

NM WRI Student Water Research Grant Progress Report Form

Progress Report due October 1, 2020

Draft Final Report due July 9, 2021

Final Report due August 9, 2021

1. Student Researcher: Zahra Abbasian
Faculty Advisor: Dr. Reza Foudazi

2. Project title:

The Effect of Concentration and Composition on PFAS Adsorption at Air-water Interface

3. Description of research problem and research objectives.

In October 2018, The New Mexico Environment Department released news about a Cannon Air Force Base groundwater contamination by per- and polyfluoroalkyl substances (PFAS) associated with firefighting foams used in military fire training exercises.¹ PFAS concentrations range from 25 to 1,600 nanograms per liter (ng/L) in off-base wells and more than 26000 ng/L in on-base monitoring wells. Although the federal advisory level for drinking water is 70 ng/L², some of these contaminated wells supply drinking water to local dairies. PFAS contamination has also detected in wells number 2 and 4 of The Brackish Groundwater National Desalination Research Facility (BGNDRF). In the U.S., PFAS contaminated water supplies have been found in 49 states as of July 2019. Due to toxicity, bioaccumulation, and environmental persistence, PFAS have been recognized as contaminants of emerging concern (CECs) and listed in a top priority list of unregulated contaminants by The United States Environmental Protection Agency (EPA). The stable carbon-fluorine bond in PFAS structure leads to their stability against environmental degradation, which results in their broad accumulation in air, soil, and groundwater.³

According to the wide distribution of PFAS in the environment, an accurate perception of PFAS fate and transport is essential to develop efficient remediation methods and determine the exposure risks. Therefore, the objective of this research is to conduct a fundamental investigation of PFAS adsorption at air-water interface. The study of interfacial properties of PFAS is of great importance as the air-water interface is a retention source for PFAS transport in atmosphere, soil, and groundwater. In the present study, PFAS adsorption kinetics and equilibrium at the air-water interface are studied by measuring the dynamic surface tension. We evaluate the effect of perfluoroalkyl chain length, PFAS concentration, and composition of PFAS contaminants on their adsorption at the interface.

4. Description of methodology employed.

Perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and perfluorobutanesulfonic acid (PFBS), all at $\geq 96\%$ purity, are purchased from Sigma-Aldrich. These compounds are selected from the most prevalent PFAS in water resources and contain both short and long chain PFAS. PFOA and PFOS were phased out of production and use in 2002, but they are still persistent in the environment. PFBS is still used⁴ as a surfactant in industrial processes and in water and stain resistant coating products. Molecular structures of PFAS are shown in Figure 1. The PFAS solutions are prepared in deionized water at desired concentration.

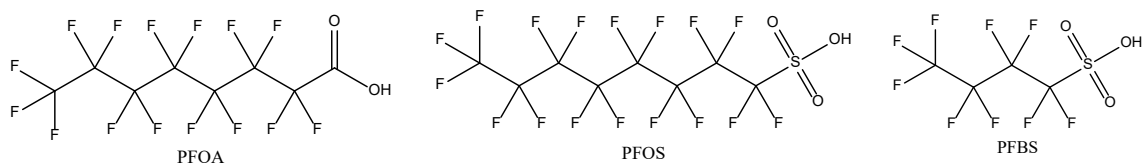


Figure 1. Molecular structures of PFOA, PFOS and PFBS

After preparation of PFAS solution, the adsorption rate and degree of PFAS molecules at the air-water interface are studied through surface tension measurements versus time. Pendant drop method is used to study the dynamic surface tension and the amount of PFAS adsorbed at the interface. The obtained results are used to evaluate the adsorption kinetic, and the amount of PFAS adsorbed at the interface. Different concentrations and compositions, separately and as mixtures, of PFAS are examined during these experiments.

5. Description of results; include findings, conclusions, and recommendations for further research.

The current project was started with a broad literature review on PFAS properties, remediation methods, and their fate and transport (F&T).

PFAS are directly released into the environment through AFFF used in firefighting training areas and in emergency situations, effluent of wastewater treatment plants, land applications of biosolids, and disposal of PFAS-containing products in landfills.⁵⁻⁸ Figure 2 shows a conceptual model of PFAS F&T. According to the most recent EPA PFAS action plan in 2020, EPA is still analyzing PFAS industrial sources and discharges to determine which industries are most likely to discharge PFAS into the environment and which compounds are currently used.⁹

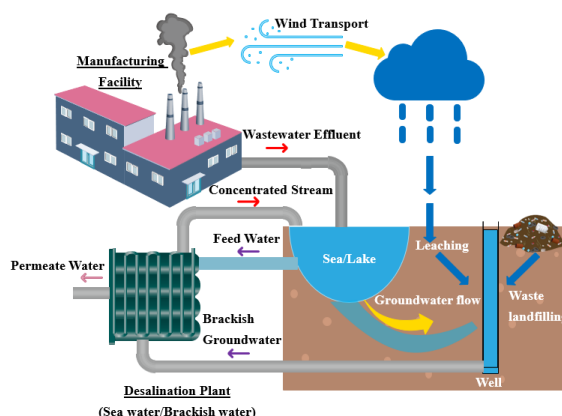


Figure 2. Conceptual model of PFAS fate and transport (F&T).

The awareness of PFAS environmental impacts is very recent; thus, several conventional technologies, mostly granular activated carbon (GAC), ion exchange and reverse osmosis (RO) have been utilized for PFAS remediation. The limitations of the conventional methods can be generally summarized as follows:¹⁰

- inefficient removal of short-chain PFAS;
- high energy demand; and,
- generation of high volumes of secondary wastes.

Destructive methods, such as sonolysis and electrochemical treatment, have also been studied to remove PFAS, but these energy-intensive methods have limitations for large-scale applications.¹¹ Foam fractionation with ozone has been used for PFAS removal from water¹²; however, there are serious concerns about ozone treatment for drinking water since it is a potential carcinogenic to humans. There is evidence that biosparging activity, as a very routine remedial activity in groundwater well facilities, has led to the transformation of polyfluorinated precursors into perfluoroalkyl acids rather than removing or destroying them, in case of PFAS contamination of well.¹⁰

After the literature review, the experimental work began with the surface tension measurement of PFOA solutions at concentrations ranging from 1 mg/L to 1000 mg/L as a function of time by using pendant drop method (Figure 3).

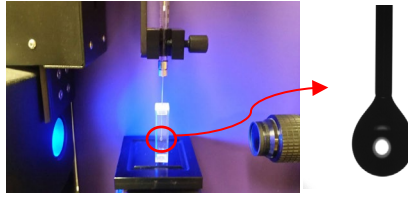


Figure 3. Pendant drop method to measure the dynamic surface tension of PFAS solution

Figure 4 shows the surface tension versus time for different PFOA solutions.

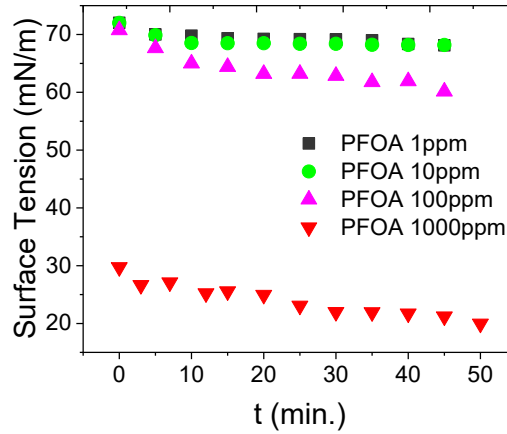


Figure 4. Dynamic surface tension of PFOA solutions at the air-water interface

The adsorption mechanism of PFOA solutions is investigated by using a diffusion-controlled adsorption model, Ward and Tordai model. The following equations are used to calculate the surfactant diffusion coefficient, D , using dynamic surface tension data during short and long times, respectively:¹³

$$\gamma - \gamma_0 = -2C_0RT\left(\frac{Dt}{\pi}\right)^{1/2} \quad (1)$$

$$\gamma - \gamma_e = \frac{RT\Gamma^2}{2C_0}\left(\frac{\pi}{Dt}\right)^{1/2} \quad (2)$$

where t is the time, C_0 is the surfactant bulk concentration, R is the gas constant, T is the absolute temperature, γ_0 is the surface tension of the solvent, γ_e is the equilibrium surface tension at infinite

time, and Γ is the surface excess concentration of the surfactant which can be obtained from the equilibrium surface tension measurements. At a constant surfactant concentration C_0 , if the adsorption is diffusion-controlled, the variation of γ versus $t^{1/2}$ based on eq. (1) for short times and γ versus $t^{-1/2}$ based on eq. (2) for long times should be linear. Consequently, D is calculated from the slope of each plot. The diffusion coefficient of different PFOA solutions, estimated from the slope of surface tension plotted versus $t^{1/2}$ (Figure 5), is summarized in Table 1.

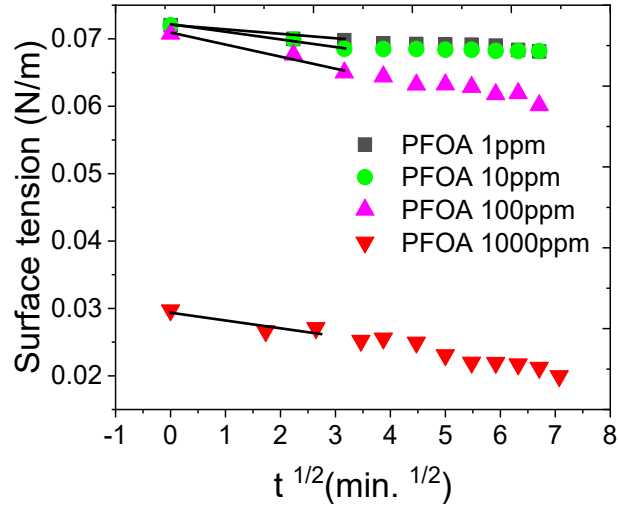


Figure 5. PFOA surface tension versus $t^{1/2}$ to calculate PFOA diffusion coefficient (D)

Table 1. Diffusion coefficient of PFOA solutions

Concentration (ppm)	Diffusion Coefficient (m ² /s)
1	8.20×10^{-9}
10	5.69×10^{-11}
100	5.12×10^{-12}
1000	3.77×10^{-15}

The PFOA concentration at the air-water concentration (Γ) is estimated from the slope of γ - $\ln c$ curve (Figure 6) by using the Gibbs adsorption equation, eq. (3):¹⁴

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d(\ln c)} \quad (3)$$

From Figure 6, Γ is estimated to be 7.16×10^{-6} mol/m².

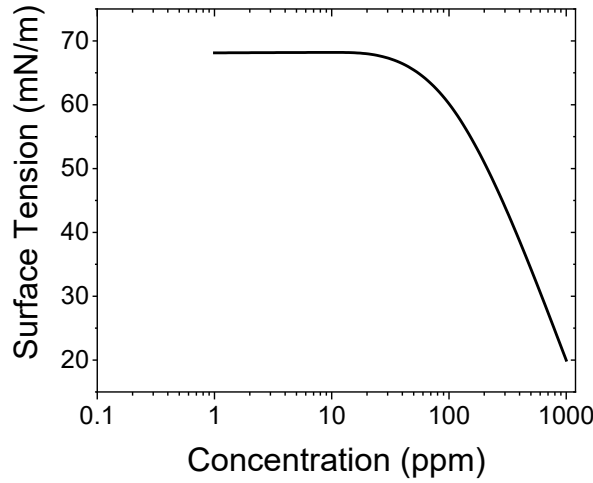


Figure 6. PFOA surface tension versus concentration to estimate surface excess concentration (Γ)

According to the results achieved from this part of the project, the following conclusions are drawn:

- Kinetics of PFOA adsorption at air-water interface is low according to the low diffusion coefficients.
- Diffusion coefficient values decrease with an increase in the PFOA concentration. It can be resulted from probable micelle formation in the solutions.
- Initial adsorption is a rapid diffusive process at concentrations of 1000 ppm and requires the measurements on a shorter time scale (<5 ms). Because the intercept of the plots in Figure 5 (at $t = 0$) should be close to the water surface tension (according to eq. 1), it is less than the concentrations of 1000 ppm.

In the next experiments the dynamic surface tension of PFOS and PFBS solutions at different concentrations were measured using the pendant drop method. The results are shown in Figure 7.

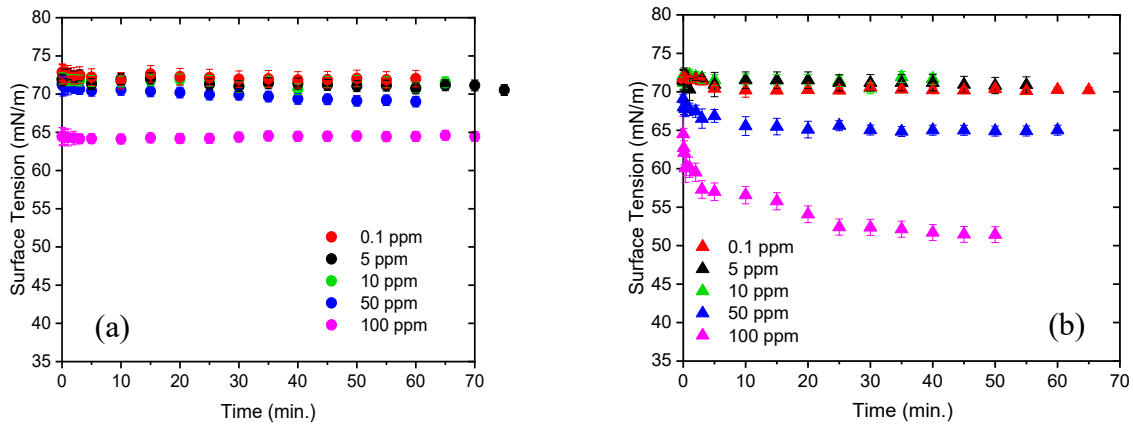


Figure 7. Dynamic surface tension of (a) PFBS and (b) PFOS

According to Figure 7, lower equilibrium surface tension (γ_{eq}) of PFOS is obtained compared to PFBS at higher concentration. The equilibrium surface tension (γ_{eq}) is achieved in the first 20 minutes for both PFAS. Furthermore, an initial rapid decrease is observed in the surface tension at high PFOS or PFBS concentration indicating a diffusion-controlled adsorption mechanism. Also, it should be mentioned that there is a difficulty in measuring the surface tension change at low concentration (lower than 10 ppm), which is not the problem associated only with the pendent drop method and have been seen by other researchers using different methods. The Szyszkowski equation, eq. (4) is used to substitute in Gibbs eq. (3) and then obtain PFAS maximum surface excess and surface activity¹⁵:

$$\gamma = \gamma_0 [1 - a \times \ln(\frac{C}{b} + 1)] \quad (4)$$

Substituting in eq. (3):

$$\Gamma = \frac{\alpha \gamma_0}{RT} \frac{C}{C+b} \quad (5)$$

where b is the surface activity and is related to the free energy of PFAS transfer from bulk solution to the interface, ΔG , as follows:

$$b(\frac{mol}{L}) = 55.3 \exp(\frac{\Delta G}{RT}) \quad (6)$$

Table 2 shows two parameters of the maximum surface excess and the surface activity for PFOS and PFBS obtained from fitting the plot Γ vs C by using eq. (5):

Table 2. Maximum surface excess and surface activity of PFOS and PFBS

Component	$\Gamma_m (\frac{mg}{m^2})$	$b (\frac{mg}{L})$
PFOS	1.63	18
PFBS	0.36	9

The higher maximum surface excess and surface activity of PFOS compared to PFBS is contributed to the longer hydrophobic tail of PFOS which pushes the PFOS molecules to the air-water interface more than PFBS molecules.

The dynamic surface tension of binary mixtures of PFOS and PFBS were also studied in the last stage of the current research. Figure 8-a represents the dynamic surface tension of the binary mixture. The binary mixture was prepared by using a 1:1 wt% of PFOS and PFBS.

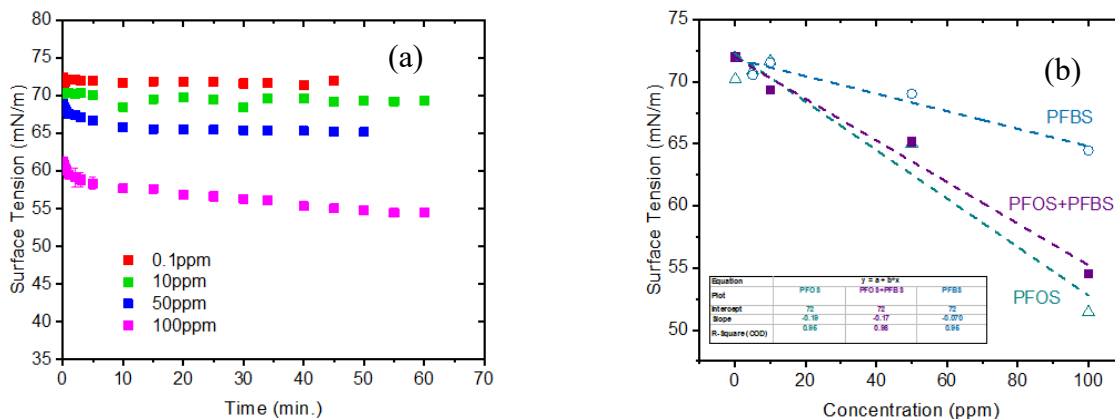


Figure 8. (a) Dynamic surface tension of the binary mixture of PFOS and PFBS and (b) equilibrium surface tension of single and dual solute solutions of PFAS vs concentration

The equilibrium surface tension of PFOS, PFBS and the mixture solution of PFOS and PFBS versus concentration was plotted in Figure 8-b to provide a clear comparison among solutions. According to this graph, the surface tension of mixture is positioned between the single-component isotherms, suggesting a lack of synergistic adsorption at the interface. Furthermore, positioning of the mixture isotherm is weighted toward the most surface-active component (PFOS). This result suggests a competitive adsorption of PFOS and PFBS at the air-water interface.

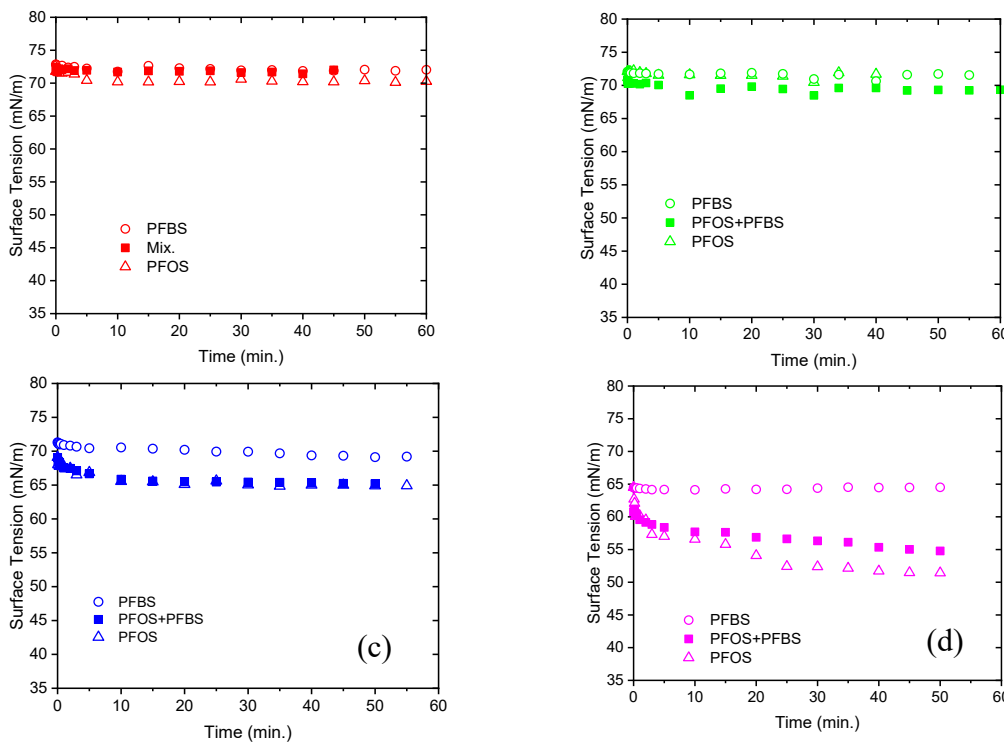


Figure 9. Dynamic surface of PFOS, PFBS and their mixture at concentration (a) 0.1 ppm (b) 10 ppm, (c) 50 ppm and (d) 100 ppm.

Figure 9 compares the dynamic surface tension of PFOS, PFBS and their mixture at the same concentration in one plot for different concentration levels. As it can be seen, the mixture isotherm is again weighted toward the most surface-active component. This effect is more pronounced at higher concentration.

In conclusion, a higher concentration of PFAS in the solution resulted in lower surface tension at air-water interface as it was expected. A higher surface activity and concentration was observed for PFOS compared to PFBS in the single solute solution. The reason could be due to the longer hydrophobic tail of PFOS which increases the PFOS tendency to accumulate at the air-water interface. Also, a competitive adsorption was suggested for PFOS and PFBS adsorption in a binary mixture according to the mixture isotherm achieved for these PFAS.

A mixture of more PFAS compounds in the presence of other background ions is recommended as future work to simulate a real water matrix and obtain a comprehensive knowledge of PFAS competition for adsorption at the air-water interface. The importance of PFAS behavior at the air-water interface plays a major role in PFAS environmental fate and transport due to the existence of the air-water interface in the media such as air and soil.

6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results.

This research sheds light on F&T analysis of PFAS in the environment for developing efficient remediation methods and determining exposure risks based on the obtained results. Due to the current PFAS contamination level of NM groundwater and the fact that this toxic plume is spreading slowly to new areas, the present study provides useful and effective data for environmental scientists and water treatment facilities.

7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after May 31, 2021, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)

Budget balance:

- paying student tuition fees (\$3155)
- supplying materials (\$609.58)
- conference registration (\$284)
- paying students' salary (\$3051.4)

8. List presentations you have made related to the project.

- Z. Abbasian Chaleshtari, R. Foudazi, "Per- and polyfluoroalkyl substances (PFAS) adsorption at the air-water interface", 65th NM Water Conference, Poster, October 26-29, 2020, Online Conference.

- Z. Abbasian Chaleshtari, R. Foudazi, "Adsorption of Poly- and Perfluoroalkyl Substances at the Air-Water Interface", AIChE, Poster, November 16-20, 2020, Virtual.

- Z. Abbasian Chaleshtari, R. Foudazi, “Interfacial properties of poly- and perfluoroalkyl substances at the air-water interface”, APS March Meeting, 2021.

9. List publications or reports, if any, that you are preparing. For all publications/reports and posters resulting from this award, please attribute the funding to NM WRI and the New Mexico State Legislature by including the account number: NMWRI-SG-2020.
10. List any other students or faculty members who have assisted you with your project.
11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.
12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.

This project is a part of a PhD research project attempting to evaluate/develop an efficient method for PFAS removal from water resources. Due to the nature of this experience being achieved in the field of water treatment, it seems likely the students involved will continue their research in water-related areas after degree completion dependent on their interest and background.

You are encouraged to include graphics and/or photos in your draft and final report.

Final reports will be posted on the NM WRI website.

References:

- (1) New Mexico Environment Department. *Cannon Air Force Base Groundwater Contamination : Per- and Poly-Fluoroalkyl Substances Detected in Cannon Air Force Base Groundwater*; 2018.
- (2) U.S. Environmental Protection Agency. *EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan*; 2019.
- (3) Oyetade, O. A.; Varadwaj, G. B. B.; Nyamori, V. O.; Jonnalagadda, S. B.; Martincigh, B. S. A Critical Review of the Occurrence of Perfluoroalkyl Acids in Aqueous Environments and Their Removal by Adsorption onto Carbon Nanotubes. *Rev. Environ. Sci. Bio/Technology* **2018**, *17*, 603–635. <https://doi.org/10.1007/s11157-018-9479-9>.
- (4) U.S. Environmental Protection Agency. Basic Information on PFAS | Per- and Polyfluoroalkyl Substances (PFAS) | US EPA <https://www.epa.gov/pfas/basic-information-pfas>.
- (5) Lang, J. R.; Allred, B. M. K.; Field, J. A.; Levis, J. W.; Barlaz, M. A. National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. *Environ. Sci. Technol.* **2017**, *51* (4), 2197–2205. <https://doi.org/10.1021/acs.est.6b05005>.
- (6) Gallen, C.; Eaglesham, G.; Drage, D.; Nguyen, T. H.; Mueller, J. F. A Mass Estimate of Perfluoroalkyl Substance (PFAS) Release from Australian Wastewater Treatment Plants. *Chemosphere* **2018**, *208*, 975–983. <https://doi.org/10.1016/j.chemosphere.2018.06.024>.
- (7) Järnberg, U.; Holmström, K. Perfluoroalkylated Acids and Related Compounds (PFAS) in the Swedish Environment. *Chem. Sources, Expo.* **2006**, 1–47.
- (8) ITRC. *Environmental Fate and Transport for Per-and Polyfluoroalkyl Substances*; 2018; p 18.
- (9) U.S. Environmental Protection Agency. *EPA PFAS Action Plan: Program Update*; 2020. <https://doi.org/10.1017/CBO9781107415324.004>.
- (10) Horst, J.; McDonough, J.; Ross, I.; Dickson, M.; Miles, J.; Hurst, J.; Storch, P. Water Treatment Technologies for PFAS: The Next Generation. *Groundw. Monit. Remediat.* **2018**, *38* (2), 13–23.
- (11) Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Thelakkat Kochunarayanan, P.; Kalve, E.; Hurst, J.; S. Dasgupta, S.; Burdick, J. A Review of Emerging Technologies for Remediation of PFASs. *Remediation* **2018**, *28* (2), 101–126.
- (12) McDonough, J.; Ross, I.; Miles, J.; Houtz, E.; Burdick, J. Optimizing The PFAS Puzzle : Piecing Together A Holistic PFAS Restoration Strategy. In *Eleventh International Conference on Remediation of Chlorinated and Recalcitrant Compound*; 2018. <https://doi.org/10.13140/RG.2.2.25366.04163>.
- (13) Yoshimura, T.; Ohno, A.; Esumi, K. Equilibrium and Dynamic Surface Tension Properties of Partially Fluorinated Quaternary Ammonium Salt Gemini Surfactants. *Langmuir* **2006**, *22* (10), 4643–4648.
- (14) Brusseau, M. L.; Van Glubt, S. The Influence of Surfactant and Solution Composition on PFAS Adsorption at Fluid-Fluid Interfaces. *Water Res.* **2019**, *161*, 17–26. <https://doi.org/10.1016/j.watres.2019.05.095>.
- (15) Rosen, M. J., Kunjappu, J. T. *Surfactants and Interfacial Phenomena*; 2012. <https://doi.org/10.5860/choice.42-2832>.