



**Environmental
Science**
Processes & Impacts

**Enhanced Aggregation and Interfacial Adsorption of an
Aqueous Film Forming Foam (AFFF) in High Salinity
Matrices**

Journal:	<i>Environmental Science: Processes & Impacts</i>
Manuscript ID	EM-ART-06-2023-000247.R1
Article Type:	Paper

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12 **Environmental Significance Statement**
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14 Per- and polyfluoroalkyl substances (PFAS) are worldwide concerns, with much of the
15 contamination attributable to use of aqueous film forming foams (AFFFs) for fire-fighting
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17 activities. PFAS surfactant properties impart them with unique environmental behavior, such as
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19 their tendency to aggregate, ‘salt-out’, and adsorb at air-water interfaces, all which impact their
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21 interactions with surfaces and consequently their detection, fate, and transport. This work
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23 demonstrates that salinity increases PFAS aggregation in bulk solution and drives adsorption of
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25 PFAS at the air-water interface in AFFF solutions. Our findings suggest that AFFF
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27 contamination in high salinity environments may lead to enhanced retention of PFAS at the point
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29 of contamination, necessitating increased attention to source zone treatment and monitoring.
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3 Enhanced Aggregation and Interfacial Adsorption of an Aqueous Film Forming Foam (AFFF)
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49 **Key Words:** PFAS, AFFF, aggregation, air-water interface, surfactant
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Abstract

Per- and polyfluoroalkyl substances (PFAS) exist in contaminated groundwater, surface water, soil, and sediments from use of aqueous film forming foams (AFFFs). Under these conditions PFAS exhibit unusual behavior due to their surfactant properties, namely, aggregation and surface activity. Environmental factors such as salinity can affect these properties, and complicate efforts to monitor PFAS. The effect of high salinity matrices on the critical micelle concentration (CMC) of a AFFF formulation manufactured by 3M and the surface accumulation of PFAS was assessed with surface tension isotherm measurements and bench-scale experiments quantifying PFAS at the air-water interface. Conditions typical of brackish and saline waters substantially depressed the CMC of the AFFF by over 50% and increased the interfacial mass accumulation of PFAS in the AFFF mixture by up to a factor of 3, relative to values measured in ultrapure water. These results indicate that high salinity matrices increase the aggregation and surface activity of PFAS in mixtures, which are key properties affecting their transport.

Introduction

Aqueous film-forming foam (AFFF) contamination often eludes conventional approaches to remediation and monitoring. Legacy AFFF formulations contain per- and polyfluoroalkyl substances (PFAS), a class of compounds which provides these liquids with film-forming properties and fast spreading coefficients,^{1,2} yielding rapid fire-extinction performance when used for firefighting applications.^{2,3} While extremely valuable for this technical application, many PFAS have proven to be toxic and bio-accumulative,⁴ and can be detected in water globally due to their widespread use.⁵ Accurate monitoring of PFAS, with the end goal of reducing human exposure, has proved to be challenging because of their unusual surfactant properties.

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3 Many PFAS are surface active compounds (surfactants) that exhibit a high affinity for
4 interfaces (e.g., air-water interface). They also form aggregates and/or micelles at concentrations
5 near and above the critical micelle concentration (CMC). These surfactant-specific phenomena
6 affect compound detection and transport in aqueous systems.⁶⁻⁸ The surface activity and CMC of
7 PFAS varies based on structural characteristics such as chain length, head group, and degree of
8 fluorination. Within a specific AFFF formulation, these parameters also are affected by
9 concentration, background ions, temperature, other formulation components and co-
10 contaminants (e.g., concentrations of hydrocarbon surfactants and solvents).⁹⁻¹¹ As a result,
11 PFAS environmental behavior is challenging to predict and varies depending not only on the
12 identity of the compound being evaluated, but on the environmental conditions themselves.¹²⁻¹⁵
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14 Considering that thousands of individual PFAS have been associated with AFFF,¹⁶ a
15 comprehensive understanding of the relationship between environmental factors and the
16 contaminant physicochemical properties is essential for accurate monitoring and modeling of
17 fate and transport.
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PFAS contamination is prevalent at coastal military bases where PFAS-containing AFFF was applied during firefighter training and emergencies.¹⁶ Salinity has been shown to alter the environmental behavior and detection of PFAS through processes such as ‘salting-out’^{8,17-20} but thus far, researchers have only examined simplified systems (e.g., one or two PFAS compounds) in the presence of high salt concentrations. Processes such as ‘salting-out’ can lead to both aggregate formation and enhanced sorption to sediments and soils, which have the potential to reduce PFAS migration.^{20,21} To further understand the behavior of PFAS mixtures in saline waters, we evaluated the CMC of a legacy 3M AFFF formulation under conditions typical of brackish and saline water. Additionally, we measured the interfacial mass accumulation of

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3 individual compounds in the AFFF formulation in the presence of different salts to assess the
4 effects of varying specific cations and anions. This analysis will inform interpretation of PFAS
5 fate under saline conditions and improve efforts to model PFAS transport in saline matrices.
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7 Understanding the interfacial behavior of PFAS under conditions mimicking those encountered
8 at coastal source zones will support treatment strategies for contaminant clean up.
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17 **Methods**

18 Chemicals

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20 PFAS containing solutions were prepared in 50-mL polypropylene centrifuge tubes
21 (Corning) with Milli-Q water and specified salt concentrations. Reagent grade salts purchased
22 from Sigma-Aldrich were used to prepare electrolyte solutions. Artificial brackish water (ABW)
23 and artificial seawater (ASW) solutions were prepared as 1L solutions with compositions
24 representative of those likely to be encountered in the environment (Supporting Information
25 Table S1).²² AFFF solutions were prepared using a legacy 3M Guardian AFFF concentrate
26 (manufactured 2000-2002, provided by Dr. Jennifer Field of Oregon State University). Dilution
27 series were prepared by weighing out portions of the 3M concentrate and diluting with Milli-Q
28 water, ABW, or ASW (Supporting Information Table S2). PFAS analytes were quantified by
29 liquid chromatography tandem mass spectrometry (LC-MS/MS) using a PFAS analytical
30 standard mixtures obtained from Wellington Laboratories, Inc.; a detailed list of analytes,
31 transition energies, and the chromatography method can be found in the Supporting Information
32 Table S3, Text S1.
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51 Surface Tension Experiments

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3 Surface tension isotherms were measured using pendant drop tensiometry (PDT) on a
4 KRÜSS tensiometer with a glass syringe and needle attachment. Surface tension measurements
5 obtained on three drops were averaged for each solution in the dilution series; surface tension
6 measurements were taken over a minimum of three minutes at ten second intervals. Typically,
7 surface tension was observed to decrease steadily in the early measurement intervals (i.e., 30-60
8 seconds), and then reach an equilibrium. The CMC of the 3M AFFF formulation was determined
9 from slope of the surface tension isotherm in the pre-micellar region (Supporting Information
10 Figure S1, Table S5); the surface tension data were analyzed using the Langmuir-Szyszkowski
11 (LS) model (Supporting Information Text S2). The fitted parameters *a* and *b*, related to the
12 maximum surface excess and surface activity, respectively, were determined using a non-linear
13 regression using the *SciPy* package in Python 3.8.5. Maximum surface excess was calculated
14 from the first term of the Langmuir-Szyszkowski equation (Supporting Information Eq. S2).
15 Target AFFF concentrations were used to fit the surface tension data; validation of the target
16 concentrations was performed by comparing perfluorooctane sulfonic acid (PFOS) concentration
17 measured in the AFFF dilution series (Supporting Information Figure S2, Table S4).

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19 By fitting the Szyszkowski equation to the surface tension isotherms, the parameters
20 related to the surface excess (*a*) and surface activity (*b*) were calculated from the Szyszkowski
21 equation (Supporting Information Text S2, Table S6). The parameter *a* can be substituted into
22 the first term of the Langmuir-Szyszkowski equation (Eq. 1) which represents the maximum
23 surface excess, Γ_{max} , and γ_0 represents the surface tension of ultrapure water, *R* is the universal
24 constant, and *T* is the temperature.

$$\Gamma_{max} = \frac{\gamma_0 a}{RT} \quad (\text{Eq. 1})$$

Interfacial Mass Accumulation Experiments

AFFF solutions were prepared in Milli-Q water in polypropylene tubes; AFFF was diluted 1000-fold to a target concentration of 10 mg/L PFOS to compare observations to prior measurements made in PFOS solutions.⁸ For single salt experiments (e.g., NaCl and CaCl₂), solid salts were added directly to dilute AFFF solutions in tubes; for experiments in ABW and ASW, AFFF was diluted directly into centrifuge tubes containing ABW or ASW.

PFAS adsorption at the air-water interface was analyzed using an experimental procedure described by Schaefer et al. 2019²³ and modified in Steffens et al. 2021.⁸ The 50-mL centrifuge tubes (d= 29.1 mm) were prepared with a small hole drilled at the bottom and temporarily sealed with PFAS-free tape; solutions were prepared in triplicate for each condition studied. Solutions were left to equilibrate at room temperature for 48-hours; the bulk solution from each tube was then drained into a catch tube and the ‘film’-containing volume (approximately 0.5 mL) was collected in a microcentrifuge tube by draining the volume through the drilled hole. The collected solutions were weighed to ensure accuracy in subsequent concentration calculations. The interfacial mass of PFAS was determined from the detected concentration and volume of the collected film.

Results & Discussion

Previous research has demonstrated the effect of salinity on enhancing the interfacial sorption of PFAS, but these systems have only considered one or two analytes in the presence a limited set of salts.^{6-8,23,24} Considering that AFFF contamination typically involves complex mixtures of PFAS in the presence of high concentrations of other organic compounds and dissolved ions, it is important to quantify the aggregation behavior and air-water sorption

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3 behavior of complex mixtures under more realistic conditions. Legacy 3M AFFF formulations
4 contain a mixture of fluoro- and hydrocarbon surfactants in addition to organic solvents, e.g.,
5 diethylene glycol monobutyl ether (DGBE).^{12,25,26} The primary compound identified in the 3M
6 AFFF solution was the anionic compound PFOS (~1.3%), which is consistent with previous
7 findings²⁶ and reports of AFFF composition, despite the exact formulations being proprietary.²⁵
8 Note the wide variation in PFAS concentrations in the AFFF formulation (Figure 1). The
9 formulation tested here also contained perfluorosulfonamido compounds, mainly, *N*-dimethyl
10 ammonio propyl perfluorohexane sulfonamide (AmPr-FhxSA, ~0.12%) as well as low
11 concentrations (<250 µg/L) of the perfluorocarboxylic acids, perfluorohexanoic acid (PFHxA),
12 perfluoroheptanoic acid (PFHpA), and perfluorooctanoic acid (PFOA) (Supporting Information
13 Tables S7-S10, Figure S3). The hydrocarbon surfactants and solvents in the formulation were not
14 evaluated in this study.
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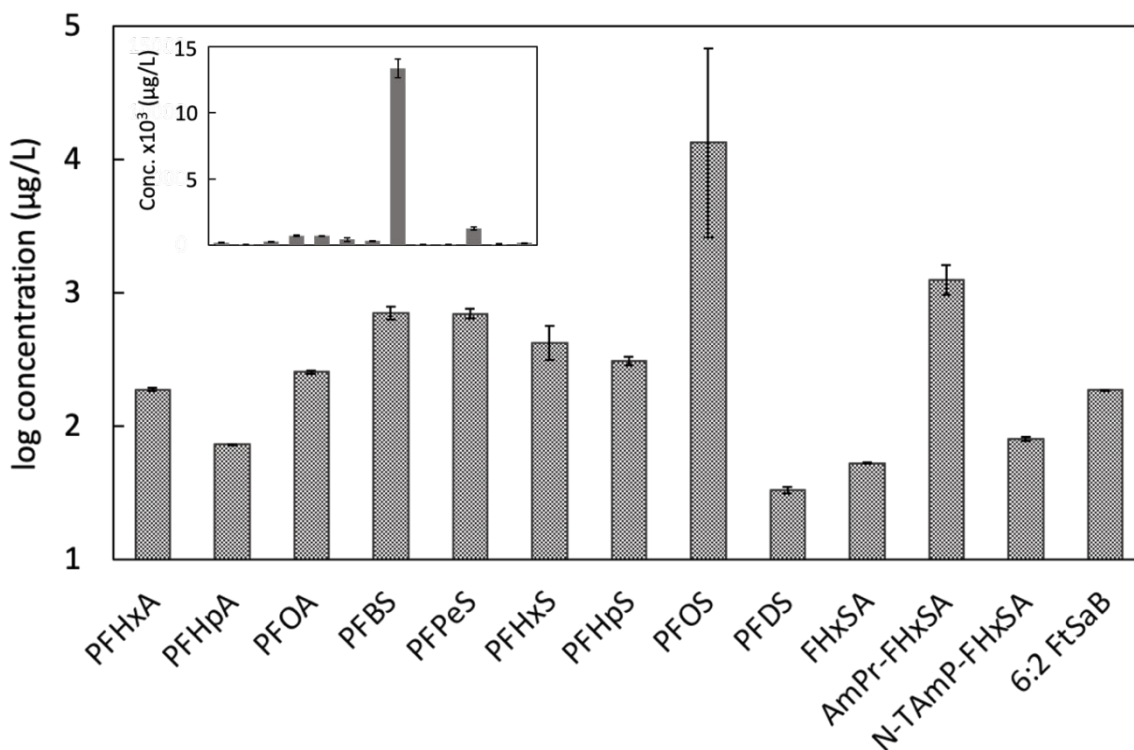


Figure 1. PFAS analytes detected in 1000x diluted 3M AFFF in ultrapure water (bulk solution) reported on a log scale with inset of a linear scale. Values and error bars are the mean and standard deviation of triplicate samples.

PFAS aggregation behavior was assessed by surface tension isotherms in ultrapure, artificial brackish water (ABW) and artificial saline water (ASW) (Figure 2). In ultrapure water, the CMC of the 3M AFFF was 3780 mg/L ($R^2 = 0.975$). In both ABW and ASW, the CMC was over 50% lower than values measured in deionized water; in ABW, the CMC was 1690 mg/L ($R^2 = 0.949$) and for the ASW, the CMC was 1540 mg/L ($R^2 = 0.935$) (Table 1, Table S5). It was expected that the CMC would be lower in the saline matrices, as cations can increase the activity of the hydrophobic fluorinated tails in solution and decrease the electrostatic repulsion between anionic PFAS headgroups, thereby favoring micellization.^{12,27} The difference between the CMC in ABW and ASW was minimal, despite the higher ionic strength of the ASW (i.e., $I=0.32$ M for

the ABW and 0.64 M for ASW). When compared to the previously investigated PFOS-only system in single salt solutions,⁸ the 3M AFFF had a similar CMC in ABW (225 mM NaCl) and ASW (450 mM NaCl) to PFOS in 500-mM NaCl (Table 1). This similarity is consistent with an analysis by Costanza et al.²⁷ and can be attributed to the surfactant with greater surface activity and highest concentration in the formulation (PFOS) controlling the surface activity and CMC in a mixed surfactant system.^{12,28} This may explain why the manufacturer relied on PFOS in its formulations to drive surface activity and ‘film-forming’ properties of the formulation.²⁵ While deionized water was used in this study, the use of a background electrolyte could improve the variability observed in the surface tension profile for the Ultrapure solution.^{6,7,35}

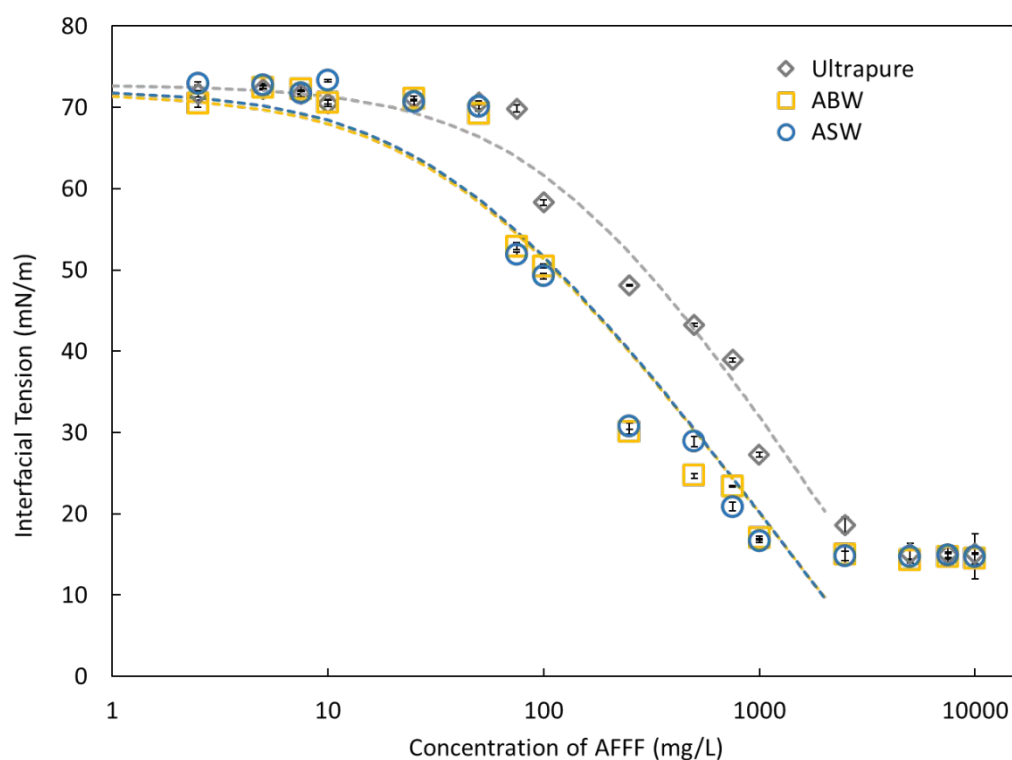


Figure 2. Surface tension isotherms for 3M AFFF formulation in ultrapure, artificial brackish (ABW), and artificial seawater (ASW). Dotted lines are the Szyszkowski equation fit; note that the ABW fit and ASW fit are nearly overlapping. AFFF concentration is based on the total mass of AFFF added and was validated by measuring the PFOS concentrations for the AFFF dilution series (Supporting Information Figure S2). Error bars are the standard deviation of three drop measurements.

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3 The driving force for surfactant aggregation is related to three energetic parameters: the
4 free energy due to transfer of the monomer tail from the bulk solution into the aggregate, the free
5 energy due to residual interactions between the surfactant tails in the aggregate core and water
6 molecules, and the free energy due to surfactant headgroup repulsions.²⁹ For anionic surfactants
7 (e.g., PFOS), the addition of salt decreases the electrostatic repulsion between surfactant
8 headgroups, affecting the free energy contribution from headgroup repulsions and decreasing the
9 CMC.^{30–32} However, for zwitterionic surfactants such as AmPr-FhxSA, which was also present
10 in the 3M AFFF solution, decreases in the CMC at high salt concentrations can be mainly
11 attributed to the salting-out of the hydrophobic monomer tail.^{32–34} The mixture of anionic and
12 zwitterionic PFAS in the 3M formulation, in addition to the highly saline solutions, suggest that
13 the aggregation behavior is driven by both the electrostatic effect of decreased headgroup
14 repulsions and the salting-out effect. The increased ionic strength of ABW relative to ASW did
15 not substantially alter the CMC, possibly due to limits on packing density between the surfactant
16 tails that cannot be energetically overcome with the addition of more salt.

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35 Surface excess can be an indicator of PFAS retention on solids and is of particular
36 importance for modeling PFAS transport in the vadose zone where there is high air-water
37 interfacial area.^{7,35–37} We found that surface excess (Γ_{\max}) did not vary substantially among the
38 conditions tested (ultrapure, ABW, ASW). An equivalent minimum surface tension was
39 observed in all three aqueous systems (Figure 2), indicating that surface adsorption of the 3M
40 AFFF formulation is not substantially altered by the presence of high salt concentrations. The
41 mixture of zwitterions and anions in the 3M formulation may serve to increase the packing of the
42 monomers at the air-water interface due to interactions between the cationic moieties of the
43 zwitterions, and the negative headgroups of the anions.²⁵ The dissolved ions, while affecting the
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aggregation and CMC in the bulk solution due to hydrophobic interactions as discussed earlier, do not appear to enhance the packing at the air-water interface for the surfactant mixture.

Table 1. Summary of CMC and Γ_{\max} for the 3M AFFF formulation in ultrapure, ABW, and ASW. PFOS-only* values are from previously published work for comparison.²³ Values were calculated by fitting the Langmuir-Szyszkowski equation to the surface tension isotherms. Confidence intervals for the CMC linear fit are reported in the Supporting Information Table S5.

	CMC (mg/L)	Γ_{\max} ($\times 10^{-7}$ mol/cm ²)	R ² (for Γ_{\max})
Ultrapure	3780	7.32	0.976
Artificial Brackish	1690	6.20	0.943
Artificial Seawater	1540	6.24	0.944
PFOS-only in 500 mM NaCl*	1860	4.57	0.991

Given the complexity of the system being studied— a mixture of fluorocarbon surfactants, hydrocarbon surfactants, and solvents in mixed salt matrices— it is likely that the system deviated from ideal surface adsorption behavior expected when analyzing a single surfactant. To gain additional insight into the measurable interfacial mass accumulation of the individual PFAS components in the 3M AFFF formulation, we used a procedure previously described by Schaefer et al.²³ and employed in our work investigating a perfluorooctanesulfonic acid (PFOS)-only system.^{12,18} We compared solutions containing single salts, NaCl and CaCl₂, to the ABW and ASW conditions to provide mechanistic insight for sorption behavior and inform modeling of interfacial behavior in various real water matrices, which may vary in ion composition.^{8,34}

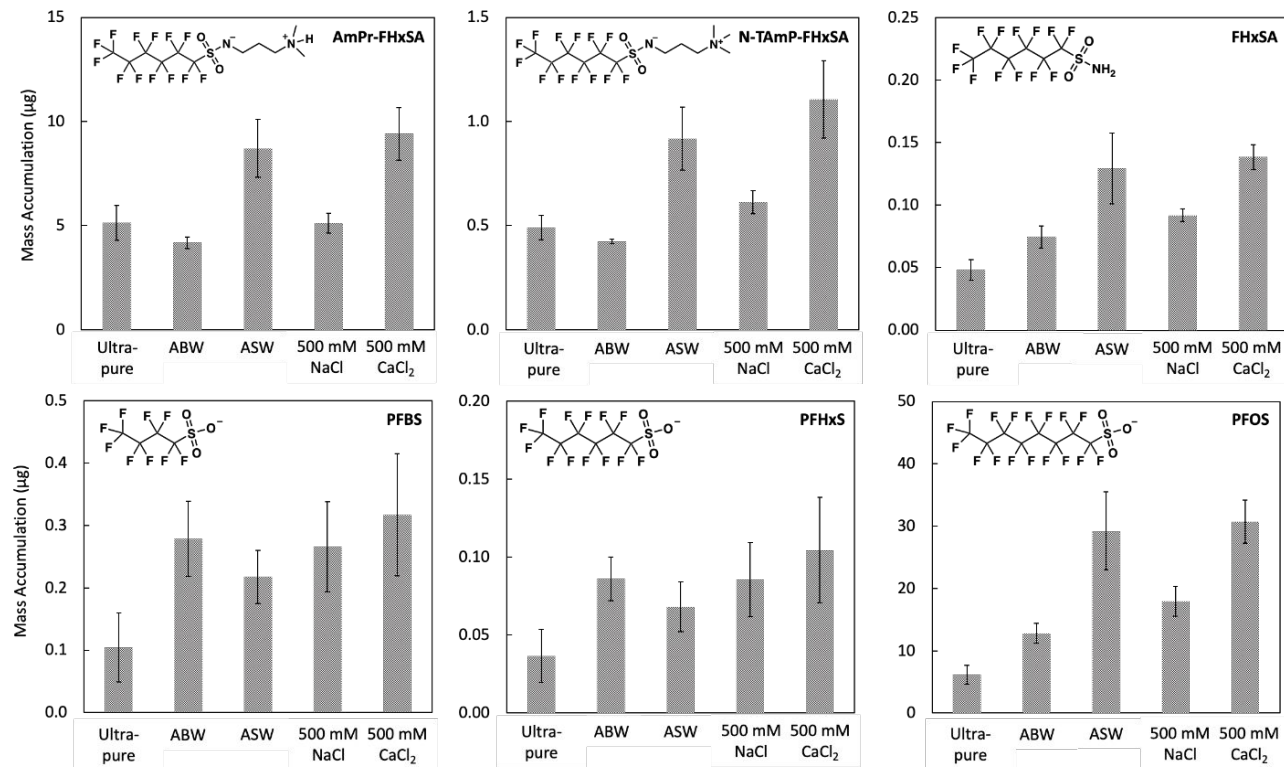


Figure 3. Interfacial mass accumulation of PFASs in an AFFF solution in ABW, ASW, NaCl, and CaCl₂ solutions. Mass accumulation calculated from interfacial concentration and volume. Error bars are the standard deviations of triplicate samples.

In comparing the single salt to ABW and ASW conditions, the 500 mM NaCl condition was most comparable to the ASW solution for differentiating single-salt and mixed-salt solution effects. Although the high CaCl₂ concentration was not comparable with a real water saline matrix, we hypothesized that the CaCl₂ solution would exhibit different behavior from the NaCl system based on previous findings.^{8,35} It has been shown that the presence of divalent cations, calcium in particular, can increase sorption of PFAS onto sediments.^{38,39} Given that sodium is the dominant monovalent cation in seawater, NaCl and CaCl₂ were compared in an attempt to evaluate the effect of cation valence state on surface activity of a PFAS mixture.

Concentrations of PFAS in the interfacial solutions were quantified by LC-MS/MS to determine the accumulation of compounds present in the 3M AFFF (Figure 3). It was observed

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3 that amine-functionalized perfluorosulfonates (e.g., AmPr-FHxSA, N-TAmP-FHxSA, FHxSA),
4 commonly referred to as precursors, exhibited higher accumulation in the ASW and CaCl₂
5 matrices. Typically, amine-functionalized perfluorosulfonates can achieve lower surface tensions
6 than the carboxylic or sulfonic acids, indicating their higher surface activity;⁴⁰ therefore, the
7 amine moiety of the studied precursor compounds was expected to increase the propensity for
8 interfacial accumulation in the ASW and CaCl₂ matrices, compared with the PFASs. The
9 sulfonic acid compounds perfluorobutane sulfonic acid (PFBS) and perfluorohexane sulfonic
10 acid (PFHxS), exhibited similar mass accumulation in all saline matrices studied, on the order of
11 a two-fold increase compared to the ultrapure solution. This indicates that the increase in chain
12 length and hydrophobicity between PFBS and PFHxS does not substantially impact the
13 interfacial sorption of these two compounds; however, at significantly higher concentrations of
14 both compounds, some difference may be observed.

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31 The interfacial accumulation of PFOS, which was present at significantly higher
32 concentrations than any of the other PFAS detected in the solutions (Figure 1, Supporting
33 Information Table S10), exhibited substantially greater mass accumulation in the CaCl₂ solution
34 and ASW solutions than in the NaCl solution; a similar effect was observed in comparing NaCl
35 and CaCl₂ effects in a PFOS-only system.⁴⁰ Research by others has also shown that divalent
36 cations can significantly increase the monolayer packing of anionic surfactants at the interface,
37 thereby increasing the interfacial mass accumulation.⁴¹ Overall, this result indicates that the
38 addition of other PFAS to the mixture, as well as the hydrocarbon surfactants (which were not
39 quantified), do not substantially alter the interfacial sorption behavior of PFOS, a dominant
40 compound at AFFF-impacted contamination sites. The increased mass accumulation of amine-
41 functionalized precursors suggests that the retention of these compounds, in addition to PFOS,
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3 may increase in high salinity source zones. Transformation of precursors in the source zone
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5 could impact long term release of carboxylic and sulfonic acids and would necessitate increased
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7 monitoring at sites impacted by high salinity.
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10 11 12 **Conclusions** 13

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15 As evidenced by the growing body of literature on PFAS interfacial properties and
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17 partitioning behavior,^{6,7,12,17,23,24,42} there is heightened recognition within the research community
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19 of the ways that the surfactant behavior of PFAS affects the compounds' environmental fate.
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21 Interfacial accumulation has the potential to enhance the retention of these compounds, resulting
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23 in unexpected retention of PFAS within the source zone.
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27 In evaluating the interfacial behavior and mass accumulation of PFAS in a 3M AFFF
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29 formulation, we observed that high salinity matrices decrease the CMC of the formulation and
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31 increase the mass accumulation of certain PFAS in solution. The increase in interfacial mass
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33 accumulation in the evaluated matrices indicates that higher salinity substantially enhances
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35 accumulation and may be a major explanation for PFAS retention in coastal environments. This
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37 work demonstrates that particular attention should be paid to PFOS and amine-functionalized
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39 precursor compounds, which appear to drive the aggregation and surface behavior in PFAS
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41 mixtures and whose aqueous behavior is substantially impacted in high salinity matrices.
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45 It is challenging to draw precise conclusions based on structural attributes of the
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47 individual PFAS compounds, because surface accumulation is concentration-dependent, and the
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49 compounds are present at varying concentrations in the formulation.^{12,23,24} Variations of the
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51 relative proportions of fluorocarbon and hydrocarbon surfactants in different AFFF formulations
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53 could impact interfacial behavior in mixed contaminant systems. As PFAS contamination
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3 spreads from a source zone, the characteristics of the mixture will change, which may further
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5 impact interfacial accumulation and contaminant fate. Additionally, as lab and pilot scale studies
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7 have demonstrated, the interfacial and foaming properties of PFAS can be advantageous in foam
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9 fractionation removal technologies.^{43,44} In such technologies, increasing ionic strength of
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11 treatment solutions has the potential to further improve foaming properties and enhance removal.
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13 This research improves our understanding and informs modeling studies of AFFF retention
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15 processes in salt-impacted source zones. Additionally, these results emphasize the impact of
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17 retention of PFAS due to surface activity, which may prove to be a useful for managing PFAS
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19 contaminated zones.
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26 **Appendix A. List of Acronyms**

28 Acronym	29 Meaning
30 ABW	artificial brackish water
31 AFFF	aqueous film-forming foam
32 AmPr-FHxSA	<i>N</i> -dimethyl ammonio propyl perfluorohexane sulfonamide
33 ASW	artificial sea water
34 CMC	critical micelle concentration
35 DGBE	DGBE diethylene glycol monobutyl ether
36 FHxSA	FHxSA perfluorohexane sulfonamide
37 LC-MS/MS	liquid chromatography tandem mass spectrometry
38 N-TAmP-FHxSA	<i>N</i> -[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]- <i>N,N,N</i> - 39 trimethylammonium
40 PDT	pendant drop tensiometry
41 PFAS	per- and polyfluoroalkyl substances
42 PFBS	perfluorobutane sulfonic acid
43 PFHpA	perfluoroheptanoic acid
44 PFHxA	perfluorohexanoic acid

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3	PFHxS	perfluorohexane sulfonic acid
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5	PFOA	perfluorooctanoic acid
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7	PFOS	perfluorooctane sulfonic acid
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9	3M AFFF	aqueous film forming-foam manufactured by 3M Company
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13 Acknowledgments

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15 This work was supported by SERDP (Project ER-2715) and the National Science Foundation
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17 Graduate Research Fellowship under Grant No. 1752814.
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22 Supporting Information

23
24 Details on experimental and analytical procedures and additional data tables.
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