% of C–F bonds should be in the H-rich transformation products, which underwent deep destruction by the oxidation with HO•. We measured the results of the two treatment sequences (Table E4). No significant difference between the two sequences was observed. However, we must highlight that the **similarity between the two treatment strategies can only be applied to the case where n=6 fluorotelomers are the dominant AFFF component**. If the IDW contained species other than 6:2 FTSA structures, the sequence of applying AOP and ARP may have a significant difference. For example, if 4:2 FTSA is the dominant species, the use of ARP as the first step will incur a long treatment time or limited defluorination. If the IDW mainly contained perfluorocarboxylates or sulfonates (i.e., other than telomeric structures), the first application of AOP will not achieve any defluorination because HO• only works for the degradation of telomeric PFAS.

Table E4. The comparison between ARP-AOP and AOP-ARP treatment chain.

AFFF sample	ARP-AOP			AOP-ARP		
	Step 1 ARP	Step 2 AOP	Total	Step 1 AOP	Step 2 ARP	Total
10,000x diluted	5750 ppm	1760 ppm	7510 ppm	4800 ppm	2800 ppm	7600 ppm
100,000x diluted	5000 ppm	3100 ppm	8100 ppm	4900 ppm	3700 ppm	8600 ppm

The ARP-AOP and AOP-ARP treatment strategies were further optimized (Figure E3). The results collectively show that ARP-AOP could achieve a higher overall defluorination to about 9100 ppm F⁻ (9.1 g/L or 0.479 M) from the original 3% AFFF.

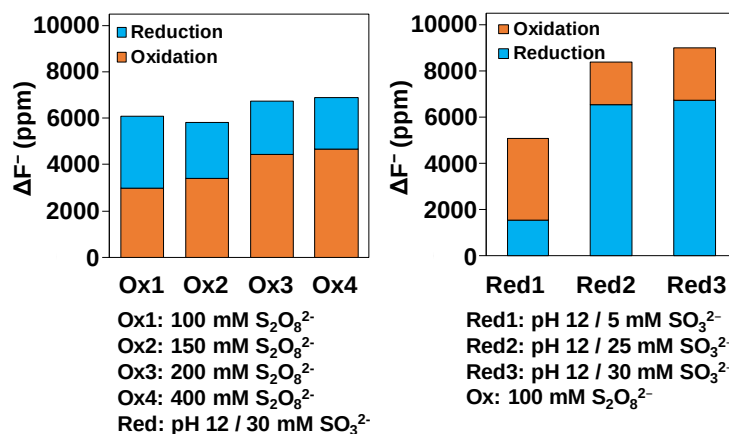


Figure E3. Comparison of AOP-ARP (left) and ARP-AOP (right) at varying operation parameters. The AOP-ARP started from 1000x diluted AFFF (then further diluted for 10x for ARP), and the ARP-AOP directly started from 10000x diluted AFFF (then oxidized without further dilution).

Treatment of NF separated streams. The initial NF separation tests were conducted by using the two membrane materials, NFX and L-NFW (Table E1), with a low [permeate:reject] ratio of 30:70. The feed contained two dilution factors for AFFF- 100x and 1000x in DI water. The reject and permeate were further diluted for 100x and 10x, respectively, so that the samples are at the 10,000x level for efficient ARP defluorination. The results are shown in Figure E4. The two membrane materials showed similar retention of PFAS compounds from the AFFF solution feed. The high solution pH was critical for the level of defluorination. The two dilution folds of AFFF in the NF feed does not show a significant difference in the defluorination treatment by ARP. In stark comparison, all NF permeates did not show a significant defluorination by ARP (Figure E5), indicating that the majority of, if not all, the PFAS components in AFFF has been rejected by both NF membrane materials.

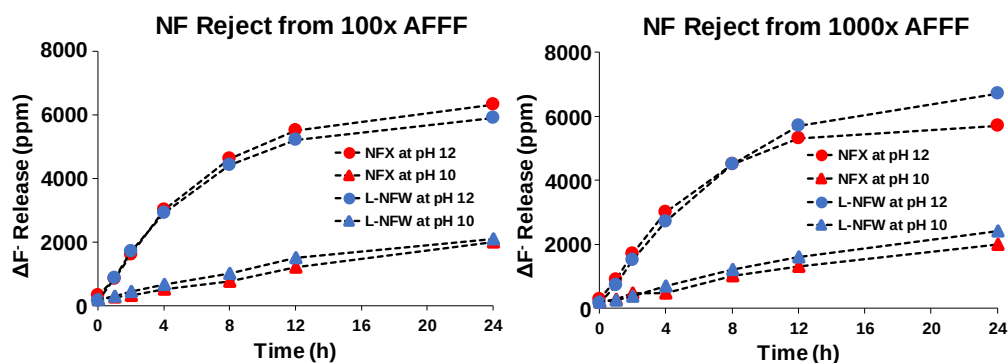


Figure E4. Defluorination of the NF reject of AFFF solutions with two dilution levels, at two pH values, and from two membrane materials. Reaction conditions: 10 mM Na₂SO₃ and 5 mM NaHCO₃ at 20 °C.

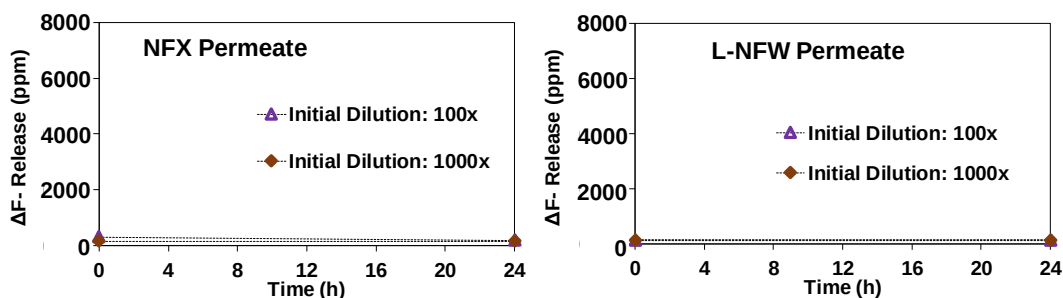


Figure E5. Defluorination of the NF permeate of AFFF solutions with two dilution levels and from two membrane materials at pH 12.

The LC/MS/MS analysis (Table E5) identified high concentrations of PFCAs in the ARP-AOP treated feed. This is strong evidence for the presence of telomeric PFAS in the AFFF. In particular, the dominating PFCA is n=4 PFPeA. The n=3 PFBA and n=5 PFHxA are less than n=4 PFPeA. From our and other earlier studies,¹ n=4 PFCA is the dominating product from the oxidative decomposition of n=6 FTSA and FTCA. This result evidences the dominance of n=6 telomeric precursor in the AFFF. The sum of all quantifiable PFAS compounds in the treated feed was 577 μg/L in the treated feed, or normalized to 577 mg/L (including carbon and other atoms) in the original AFFF. In comparison to the lost 3500 ppm of ΔF⁻, there should be more precursors not degraded yet. More interestingly, from the comparison shown in Table E6, although NF rejected most quantifiable PFAS compounds from entering the permeate, after the ARP-AOP

treatment, increased concentrations of PFCAs also showed up. All perfluorosulfonates in the treated permeate remained < 50 ng/L. This is a strong evidence that no precursor of perfluorosulfonates could penetrate the NF membrane, or the AFFF does not contain a significant amount of sulfonate precursors.

Table 1. LC/MS/MS analysis results for ARP-AOP treated AFFF-added groundwater samples (unit: ng/L).^a

<i>Treated AFFF+GW</i>	PFBS	PFPeS	PFHxA	PFHpS	PFOS	PFNS	PFDS
<i>Treated Feed</i>	340.9	617.3	2259.5	<LOQ	88.6	<LOQ	ND
<i>Treated Permeate</i>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND

<i>Treated AFFF+GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA
<i>Treated Feed</i>	165433	247106	95786	38893	22350	3798.4	107.1	<LOQ	<LOQ
<i>Treated Permeate</i>	823.2	1396.2	2463.8	2964.4	4484.3	3257.3	107.5	<LOQ	<LOQ

<i>Treated AFFF+GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
<i>Treated Feed</i>	ND	262.4	61.0	<LOQ	ND	<LOQ
<i>Treated Permeate</i>	ND	381.2	<LOQ	<LOQ	ND	<LOQ

^aThe ARP-AOP treatment on the NF reject was not conducted due to the formation of a high concentration of PFCAs (indicating incomplete treatment) from the feed. The NF reject contained 10x higher concentration of PFAS than the feed.

Table 2. Comparison of the individual PFAS compound concentrations in the AFFF-added original groundwater before and after the ARP-AOP treatment (concentration unit is ng/L).

PFAS	Feed			Permeate			Reject		
	Before	After	Change	Before	After	Change	Before	After ^a	Change ^a
PFBS	181.7	340.9	↑ 88%	<LOQ	<LOQ	-	939.9	N.A.	N.A.
PFPeS	206.2	617.3	↑ 199%	<LOQ	<LOQ	-	1042.4	N.A.	N.A.
PFHxA	781.0	2259.5	↑ 189%	75.5	<LOQ	↓ 34+%	4166.9	N.A.	N.A.
PFHpS	<LOQ ^b	<LOQ	-	<LOQ	<LOQ	-	<LOQ	N.A.	N.A.
PFOS	488.8	88.6	↓ 82%	<LOQ	<LOQ	-	3610.4	N.A.	N.A.
PFNS	<LOQ	<LOQ	-	<LOQ	<LOQ	-	92.2	N.A.	N.A.
PFDS	ND	ND	-	ND	ND	-	ND	N.A.	N.A.
PFBA	489.2	165433	↑ 33717%	<LOQ	823.2	↑ 1546+%	4368.0	N.A.	N.A.
PFPeA	378.0	247106	↑ 65272%	ND	1396.2	↑ 2692+%	1123.8	N.A.	N.A.
PFHxA	5109.4	95786	↑ 1775%	132.9	2463.8	↑ 1754%	14786	N.A.	N.A.
PFHpA	479.8	38893	↑ 8006%	ND	2964.4	↑ 5829+%	526.6	N.A.	N.A.
PFOA	6490.5	22350	↑ 244%	95.6	4484.3	↑ 4591+%	663.6	N.A.	N.A.
PFNA	<LOQ	3798.4	↑ 7497+%	<LOQ	3257.3	↑ 6415+%	<LOQ	N.A.	N.A.
PFDA	<LOQ	107.1	↑ 114+%	<LOQ	107.5	↑ 115+%	88.4	N.A.	N.A.
4:2 FTS	308.4	ND	↓ 84+%	<LOQ	ND	-	1454.2	N.A.	N.A.
6:2 FTS	4044.2	262.4	↓ 94%	1234.6	381.2	↓ 69%	8097.7	N.A.	N.A.
8:2 FTS	2840.7	61.0	↓ 98%	133.3	<LOQ	↓ 62+%	2559.0	N.A.	N.A.
FOSA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	63.7	N.A.	N.A.

^aComparison not made yet because effective treatment of the 5x concentrate of the 1000x AFFF seemed challenging using the current chemical dosing.

^bComparisons involving “<LOQ” and “ND” used <50 ng/L as the calculation basis.

Because the total PFAS in the permeate should be much less than in the feed, the reason for the incomplete destruction of the precursors for those PFCAs during the ARP is unknown. The most probable reason is the penetration of neutral organic additives into the permeate. **If this is true, an oxidation treatment before the membrane filtration could be imperative. We will systematically investigate the effect of pre-oxidation in future work.** More importantly, although the majority of quantifiable PFAS compounds in the untreated permeate is < 50 ng/L, the release of a total of 15.5 µg/L of PFCAs in the treated permeate suggests that some PFAS precursors can penetrate NF. Because NF material has been confirmed to be able to reject most charged PFAS compounds, it is highly possible that **a small fraction of PFAS compounds in AFFF might be in the neutral molecular form** (e.g., alcohol, or some other neutral molecules as the unreacted building materials used for the synthesis of fluoro-surfactant molecules). Future work is imperative to elucidate the underlying mechanism for the penetration through the NF membrane and the resistance against the degradation treatment.

Because PFCAs are the most susceptible PFAS for ARP-AOP destruction, the detection of PFCAs in the treated NF feed and permeate only indicates the need for further optimization of the ARP and AOP treatment modules. We have identified several effective strategies to treat highly concentrated PFAS and will apply them in the future work of this direction.

This Limited-Scope Project has investigated and obtained **highly positive main conclusions** in the following aspects:

1. The real PFAS-contaminated groundwater (low PFAS contents) and AFFF-added groundwater (high PFAS contents) can be purified by commercial nanofiltration (NF) membranes. Analytical results show that the concentrations for all C4 and longer PFAS compounds on and beyond the EPA Method 537.1 analyte list are below 50 ng/L in the NF permeate.
2. The advanced reduction (ARP, using UV/sulfite operated at pH≥12.0 and 20 °C) and advanced oxidation (AOP, using heat-activated persulfate/hydroxide at ≤120 °C) have been specifically optimized for the treatment of AFFF solutions. The combination of ARP and AOP can effectively degrade all PFAS compounds on the EPA Method 537.1 analyte list in the presence of groundwater matrix and organic additives from the AFFF. With adequate dilution (e.g., 10,000x), at least 8.6 g/L (0.45 M) of organic fluorine can be defluorinated as F⁻ ion from the original AFFF product.
3. Based on the structure-reactivity relationship established by the PI, our analytical work, including LC/MS/MS analysis, ¹⁹F NMR, and fluoride ion determination, have successfully identified the dominant PFAS component in the AFFF as a C₆F₁₃ telomeric structure. Other minor impurities with various chain lengths are also present. Perfluorosulfonates are not a significant component in the AFFF. We have also identified different types of PFAS pollution and transformation in the fresh NAS JRB Willow Grove groundwater and the AFFF-added groundwater.
4. The results achieved to date have confirmed that, upon further optimization of the NF and ARP/AOP modules, most PFAS species in the groundwater and AFFF-added groundwater can be deeply or completely destructed.

Implications of Future Research and Benefits

This Limited-Scope Project has also identified **a series of technical challenges and unexpected/intriguing phenomena** that are imperative for IDW treatment in the following aspects:

1. Although NF treatment can produce the permeate containing <50 ppt of each PFAS compound, after the ARP-AOP treatment, a small amount of PFCA mixtures was detected in the treated permeate from both the fresh groundwater and AFFF-added groundwater. This is a critical point for the application of membrane filtration in PFAS remediation. The precursors for the generated PFCAs may be neutral molecules that can penetrate the NF membrane. Further detailed studies on the structure-selectivity relationship by the membrane interception are essential for the design and application of separation technology for the PFAS remediation practice.
2. The current UV/sulfite using 10–30 mM Na₂SO₃ as the source of hydrated electrons, 254 nm UV low-pressure mercury lamp, and the maintained 20 °C reaction temperature could not effectively treat AFFF with 1000x or lower dilution folds. However, treating concentrated PFAS in a small volume of water is highly desirable to save the capital cost and the consumption of both chemicals and electricity. Currently, we believe that PFAS degradation enabled by UV-generated hydrated electron is one of the few highly competitive methods for the practical treatment of concentrated PFAS. Further improvement of the ARP process is thus imperative to provide an effective and efficient technology for the remediation efforts led by SERDP and ESTCP.
3. We have observed significant defluorination from the AFFF and the transformation of a wide collection of PFAS compounds in the fresh groundwater and AFFF-added groundwater. A limited set of data also suggests that the NF filtration may improve the defluorination in the reject, probably by allowing the organic additives to go with the permeate. Detailed studies on the molecular transformation of individual PFAS structures, especially in the mixture of multiple PFAS species and in the groundwater mineral matrix and AFFF organic matrix, are necessary toward further optimizing the degradation technologies for IDW treatment, safe AFFF disposal, and fire-fighting pipeline cleaning, and so on.

Continued works on this project will be highly beneficial. The plans have been proposed in the full report and the project continuation proposal. We expect that all technical details to be studied by the extended work will push the NF-ARP-AOP treatment train into the practical application to treat either groundwater or specific concentrated samples (e.g., IDW and decommissioned AFFF) to the desired level that allows either safe discharge or reuse. We have high confidence in the working nature of this technology and our research capability to achieve the desired results.

Objective

This SERDP Limited Scope project aims at developing a cost-effective and practical treatment train for the decontamination of investigation-derived waste (IDW) generated from DoD sites. The main target of treatment is the aqueous wastes that contain per- and polyfluoroalkyl substances (PFAS) from the use of aqueous film-forming foam (AFFF). The destruction of PFAS is achieved by the application of the advanced reduction process (ARP) using hydrated electrons (e_{aq}^-) and the advanced oxidation process (AOP) using hydroxyl radicals ($HO\bullet$). To ensure the efficient use of chemicals and energies, we combine nanofiltration (NF) membrane to reduce the volume of IDW.

The project has three central technical hypotheses. **First**, NF can significantly reduce the IDW volume for PFAS destruction. Concentrated PFAS in the NF reject (or retentate) can be treated with minimal amounts of chemical and energy in the following ARP and AOP. The NF permeate contains no (ideally) or significantly reduced concentrations of PFAS, and can thus be reused on-site or discharged safely. Therefore, the NF can significantly reduce the spatial footprint, treatment time, energy input, and chemical dosing of the subsequent destruction treatment. This step is optional, depending on the concentration and volume of specific IDW samples. **Second**, the ARP utilizing e_{aq}^- generated from UV/sulfite system is the core of the treatment train for PFAS destruction. This defluorination technology is one of the very few options that are both effective in PFAS degradation and compatible with practical water treatment conditions. **Third**, AOP can convert PFAS precursors into perfluorocarboxylates (PFCAs) that are more susceptible to defluorination by ARP. Our earlier studies have revealed that PFCAs are the most susceptible substrate for the defluorination by ARP. AOP can also release the residual fluorines after a deep defluorination by ARP.

Specific objectives and the associated technical questions we have answered include:

Objective 1. Optimize the effectiveness of each treatment module on PFAS removal and degradation

- Whether NF can achieve the energy-efficient concentration of IDW, rejecting most of the target contaminants, and resulting in a permeate for safe liquid discharge?
- What parameters for ARP and AOP can achieve intensive defluorination in concentrated IDW?

Objective 2. Investigate the effectiveness of the integrated treatment train on IDW treatment

- What combination and sequence of process modules can achieve optimized PFAS removal?
- What are the contaminant removal percentage and end products from the treatment train?

In this Limited Scope project, we have focused on examining the above hypotheses in treating three typical IDW samples: (i) groundwater with historical PFAS pollution, (ii) groundwater after immediate exposure to AFFF, and (iii) relatively concentrated AFFF solutions for harmless disposal. To verify the hypotheses and provide a set of proof-of-concept data for the proposed treatment strategy, the research team has constructed an integrated treatment process that

combines chemical treatment and membrane concentration, and used instrumental analysis to evaluate and optimize the treatment.

In the one-year time window, we have optimized the operation parameters for the three treatment modules (NF, ARP, and AOP) and evaluated the treatment train of combined processes on the IDW samples. The results obtained to date have shown multiple advantages over a single treatment step and other competing technologies. The findings have identified key technical aspects to further improve the treatment of IDW in a more comprehensive follow-on project. The extended study will allow potential pilot-scale or field-scale validations of the proposed treatment train. The full development of this treatment train will meet the criteria of decontaminating IDW for unrestricted disposal and water reuse with reduced space, energy, and chemicals.

Background

General analysis of the problem and proposed technology

AFFF-contaminated groundwater contains a complicated mixture of PFASs, including carboxylic acids, sulfonic acids, sulfonamides, and many other structures with variable terminal groups and variable lengths.²⁻⁴ In particular, a large number of fluorotelomers with $-(CH_2)_n-$ linkers connecting to a vast diversity of end groups and hydrocarbon moieties have been used in AFFF.⁴⁻⁶ For a safe treatment, reuse, and disposal of aqueous IDW samples, the prior technical focus is on the effective and efficient destruction of most PFAS structures.

The contaminated groundwater also contains other organic ingredients (e.g., ethylene glycol, propanol, and hydrocarbon surfactants), and possibly petroleum compounds and chlorinated solvents as the co-contaminants. Compared to groundwater, IDW may contain more organic species introduced from the processes of soil extraction, chemical reaction, drilling equipment cleaning, etc. The presence of these co-contaminants complicates the processes for PFAS destruction.

The remediation effort requires a destructive treatment of PFASs in IDW. However, current incineration or landfilling treatment of PFAS in liquid wastes requires very high energy consumption and cost in transportation. Recent findings suggest that incomplete PFAS destruction during the incineration of soil and surface water samples may further spread PFAS pollutants through the air.⁷ Physical removal such as carbon adsorption and ion-exchange is suitable for groundwater remediation,⁸⁻¹⁰ but disposal or regeneration of the exhausted materials requires additional steps and might not be suitable for IDW treatment. In addition, IDW liquid composition is much more complicated than groundwater, and the capacity of sorption methods may be quickly exhausted by competition from non-target co-contaminants, thus reducing the removal efficiency of PFAS and increasing the demand of adsorbents. Since IDW treatment needs comprehensive contaminant destruction, direct chemical degradation of a wide variety of PFAS in aqueous IDW at ambient temperature is highly desirable.

The PI has been conducting a regular SERDP project (ER18-1289), which focuses on (1) elucidating the fundamental structure-reactivity mechanisms for PFAS destruction and (2) developing a sorption-destruction treatment train for groundwater remediation. The treatment of IDW in this Limited Scope project (ER18-1497) has very different emphases. First, the volume of IDW is much smaller than a large area of groundwater for remediation. Second, higher concentrations of PFAS may be present in IDW than in groundwater, such as relatively

concentrated AFFF diluted in groundwater. Third, IDW may contain a more complicated water matrix than the sorbent regeneration wastes that mainly contain inorganic ions (e.g., chloride, sulfate, nitrate, etc.) and residual methanol.^{11, 12} Hence, it is reasonable to use more aggressive methods to treat IDW at a reasonably higher cost per volume of water than groundwater remediation. Accordingly, we used relatively intense operation conditions for IDW treatment, including (1) elevated dose of chemicals for ARP and AOP and (2) use NF separation to pre-treat IDW by concentrating the PFAS and removing neutral organics. These measures could minimize the spatial footprint, treatment time, energy input, and chemical dosing for IDW decontamination.

A brief review of defluorination technologies

A complete destruction of PFAS requires breaking the highly recalcitrant C–F bonds (i.e., defluorination). In general, biological degradation is still ineffective in PFAS degradation. Many early proposed chemical defluorination technologies have been out of consideration for engineering applications. Major limitations of those technologies include (1) extreme working pH and/or temperature, (2) need for expensive or exotic reagents/materials, (3) limited PFAS species that can be effectively treated, and (4) lack of information on the performance in the practical water matrix.¹³ Currently, ARP and AOP principles have been utilized by a series of promising technologies, such as plasma treatment, electrochemical treatment, ultrasonication, photocatalysis, or homogeneous photochemical reactions. Details of these technologies will not be discussed in this report. It is important to note the unique advantage of the homogeneous photochemical approach; the reaction is not limited by the mass transfer at the heterogeneous water-solid or water-gas interface. For example, short-chain substrates such as TFA, PFBA, and PFBS have been challenging for most heterogeneous treatment, but they can be effectively degraded by UV/sulfite ARP. Therefore, defluorination using UV/sulfite is a viable option for IDW treatment. In particular, our own tests have confirmed that the PFAS defluorination activity by UV/sulfite is not hindered in water matrices containing carbonate, ammonia, chloride, and methanol. These features make the UV/sulfite a highly competitive technology for IDW treatment.

Technical background of ARP and AOP used in this project

Hydrated electrons can be generated from sulfite (SO_3^{2-}), iodide (I^-), and selected organic molecules under UV irradiation.¹⁴⁻¹⁶ The UV/sulfite system holds high promise in destructing PFASs in IDW because (1) UV irradiation has been widely-adopted water and wastewater treatment process for disinfection and organics destruction, (2) sulfite is inexpensive and readily oxidized to sulfate (SO_4^{2-}), a ubiquitous and nontoxic natural water component, and (3) sulfite has already been widely used in wastewater treatment (e.g., eliminating the residual chlorine).¹⁷⁻¹⁹ All reactions used the very common 254 nm low-pressure mercury lamp at 20 °C. The PI's lab has elucidated the structure-reactivity relationship of major PFAS categories, including perfluorocarboxylates, perfluorodicarboxylates, perfluorosulfonates, fluorotelomers, and perfluoro ether carboxylates.^{20, 21} PFCAs are the most susceptible structures to be degraded and mineralized. The carboxylate group allows a special decarboxylation pathway, which is critical for a deep defluorination. The rate and extent of degradation of other PFAS structures are highly dependent on the chain length. A treatment of 60,000-fold diluted AFFF using the same reaction system has observed a very similar degradation profile for individual PFAS compounds.²² The PI's lab has also significantly improved the efficacy and efficiency of UV/sulfite system by operating the reaction at pH 12.²³ At pH 12, the favorable decarboxylation pathway can be further enhanced so that the defluorination percentage (deF%) became much higher than the previously

used pH 9.5. The other unfavorable pathway is H/F exchange. The pH 12 enabled the cleavage of multiple recalcitrant C–F bonds that could not be cleaved at pH 9.5. However, as the formation of C–H bonds significantly enhance the neighboring C–F bonds, the defluorination through H/F exchange will eventually stop when all remaining C–F bonds are too strong.

For the same reason, the direct treatment of fluorotelomers using ARP is not efficient. For example, without the decarboxylation degradation pathway that only applies to PFCA, the 6:2 FTCA and 6:2 FTSA degraded much slower than PFHpA, which has the same $C_6F_{13}-$ chain. For short fluorotelomers, the ARP degradation was very sluggish because of the strong C–F bonds in short fluoroalkyl chains.¹⁹ In reality, for IDW treatment, numerous fluorotelomer-based surfactants have been identified in AFFF and contaminated groundwater. A large number of PFAS surfactants have been used for AFFF formulations.^{24, 25} Early studies on PFAS detection used the total oxidizable precursor (TOP, using persulfate in alkaline solutions) assay to convert fluorotelomers into PFCAs in various chain lengths.¹ Our mechanistic study under ER18-1289 has systematically investigated the details. The AOP treatment of fluorotelomers not only generates PFCAs but also releases a significant portion of molecular fluorines as F^- ion. Because $HO^\bullet$ cannot degrade the PFCA products, the following ARP is critical for further defluorination. Reversely, AOP will be useful to further defluorinate the ARP treatment residuals that are rich in C–H bonds. The AOP-ARP and ARP-AOP sequential strategies are expected to be helpful in the treatment of IDW, which always contains a mixture of various PFSA structures.

Technical background of NF separation used in this project

Because both ARP and AOP require at least mM-levels of chemicals (sulfite and persulfate, respectively) as the source of e_{aq}^- and $HO^\bullet$, if IDW contained only ppt or ppb level of PFAS, the efficiency of chemical use will be very low. A concentration of the PFAS in IDW through nanofiltration is thus highly beneficial to minimizing the chemical consumption and capital costs (e.g., number of UV lamps, energy consumption, and space requirement). Hence, if IDW can be concentrated, a relatively small amount of Na_2SO_3 will achieve adequate sulfite concentration. Earlier studies have shown that nanofiltration (NF) can effectively remove charged PFAS compounds.²⁶⁻²⁸ In comparison, ultrafiltration (UF) has poor rejection for low molecular weight PFAS,^{26, 29} and reverse osmosis (RO), though capable of rejecting most charged PFAS very effectively,^{30, 31} requires much higher applied pressure (and thus higher capital cost and energy consumption). In this project, we used NF concentration to treat the original groundwater and AFFF-added groundwater. The concentrate/reject is expected to have significantly elevated concentrations of PFAS for AOP-ARP degradation. Because NF treatment will let neutral molecules pass the membrane, we also expected to have lower organic content in the concentrate/reject than in the feed. This aspect may be an additional benefit to the AOP treatment.

Materials and Methods

Advanced reduction with hydrated electrons

A 600-mL aqueous sample (e.g., original groundwater, AFFF-spiked groundwater, NF concentrates, and NF permeates) was added with Na_2SO_3 (in varying concentrations) and 5 mM $NaHCO_3$ (only added in non-groundwater samples). The pH was adjusted by 1 M NaOH solution. For a typical sulfite loading at 10 mM in the 600-mL solution, the powder of Na_2SO_3 (756 mg) was directly added without on-shelf storage as a stock solution.

The closed-system cylindrical photochemical reactor (**Figure 1**) consisted of a borosilicate glass shell and a quartz immersion well, both of which are double-layered for cooling with circulated water (20 °C) in the jacket. The space between the glass shell and immersion well (~1 cm thickness ring column) was loaded with the 600-mL reaction solution. A magnetic stir bar was placed at the bottom of the reactor, and the stirring speed was set at 360 rpm. An 18 W low-pressure mercury lamp (GPH212T5L/4P/HO) in the immersion well delivered 254 nm UV irradiation to the surrounding solution. The reactor assembly was wrapped in heavy-duty aluminum foil to prevent UV irradiation leaking. After the UV lamp was turned on, aliquots of solution (5 mL each) were taken at time intervals through a 16-gauge stainless steel needle that penetrated the rubber-sealed sampling port. The samples were stored in 7-mL glass scintillation vials at 4 °C prior to analysis.

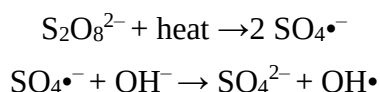


Figure 3. The UV reactors at UC Riverside.

The reason for choosing carbonate as the buffer/additive is that carbonate is ubiquitous in all natural waters, especially in groundwater. Because dissolved oxygen (DO) can be rapidly eliminated by a small portion of the added sulfite, all reactions did not have the N₂ sparging step for DO removal. More experimental details of the UV/sulfite treatment can be found from the PI's publications.²⁰

Advanced oxidation with hydroxyl radicals

A 30-mL aqueous sample was added with varying concentration of K₂S₂O₈ and KOH (2.5 molar equivalent of persulfate). The mixture was loaded in a pressure tube, which was then put into an autoclave at 120 °C for 40 min. Samples were cooled to room temperature naturally prior to analysis. The molar ratio between K₂S₂O₈ and KOH ensures that most sulfate radical is converted to hydroxyl radical:



More details of oxidative treatment can be found from the previous publication by Houtz and Sedlak.¹ The main difference is that we used 120 °C as the standard configuration for oxidative digestion of environmental samples.³²

Measurement of Fluoride Ion Release

The concentration of fluoride ion (F^-) released from PFAS degradation was primarily determined by an ion-selective electrode (ISE, Fisherbrand accumet solidstate) connected to a Thermo Scientific Orion Versa Star Pro meter. A 2-mL aliquot of reaction sample was added in the equal volume of the total ionic strength adjustment buffer (TISAB for fluoride electrode, Thermo Scientific), and the F^- concentration was determined with the ISE. The accuracy of F^- measurement by the ISE in the solution matrix was validated by the measurement of representative reaction samples using ion chromatography. A Dionex ICS-5000 ion chromatography (IC) system equipped with a conductivity detector and a Dionex IonPac AS11-HC column (4×250 mm) with a AG11-HC guard column (4×50 mm) was used for the ISE validation. For IC analysis, the original samples were diluted for 10 fold with DI water. The column was used at 30 °C, with a 20 mM NaOH isocratic eluent at 1.5 mL min⁻¹, and a suppressor current at 75 mA. More experimental details of the fluoride ion measurement can be found from the PI's publication.²⁰

AFFF and Groundwater Collection and Handling

The 3% MS-AFFF (Buckeye 50285) was purchased from Amazon.com by the PI and distributed to the labs of the two co-PIs at Vanderbilt and UNCC. The 10 gallons of groundwater sample from NAS JRB Willow Grove was collected by Geosyntec on June 27th, 2019, and shipped to Vanderbilt, where the NF separation experiment was conducted. All water samples were kept at 4 °C. The feed, NF permeate, and NF concentrate were shipped from Vanderbilt to UCR and UNCC, where the AOP-ARP degradation and LC/MS/MS characterization were conducted, respectively.

Of the ten gallons of the collected Willow Grove groundwater:

- 1 L was labeled as “fresh-GW feed”.
- 9 L was treated by NF at the 10:90 of [reject: permeate] ratio, so 900 mL was collected as “fresh-GW reject” and 8100 mL as “fresh-GW permeate”.
- 10 L was added with 10 mL AFFF (1000x dilution), and 1000 mL was labeled as “AFFF-GW feed”.
- 9 L out of the AFFF-added GW was treated by NF at the 10:90 of [reject: permeate] ratio, so 900 mL was collected as “AFFF-GW reject” and 8100 mL as “AFFF-GW permeate”.

The left ~18 L of unused groundwater was stored at UNCC for future use.

LC/MS/MS quantification

Analytical standards. Standard mix stock solutions (PFAC-24PAR) containing 2 µg/mL of each PFAS in methanol, as well as the internal standards containing 1 µg/mL of each mass-labeled PFAS in methanol, were purchased from Wellington Laboratories (Ontario, Canada). The list of analytes and corresponding internal standards are summarized in [Table 1](#) and [Table 2](#), respectively.

Table 3. List of analytes used in this project.

Compound Name	Acronym	CAS no.
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnDA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTriA	72629-94-8
Perfluorotetradecanoic acid	PFTreA	376-06-7
Perfluorobutane sulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexane sulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctane sulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	474511-07-4
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorooctanesulfonamide	PFOSA	754-91-6
Fluorotelomer sulfonic acid 8:2	FtS 8:2	39108-34-4
Fluorotelomer sulfonic acid 6:2	FtS 6:2	27619-97-2
Fluorotelomer sulfonic acid 4:2	FtS 4:2	757124-72-4
2-(N-Ethylperfluorooctanesulfonamido)acetic acid	NEtFOSAA	2991-50-6
2-(N-Methylperfluorooctanesulfonamido)acetic acid	NMeFOSAA	2355-31-9

Table 4. List of internal standards used in this project.

Isotope Labeled Standards	Abbreviation	Assigned Analyte(s)
Perfluoro[¹³ C ₄]butanoic acid	MPFBA	PFBA
Perfluoro[¹³ C ₅]pentanoic acid	M5PFPeA	PFPeA
Perfluoro[¹³ C ₅]hexanoic acid	M5PFHxA	PFHxA
Perfluoro[¹³ C ₄]heptanoic acid	M4PFHpA	PFHpA
Perfluoro[¹³ C ₈]octanoic acid	M8PFOA	PFOA
Perfluoro[¹³ C ₉]nonanoic acid	M9PFNA	PFNA
Perfluoro[¹³ C ₆]decanoic acid	M6PFDA	PFDA
Perfluoro[¹³ C ₇]undecanoic acid	M7PFUdA	PFUdA
Perfluoro[¹³ C ₂]dodecanoic acid	MPFDoA	PFDoA, PFTTrDA
Perfluoro[¹³ C ₄]tetradecanoic acid	M2PFTeDA	PFTeDA
Perfluoro[¹³ C ₃]butane sulfonate	M3PFBS	PFBS, PFPeS
Perfluoro[¹³ C ₃]hexane sulfonate	M3PFHxS	PFHxS, PFHpS
Perfluoro[¹³ C ₈]octane sulfonate	M8PFOS	PFOS, PFNS, PFDS
Perfluoro[¹³ C ₈]octane sulfonamide	M8PFOSA	PFOSA
N-[d ₃]methylperfluorooctane sulfonamidoacetic acid	d3-N-MeFOSAA	N-MeFOSAA
N-[d ₅]ethylperfluorooctane sulfonamidoacetic acid	d5-N-EtFOSAA	N-EtFOSAA
1H,1H,2H,2H-perfluoro[1,2- ¹³ C ₂]hexane sulfonate	M2-4:2 FTS	4:2 FTS
1H,1H,2H,2H-perfluoro[1,2- ¹³ C ₂]octane sulfonate	M2-6:2 FTS	6:2 FTS
1H,1H,2H,2H-perfluoro[1,2- ¹³ C ₂]decane sulfonate	M2-8:2 FTS	8:2 FTS

Solid phase extraction (SPE). Analytes were extracted using Oasis WAX Plus 225 mg, 60 μm extraction cartridge (Waters, Milford, MA). The cartridges were conditioning by 5 mL methanol and 25 mL ultrapure water, washed by 4 mL of 25 mM sodium acetate buffer (pH 4). After loading 50 mL of samples (either original or diluted to be included in the calibration range), the analytes were eluted by 4 mL methanol, then 4–8 mL 0.05% v/v ammonia hydroxide in methanol. The elutes were combined and evaporated by nitrogen gas to 1 mL in a 40°C water bath. For each sample, 200 μL concentrated elute was mixed with 20 μL internal standard and 580 μL of MS-grade water to make the total volume of 800 μL in 1 mL polypropylene vials. All blanks and calibration standards were treated the same way as the samples.

PFAS analysis. The concentration of each PFAS was analyzed by an Agilent 1100 liquid chromatography (LC) coupled with an Agilent 6410 triple quadrupole tandem mass spectrometry (MS/MS). A delay column (4.6 x 50 mm, 3.5 μm , Agilent Eclipse plus C18), was installed between the mixing valve and the autosampler in order to trap any PFAS from the LC pump system. A 750 μL aliquot of sample was injected each time, and the analytes were separated through an Agilent InfinityLab Poroshell 120 EC-C18 column (4.6 x 50 mm, 4 μm). The Mobile phase A was 2 mM ammonium acetate in MS-grade water, and the mobile phase B was 2mM ammonium acetate in MS-grade methanol. Gradient elution at 0.5 mL/min ramped from 10% B to 95% B in 10 minutes, held for 5 minutes, and reduced back to 10% B in 0.1 minute. The runtime was 21 minutes, in which the analytes were eluted to MS/MS during 4-16 minutes, and the post-run time is 4 minutes. The MS/MS with dynamic multiple reaction monitoring (dMRM) was in electrospray ionization (ESI) negative mode. The gas source for MS/MS operation was at 300 °C in 13 L/min, and the nebulizer pressure was 13 psi. The optimized MRM parameters for each PFAS analyte, such as the precursor and product ions, and the limit of quantification (LOQ) are summarized in [Table 3](#). Calibration was made based on isotopic dilution in the range of 50-400 ng/L.

Table 5. MS/MS parameters for each analyte and internal standard.

Compound	Precursor ion	Product ion 1	Product ion 2	Fragmentor volt (V)	Collision Energy-1 (V)	Collision Energy-2 (V)
PFBA	212.98	169	n.a.	83	4	n.a.
PFPeA	262.97	219	n.a.	83	4	n.a.
PFHxA	312.94	269	119	83	4	20
PFHpA	362.97	319	169	88	4	20
PFBS	298.94	80	99	73	40	36
PFPeS	348.94	80	99	84	48	40
PFHxS	398.93	80	99	84	52	40
4:2FTS	326.97	307	186	73	20	52
PFOA	412.96	369	169	88	8	20
PFNA	462.96	419	219	88	8	16
PFDA	512.96	469	269	98	8	16
PFUdA	562.95	519	307	73	12	40
PFDoA	612.95	569	269	73	12	20
PFTTrDA	662.95	619	169	73	12	32
PFTeDA	712.94	669	169	112	12	36

Compound	Precursor ion	Product ion 1	Product ion 2	Fragmentor volt (V)	Collision Energy-1 (V)	Collision Energy-2 (V)
PFHpS	448.93	80	99	84	52	48
PFOS	498.93	80	99	50	68	48
PFNS	548.92	80	99	50	72	48
PFDS	598.92	80	99	50	76	56
6:2FTS	426.97	81	407	73	52	20
8:2FTS	526.96	277	507	50	24	24
FOSA	497.94	78	478	73	40	20
N-MeFOSAA	569.96	419	251	107	20	8
N-EtFOSAA	582.97	312	526	112	32	12
MPFBA	216.99	172	n.a.	64	4	n.a.
MPFPeA	267.99	223	n.a.	78	4	n.a.
MPFHxA	314.99	273	119	95	0	16
MPFHpA	366.99	322	169	88	8	16
MPFOA	416.99	372	169	105	0	12
MPFNA	471.99	427	223	93	8	16
MPFDA	518.99	474	270	103	8	20
MPFUdA	569.99	525	274	73	8	20
MPFDoA	614.99	570	270	117	12	20
MPFBS	301.99	80	99	73	36	32
MPFHxS	401.99	80	99	190	56	40
MPFOS	506.99	80	99	84	56	52
M4:2FTS	328.99	309	81	107	24	32
M6:2FTS	428.99	409	81	185	28	44
M8:2FTS	528.99	81	64	185	64	24
MFOSA	505.99	78	486	185	40	20
d-N-MeFOSAA	572.99	419	483	156	20	16
d-N-EtFOSAA	588.99	419	531	151	20	24

Nanofiltration separation

Membrane element. Two commercial spiral-wound polyamide-TFC NF membranes, NFX and NFW (manufactured by Synder Filtration), were used in this project. The membrane element has a dimension of 1.8 in diameter $\times$ 12 in length, with 0.37 m² active membrane area. Other membrane element specifications reported by the manufacturer are summarized in [Table 4](#).

Table 6. Membrane specifications provided by the manufacturer.^a

Membrane	MWCO (Da)	Flux (LMH/bar)	Rejection MgSO ₄ (NaCl)	pH Range (25 °C)	Cl Tolerance (ppm.hrs)	Max. Temp. (°C)	Spacer
NFX	150-300	34-43/7.6	99% (40%)	3-9.5	500	50	31 mil
NFW	300-500	77-85/7.6	97% (20%)	4-9	500	50	31 mil

^aMore details can be found:

<https://synderfiltration.com/2014/wp-content/uploads/2018/11/NFX-TFC-150-300Da-Sanitary-Specsheet.pdf>

<https://synderfiltration.com/2014/wp-content/uploads/2018/11/NFW-TFC-300-500Da-Sanitary-Specsheet.pdf>

LMH: liter per square meter per hour (flux unit).

Membrane apparatus. The NF performance was tested using a stainless steel cross-flow filtration system (Sterlitech™ 1812, **Figure. 2**). The cross-flow filtration system has an operating pressure range of 0-41 bar (0-600 psi) and a maximum feed flow rate of 1.8 GPM (6.7 LPM). The photos of the membrane module and the entire filtration system are shown in **Figure 3**.

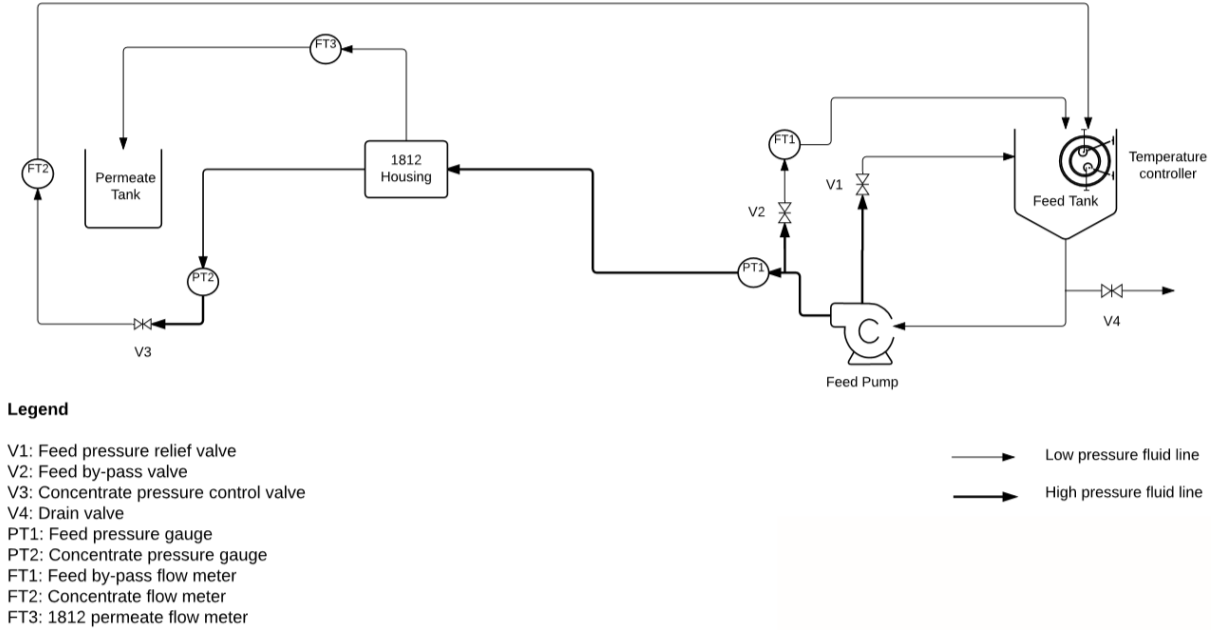


Figure 4. Sterlitech™ 1812 cross-flow filtration system.

(Source: https://www.sterlitech.com/media/wysiwyg/Analog_1812_Skid_Data_Sheet_2_.pdf)

Nanofiltration operations. Before each filtration experiment, the membrane element was compacted with deionized water feed under operating conditions for at least 30 min until the flux and crossflow had stabilized. 100 mL permeate and 100 mL retentate of the stabilized system were collected for quality control. The following operating conditions were used: the cross-flow rate was 6 LPM and the applied pressure was 10 bar. Retentate stream was recycled to the feed tank and permeate was collected until target water recovery was reached. In the Willow Grove Groundwater nanofiltration experiment, the NFX membrane was used, and the target recovery was 90%, equivalent to a concentration factor (CF) of 10. The permeate flux, J (unit: LMH), was determined by measuring the rate of permeate volume change (which was converted from mass change), ΔV , in the time interval, Δt , for a given membrane-active area, S , and (**Eq. 1**). The solute rejection, R (%), was calculated using the solute concentrations of permeate, C_p , and feed solution, C_f based on **Eq. 2**. After each filtration experiment, the membrane element was flushed with DI water for at least one hour for cleaning.

$$J = \frac{\Delta V}{S \Delta t} \quad (1)$$

$$R = 1 - \frac{C_p}{C_f} \quad (2)$$

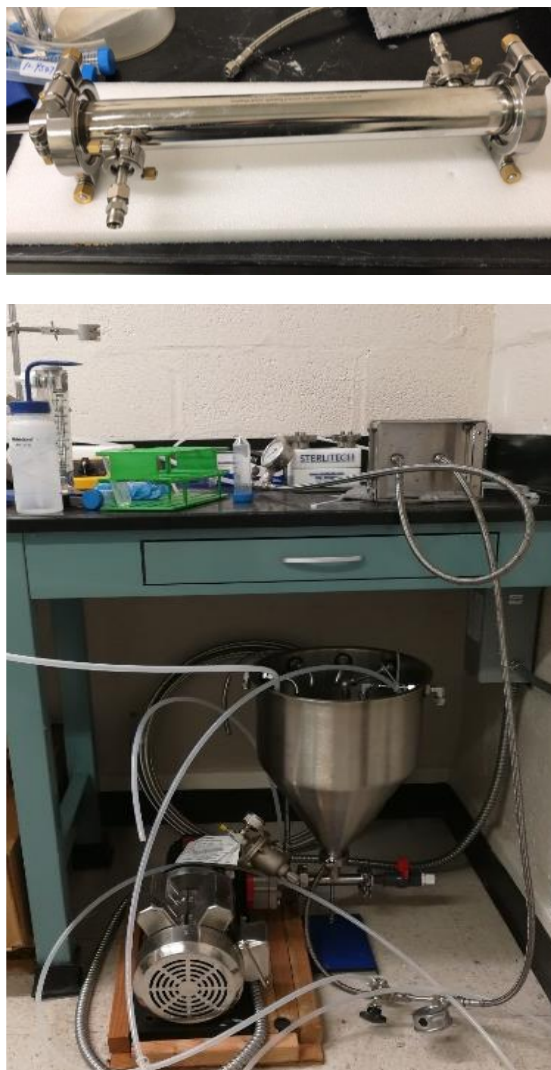


Figure 5. The membrane module and experimental setup of the NF system at Vanderbilt University.

Results and Discussion

NF separation for PFAS removal

Hardness, alkalinity and pH. The hardness and alkalinity of fresh groundwater were 137 mg/L as CaCO₃ and 200 mg/L as CaCO₃, respectively, measured using Total Hardness Test Kit (Model 5-B, HACH) and Alkalinity Test Kit (Model AL-AP, HACH). The pH of feed, permeate, and reject (**Table 5**) were measured by an Oakton PC700 pH meter.

Table 7. pH measurements in of the groundwater samples before and after NF separation.

pH	Feed	Permeate	Reject
Fresh GW	6.20	6.43	7.90
AFFF+GW	6.47	7.40	7.98

Fouling evaluation. The total filtration time was around 40 min. The membrane fouling was evaluated by permeate flux change during filtration (**Table 6**) and by comparing the pure water flux before and after each filtration experiment (**Table 7**). Pure water flux was measured using DI water as feed under the same operating conditions as the groundwater filtration experiments. After each filtration of groundwater, the membrane element was temporarily removed from the membrane vessel, the system was flushed with DI water, and the fouled element was placed back into the vessel. Then the pure water flux was measured again. Results in Table 3 show that there was a substantial drop in flux when the GW was used as the feed solution (as compared to DI water as the feed solution), but the flux gradually returned back to the level for DI water. Such results are untypical of membrane fouling experiments and its cause needs to be further investigated. Nonetheless, results from Table 4 showed negligible irreversible fouling of the NF membrane upon filtrating the given volume of groundwater and AFFF-added groundwater, i.e., the filtration process did not result in any considerable change of the pure water permeability.

Table 8. Permeate flux (unit: LMH) during the filtration operation.

Recovered Permeate volume (L)	0	1	2	4	6	8
Fresh GW	23.0	24.8	26.6	29	32	35.2
AFFF+GW	25.4	24.8	26.6	31.2	32.2	33.8

Table 9. Pure water flux before and after NF in Willow Grove Groundwater Experiment.

Pure water flux (LMH)	Before	After
Fresh GW	33.92	34.96
AFFF+GW	37.04	36.08

PFAS removal from groundwater. The LC/MS/MS analyte list contained C4 to C10 perfluorosulfonates, C4 to C14 perfluorocarboxylates, 4:2, 6:2, and 8:2 fluorotelomer sulfonates, and three perfluorooctane sulfonamides with -NH₂, -NHMe and -NHEt end groups. **Table 8** shows the quantification of all these PFAS compounds in the feed, permeate, and reject from NF treated fresh groundwater (Fresh GW). In the contaminated groundwater, PFOS and PFHxS are the two dominating species, followed by PFOA and PFHxA. C4, C5, and C7 PFCAs and PFASs also take significant portions of the total quantifiable PFAS. In this project, the limit of

quantification (LOQ) of the LC/MS/MS analysis is 50 ng/L (or 50 ppt) for each compound. Structures longer than C9 either had concentrations lower than 50 ng/L (<LOQ) or not detected (ND). With a few exceptions (see the footnotes in tables), most individual compounds had a concentration factor of 3 to 7. **Most importantly, all compounds in the NF permeate went below 50 ng/L, showing the promise of using nanofiltration to remove the listed PFAS compounds from groundwater IDW.** At the USEPA's current health advisory level for PFOA and PFOS, **the NF-treated permeate may be allowed for disposal.** We note that DI water flushing of the membrane system contained 6:2 FTS so that this structure may also come from certain parts of the membrane system. We also note that if a total concentration of 70 ppt for all PFAS compounds is the treatment goal, the LC/MS/MS analysis will need to further lower the LOQ to quantify the ΣPFAS. At this low concentration, total fluorine analysis does not apply because the detection of < 70 ppt fluoride ion is very difficult.

Table 10. LC/MS/MS analysis results for groundwater samples (unit: ng/L).

<i>Fresh GW</i>	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
<i>Feed</i>	233.3	278.6	1062.1	101.3	1110.6	<LOQ ^a	ND ^b
<i>Permeate</i>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
<i>Reject</i>	1101.8	1496.1	7516.9	338.4	1022.0 ^c	<LOQ	ND

<i>Fresh GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA ^d
<i>Feed</i>	133.9	136.9	506.9	99.2	408.8	<LOQ	<LOQ	<LOQ	<LOQ
<i>Permeate</i>	<LOQ	ND	<LOQ	ND	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<i>Reject</i>	605.3	799.1	2567.1	531.5	1788.5	<LOQ	<LOQ	<LOQ	<LOQ

<i>Fresh GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
<i>Feed</i>	ND	306.9	<LOQ	<LOQ	ND	<LOQ
<i>Permeate</i>	ND	181.6 ^e	<LOQ	<LOQ	ND	<LOQ
<i>Reject</i>	ND	1564.4	397.6	92.6	ND	<LOQ

^aLOQ = limit of quantitation (50 ng/L for each compound), <LOQ indicates the detection of peaks with a calculated concentration below 50 ng/L.

^bND = not detected.

^cDubious result that does not follow the concentration factor suggested by other data.

^dPFDoA (C12), PFTrDA (C13), and PFTeDA (C14) were not detected in all samples.

^eThe detection of 6:2 FTS in this sample might be from the NF system as the flushing using DI water also observed this compound.

PFAS removal from AFFF-added groundwater. For AFFF-added groundwater, a majority of PFAS compounds are still <LOQ in the NF permeate (**Table 9**), with the exceptions of PFHxS, PFHxA, PFOA, and 8:2 FTS. Nanofiltration is supposed to remove long-chain charged PFAS. The detection of those C6, C8, and even C10 structures is thus attributed to the presence of some neutral PFAS structures that can penetrate NF membrane. As the 3% AFFF is a highly viscous mixture of multiple organics, even after 1000x dilution the organics might also be able to interfere with the normal PFAS interception by NF membrane. We point this out because we later realized that some PFAS compounds were also observed after the fresh groundwater permeate was treated by ARP-AOP (see the section of “*Treatment of NF separation streams*”). Nevertheless, comparing with the concentrations in the feed and reject, **the NF treatment is highly effective in rejecting most PFAS from entering the permeate.**

Table 11. LC/MS/MS analysis results for AFFF-added groundwater samples (unit: ng/L).^a

AFFF+GW	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
Feed	181.7	206.2	781.0	<LOQ ^b	488.8 ^b	<LOQ	ND
Permeate	<LOQ	<LOQ	75.5	<LOQ	<LOQ	<LOQ	ND
Reject	939.9	1042.4	4166.9	<LOQ ^b	3610.4	92.2	ND

AFFF+GW	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA
Feed	489.2	378.0	5109.4	479.8	6490.5	<LOQ	<LOQ	<LOQ	<LOQ
Permeate	<LOQ	ND	132.9	ND	95.6	<LOQ	<LOQ	<LOQ	<LOQ
Reject	4368.0	1123.8	14786.0 ^c	526.6 ^d	663.6 ^d	<LOQ	88.4	<LOQ	<LOQ

AFFF+GW	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
Feed	308.4	4044.2	2840.7	<LOQ	ND	<LOQ
Permeate	<LOQ	1234.6 ^e	133.3	<LOQ	ND	<LOQ
Reject	1454.2	8097.7	2559.0	63.7	ND	<LOQ

^aLC-MS/MS analysis in the samples with diluted AFFF matrix is more challenging than the original groundwater.^bDubious results that are lower than in the original groundwater.^cDubious result that does not follow the concentration factor suggested by other data, probably due to the deviation from the calibration curve at a high concentration.^dDubious result that does not follow the concentration factor suggested by other data by unknown reasons.^eThe detection of 6:2 FTS in this sample might be from the NF system as the flushing using DI water also observed this compound.**Table 12.** Comparison of the PFAS compound concentrations before and after adding the AFFF in the groundwater (without ARP-AOP treatment, the concentration unit is ng/L).

PFAS	Feed			Permeate			Reject		
	Fresh	+AFFF	Change	Fresh	+AFFF	Change	Fresh	+AFFF	Change
PFBS	233.3	181.7	↓ 22%	<LOQ	<LOQ	-	1101.8	939.9	↓ 15%
PFPeS	278.6	206.2	↓ 26%	<LOQ	<LOQ	-	1496.1	1042.4	↓ 30%
PFHxS	1062.1	781.0	↓ 26%	<LOQ	75.5	↑ 51+%	7516.9	4166.9	↓ 45%
PFHpS	101.3	<LOQ ^a	↓ 51+%	<LOQ	<LOQ	-	338.4	<LOQ	↓ 85%
PFOS	1110.6	488.8	↓ 56%	<LOQ	<LOQ	-	1022.0	3610.4	↑ 253%
PFNS	<LOQ	<LOQ	-	<LOQ	<LOQ	-	<LOQ	92.2	↑ 84+%
PFDS	ND	ND	-	ND	ND	-	ND	ND	-
PFBA	133.9	489.2	↑ 265%	<LOQ	<LOQ	-	605.3	4368.0	↑ 622%
PFPeA	136.9	378.0	↑ 176%	ND	ND	-	799.1	1123.8	↑ 41%
PFHxA	506.9	5109.4	↑ 908%	<LOQ	132.9	↑ 165+%	2567.1	14786	↑ 476%
PFHpA	99.2	479.8	↑ 384%	ND	ND	-	531.5	526.6	↓ 1%
PFOA	408.8	6490.5	↑ 1488%	<LOQ	95.6	↑ 91+%	1788.5	663.6	↓ 63%
PFNA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	<LOQ	<LOQ	-
PFDA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	<LOQ	88.4	↑ 77+%
4:2 FTS	ND	308.4	↑ 517+%	ND	<LOQ	-	ND	1454.2	↑ 2808+%
6:2 FTS	306.9	4044.2	↑ 1218%	181.6 ^b	1234.6	-	1564.4	8097.7	↑ 418%
8:2 FTS	<LOQ	2840.7	↑ 5581+%	<LOQ	133.3	↑ 167+%	397.6	2559.0	↑ 544%
FOSA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	92.6	63.7	↓ 31%

^aComparisons involving “<LOQ” and “ND” used <50 ng/L as the calculation basis.^bComparison not made due to the potential interference of 6:2 FTS from the NF system.

The data between the fresh groundwater and AFFF-added groundwater are compared in **Table 10**. The slight decrease of sulfonates after the addition of AFFF is within the expected error range (due to instrument factors, interfering matrix components from AFFF, etc.) However, all PFCAs and FTSAAs showed significantly increased concentrations, indicating that AFFF contained these species or their precursors. We note that all of these quantifiable species are not the major PFAS components in the AFFF. As to be seen in later sections, the major PFAS components should be some telomeric structures with the C6 fluoroalkyl moiety.

Destruction of PFAS compounds in AFFF

This section focuses on the degradation and defluorination of PFAS components in AFFF using ARP and AOP. AFFF-polluted groundwater can be either directly treated or treated after a membrane separation into the concentrated NF reject.

Optimization of the UV/sulfite ARP treatment. Using reaction conditions that have been optimized for individual PFAS²³ (pH 12, 10 mM sulfite, 254 nm irradiation), we conducted UV/sulfite treatment on AFFF solutions with a wide range of dilution from 10x to 100,000x in DI water. As shown in **Figure 4**, after the release of F^- ion were normalized by the dilution factor, the defluorination profile shows that sufficient defluorination was achieved when the original AFFF was diluted for 10,000x or 100,000x. At the specific reaction condition, up to 5000 ppm of F^- (5 g/L or 0.26 M) can be released from the original 3% AFFF product. In our earlier study, the lifetime of the 10 mM sulfite under UV irradiation was < 24 h.²³ Therefore, the continuous release of F^- ion from 10x to 1000x samples after 24 h should be attributed to the presence of unknown photosensitizer contained in the AFFF product. This phenomenon has also been observed in another recent publication treating a different AFFF product.²² However, although the reductive defluorination can continue by this novel mechanism, the rate was very slow and would consume a great amount of electrical energy. The higher the dilution factor, the faster the defluorination profile could reach the plateau. At the 100,000x dilution, the measurement of F^- became challenging. Therefore, the following ARP optimization tests mainly used 10,000x dilution.

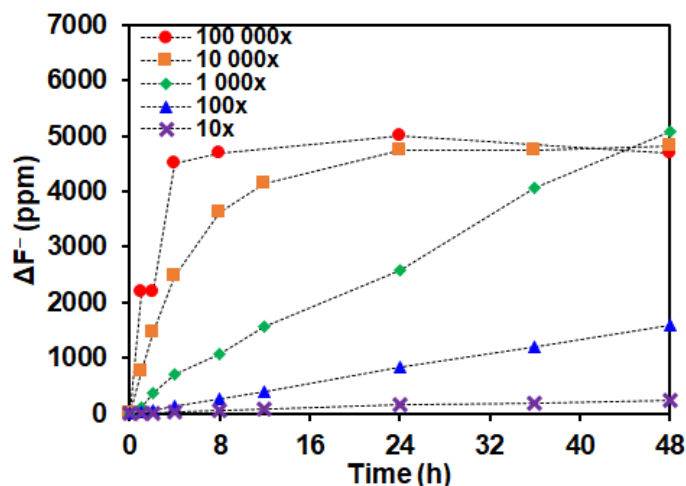


Figure 6. Defluorination from the AFFF solution at varying dilution factors.

Reaction conditions: 600 mL solution containing 10 mM Na_2SO_3 , 5 mM $NaHCO_3$, pH 12.0, one 18 W low-pressure 254 nm UV lamp, 20 °C. The ΔF^- indicates the F^- release after the measured F^- concentration was normalized by the dilution factor.

We also examined the effect of varying solution pH on the defluorination of 10,000x diluted AFFF. The result was different from the results using pure PFOA in our earlier study²³ where pH 12.0 showed the highest performance. In the case of AFFF treatment, pH higher than 12.0 provided better defluorination performance (**Figure 5**). We did not further test pH values above 13 because the addition of NaOH to over 0.1 M was not considered practical. At least, the result suggests that the PFAS compounds in the AFFF have different degradation behavior from the perfluorocarboxylates (i.e., no more significant defluorination at pH >12). For simplicity, we kept using pH 12 in the following studies.

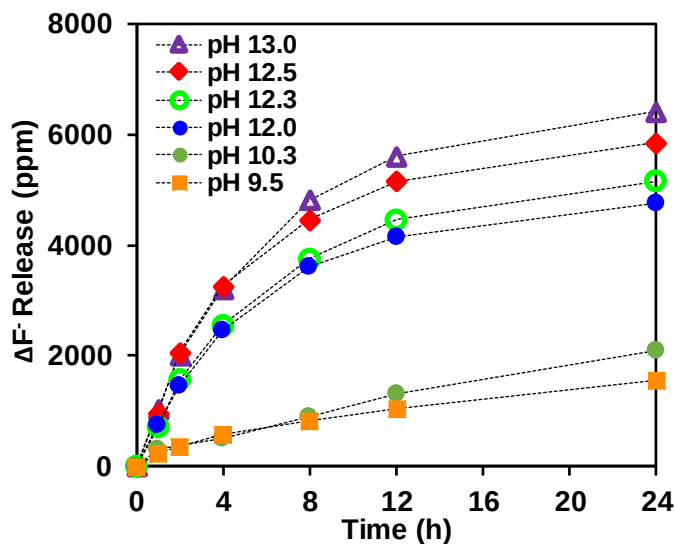


Figure 7. Defluorination from 10,000x diluted AFFF solution with 10 mM at varying pH values.

At pH 12, we further investigated the effect of sulfite concentration. For the 10,000x diluted AFFF, 20 mM sulfite provided the optimal defluorination (**Figure 6**).

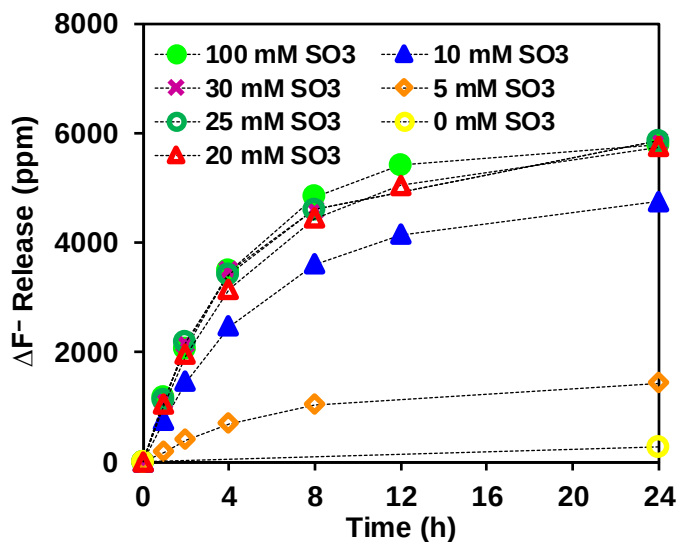


Figure 8. Defluorination from 10,000x diluted AFFF solution with varying concentrations of sulfite at pH 12.0.

As the sulfite decays itself under UV irradiation in first-order kinetics²³, we also examined the sequential sulfite addition strategy (i.e., additions of two portions of 10 mM at different time intervals instead of one-time addition of 20 mM sulfite in the beginning). Results showed no significant difference between the sequential and one-time sulfite addition (Figure 7). We further compared the addition of 25 mM of sulfite altogether versus adding five times of 5 mM sulfite (Figure 8). Results show that although 5 mM sulfite along gave a slow defluorination at the beginning (cf. Figure 6), the following addition resumed the fast reaction rate. However, the maximum defluorination showed no significant difference. Therefore, the following experiments kept using the one-time addition of 20 mM Na₂SO₃ for simplicity.

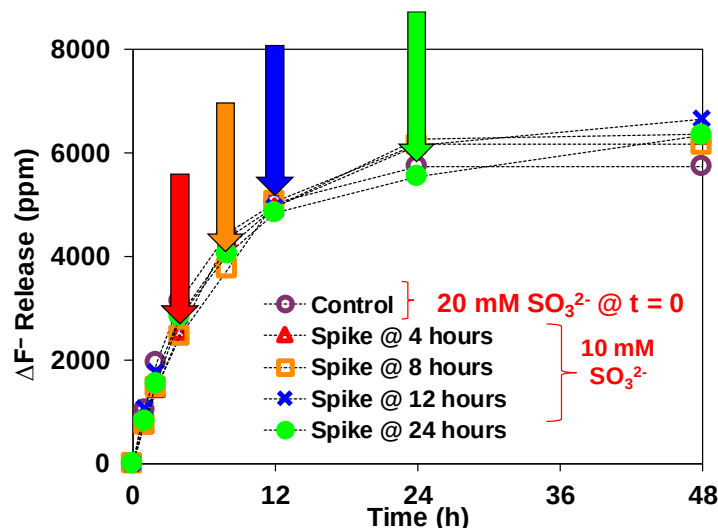


Figure 9. Defluorination from 10,000x diluted AFFF solution with different sulfite addition strategies (one-portion versus two-portion) at pH 12.0.

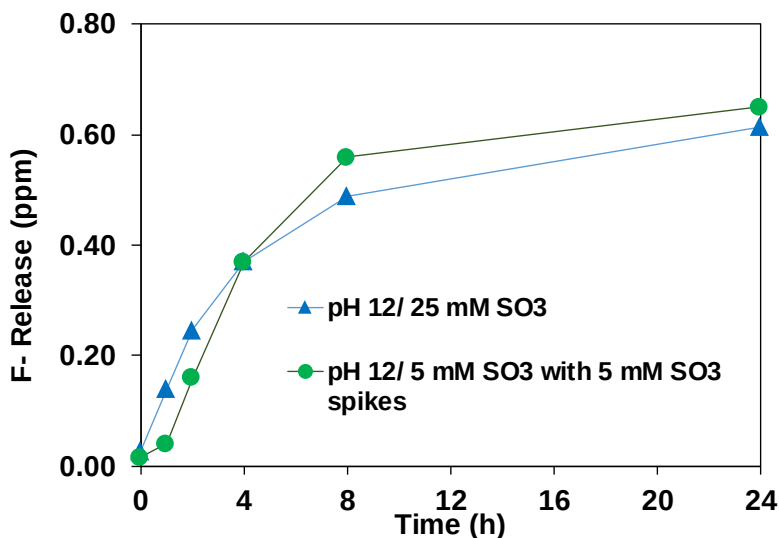


Figure 10. Defluorination from 10,000x diluted AFFF solution with different sulfite addition strategies (one-portion versus five-portion, added at each sampling time point) at pH 12.0.

In addition, Figure 6 suggests the upper limit of sulfite to be effective in AFFF defluorination. We further tested whether or not higher concentrations of sulfite can be effective

in treating the less diluted 100x AFFF (Figure 9). Although the defluorination profile has completely changed due to the highly concentrated PFAS compounds (and organic additives) present in solution, the addition of 10 mM sulfite showed the best performance. All results collectively suggest **an upper limit of PFAS concentration (e.g., 1000x) and sulfite concentration (e.g., 10 to 20 mM) for an effective defluorination from AFFF solutions.** However, we expect a significant improvement of the defluorination treatment via further system improvements, such as tuning the intensity and energy of UV irradiation.^{33, 34}

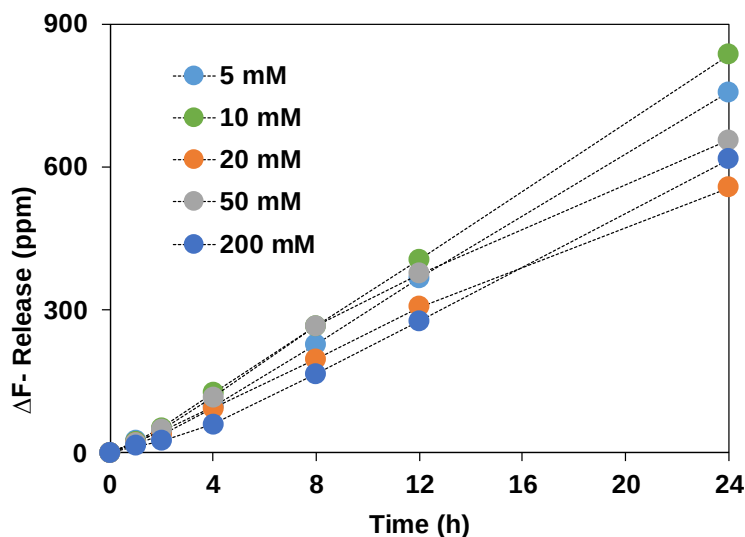


Figure 11. Defluorination from 100x diluted AFFF solution using varying sulfite concentrations at pH 12.0.

Note that the dilution-normalized ΔF^- is one order-of-magnitude lower than treating 10,000x diluted AFFF.

Optimization of the alkaline persulfate AOP treatment. Due to the effect of the dilution factor that we have observed from ARP experiments, we started the oxidative treatment of AFFF solution at three dilution factors, 1000x, 10,000x, and 100,000x. The use of 2.5 equivalent of KOH ensured that most sulfate radical from the heat activation of persulfate can be fully converted to hydroxyl radicals ($HO^\bullet$). We have the following rationales for investigating the AOP by $HO^\bullet$. First, $HO^\bullet$ can destruct organic matrix that might interfere with both separation and chemical destruction steps. Second, $HO^\bullet$ can convert telomeric structures into PFCAs for much more efficient reductive defluorination. Third, the widely applied AOP with $HO^\bullet$ typically has faster kinetics than $SO_4^{\bullet-}$ for pollutant degradation. As shown in Figure 10, the investigation with varying dilution factors and persulfate concentrations have revealed the reaction stoichiometry through F^- ion release. The defluorination through AOP is most probably from the destruction of telomeric structures. The PI's ER18-1289 has revealed the oxidative defluorination from a series of model fluorotelomer structures (manuscript in preparation). For 1000x diluted AFFF, 200 mM persulfate was necessary to yield the same defluorination as from 10,000x diluted AFFF. Similarly, for the 10,000x diluted AFFF, the use of only 25 mM persulfate yielded similar (or even higher) defluorination than the use of 200 mM persulfate. Therefore, for the following AOP investigations, we mainly used 25 mM persulfate to treat 10,000x diluted AFFF samples.

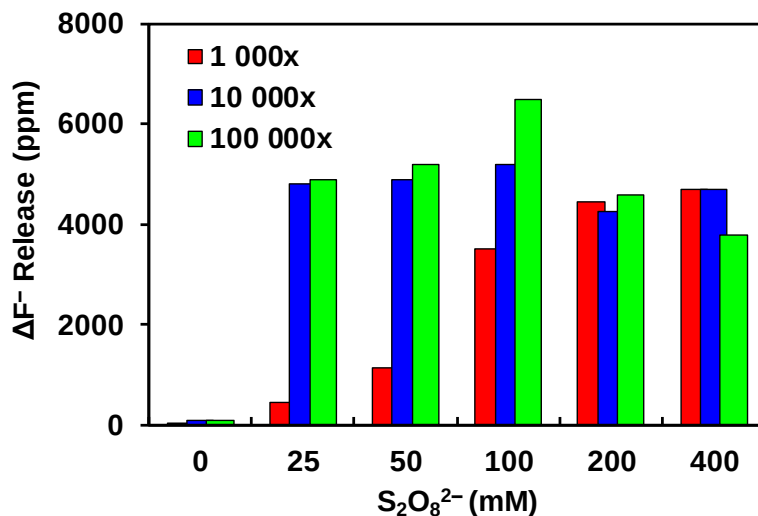


Figure 12. Defluorination from AFFF solutions of varying dilution factors and persulfate concentrations. Reaction conditions: KOH : $K_2S_2O_8$ = 2.5 : 1 and heated at 120 °C for 40 min.

Characterization of the AFFF

Since the AOP treatment released a significant amount of F^- ion (i.e., the ΔF^- from ARP is ~6000 ppm and from AOP is ~5000 ppm), we attempted using ^{19}F nuclear magnetic resonance (NMR) to probe the structure of the PFAS surfactants in AFFF. **Figure 11** shows the full spectrum of a 100x diluted AFFF in the 50/50 MeOD/ D_2O mixed solvent. There are mainly two groups of resonances (one major set, and one minor set with peaks very close to the main set).

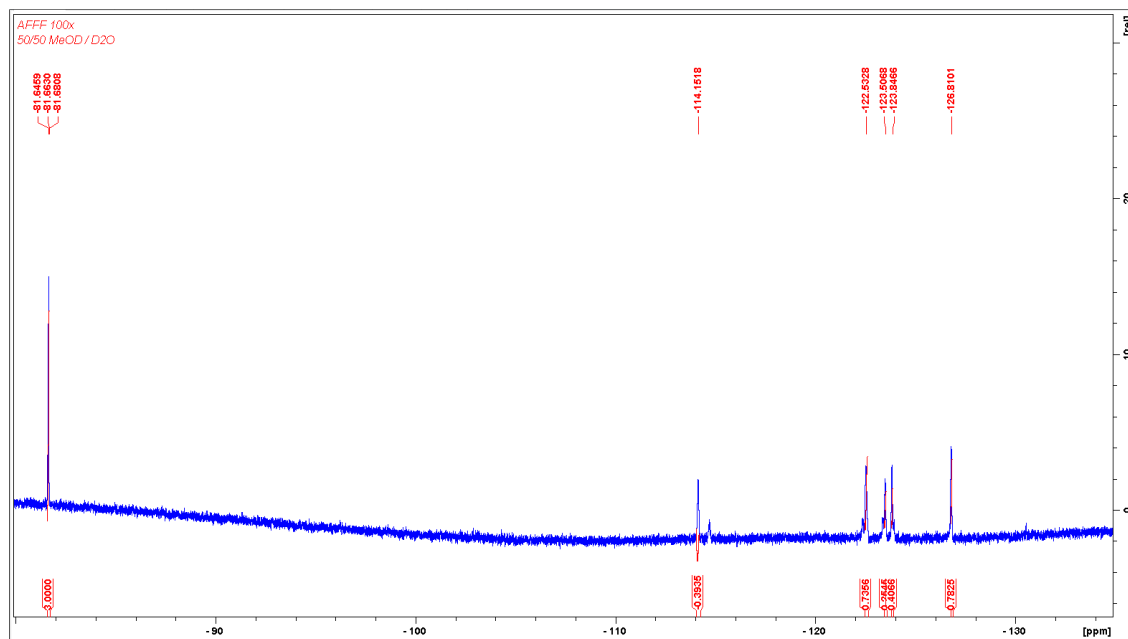


Figure 13. ^{19}F NMR spectrum of the 100x diluted AFFF in 50/50 MeOD/ D_2O .

Because C6 PFAS has been often used in new AFFF formulations, we further compared the ^{19}F NMR resonances of C6 fluoroalkyl model compounds: PFHpA, PFHxS, and 6:2 FTSA. **Figure 12** shows the CF_2 region (i.e., the terminal $-CF_3$ peak around -80 ppm not shown) that

comparison of AOP/ARP defluorination results between the 6:2 FTSA and the AFFF solution shows a high similarity. Because n:2 FSAs demonstrated high dependence of both reductive and oxidative defluorination on the chain length of the C_nF_{2n+1} moiety (Table 11), the quick comparison also suggests the dominant PFAS compound in AFFF as an n=6 telomeric structure. Note that ^{19}F NMR also observed a simple set of resonances for n=6 telomer structure (Figure 12).

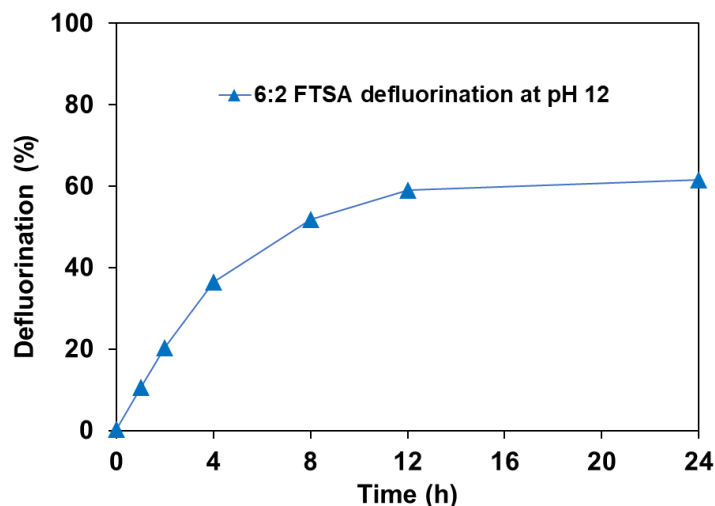


Figure 15. Defluorination from 25 μM of pure 6:2 FTSA at pH 12.0 using 10 mM sulfite.

Table 13. The comparison of defluorination results on the diluted AFFF (in ΔF^-) and three FTSA (in defluorination percentage) with varying fluoroalkyl chain lengths.

Treatment Target	Direct ARP	Direct AOP
10,000x diluted AFFF	5750 ppm	4800 ppm
4:2 FTSA	18%	62%
6:2 FTSA	62%	51%
8:2 FTSA	66%	36%

Comparison between ARP-AOP and AOP-ARP sequential treatment strategies

It seems that both ARP and AOP can be used as the first treatment step of the combined reduction/oxidation treatment chain for the specific AFFF that mainly contained an n=6 telomeric structure. Because the telomeric structure was oxidized into a series of PFCAs¹ that are inert to further oxidation with $HO^\bullet$, ARP was used to treat the PFCA products. On the other hand, if ARP was used first, the remaining ~40% of C–F bonds should be in the H-rich transformation products, which underwent deep destruction by the oxidation with $HO^\bullet$. We measured the results of the two treatment sequences (Table 12). No significant difference between the two sequences was observed. However, we must highlight that the **similarity between the two treatment strategies can only be applied to the case where n=6 fluorotelomers are the dominant AFFF component**. As shown in Table 11, if the IDW contained species other than 6:2 FTSA structures, the sequence of applying AOP and ARP may have a significant difference. For example, if 4:2 FTSA is the dominant species, the use of ARP as the first step will incur a long treatment time or limited defluorination. If the IDW mainly contained perfluorocarboxylates or sulfonates (i.e., other than

telomeric structures), the first application of AOP will not achieve any defluorination because HO• only works for the degradation of telomeric PFAS.

Table 14. The comparison between ARP-AOP and AOP-ARP treatment chain.

AFFF sample	ARP-AOP			AOP-ARP		
	Step 1 ARP	Step 2 AOP	Total	Step 1 AOP	Step 2 ARP	Total
10,000x diluted	5750 ppm	1760 ppm	7510 ppm	4800 ppm	2800 ppm	7600 ppm
100,000x diluted	5000 ppm	3100 ppm	8100 ppm	4900 ppm	3700 ppm	8600 ppm

The ARP-AOP and AOP-ARP treatment strategies were further optimized (**Figure 14**). The results collectively show that ARP-AOP could achieve a higher overall defluorination to about 9100 ppm F⁻ (9.1 g/L or 0.479 M) from the original 3% AFFF.

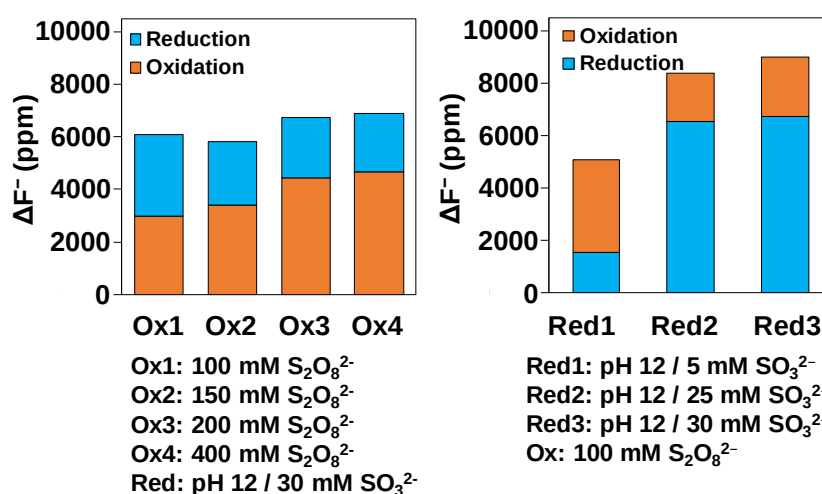


Figure 16. Comparison of AOP-ARP (left) and ARP-AOP (right) at varying operation parameters. The AOP-ARP started from 1000x diluted AFFF (then further diluted for 10x for ARP), and the ARP-AOP directly started from 10000x diluted AFFF (then oxidized without further dilution).

Treatment of NF separated streams

The initial NF separation tests were conducted by using the two membrane materials, NFX and L-NFW (**Table 4**), with a low [permeate:reject] ratio of 30:70. The feed contained two dilution factors for AFFF- 100x and 1000x in DI water. The reject and permeate were further diluted for 100x and 10x, respectively, so that the samples are at the 10,000x level for efficient ARP defluorination. The results are shown in **Figure 15**. The two membrane materials showed similar retention of PFAS compounds from the AFFF solution feed. The high solution pH was critical for the level of defluorination. The two dilution folds of AFFF in the NF feed does not show a significant difference in the defluorination treatment by ARP. In stark comparison, all NF permeates did not show a significant defluorination by ARP (**Figure 16**), indicating that the majority of, if not all, the PFAS components in AFFF has been rejected by both NF membrane materials.

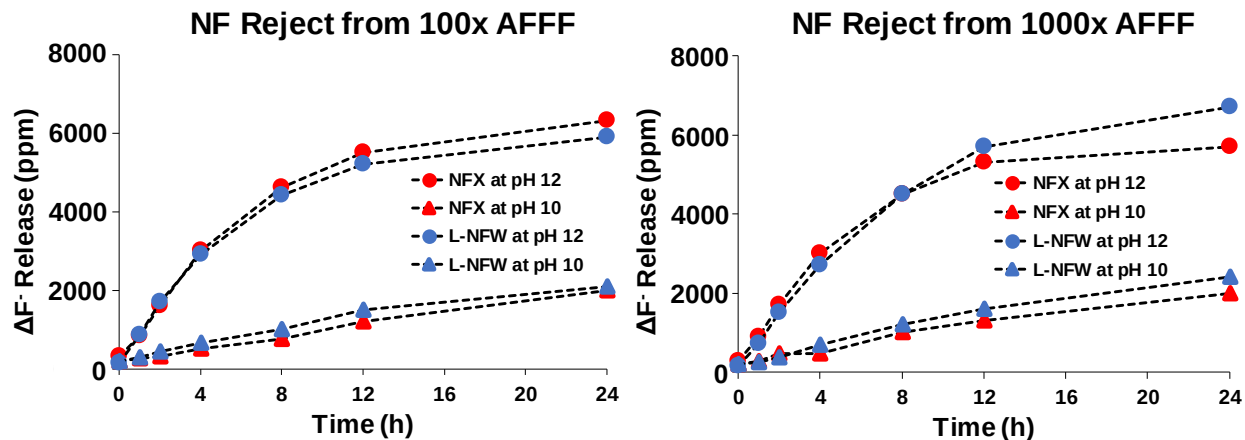


Figure 17. Defluorination of the NF reject of AFFF solutions with two dilution levels, at two pH values, and from two membrane materials. Reaction conditions: 10 mM Na₂SO₃ and 5 mM NaHCO₃ at 20 °C.

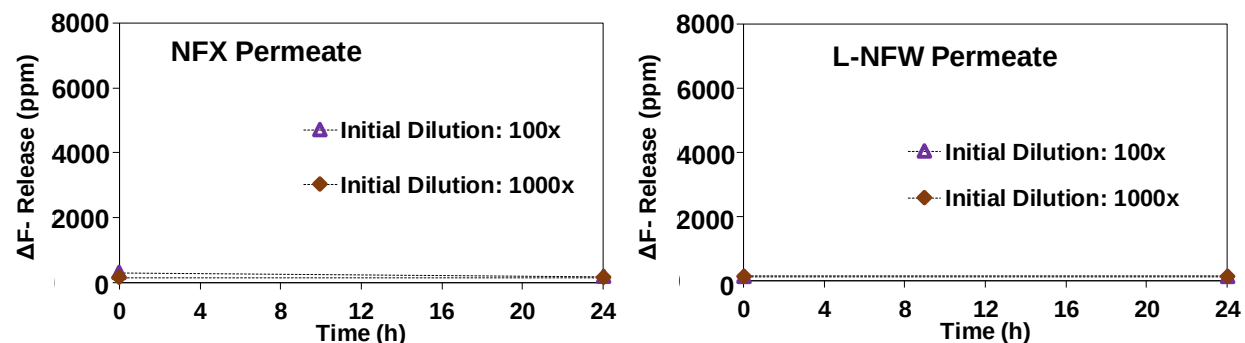


Figure 18. Defluorination of the NF permeate of AFFF solutions with two dilution levels and from two membrane materials at pH 12.

After the initial explorations, the later separation tests were conducted with the NFX membrane, and the [permeate:reject] ratio was increased to 90:10 (i.e., 10x concentration) for the treatment of the fresh and AFFF-added NAS JRB Willow Grove groundwater. [Table 8](#) and [Table 9](#) have shown that the NF filtration could reject most quantifiable PFAS compounds to <50 ng/L. Here we show the defluorination results of applying the ARP-AOP treatment train. [Figure 17](#) shows the data of F⁻ ion concentrations throughout the reduction and the following oxidation. The data at t=0 indicates the F⁻ ion concentrations of the feed (0.12 ppm), permeate (0.14 ppm), and reject (0.51 ppm). This data set roughly agrees with the NFX manufacturer's information on the 40% rejection of NaCl. The rejection of F⁻ ion in this case is also ~40%:

$$(0.51 \text{ ppm} \times 0.1) / (0.51 \text{ ppm} \times 0.1 + 0.14 \text{ ppm} \times 0.9) = 40.5\%$$

Because the fresh groundwater contains < 5 µg/L of total quantifiable PFAS and the reject contains < 20 µg/L of total quantifiable PFAS, the ARP treatment could not detect a significant increase of F⁻ ion concentration. However, the following AOP treatment increased the F⁻ ion concentration from 0.57 ppm to 0.63 ppm in the NF reject and from 0.13 to 0.21 ppm in the feed, respectively. **The higher increase in the feed than in the reject may suggest that some PFAS**

precursors were able to penetrate the NF membrane. LC/MS/MS analysis observed a series of PFCAs appeared in the NF permeate after the ARP-AOP process (Table 13).

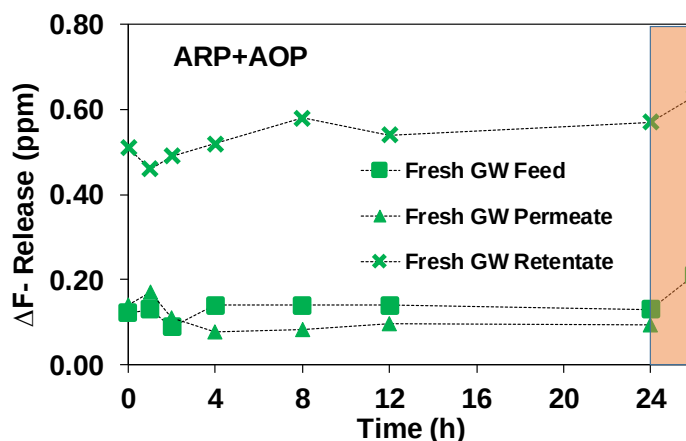


Figure 19. ARP-AOP defluorination from the fresh groundwater samples processed by NF. The AOP step is highlighted in orange.

ARP Reaction conditions: 20 mM Na₂SO₃, pH 12.0, 20 °C. AOP reaction conditions: 50 mM K₂S₂O₈, 125 mM KOH, 120 °C, 40 min.

Table 15. LC/MS/MS analysis results for ARP-AOP treated groundwater (unit: ng/L).

<i>Treated GW</i>	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
<i>Treated Feed</i>	67.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
<i>Treated Permeate</i>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
<i>Treated Reject</i>	179.3	<LOQ	290.0	<LOQ	61.6	<LOQ	ND

<i>Treated GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA
<i>Treated Feed</i>	440.6	502.3	1106.2	1744.7	2685.0	312.3	<LOQ	<LOQ	<LOQ
<i>Treated Permeate</i>	253.1	356.9	650.8	442.8	340.9	52.4	<LOQ	<LOQ	<LOQ
<i>Treated Reject</i>	606.5	246.4	601.2	992.4	2021.8	189.8	73.2	<LOQ	<LOQ

<i>Treated GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
<i>Treated Feed</i>	ND	229.7	89.3	<LOQ	ND	<LOQ
<i>Treated Permeate</i>	ND	<LOQ	<LOQ	<LOQ	ND	<LOQ
<i>Treated Reject</i>	ND	76.1	279.3	<LOQ	ND	<LOQ

The data in Table 8 and Table 13 clearly show the difference before and after the ARP-AOP treatment (data rearranged in Table 14). In all three samples (feed, permeate, and reject), all perfluorosulfonates were significantly degraded (the removal ratio ranging from 51 to 96%). As a stark comparison, most perfluorocarboxylic acids had concentrations increased for up to 17 folds. This observation is strong evidence that the groundwater contained other PFAS precursors, which could be converted into PFCAs. As PFHpA, PFOA, and PFNA are the three mostly increased species, we postulate that in the real groundwater, long-chain PFAS surfactants are the precursors for those PFCAs. We must note that due to the low concentration of PFAS and organic matter, as well as the optimized ARP and AOP reaction conditions, many relatively labile PFAS compounds

(e.g., PFHpS and 8:2 FTS) were supposed to be deeply degraded. **The observed partial degradation (e.g., 30%, 51%, or 85%) could only be caused by the balance between the degradation by ARP/AOP and the formation from precursors.** The formation of 8:2 FTS is also a strong indicator of the presence of long-chain precursors in the historical AFFF used at the contaminated site. The outstanding “recalcitrance” of PFHpS among all sulfonates (shown in [Table 14](#)) may also indicate that the historical AFFF products contained C7 sulfonamides in relatively high quantities, together with other sulfonates ranging from C4 to C9. The sum of the total quantifiable PFAS compounds in the ARP-AOP treated feed, permeate, and reject are 7.2, 2.1, and 5.6 µg/L, respectively. **Future works are necessary to identify the factors that prevent a complete degradation of most PFAS compounds in the data table.**

Table 16. Comparison of the individual PFAS compound concentrations in the fresh groundwater before and after the ARP-AOP treatment (concentration unit is ng/L).

PFAS	Feed			Permeate			Reject		
	Before	After	Change	Before	After	Change	Before	After	Change
PFBS	233.3	67.7	↓ 71%	<LOQ	<LOQ	-	1101.8	179.3	↓ 84%
PFPeS	278.6	<LOQ ^a	↓ 82+%	<LOQ	<LOQ	-	1496.1	<LOQ	↓ 97+%
PFHxS	1062.1	<LOQ	↓ 95+%	<LOQ	<LOQ	-	7516.9	290.0	↓ 96%
PFHpS	101.3	<LOQ	↓ 51+%	<LOQ	<LOQ	-	338.4	<LOQ	↓ 85+%
PFOS	1110.6	<LOQ	↓ 95+%	<LOQ	<LOQ	-	1022.0	61.6	↓ 94%
PFNS	<LOQ	<LOQ	-	<LOQ	<LOQ	-	<LOQ	<LOQ	-
PFDS	ND	ND	-	ND	ND	-	ND	ND	-
PFBA	133.9	440.6	↑ 229%	<LOQ	253.1	↑ 406+%	605.3	606.5	↑ 0.2%
PFPeA	136.9	502.3	↑ 267%	ND	356.9	↑ 614+%	799.1	246.4	↓ 69%
PFHxA	506.9	1106.2	↑ 118%	<LOQ	650.8	↑ 1202+%	2567.1	601.2	↓ 77%
PFHpA	99.2	1744.7	↑ 1659%	ND	442.8	↑ 786+%	531.5	992.4	↑ 87%
PFOA	408.8	2685.0	↑ 557%	<LOQ	340.9	↑ 582+%	1788.5	2021.8	↑ 13%
PFNA	<LOQ	312.3	↑ 525+%	<LOQ	52.4	↑ 4.8+%	<LOQ	189.8	↑ 280+%
PFDA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	<LOQ	73.2	↑ 46+%
4:2 FTS	ND	ND	-	ND	ND	-	ND	ND	-
6:2 FTS	306.9	229.7	↓ 25%	181.6 ^b	<LOQ	-	1564.4	76.1	↓ 95%
8:2 FTS	<LOQ	89.3	↑ 79+%	<LOQ	<LOQ	-	397.6	279.3	↓ 30%
FOSA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	92.6	<LOQ	↓ 46+%

^aComparisons involving “<LOQ” and “ND” used <50 ng/L as the calculation basis.

^bComparison not made due to the potential interference of 6:2 FTS from the NF system.

For the treatment of AFFF-added groundwater, due to the limited time window and the amount of groundwater, we directly challenged the treatment system with the 1000x diluted AFFF. As shown in the previous sections, the ARP-AOP treatment of 10,000x and 100,000x diluted AFFF seemed to be adequate. We were mainly interested in challenging the system for the treatment of more concentrated IDW. As already shown in earlier comparisons (e.g., [Figure 4](#)), the treatment of 1000x AFFF in the feed could be challenging, and the treatment of the 100x equivalent AFFF in the reject would be difficult. We have stored the very limited 0.9 L of AFFF-GW reject for future studies that aim at the effective defluorination of most PFAS in the high-concentration samples. Assuming the original AFFF contained >9000 ppm F (see [Table 12](#)), a 100x diluted sample will contain >90 ppm F, which is higher than the typical concentration in our common

ARP reactions that contains 25 μM PFAS compound (e.g., 7 ppm F⁻ in PFOA). **Figure 18** shows the defluorination results. Similar to the data in **Figure 4**, the dilution-normalized ΔF^- from ARP after 24 h was 1300 ppm, merely 20% of the values from 10,000x and 100,000x diluted samples. The following AOP released 3800 ppm of ΔF^- , making the total ΔF^- of 5,100 ppm. This value was 59% of the maximum ΔF^- achieved from the 100,000x dilution samples. Therefore, an incomplete destruction of PFAS in the samples was expected. **This result indicates the necessity of further developing the ARP details to treat relatively concentrated IDW or slightly diluted AFFF.** For example, ESTCP's FY2020 Topic B12 "*Demonstration and Validation of Environmentally Sustainable Methods to Clean Firefighting Delivery Systems*" may benefit from this effort to fully destruct AFFF components within a minimal volume of system cleaning water. The UV/sulfite ARP and alkaline persulfate AOP has demonstrated high PFAS destruction efficiency when the AFFF was diluted for >10,000 fold. Hence, a technical solution toward further reducing the volume (and thus elevated concentration) would be highly desirable. We have obtained a suite of promising findings to achieve this goal (to be discussed during the presentation).

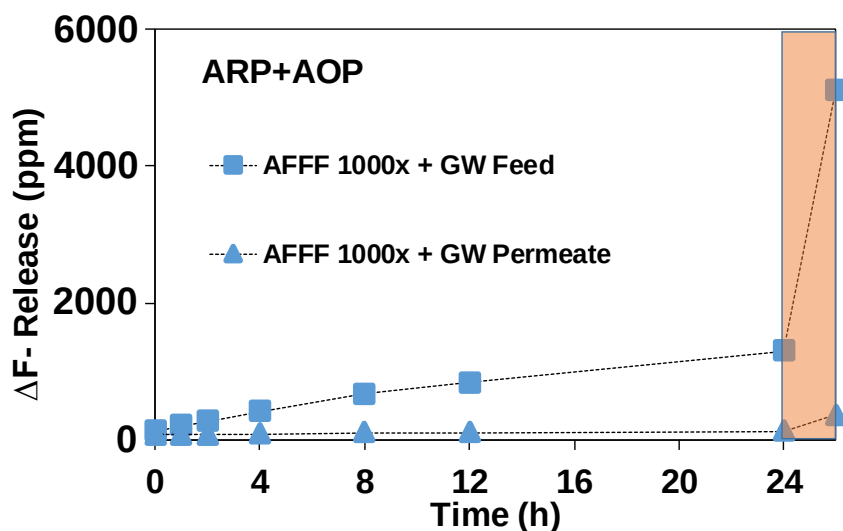


Figure 20. ARP-AOP defluorination from the AFFF-added groundwater samples (1000x dilution in the feed) processed by NF.

ARP Reaction conditions: 20 mM Na_2SO_3 , pH 12.0, 20 °C. AOP reaction conditions: 50 mM $\text{K}_2\text{S}_2\text{O}_8$, 125 mM KOH, 120 °C, 40 min.

As expected, the LC/MS/MS analysis (**Table 15**) identified high concentrations of PFCAs in the ARP-AOP treated feed. This is strong evidence for the presence of telomeric PFAS in the AFFF. In particular, the dominating PFCA is $n=4$ PFPeA. The $n=3$ PFBA and $n=5$ PFHxA are less than $n=4$ PFPeA. From our and other earlier studies,¹ $n=4$ PFCA is the dominating product from the oxidative decomposition of $n=6$ FTSA and FTCA. This result evidences the dominance of $n=6$ telomeric precursor in the AFFF. The sum of all quantifiable PFAS compounds in the treated feed was 577 $\mu\text{g/L}$ in the treated feed, or normalized to 577 mg/L (including carbon and other atoms) in the original AFFF. In comparison to the lost 3500 ppm of ΔF^- (5100 ppm shown in **Figure 18** versus 8600 ppm shown in **Table 12**), there should be more precursors not degraded yet. More interestingly, from the comparison shown in **Table 16**, although NF rejected most quantifiable PFAS compounds from entering the permeate, after the ARP-AOP treatment, increased concentrations of PFCAs also showed up. All perfluorosulfonates in the treated permeate

remained < 50 ng/L. This is a strong evidence that no precursor of perfluorosulfonates could penetrate the NF membrane, or the AFFF does not contain a significant amount of sulfonate precursors.

Table 17. LC/MS/MS analysis results for ARP-AOP treated AFFF-added groundwater samples (unit: ng/L).^a

<i>Treated AFFF+GW</i>	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS
<i>Treated Feed</i>	340.9	617.3	2259.5	<LOQ	88.6	<LOQ	ND
<i>Treated Permeate</i>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND

<i>Treated AFFF+GW</i>	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDaA
<i>Treated Feed</i>	165433	247106	95786	38893	22350	3798.4	107.1	<LOQ	<LOQ
<i>Treated Permeate</i>	823.2	1396.2	2463.8	2964.4	4484.3	3257.3	107.5	<LOQ	<LOQ

<i>Treated AFFF+GW</i>	4:2 FTS	6:2 FTS	8:2 FTS	FOSA	N-EtFOSAA	N-MeFOSAA
<i>Treated Feed</i>	ND	262.4	61.0	<LOQ	ND	<LOQ
<i>Treated Permeate</i>	ND	381.2	<LOQ	<LOQ	ND	<LOQ

^aThe ARP-AOP treatment on the NF reject was not conducted due to the formation of a high concentration of PFCAs (indicating incomplete treatment) from the feed. The NF reject contained 10x higher concentration of PFAS than the feed.

Table 18. Comparison of the individual PFAS compound concentrations in the AFFF-added original groundwater before and after the ARP-AOP treatment (concentration unit is ng/L).

PFAS	Feed			Permeate			Reject		
	Before	After	Change	Before	After	Change	Before	After ^a	Change ^a
PFBS	181.7	340.9	↑ 88%	<LOQ	<LOQ	-	939.9	N.A.	N.A.
PFPeS	206.2	617.3	↑ 199%	<LOQ	<LOQ	-	1042.4	N.A.	N.A.
PFHxS	781.0	2259.5	↑ 189%	75.5	<LOQ	↓ 34+%	4166.9	N.A.	N.A.
PFHpS	<LOQ ^b	<LOQ	-	<LOQ	<LOQ	-	<LOQ	N.A.	N.A.
PFOS	488.8	88.6	↓ 82%	<LOQ	<LOQ	-	3610.4	N.A.	N.A.
PFNS	<LOQ	<LOQ	-	<LOQ	<LOQ	-	92.2	N.A.	N.A.
PFDS	ND	ND	-	ND	ND	-	ND	N.A.	N.A.
PFBA	489.2	165433	↑ 33717%	<LOQ	823.2	↑ 1546+%	4368.0	N.A.	N.A.
PFPeA	378.0	247106	↑ 65272%	ND	1396.2	↑ 2692+%	1123.8	N.A.	N.A.
PFHxA	5109.4	95786	↑ 1775%	132.9	2463.8	↑ 1754%	14786	N.A.	N.A.
PFHpA	479.8	38893	↑ 8006%	ND	2964.4	↑ 5829+%	526.6	N.A.	N.A.
PFOA	6490.5	22350	↑ 244%	95.6	4484.3	↑ 4591+%	663.6	N.A.	N.A.
PFNA	<LOQ	3798.4	↑ 7497+%	<LOQ	3257.3	↑ 6415+%	<LOQ	N.A.	N.A.
PFDA	<LOQ	107.1	↑ 114+%	<LOQ	107.5	↑ 115+%	88.4	N.A.	N.A.
4:2 FTS	308.4	ND	↓ 84+%	<LOQ	ND	-	1454.2	N.A.	N.A.
6:2 FTS	4044.2	262.4	↓ 94%	1234.6	381.2	↓ 69%	8097.7	N.A.	N.A.
8:2 FTS	2840.7	61.0	↓ 98%	133.3	<LOQ	↓ 62+%	2559.0	N.A.	N.A.
FOSA	<LOQ	<LOQ	-	<LOQ	<LOQ	-	63.7	N.A.	N.A.

^aComparison not made yet because effective treatment of the 5x concentrate of the 1000x AFFF seemed challenging using the current chemical dosing.

^bComparisons involving “<LOQ” and “ND” used <50 ng/L as the calculation basis.

Because the total PFAS in the permeate should be much less than in the feed (see the defluorination profile of permeate in [Figure 18](#)), the reason for the incomplete destruction of the precursors for those PFCAs during the ARP is unknown. The most probable reason is the penetration of neutral organic additives into the permeate. **If this is true, an oxidation treatment before the membrane filtration could be imperative. We will systematically investigate the effect of pre-oxidation in future work.** More importantly, although the majority of quantifiable PFAS compounds in the untreated permeate is < 50 ng/L, the release of a total of 15.5 µg/L of PFCAs in the treated permeate suggests that some PFAS precursors can penetrate NF. Because NF material has been confirmed to be able to reject most charged PFAS compounds, it is highly possible that **a small fraction of PFAS compounds in AFFF might be in the neutral molecular form** (e.g., alcohol, or some other neutral molecules as the unreacted building materials used for the synthesis of fluoro-surfactant molecules). Future work is imperative to elucidate the underlying mechanism for the penetration through the NF membrane and the resistance against the degradation treatment.

Lastly, since PFCAs are the most susceptible PFAS for ARP-AOP destruction, the detection of PFCAs in the treated NF feed and permeate only indicates the need for further optimization of the ARP and AOP treatment modules. We have identified several effective strategies to treat highly concentrated PFAS (not discussed in this final report) and will apply them in the future work of this direction.

Conclusions and Implications for Future Research

This Limited-Scope Project has investigated and obtained **highly positive main conclusions** in the following aspects:

5. The real PFAS-contaminated groundwater (low PFAS contents) and AFFF-added groundwater (high PFAS contents) can be purified by commercial nanofiltration (NF) membranes. Analytical results show that the concentrations for all C4 and longer PFAS compounds on and beyond the EPA Method 537.1 analyte list are below 50 ng/L in the NF permeate.
6. The advanced reduction (ARP, using UV/sulfite operated at $\text{pH} \geq 12.0$ and $20\text{ }^{\circ}\text{C}$) and advanced oxidation (AOP, using heat-activated persulfate/hydroxide at $\leq 120\text{ }^{\circ}\text{C}$) have been specifically optimized for the treatment of AFFF solutions. The combination of ARP and AOP can effectively degrade all PFAS compounds on the EPA Method 537.1 analyte list in the presence of groundwater matrix and organic additives from the AFFF. With adequate dilution (e.g., 10,000x), at least 8.6 g/L (0.45 M) of organic fluorine can be defluorinated as F^- ion from the original AFFF product.
7. Based on the structure-reactivity relationship established by the PI, our analytical work, including LC/MS/MS analysis, ^{19}F NMR, and fluoride ion determination, have successfully identified the dominant PFAS component in the AFFF as a C_6F_{13} telomeric structure. Other minor impurities with various chain lengths are also present. Perfluorosulfonates are not a significant component in the AFFF. We have also identified different types of PFAS pollution and transformation in the fresh NAS JRB Willow Grove groundwater and the AFFF-added groundwater.
8. The results achieved to date have confirmed that, upon further optimization of the NF and ARP/AOP modules, most PFAS species in the groundwater and AFFF-added groundwater can be deeply or completely destructed.

This Limited-Scope Project has also identified **a series of technical challenges and unexpected/intriguing phenomena** that are imperative for IDW treatment in the following aspects:

4. Although NF treatment can produce the permeate containing <50 ppt of each PFAS compound, after the ARP-AOP treatment, a small amount of PFCA mixtures was detected in the treated permeate from both the fresh groundwater and AFFF-added groundwater. This is a critical point for the application of membrane filtration in PFAS remediation. The precursors for the generated PFCAs may be neutral molecules that can penetrate the NF membrane. Further detailed studies on the structure-selectivity relationship by the membrane interception are essential for the design and application of separation technology for the PFAS remediation practice.
5. The current UV/sulfite using 10–30 mM Na_2SO_3 as the source of hydrated electrons, 254 nm UV low-pressure mercury lamp, and the maintained $20\text{ }^{\circ}\text{C}$ reaction temperature could not effectively treat AFFF with 1000x or lower dilution folds. However, treating concentrated PFAS in a small volume of water is highly desirable to save the capital cost and the consumption of both chemicals and electricity. Currently, we believe that PFAS degradation enabled by UV-generated hydrated electron is one of the few highly

competitive methods for the practical treatment of concentrated PFAS. Further improvement of the ARP process is thus imperative to provide an effective and efficient technology for the remediation efforts led by SERDP and ESTCP.

6. We have observed significant defluorination from the AFFF and the transformation of a wide collection of PFAS compounds in the fresh groundwater and AFFF-added groundwater. A limited set of data also suggests that the NF filtration may improve the defluorination in the reject, probably by allowing the organic additives to go with the permeate. Detailed studies on the molecular transformation of individual PFAS structures, especially in the mixture of multiple PFAS species and in the groundwater mineral matrix and AFFF organic matrix, are necessary toward further optimizing the degradation technologies for IDW treatment, safe AFFF disposal, and fire-fighting pipeline cleaning, and so on.

Accordingly, to fully develop this NF-ARP/AOP strategy, we have the **following future research objectives and corresponding research plans**:

1. Obtain a comprehensive understanding of the structure-selectivity relationship by nanofiltration membranes: Co-PI Lin at Vanderbilt University will test the interception of a large number of charged and neutral PFAS compounds, especially those at the molecular weight cut-off “borderline” of nanofiltration, by a variety of commercial and lab-tailored membranes. The separation of the organic additives used in AFFF will also be systematically studied. PI Liu (UCR) and co-PI Sun (UNCC) will provide the analytical support with an Orbitrap high-resolution mass spectrometer and a triple quad mass spectrometer, respectively. Co-PI Lin will also study the fouling of the membrane materials by the groundwater minerals and AFFF organics after long-term operations.
2. Further improve the PFAS degradation technology to (1) treat highly concentrated PFAS mixture in less diluted AFFF solution and (2) achieve the complete destruction of most PFAS compounds in both the permeate and reject from NF treatment. By the assistance of co-PI Lin’s group, PI Liu will build a replicate NF system, which was initially developed at Vanderbilt U, at UCR. Without long-distance shipping of water samples, the NF-separated water samples can be produced in much larger quantities and immediately treated by the rapidly improving ARP and AOP methods in the same lab. The main guideline is to (1) improve the treatment efficiency for highly concentrated PFAS and (2) understand the effect of water matrix and provide solutions if major inhibiting species are identified. The improvement of ARP efficiency will rely on (but not limited to) the control of UV energy and intensity and the reaction temperature.

The majority of sample analysis (quantification of parent PFAS and transformation product analysis) will be immediately conducted at UCR. The Orbitrap high-resolution mass spec at the PI’s department Water Research Center has become available since February 2020. NMR analysis of the treated water samples will be further developed by PI Liu to obtain more chemical information during the reactions. Co-PI Sun will conduct the quantification of low-concentration PFAS analytes and total fluorine in her lab at UNCC. We will also systematically characterize other important parameters, such as total organic carbon level upon AOP and the concentrations of various metals

and anions that we did not have sufficient time or resources to conduct during the Limited-Scope project.

3. Evaluate the varying combination of NF/ARP/AOP treatment modules. The further improved membrane module (in terms of PFAS rejection and resistance to fouling) and the PFAS degradation module (in terms of the robustness and effectiveness of treating high-concentration PFAS mixtures) will be integrated into different sequences and evaluated. Based on the promising results from the Limited-Scope project, we aim at achieving thorough destruction of all PFAS compounds in both permeate and reject for safe disposal or reuse, and meanwhile save the energy and chemicals. For example, if the presence of PFAS in the permeate is caused by the organic additives or by the neutral PFAS precursors, we will evaluate the benefits and challenges of an AOP pretreatment before the NF step. The team still has 5 gallons of un-used NAS JRB Willow Grove groundwater to enable another round of final test. If needed, we will take more water samples from the same site in Pennsylvania or other sites in California. With all data in hand, we will conduct the techno-economic analysis (this skill can be quickly learned) to compare with other PFAS treatment technologies that are in or close to practical application.

The benefit of these future works is straightforward. We expect that all technical details to be studied by the extended work will push the NF-ARP-AOP treatment train into the practical application to treat either groundwater or specific concentrated samples (e.g., IDW and decommissioned AFFF) to the desired level that allows either safe discharge or reuse. We have high confidence in the working nature of this technology and our research capability to achieve the desired results.

Literature Cited

1. Houtz, E. F.; Sedlak, D. L., Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental science & technology* **2012**, 46, (17), 9342-9349.
2. Singh, R. K.; Multari, N.; Nau-Hix, C.; Anderson, R. H.; Richardson, S. D.; Holsen, T. M.; Mededovic Thagard, S., Rapid Removal of Poly-and Perfluorinated Compounds from Investigation-Derived Waste (IDW) in a Pilot-Scale Plasma Reactor. *Environmental science & technology* **2019**, 53, (19), 11375-11382.
3. Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L., Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environmental science & technology* **2013**, 47, (15), 8187-8195.
4. Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A., Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. *Environmental science & technology* **2017**, 51, (4), 2047-2057.
5. Harding-Marjanovic, K. C.; Houtz, E. F.; Yi, S.; Field, J. A.; Sedlak, D. L.; Alvarez-Cohen, L., Aerobic biotransformation of fluorotelomer thioether amido sulfonate (Lodyne) in AFFF-amended microcosms. *Environmental science & technology* **2015**, 49, (13), 7666-7674.
6. Yi, S.; Harding-Marjanovic, K. C.; Houtz, E. F.; Gao, Y.; Lawrence, J. E.; Nichiporuk, R. V.; Iavarone, A. T.; Zhuang, W.-Q.; Hansen, M.; Field, J. A., Biotransformation of AFFF component 6: 2 fluorotelomer thioether amido sulfonate generates 6: 2 fluorotelomer thioether carboxylate under sulfate-reducing conditions. *Environmental science & technology letters* **2018**, 5, (5), 283-288.
7. Hogue, C., Incinerators may spread, not break down PFAS. *Chemical & Engineering News* **APRIL 27, 2020**, <https://cen.acs.org/environment/persistent-pollutants/Incinerators-spread-break-down-PFAS/98/web/2020/04>.
8. Rahman, M. F.; Peldszus, S.; Anderson, W. B., Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review. *Water research* **2014**, 50, 318-340.
9. Xiao, X.; Ulrich, B. A.; Chen, B.; Higgins, C. P., Sorption of poly- and perfluoroalkyl substances (PFASs) relevant to aqueous film-forming Foam (AFFF)-impacted groundwater by biochars and activated carbon. *Environmental Science & Technology* **2017**, 51, (11), 6342-6351.
10. Boo, C.; Wang, Y.; Zucker, I.; Choo, Y.; Osuji, C. O.; Elimelech, M., High performance nanofiltration membrane for effective removal of perfluoroalkyl substances at high water recovery. *Environmental Science & Technology* **2018**, 52, (13), 7279-7288.
11. Deng, S.; Yu, Q.; Huang, J.; Yu, G., Removal of perfluorooctane sulfonate from wastewater by anion exchange resins: effects of resin properties and solution chemistry. *Water Research* **2010**, 44, (18), 5188-5195.
12. Du, Z.; Deng, S.; Chen, Y.; Wang, B.; Huang, J.; Wang, Y.; Yu, G., Removal of perfluorinated carboxylates from washing wastewater of perfluorooctanesulfonyl fluoride using activated carbons and resins. *Journal of hazardous materials* **2015**, 286, 136-143.
13. Merino, N.; Qu, Y.; Deeb, R. A.; Hawley, E. L.; Hoffmann, M. R.; Mahendra, S., Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water. *Environmental Engineering Science* **2016**, 33, (9), 615-649.

14. Song, Z.; Tang, H.; Wang, N.; Zhu, L., Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system. *Journal of hazardous materials* **2013**, 262, 332-338.
15. Park, H.; Vecitis, C. D.; Cheng, J.; Choi, W.; Mader, B. T.; Hoffmann, M. R., Reductive defluorination of aqueous perfluorinated alkyl surfactants: effects of ionic headgroup and chain length. *The Journal of Physical Chemistry A* **2009**, 113, (4), 690-696.
16. Tian, H.; Gao, J.; Li, H.; Boyd, S. A.; Gu, C., Complete Defluorination of Perfluorinated Compounds by Hydrated Electrons Generated from 3-Indole-acetic-acid in Organomodified Montmorillonite. *Scientific Reports* **2016**, 6.
17. Kulkarni, U. S.; Dixit, S. G., Destruction of phenol from wastewater by oxidation with sulfite-oxygen. *Industrial & engineering chemistry research* **1991**, 30, (8), 1916-1920.
18. MacCrehan, W. A.; Jensen, J. S.; Helz, G. R., Detection of sewage organic chlorination products that are resistant to dechlorination with sulfite. *Environmental science & technology* **1998**, 32, (22), 3640-3645.
19. Sun, B.; Guan, X.; Fang, J.; Tratnyek, P. G., Activation of manganese oxidants with bisulfite for enhanced oxidation of organic contaminants: the involvement of Mn (III). *Environmental science & technology* **2015**, 49, (20), 12414-12421.
20. Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Defluorination of per- and polyfluoroalkyl substances (PFASs) with hydrated electrons: structural dependence and implications to PFAS remediation and management. *Environmental science & technology* **2019**, 53, (7), 3718-3728.
21. Bentel, M. J.; Yu, Y.; Xu, L.; Kwon, H.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Degradation of perfluoroalkyl ether carboxylic acids with hydrated electrons: Structure–reactivity relationships and environmental implications. *Environmental Science & Technology* **2020**, 54, (4), 2489-2499.
22. Tenorio, R.; Liu, J.; xiao, x.; Maizel, A. C.; Higgins, C. P.; Schaefer, C. E.; Strathmann, T. J., Destruction of per- and polyfluoroalkyl substances (PFASs) in aqueous film-forming foam (AFFF) with UV-sulfite photo-reductive treatment. *Environmental Science & Technology* **2020**.
23. Bentel, M. J.; Liu, Z.; Yu, Y.; Gao, J.; Men, Y.; Liu, J., Enhanced Degradation of Perfluorocarboxylic Acids (PFCAs) by UV/Sulfite Treatment: Reaction Mechanisms and System Efficiencies at pH 12. *Environmental Science & Technology Letters* **2020**, 7, (5), 351-357.
24. Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T., A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environmental Science & Technology* **2017**, DOI: 10.1021/acs.est.6b04806.
25. Kleiner, E.; Jho, C. In *Recent developments in 6: 2 fluorotelomer surfactants and foam stabilizers*, 4th Reebok Foam Seminar, 2009; 2009; pp 6-7.
26. Pramanik, B. K.; Pramanik, S. K.; Sarker, D. C.; Suja, F., Removal of emerging perfluorooctanoic acid and perfluorooctane sulfonate contaminants from lake water. *Environmental technology* **2017**, 38, (15), 1937-1942.
27. Appleman, T. D.; Dickenson, E. R.; Bellona, C.; Higgins, C. P., Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. *Journal of hazardous materials* **2013**, 260, 740-746.
28. Steinle-Darling, E.; Reinhard, M., Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. *Environmental science & technology* **2008**, 42, (14), 5292-5297.
29. Rattanaoudom, R.; Visvanathan, C., Removal of PFOA by hybrid membrane filtration using PAC and hydrotalcite. *Desalination and Water Treatment* **2011**, 32, (1-3), 262-270.

30. Baudequin, C.; Mai, Z.; Rakib, M.; Deguerry, I.; Severac, R.; Pabon, M.; Couallier, E., Removal of fluorinated surfactants by reverse osmosis–role of surfactants in membrane fouling. *Journal of Membrane Science* **2014**, *458*, 111-119.
31. Tang, C. Y.; Fu, Q. S.; Robertson, A.; Criddle, C. S.; Leckie, J. O., Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater. *Environmental science & technology* **2006**, *40*, (23), 7343-7349.
32. Hosomi, M.; Sudo, R., Simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulfate digestion. *International Journal of Environmental Studies* **1986**, *27*, (3-4), 267-275.
33. Bao, Y.; Deng, S.; Jiang, X.; Qu, Y.; He, Y.; Liu, L.; Chai, Q.; Mumtaz, M.; Huang, J.; Cagnetta, G., Degradation of PFOA substitute: GenX (HFPO–DA ammonium salt): oxidation with UV/persulfate or reduction with UV/sulfite? *Environmental science & technology* **2018**, *52*, (20), 11728-11734.
34. Gu, Y.; Liu, T.; Zhang, Q.; Dong, W., Efficient decomposition of perfluorooctanoic acid by a high photon flux UV/sulfite process: Kinetics and associated toxicity. *Chemical Engineering Journal* **2017**, *326*, 1125-1133.

Appendix. QA/QC Report on LC-MS/MS quantitation.

QC ID	Type	4:2FTS			6:2FTS		8:2FTS	
		True Value (ng/L)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)
Standard 1	Calibration Standard	50.00	44.31	88.62	44.08	88.16	65.99	131.99
Standard 2	Calibration Standard	100.00	108.50	108.50	107.77	107.77	102.05	102.05
Standard 3	Calibration Standard	150.00	155.04	103.36	152.45	101.63	143.57	95.71
Standard 4	Calibration Standard	200.00	194.11	97.05	192.92	96.46	180.66	90.33
Standard 5	Calibration Standard	250.00	250.18	100.07	259.20	103.68	247.51	99.00
Standard 6	Calibration Standard	300.00	293.33	97.78	291.65	97.22	296.37	98.79
Standard 7	Calibration Standard	400.00	404.53	101.13	401.93	100.48	413.85	103.46
QC 300 ppt	Calibration verification	300.00	300.11	100.04	263.84	87.95	296.37	98.79

QC ID	Type	FOSA			N-EtFOSAA		N-MeFOSAA	
		True Value (ng/L)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)
Standard 1	Calibration Standard	50.00	56.20	112.40	45.36	90.73	65.51	131.02
Standard 2	Calibration Standard	100.00	108.04	108.04	124.71	124.71	116.75	116.75
Standard 3	Calibration Standard	150.00	150.78	100.52	143.87	95.92	146.90	97.93
Standard 4	Calibration Standard	200.00	177.80	88.90	183.92	91.96	179.79	89.89
Standard 5	Calibration Standard	250.00	245.03	98.01	246.56	98.62	222.20	88.88
Standard 6	Calibration Standard	300.00	304.10	101.37	294.74	98.25	285.36	95.12
Standard 7	Calibration Standard	400.00	408.05	102.01	410.84	102.71	433.50	108.37
QC 300 ppt	Calibration verification	300.00	283.59	94.53	294.75	98.25	285.37	95.12

QC ID	Type	PFBA			PFBS		PFDA		PFDoA	
		True Value (ng/L)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)
Standard 1	Calibration Standard	50.00	40.81	81.63	48.00	96.00	74.70	149.39	57.91	115.83
Standard 2	Calibration Standard	100.00	74.99	74.99	106.42	106.42	109.71	109.71	108.10	108.10
Standard 3	Calibration Standard	150.00	160.96	107.31	156.28	104.19	142.16	94.77	151.33	100.89
Standard 4	Calibration Standard	200.00	194.86	97.43	191.03	95.52	170.25	85.12	185.11	92.56
Standard 5	Calibration Standard	250.00	329.44	131.78	253.55	101.42	233.21	93.28	230.07	92.03
Standard 6	Calibration Standard	300.00	270.88	90.29	284.66	94.89	288.74	96.25	304.35	101.45
Standard 7	Calibration Standard	400.00	378.05	94.51	410.06	102.51	431.24	107.81	413.13	103.28
QC 300 ppt	Calibration verification	300.00	298.55	99.52	299.59	99.86	288.75	96.25	304.34	101.45

QC ID	Type	PFDS			PFHpA		PFHpS		PFHxA	
		True Value (ng/L)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)
Standard 1	Calibration Standard	50.00	43.62	87.24	60.59	121.18	54.99	109.97	50.06	100.12
Standard 2	Calibration Standard	100.00	94.20	94.20	99.15	99.15	105.06	105.06	102.33	102.33
Standard 3	Calibration Standard	150.00	159.27	106.18	150.81	100.54	150.80	100.54	153.18	102.12
Standard 4	Calibration Standard	200.00	213.70	106.85	187.25	93.62	193.41	96.71	197.81	98.91
Standard 5	Calibration Standard	250.00	250.26	100.10	255.94	102.38	245.86	98.35	253.87	101.55
Standard 6	Calibration Standard	300.00	288.75	96.25	280.05	93.35	284.73	94.91	283.42	94.47
Standard 7	Calibration Standard	400.00	400.19	100.05	416.21	104.05	415.14	103.79	409.33	102.33
QC 300 ppt	Calibration verification	300.00	288.76	96.25	300.37	100.12	256.96	85.65	293.57	97.86

QC ID	Type	PFHxS			PFNA		PFNS		PFOA	
		True Value (ng/L)	Measur ed Value (ng/L)	Recove ry (%)	Measur ed Value (ng/L)	Recove ry (%)	Measur ed Value (ng/L)	Recove ry (%)	Measur ed Value (ng/L)	Recove ry (%)
Standard 1	Calibration Standard	50.00	64.00	128.01	46.16	92.32	62.59	125.17	48.40	96.79
Standard 2	Calibration Standard	100.00	104.17	104.17	132.45	132.45	104.48	104.48	106.49	106.49
Standard 3	Calibration Standard	150.00	164.59	109.72	140.10	93.40	156.74	104.50	153.46	102.30
Standard 4	Calibration Standard	200.00	184.99	92.49	177.16	88.58	177.42	88.71	189.84	94.92
Standard 5	Calibration Standard	250.00	232.21	92.88	249.75	99.90	243.97	97.59	252.54	101.02
Standard 6	Calibration Standard	300.00	258.74	86.25	286.88	95.63	279.84	93.28	294.00	98.00
Standard 7	Calibration Standard	400.00	441.31	110.33	417.49	104.37	424.95	106.24	405.27	101.32
QC 300 ppt	Calibration verification	300.00	305.78	101.93	280.29	93.43	279.85	93.28	289.70	96.57

QC ID	Type	PFOS			PFPeA		PFPeS		PFUdA	
		True Value (ng/L)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)	Measured Value (ng/L)	Recovery (%)
Standard 1	Calibration Standard	50.00	69.12	138.23	0.00	0.00	50.03	100.05	62.81	125.62
Standard 2	Calibration Standard	100.00	102.46	102.46	141.51	141.51	103.19	103.19	108.10	108.10
Standard 3	Calibration Standard	150.00	143.41	95.61	134.88	89.92	156.66	104.44	153.44	102.30
Standard 4	Calibration Standard	200.00	180.18	90.09	274.66	137.33	193.19	96.59	179.74	89.87
Standard 5	Calibration Standard	250.00	243.04	97.22	245.98	98.39	250.42	100.17	232.81	93.12
Standard 6	Calibration Standard	300.00	292.26	97.42	276.52	92.17	286.71	95.57	288.56	96.19
Standard 7	Calibration Standard	400.00	419.53	104.88	385.47	96.37	409.82	102.45	424.54	106.13
QC 300 ppt	Calibration verification	300.00	292.27	97.42	343.41	114.47	325.48	108.49	288.56	96.19

Blanks

QC ID	All individual PFAS shown in the previous pages (ng/L)
SPE Blank	<50.00
LC-Blank 1	<50.00
LC-Blank 2	<50.00
LC-Blank 3	<50.00
LC-Blank 4	<50.00
LC-Blank 5	<50.00
LC-Blank 6	<50.00
LC-Blank 7	<50.00
LC-Blank 8	<50.00
LC-Blank 9	<50.00
LC-Blank 10	<50.00