Aqueous photolysis of 6:2 fluorotelomer sulfonamide alkylbetaine

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Abstract

The aqueous photolytic fate of 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) was determined experimentally. The PhotoFate system was used to compare the kinetic and mechanistic differences between direct and indirect aqueous photolysis of 6:2 FTAB. Differences attributable to varying aqueous components (nitrate, bicarbonate, and dissolved organic matter (DOM)) were investigated. DOM had a major role in modulating the photolysis rate of 6:2 FTAB, likely by attenuating radical production and quenching radicals in solution. A mechanistic investigation found that the major intermediate of 6:2 FTAB photolysis is 6:2 fluorotelomer sulfonamide (6:2 FTSAm), followed by 6:2 fluorotelomer sulfonate (6:2 FTSA), 6:2 fluorotelomer sulfonamide alkylamine (6:2 FTAA), 6:2 fluorotelomer alcohol (6:2 FTOH) and 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA). As well, the significant production of perfluoroalkyl carboxylic acids (PFCAs) was observed. A high mass balance (51 to 68 mol % recovery) enabled the proposal of a degradation mechanism for the aqueous photolysis of 6:2 FTAB.
Acknowledgements

Thank you to Scott taking me on as a student. No one leaves your lab without appreciating the value of experimental work and chemical intuition, and I’m glad I could learn that from you. Thanks also to my second reader, Derek Muir, and to Frank Wania, for serving on my committee.

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Chapter One

Introduction to Aqueous Photolysis and Fluorinated Surfactants
1.1 Aqueous Film Forming Foams – Chemistries and Fate

Aqueous film forming foams (AFFFs) are used to fight liquid fuelled fires. When combined with water and sprayed on the fire, the foam covers the liquid fuel and limits contact with oxygen, helping to choke the fire.[1] AFFFs are used primarily in the petroleum industry, aviation, and military, where significant quantities of flammable liquids are regularly used.[2] The foam concentrates are a mix of hydrocarbon and fluorinated surfactants. The hydrocarbon surfactants primarily interact with the organic liquid/foam interface, while the fluorinated surfactants interact at the foam/air interface.[2] Fluorinated surfactants are ideal for use in AFFFs since they are much more thermally stable than their non-fluorinated counterparts. Furthermore, fluorinated surfactants also exhibit higher surface activity than their hydrocarbon analogues, indicating that much less surfactant can be used to achieve desired surface tension reduction or foaming.[3] The major fluorinated surfactant used for many years in AFFFs was perfluorooctane sulfonate (PFOS), a persistent and bioaccumulative chemical now listed on Annex B of the Stockholm Convention.[2]

However, PFOS was never the sole fluorinated surfactant used in AFFF formulations. Material Safety Data Sheets of AFFF formulations, as well as patent literature, revealed that these products contained a diverse group of surfactants: a typical formulation contained approximately 1% perfluoroalkyl sulfonates (e.g. PFOS) and up to 5% amphoteric fluoroalkylamide derivatives.[2] This was also confirmed when a study simultaneously investigated the accidental release of AFFF material in Toronto, ON by traditional LC-MS and $^{19}$F NMR. The investigators found that the perfluoroalkyl region of the samples’ NMR spectra accounted for as much as 5 times more fluorinated material than was identified as
targeted analytes (e.g. PFOS) in their LC-MS analysis.[4,5] Furthermore, a later investigation into the organic fluorine content of AFFFs found that simple LC-MS analysis of known fluorinated chemicals far underestimated the true concentration of organofluorine in the formulations.[6] This confirms that other perfluoroalkyl surfactants are present in AFFF formulations and are being released into the environment.

Recently, several major investigations have identified a plethora of diverse surfactants present in AFFF formulations.[7–9] The dominant surfactant in historic AFFF formulations was PFOS, which was manufactured by electrochemical fluorination (ECF), primarily by the 3M Company. In 2001 3M ended its electrochemical fluorination, due to the environmental concerns for PFOS, and perfluorooctanoic acid (PFOA).[10] Subsequently, fluorinated products based on the telomerization process have played a larger role in the chemical composition of recent AFFF formulations.[7,9] Today, the major fluorinated surfactants in AFFFs are fluorotelomer-based. Fluorotelomer surfactants contain a perfluoroalkyl chain bound to an alkyl moiety, which connects the chain to a polar head group. Fluorotelomer chain-based chemicals are named according to the number of perfluorinated and non-fluorinated carbon atoms they bear. Thus, 6:2 fluorotelomer sulfonate has a perfluorohexyl moiety bound to an ethyl moiety with a sulfonic acid (sulfonate at environmental pH) head group, as shown in Figure 1.1. The term fluorotelomer derives from the telomerization process by which the chains are synthesized.[3]
Depending on the alkyl moiety and the head group used in a fluorinated surfactant, the chemical can exhibit vastly different chemical properties and subsequent environmental fate.[11] The main surfactants detected can have: a negatively charged carboxylic or sulfonic acid head group, a positively charged quaternary ammonium head group, or an amphoteric head group such as a betaine.[9] Species which are charged at environmental pH are likely to be water soluble and exhibit no partitioning to the gas phase. In contrast, an uncharged neutral species would be much less water soluble and may partition strongly to solid phases or volatilize into the atmosphere. Fluorinated surfactants are frequently charged and their main fate is primarily to the aqueous environment. Due to their use in fire-fighting, AFFFs are typically drained into run-off or sewage, where their components enter the aqueous environment.[2]

Fluorotelomer-based chemicals, unlike perfluoroalkyl acids, contain abstractable H atoms and relatively electron-rich C atoms, and thus are much more susceptible to environmental oxidation.[12,13] This reduces their persistence and therefore limits their bioaccumulation potential. However, the environmental degradation byproducts of fluorotelomer-based chemicals may persist. Two investigations found that the major AFFF component 6:2 fluorotelomer mercaptoalkylamido sulfonate (FTSAS), and its 4:2 and 8:2 analogues, biodegrade to produce perfluoroalkyl carboxylic acids (PFCAs).[6,14]
Perfluoroalkyl carboxylic acids are highly persistent with no known environmentally relevant transformations, and some longer-chain congeners (7 perfluorinated carbons and greater) are known to be bioaccumulative and toxic.\cite{15} The use of volatile precursors has led to the detection of PFOS and PFOA, globally in virtually all environmental matrices.\cite{10,16}

Several investigations have identified 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), as a major fluorinated surfactant present in AFFF formulations and groundwater surrounding United States military bases.\cite{7–9} Most recently, D’Agostino and Mabury found 6:2 FTAB to be the second most frequently detected fluorinated surfactant in their analysis of AFFF concentrates. Another study identified 6:2 FTAB in soil surrounding an airport in Norway and attempted to assess the photodegradation of 6:2 FTAB.\cite{17} Unfortunately, their investigation was experimentally hindered and was unable to calculate a half-life, propose a complete mechanism, or quantify many degradation products.\cite{17} As a zwitterionic (neutral, but bearing a positive and a negative charge) fluorinated surfactant, 6:2 FTAB (shown in Figure 1.2) has a relatively high water solubility and is expected to primarily partition to the aqueous environment. Due to its fluorotelomer-based structure, 6:2 FTAB is likely to be susceptible to oxidation mechanisms such as indirect photolysis, which may play a significant role in its overall environmental transformation.
1.2 Aqueous Photolysis

Aqueous photolysis is broadly separated between direct and indirect photolysis. Direct photolysis occurs when the analyte of interest itself absorbs light radiation and undergoes a chemical reaction. Indirect photolysis occurs when light radiation is absorbed by other species that chemically produce a reactive species that acts on the analyte of interest. Aqueous reactions with hydroxyl radicals (•OH), carbonate radicals (•CO₃⁻), peroxo radicals (•OOR), or singlet molecular oxygen (¹O₂) are all initiated photolytically and thus are forms of indirect photolysis.[18] If a chemical exhibits no light absorption in the actinic spectrum (> 290 nm), it cannot undergo direct photolysis. In contrast however, nearly all chemicals are labile to indirect photolysis. Only the most recalcitrant and persistent chemicals are known to be inert to indirect photolytic processes (e.g. perfluoroalkyl carboxylic and sulfonic acids).[19,20]

Prior studies investigating the fate of AFFF surfactants have focused primarily on microbial biodegradation, since AFFFs are likely to enter the wastewater treatment system and interact with the microbial activity there. However, water soluble surfactants such as those in AFFFs are likely to be transported through the aquatic environment ultimately into surface waters. In surface waters, biodegradation typically plays a relatively minor role in comparison to photolysis.

Investigations into the photolysis of perfluoroalkyl and polyfluoroalkyl substances (PFASs) have largely been restricted to remediation-based studies. These studies use highly energetic far-UV radiation and unique photosensitizers to degrade all PFASs including PFCAs.[21–23] These conditions far from mimic the natural environment and do not elucidate the environmental transformation of PFASs. In contrast to these, some studies
have solely looked at the direct photolysis of PFASs. Given the lack of chromophores in most PFASs however, their results have frequently indicated slow photolysis or complete persistence.[19,20,24]

Realistic environmental aqueous photolysis is dependent on the concentration of a few key reactive species. In particular, •OH, carbonate radical (•CO$_3^-$), $^1$O$_2$, •OOR, triplet excited states of dissolved organic matter ($^3$DOM), and hydrated electrons (e$^{-}_{(aq)}$) have all been identified as reactive transients in natural waters.[18] The sources of all these transients are largely derived from a few main components of natural waters: •OH from nitrate photolysis,[25] •CO$_3^-$ from •OH and HCO$_3^-$/$CO_3^{2-}$,[26] $^3$DOM from direct photolysis,[27] $^1$O$_2$ and •OOR from O$_2$ and $^3$DOM,[18,28] and e$^{-}_{(aq)}$ from DOM or aromatic carboxylic acid photolysis.[29,30]

Lam et al. devised a system to combine these major components to create a rich system of photolytically produced transients to fully simulate indirect photolysis in the laboratory.[31] Their PhotoFate system combines nitrate, bicarbonate, and dissolved organic matter in different proportions to produce a broad suite of synthetic field water solutions with differing levels of radical production and quenching. Overall they found that nitrate and bicarbonate had the largest contribution to photolysis rates (i.e. via •OH and •CO$_3^-$), and that DOM was largely responsible for the quenching of radicals rather than their production, particularly at high DOM concentrations.[31]

1.3 Study Goals

The goal of this research was to investigate the aqueous photolysis of a currently used fluorinated AFFF surfactant, 6:2 FTAB. The PhotoFate system was used to assess its
half-life in various sunlit surface water conditions. This system was also used to compare the effects of different radicals, i.e. •OH vs •CO₃⁻, on the half-lives and mechanism of 6:2 FTAB photolysis. The PhotoFate system also allowed the comparison of nitrate, bicarbonate, and DOM on the overall photolytic fate of 6:2 FTAB.

A mechanistic study was undertaken with a subset of PhotoFate solutions to identify the fluorinated products of 6:2 FTAB photolysis. A diverse suite of fluorotelomer and perfluorinated chemicals were screened to fully consider the mechanism by which 6:2 FTAB is expected to degrade. In particular, the potential production of highly persistent PFCAs can give insight into the overall environmental hazard that 6:2 FTAB poses in sunlit surface waters.
Chapter Two

Aqueous photolysis of 6:2 fluorotelomer sulfonamide alkylbetaine
2.1 Introduction

Aqueous film forming foams, as used for fighting liquid-fuelled fires, have long been a source of fluorinated surfactants to the environment. The fluorinated surfactants used in AFFFs are chosen for their thermal stability and higher surface activity compared to their hydrocarbon analogues.[2,3] Investigations of sites contaminated by AFFF use have frequently found that the major fluorinated surfactant(s) analyzed for (historically PFOS), did not account for the total breadth of PFASs present. For instance, $^{19}$F NMR analysis of an accidental release of AFFF found much higher concentrations attributable to perfluoroalkyl groups than was calculated from traditional LC-MS analysis of the then-known PFASs (PFOS, perfluorohexane sulfonate, and perfluorooctanoic acid).[4,5] Following the phase-out of electrochemically fluorinated materials by 3M, the role of PFOS in AFFFs has diminished in favour of alternative fluorinated surfactants synthesized by telomerization.[7] Several investigations have uncovered a plethora of fluorinated surfactants containing perfluoroalkyl chains of vary lengths (3 to 15 carbons) associated with various diverse polar head groups.[7–9] Many replacement fluorinated surfactants are based on fluorotelomer chains rather than perfluoroalkyl chains; 6:2 fluorotelomer chains being the most frequently observed.[9] Though these surfactants are less persistent than their perfluoroalkyl analogues, they have been shown to degrade to produce perfluorinated acids such as perfluoroalkyl sulfonic acids and perfluoroalkyl carboxylic acids (PFCAs), both of which have no known environmental degradation pathways and thus are highly persistent.[6,12,32–34] Fluorotelomer-based chemicals are also of potential concern because a number of intermediates of their biodegradation have been shown to
exhibit greater protein binding and toxicity compared to their perfluorinated analogues.[35,36]

D’Agostino and Mabury detected 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) in 4 out of 10 AFFF samples collected from across Ontario, Canada.[9] It was the second most frequently detected class of fluorinated surfactant after 6:2 fluorotelomer mercaptoalkylamido sulfonate (6:2 FTSAS). As well, 6:2 FTAB has been detected in soil surrounding a fire-training facility in Norway.[17] The high water solubility of 6:2 FTAB and similar surfactants suggests that one of their major environmental sinks may be in ground and surface waters near their release.

Biodegradation of fluorinated surfactants can be relevant to their overall environmental transformation when they are present in ground water or soil. In surface waters sunlight radiation can have a large effect on their degradation. Photolysis may be rapid and can be the most significant form of degradation for many organics.[37,38] Environmental photolysis can occur via either direct photolysis, where the target molecule absorbs light radiation and undergoes bond cleavage, or indirect photolysis, where light radiation can produce oxidizing radicals which subsequently react with the molecule.[18] For many molecules with little or no absorption of light, indirect photolysis may represent a primary fate in light-exposed surface waters.[18,31]

Lam et al. introduced the PhotoFate system to study the contribution of indirect photolysis to the overall photolysis of aqueous phase organic contaminants.[31] The PhotoFate system mimics natural surface waters by combining the relevant photoactive components of natural surface waters in sixteen different combinations to reflect a broad range of environmental conditions. The components used are nitrate, bicarbonate and
dissolved organic matter (DOM). Together with molecular oxygen, these components are known to photolytically produce oxidizing species such as hydroxyl (•OH), peroxy (•OOR), and carbonate (•CO$_3^-$) radicals, singlet oxygen (¹O$_2$), and triplet DOM ($^3$DOM), amongst other species.[18,26,28,31,37]

Studies of the photolysis of PFASs have typically utilized photolytic remediation using far-UV radiation and photochemical sensitizers, both conditions unlike those found in environmental surface waters.[21-23] However, two environmentally relevant studies have looked at the aqueous photolysis of 8:2 FTOH and perfluoroalkane sulfonamides.[33,40] The analytes tested were all susceptible to indirect photolysis with half-lives of the order of days or weeks under continuous sunlight conditions. Direct photolysis was not observed for either 8:2 FTOH or perfluoroalkane sulfonamides within their experimental timeframes of 150 and 25 hours, respectively. Both studies found PFCAs to be major identifiable products of the indirect photolysis, however neither could accomplish a full mass-balance of products.

Moe et al. previously investigated the biodegradation and aqueous photolysis of Forafac 1157 (an AFFF formulation with 6:2 FTAB as the main fluorinated surfactant) in seawater.[17] Although they detected several fluorinated degradation products, their photolysis experiments were unable to detect a significant decrease in 6:2 FTAB concentrations over the course of 180 hrs and thus could not calculate a photolytic half-life. Unfortunately their investigation did not probe the possibility of direct photolysis. Further, the presence of many fluorinated impurities in the formulation, such as perfluorinated carboxylic acids and fluorotelomer sulfonates, hindered a full mechanistic investigation.
The present investigation examined the aqueous photolytic degradation of “pure” 6:2 FTAB using the PhotoFate system. The kinetics of 6:2 FTAB photolysis was determined and the relative effects of direct and indirect photolysis were compared. The fluorinated products, including many major fluorinated acids, were also monitored. Using this information, we propose a mechanism by which 6:2 FTAB undergoes phototransformation in the environment. This investigation was the first of its kind to probe the aqueous photolysis of fluorinated surfactants and therefore can provide a unique insight into the overall fate of these chemicals in the environment. Knowing the aqueous photolysis of 6:2 FTAB also provides a basis for understanding the aqueous fate of similar fluorotelomer-based AFFF surfactants.

2.2 Materials and Methods

A DOM stock was prepared as per EPA method OPPTS 835.5270,[41] using Aldrich humic acid (Sigma Aldrich). Sodium bicarbonate and potassium nitrate (ACP Chemicals) were used to create $\text{HCO}_3^-$ and $\text{NO}_3^-$ stock solutions. The PhotoFate system combines three concentrations of nitrate, two concentrations of bicarbonate, and three concentrations of DOM, in varying ratios to make a broad suite of synthetic field waters (SFWs) that simulate the range of environmental conditions in sunlit surface waters. The PhotoFate system uses sixteen different SFW solutions (denoted as A-P in Table 2.1) and deionized water (DI). The following fluorinated analytes were obtained from Wellington Laboratories: 6:2 FTSA, 6:2 FTCA, 6:2 FTUCA, 5:3 FTCA, and C4 to C8 PFCAs. Mass-labelled internal standards for all these chemicals (except 5:3 FTCA), and for perfluorooctane sulfonate (FOSA), were also obtained from Wellington Laboratories.
The analytes 6:2 FTAB, 6:2 FTAA, and 6:2 fluorotelomer sulfonamide (6:2 FTSAm), which are not commercially available, were synthesized in house to > 99% purity as described in D’Agostino and Mabury, and analyzed using LC-MS/MS. [42]

Table 2.1: Composition and pH of 16 synthetic field water solutions. Bicarbonate and nitrate are reported in mg/L, DOM in mg C/L

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2.2.1 PhotoFate setup

Synthetic field water solutions were prepared in quartz vials with a spike of 6:2 FTAB (final concentration: 10 or 250 ppb (20 or 500 nM)) to a final volume of 10 mL. Each experiment contained at least three replicate vials, and up to 6 or 12 replicates as necessary, of the SFW solutions tested and blank deionized water controls. Dark controls were in glass vials covered with aluminum foil. All sample vials were weighed after sampling and, before the next sampling time, topped up with deionized water to correct for evaporative losses. A quartz plate was also placed over all quartz vials in the sunlight simulator to minimize evaporation.

The Suntest CPS sunlight simulator (Atlas) emits light across the actinic spectrum (290-800 nm). The solutions were kept cool by a chilled water recirculator and a fan system within the simulator. The internal temperature of the solutions was approximately
30-35°C during the photolysis experiments. Spectroradiometry was conducted on the sunlight simulator to confirm its spectral characteristics and assess intensity. This was done with a Black-Comet C-50 spectroradiometer (Stellar Net). Further details are listed in Appendix A. A portion of the measured spectrum is shown in Figure 2.1. UV/Vis spectra were taken with a Lambda 25 spectrometer (Perkin Elmer).

Figure 2.1: UV/Vis spectrum of 6:2 FTAB in water. Irradiance of the solar simulator is shown on the right-hand axis.

Kinetics-based experiments using all sixteen PhotoFate solutions (n = 3 to 12) were conducted at a 6:2 FTAB concentration of approximately 10 ppb (20 nM). Mechanistic studies conducted on SFW C, F, G, and DI were done at approximately 250 ppb (500 nM). Triplicates of each solution were tested, and one outlier each (found using Grubbs’ test) from SFW C and DI were removed. Thus all mechanistic data represents n ≥ 2.

Experiments to capture volatile 6:2 FTOH were done using 100 mL of solution (SFW F or DI) in 130 mL quartz test tubes which were sealed with rubber septa. The septa were
pierced to fit XAD-2 cartridges and a single XAD-2 cartridge was fitted in each septum. The experiments were spiked to a 6:2 FTAB concentration of ~ 250 ppb and irradiated for 144 hrs. After irradiation, prior to sampling of the aqueous phase and XAD cartridges, the solutions were bubbled with purified house air for 24 hrs. Details of the XAD extraction protocol and subsequent GC-MS analysis are described in Appendix A. A spike and recovery of 5 µg of 6:2 FTOH from aqueous solutions in the same fashion had a 34 % recovery. The relatively poor recovery may be due to the use of one XAD cartridge for each solution, as space requirements inside the sunlight simulator prevented the use of two cartridges in series.

2.2.2 Analysis

Aliquots were combined with an equal volume of methanol and stored at -20°C prior to analysis. LC-MS/MS analysis was conducted on a Waters Acquity UPLC coupled to a Waters Xevo TQ-S triple quadrupole mass spectrometer. All samples detected by LC-MS/MS were injected and analyzed in triplicate. Separation was performed with an Acquity UPLC BEH C18 column (1.7µm, 2.1 x 75 mm, Waters) outfitted with a Waters VanGuard BEH C18 pre-column (1.7 µm). The elution gradient, run at 0.5 mL/min, was as follows (A: 10 mM ammonium acetate in water; B: methanol): 90% A for 1 minute, ramp to 60% A from 1 to 2 mins, then ramp to 75% B from 2 to 5.5 mins, then ramp to 95% B from 5.5 to 5.6 mins, then hold at 95% B from 5.6 to 6.5 mins, return to 90% A from 6.5 to 6.6 mins, and hold at 90% B from 6.6 to 7.5 mins, marking the end of the run. The column was maintained at 60°C throughout analysis.
All analyses were run in mixed positive and negative electrospray mode, dynamically switching between modes per ion. Mass spectral parameters include: capillary voltage 1.5 kV, source offset 50 V, nebulizer 7.0 bar, desolvation temperature 500°C, cone flow 150 L/hr, desolvation flow 800 L/hr, collision gas flow 0.15 mL/min. Nitrogen was used as the cone and desolvation gas, argon was used as a collision gas.

A suite of perfluorinated and polyfluorinated chemicals were screened for: 6:2 FTSA, 6:2 FTCA, 6:2 FTUCA, 5:3 FTCA, and C4 to C8 PFCAs. We employed mass-labelled internal standards for all analytes except for those synthesized in house. Mass-labelled FOSA was used as a surrogate for 6:2 FTSAm, and similarly mass-labelled 6:2 FTUCA for 5:3 FTCA. Analytes with internal standards or surrogates were quantified by internal calibration, those without were quantified by external calibration. Mass spectral analysis parameters for each analyte are listed in Table 5.1. Spike and recovery experiments were conducted for the analytes in SFW solutions C, F, and G, and DI, each in triplicate. No significant differences in percent recovery were seen for all four solutions tested, and thus the percent recoveries are reported as an average of all four solutions. Percent recoveries ranged from 82 to 125%, and the limits of detection and quantification ranged from 0.01 to 0.3 ng/mL and 0.03 and 1.0 ng/mL, respectively. Analyte-specific percent recoveries, limits of detection, and limits of quantification are recorded in Table 5.2.

### 2.2.3 Statistical Analysis

Statistical analyses of the data were carried out using Statistica 13 (Dell Inc.). Two-tailed Student’s t-tests were used to indirect photolysis half-lives to that of direct photolysis, at p ≤ 0.05 level of significance. A multiple linear regression was also carried out
to compare the composition of each indirect photolysis solution with its photolysis half-life with a function of $t_{1/2} = b_1[HCO_3^-] + b_2[DOM] + b_3[NO_3^-] + c$. The regression function had a p-value < 0.01, and an adjusted $R^2$ value of 0.51. Further details of the analysis can be found in the Appendix A.

### 2.3 Results and Discussion

#### 2.3.1 Kinetics of 6:2 FTAB photolysis

The target analyte, 6:2 FTAB, was found to be susceptible to both direct and indirect photolysis in this investigation. The half-life by direct photolysis was $34 \pm 18$ hrs, and the photolytic half-life by indirect photolysis was observed to vary between 14 and 108 hrs (illustrated in Figure 2.2). Overall, 8 out of 16 solutions significantly ($p \leq 0.05$) extended the half-life of 6:2 FTAB in solution beyond that in deionized water, while none significantly reduced it. The relatively rapid indirect photolysis of 6:2 FTAB is coherent with similar results for other PFASs. Gauthier and Mabury found the half-life of 8:2 FTOH by indirect photolysis to range between 30 to 163 hrs using SFW solutions A, F, and O with the PhotoFate system.[33] Plumlee et al. found the half-life of various N-substituted perfluorooctane sulfonamides ranged between 1.7 to 5.6 hrs in 10 mM $H_2O_2$ irradiated solutions.[40] They estimate the environmental half-life of $N$-ethyl perfluorooctane sulfonamidoacetate to vary from 0.47 to $4.7 \times 10^3$ days, depending on the steady state concentration of $\cdot OH$ ($10^{-14}$ to $10^{-18}$ M). In comparison, this investigation found half-lives of 14 to 108 hrs for the indirect photolysis of 6:2 FTAB. These results are marginally more rapid than those for 8:2 FTOH, but may be attributable to differences between light sources.
To understand whether solution composition played a major role in dictating the photolytic half-life of 6:2 FTAB, a multiple linear regression was conducted using the concentrations of bicarbonate, DOM, and nitrate. The results of this analysis are summarized in Table 5.3. The correlation coefficients (± standard error) of bicarbonate, DOM, and nitrate were -0.16 (± 0.18), 0.76 (± 0.18), and -0.09 (± 0.18), respectively. Only the correlation coefficient of DOM was significant (p ≤ 0.05), indicating that it had a significant effect in prolonging the photolytic half-life of 6:2 FTAB. A visual illustration of the trends for each SFW component is shown in Figure 2.3. Each bar in the figure is the mean half-life for all of the 16 solutions that fall under a certain category of their composition (i.e. the mean half-lives of all 8 solutions with 45 ppm bicarbonate, and all 8 solutions with 300 ppm bicarbonate are the first two bars in the graph). The role of DOM in
slowing aqueous photolysis was also observed by Lam et al. who found that the major role of DOM in the PhotoFate system is as a light attenuator or radical scavenger.[31] As discussed below, the mechanistic differences between any of the direct and indirect photolysis solutions in this study were relatively minor. This suggests that the major role of DOM is not in radical quenching, which would cause major mechanistic differences, but rather light attenuation. A recent investigation of direct aqueous photolysis of neonicotinoid insecticides found that depth within the water column, a corollary for light attenuation by DOM, was the major factor in reducing the rate of direct photolysis. The authors calculated that at depths of 8 and 18 cm in their mesocosm waters, light flux was attenuated by 89 and 98% respectively.[43] A similar effect is likely at play for the photolysis of 6:2 FTAB where direct photolysis that occurs is being attenuated by the highly absorbing DOM.

![Figure 2.3: Mean half-lives of 6:2 FTAB in SFW solutions according to their composition (concentrations in ppm are shown on X axis). Deionized water control is shown for comparison. Error bars represent standard deviations.](image-url)
The aqueous photolysis of 6:2 FTAB has been assessed in one prior study by Moe et al. [17] Over the course of 180 hrs of photolysis in seawater, no significant degradation of 6:2 FTAB was observed. This lies in contrast to our work which finds the half-life of 6:2 FTAB to be shorter than 110 hrs in all settings. As well, they saw limited production of 6:2 FTSAm, a major photolytic product observed in this investigation.

2.3.2 Products of 6:2 FTAB photolysis

Four solutions were tested for their photolysis product distribution: SFW C, F, and G, and DI. The three indirect photolysis solutions represent high DOM conditions (SFW C), high •OH concentrations (SFW F), and high •CO₃⁻ concentrations (SFW G). The distribution of products in the four aqueous photolysis settings used in this experiment is illustrated in Figure 2.4 and Table 5.4. The major product of photolysis in all solutions was the N-dealkylation product 6:2 FTSAm. By the end of 4 days of photolysis, 6:2 FTSAm accounted for 46 to 61 mol% of all photodegraded 6:2 FTAB. It appears to be the first stable intermediate of photolysis. N-dealkylation is known to occur via both •OH and •CO₃⁻ radicals.

The temporal production of fluorinated products in all indirect photolysis solutions is illustrated in Figure 2.5. As observed, 6:2 FTSAm was the only product we observed to peak and begin to decrease in concentration within the experiment. This trend is even more evident in the SFW solution specific trends shown in Figures 5.3 to 5.6. As well, early in the experiment, 6:2 FTSAm and 6:2 FTSA are the only products detected prior to the appearance of PFCAs. This indicates that 6:2 FTSAm is likely the first stable intermediate that photolyzes to produce lower fluorinated products.
Figure 2.4: Final product distribution after 4 days of photolysis (n = 3 for F and G, n =2 for C and DI). Error bars, when visible, represent standard deviations. Distribution of minor products is shown in Figure 5.7.

The production of 6:2 FTSAm was also reported by Moe et al. as a result of photolysis.\cite{17} The chemical properties of 6:2 FTSAm are likely comparable to its perfluoroalkyl analogue, perfluorooctane sulfonamide (FOSA) and thus it will exist as a neutral, semi-volatile species under environmental conditions. Experiments to capture volatile 6:2 FTOH were also screened for 6:2 FTSAm, but found relatively low quantities (< 1 mol %), compared to its aqueous phase concentration. Since 6:2 FTSAm is expected to be a neutral uncharged species at environmental pH, it will exhibit volatilization into the atmosphere. Similar to FOSA, 6:2 FTSAm may be susceptible to long-range transport and could be a precursor to PFCAs through atmospheric oxidation.
To understand the long-range transport potential of 6:2 FTSAm, it was assessed using the OECD overall persistence and long-range transport potential tool (available from http://www.oecd.org/exposure/povlrtp).[44] Briefly, the tool assesses three global scale compartments (air, water, and soil) and predicts transport and overall fate between these. The largest of these values, typically in air, are reported as a measure of long-range transport potential. The inputs for the tool were found using EPI Suite 4.11. The modelled EPI Suite values were: logK_{AW} 0.683, logK_{OW} 3.97, and the half-lives in air, water, and soil were 28.6 hrs, 17280 hrs, and 34560 hrs, respectively. Based on the possible degradation of 6:2 FTSAm observed in this investigation, a faster half-life in water of 200 hrs was also
proposed. The complete outputs for both scenarios are shown in Figures 5.8 and 5.9. For both water half-life values, the tool predicted the characteristic travel distance of 6:2 FTSAm in the atmosphere to be 594 km, and its transport efficiency to be 0.0003%. The fact that these values were consistent between both water half-life values indicates the strong effect of the air compartment in limiting the transport of 6:2 FTSAm. The overall persistence was 124 days with a half-life in water of 17280 hrs, or 11 days with a half-life in water of 200 hrs. The low characteristic travel distance and transport efficiency both indicate that 6:2 FTSAm is too rapidly degraded in the atmosphere to travel on a global scale. Though it is likely a source of PFCAs to the atmosphere, the range of 6:2 FTSAm limits their reach to with 500 to 1000 km of the 6:2 FTSAm emission. Further measurements of the physical properties and environmental degradations of 6:2 FTSAm (e.g. half-life in air) may affect the output of this model however.

The second major product of indirect photolysis was 6:2 FTSA. Figure 5.7 shows the final product distribution in all four solutions of the minor fluorinated products (i.e. excluding 6:2 FTSAm). By the end of the experiment, 6:2 FTSA accounted for 4.0 to 5.9 mol % of photodegraded 6:2 FTAB. It may be produced directly from 6:2 FTAB; although, since after 1 day of photolysis it represents only 2.7% of known products (average for SFW C, F, and G), it may be derived directly from 6:2 FTSAm. The biodegradation of 6:2 FTSA to form 6:2 FTCA, 6:2 FTUCA, and PFCAs (C6 and lower) has been documented in the literature.[45,46]

The photolytic production of 6:2 FTAA was primarily via direct photolysis. By the end of our experiment, 6:2 FTAA accounted for 2.6 mol % of products by direct photolysis, but only 0.06 mol % by indirect photolysis. The strong bias for 6:2 FTAA production by
direct photolysis may provide a means to assess the relative effects of direct and indirect photolysis. The lack of 6:2 FTAA in indirect photolysis may be due to one or more factors. Firstly, $\cdot$OH and $\cdot$CO$_3^-$ radicals may not easily dealkylate the quarternary nitrogen atom in 6:2 FTAB. This is unsurprising as both carbonate and hydroxyl radicals react with electron-rich atoms, and the betaine group with quarternary nitrogen and carboxylic carbon are electron-deficient. Additionally, 6:2 FTAA, with two electron-rich nitrogen atoms, may be more susceptible to further oxidation from $\cdot$OH and $\cdot$CO$_3^-$ and would have a lower steady-state concentration under indirect photolysis conditions. Coincident with this investigation, D'Agostino & Mabury have found that 6:2 FTAA biodegrades to produce 6:2 FTSAm, 6:2 FTOH, 6:2 FTCA, 6:2 FTUCA, 5:3 FTCA, and PFCAs.\cite{42}

A minor intermediate observed in all solutions was 6:2 FTUCA. It accounted for 0.05 to 0.12 mol% of 6:2 FTAB products after 4 days of indirect photolysis. Fluorotelomer unsaturated carboxylic acids have been detected in the photolysis of 8:2 fluorotelomer alcohol (8:2 FTOH).\cite{33} Both FTCAs and FTUCAs are environmentally labile compounds and readily degrade to produce shorter-chain PFCAs.\cite{32,47} The lack of detection of 6:2 FTCA may be the result of its relative insensitivity to electrospray ionization mass spectrometry (LOD: 0.2 ng/mL). The observation of PFHpA as a major product in all solutions implies the presence of 6:2 FTCA.

Though physical requirements limited the collection of volatiles during most experiments, two photolysis experiments (SFW F and Di) were conducted with sealed quartz vials and XAD-2 cartridges to capture 6:2 FTOH. We targeted 6:2 FTOH because it has been detected in the degradation similar fluorotelomer chemicals including 6:2 FTSAS and 6:2 FTSA.\cite{6,46} Solution F was chosen of the three mechanistic solutions (C, F, and G)
because it exhibited the fastest half-life, and therefore would have the best detection limit for intermediates. After 6 days of photolysis, 6:2 FTOH was detected in the cartridge extracts of both SFW F and DI, attributable to 0.85 mol % and 0.82 mol % (recovery corrected) of photolyzed 6:2 FTAB, respectively. This is indicative of 6:2 FTOH’s role as a minor intermediate in the overall photodegradation of 6:2 FTAB. This is in line with other experiments that have found that FTOHs are intermediates in the degradation of 6:2 FTSA,[46] 6:2 FTSAS,[6] 6:2 FTAA,[42] and 6:2 fluorotelomer mono- and disubstituted polyfluoroalkyl phosphates.[48] Also, FTOHs are known precursors to 6:2 FTCA, 6:2 FTUCA, and PFCAs.[12,33,49] However, since the production of 6:2 FTOH was low in these experiments, it likely does not account for the 32 to 49 mol % of missing 6:2 FTAB photolysis products (Figure 2.4). An approximately equal amount of 6:2 FTSAm was detected as 6:2 FTOH in the same XAD extracts. However, no 6:2 FTAA was detected. All told, captured species in the gas phase did not account for more than 1 to 2 mol % of photolyzed FTAB in these experiments.

The three major PFCAs produced by the photolysis of 6:2 FTAB were PFHpA, PFHxA, and PFPeA. PFHpA is consistently the most abundant PFCA product, and PFHxA and PFPeA were of a similar concentration in most cases. Analogously, Gauthier and Mabury identified perfluorononanoic acid (PFNA) as a product of the aqueous photolysis of 8:2 FTOH, proceeding via the 8:2 FTCA intermediate.[33] Likewise, the product of PFNA from 8:2 FTCA has also been observed in rainbow trout.[50] PFHpA is known to be derived from 6:2 FTCA via metabolic degradation in rat hepatocytes.[47] PFHxA and PFPeA have been identified as terminal products in the environmental degradation of several 6:2 fluorotelomer chemicals including 6:2 FTSAS, 6:2 FTSA, and 6:2 FTOH.[6,14,45,46,51,52]
2.3.3 Environmental Implications

This investigation has found that 6:2 FTAB photolyzes rapidly in sunlit aqueous environments with a half-lives of 14 to 108 hrs. Under real day/night cycles this is roughly equivalent of 1 to 9 days. Spectroradiometric measurements of the sunlight simulator were compared to spectral irradiance data on two dates in 2015 to estimate the approximate intensity of the solar simulator. Details of this are given in Appendix A. Overall, the solar simulator intensity measured beneath our quartz sample cover falls somewhere between
noon in June and midafternoon in November. Thus the half-lives in the solar simulator underestimate the environmental half-lives in sunlit surface waters at the height of summer, but may overestimate them in winter.

This is rapid in comparison to biodegradation half-lives of similar PFASs. There appears to be no significant difference between high •OH and high •CO₃⁻ environments. Both conditions produce significant quantities of 6:2 FTSAm and, ultimately, substantial quantities of PFCAs. As well, no significant differences in photolytic half-lives were observed between •OH and •CO₃⁻ conditions. Due to the higher selectivity of •CO₃⁻, its steady state concentrations are 2 to 3 orders of magnitude larger.[31] If 6:2 FTAB reacts similarly with both radical species, as indicated by the poor trend between HCO₃⁻ or NO₃⁻ concentrations and photolysis half-life, its environmental photolysis is likely dominated by reactions with •CO₃⁻ rather than •OH. This assessment of •OH vs •CO₃⁻ may equally apply to other photolysis studies that investigate chemicals bearing electron rich sulfur or nitrogen function groups. For instance, though Plumlee et al. [40] assessed the half-life of N-substituted perfluorooctane sulfonamides with respected to •OH, their true environmental aqueous photolysis may, like 6:2 FTAB, be dominated by •CO₃⁻. In such cases, photolytic half-lives based solely on the steady-state concentration of •OH may overestimate the half-lives of the analytes in real aqueous settings.

The finding that 6:2 FTSAm makes up the majority of 6:2 FTAB photolysis products has implications for the broader class of fluorotelomer surfactants. Many fluorotelomer surfactants use an N-substituted sulfonamide or amine group chemistry. In sunlit surface waters with significant steady state concentrations of •OH or •CO₃⁻, it appears that N-dealkylation to produce a neutral primary sulfonamide or amine is a major pathway. It is
possible that indirect photolysis of fluorotelomer surfactants may be an indirect source of neutral, semi-volatile fluorotelomer species to the aqueous environment. Although this study found only small amounts of fluorotelomer species in XAD extracts (< 2 mol %), there may be more volatilization in real surface waters with longer time to partition, more surface area, and more effective headspace. The relative partitioning of these chemicals may be of interest due to their volatility, potential for atmospheric transport, and ultimate oxidation to PFCAs.

By the end of our photolysis experiments, up to 2.3 mol % of 6:2 FTAB was converted to PFCAs. However, nearly all the other photolytic products (6:2 FTSA, 6:2 FTOH, 6:2 FTUCA, 6:2 FTAA) are known to be PFCA precursors in the environment. Furthermore, the present study also identifies that 6:2 FTSAm is likely to be a PFCA precursor, as well as a potentially susceptible to long range transport. Perfluoroalkyl carboxylic acids are of concern due to their extreme persistence and subsequent detection in a vast array of environmental matrices. This investigation has confirmed the hypothesis that fluorotelomer surfactants are a source of PFCAs to the environment, and that the rate of transformation of PFASs to PFCAs can be quite rapid in sunlit surface waters.
Chapter Three

Summary and Conclusions
This investigation probed the aqueous photolysis of a frequently used fluorinated surfactant, 6:2 FTAB. Since similar PFASs with hydrocarbon head groups (e.g. 8:2 FTOH) are susceptible to indirect photolysis, 6:2 FTAB was expected to be susceptible to indirect photolysis, if not direct photolysis also. As well, because it bears a fluorotelomer tail, it was expected to produce polyfluorinated and perfluorinated products including PFCAs.

It was found that 6:2 FTAB was susceptible to both direct and indirect photolysis. The half-life by indirect photolysis ranged from 14 to 108 hrs, and 34 ± 18 hrs by direct photolysis. The major factor affecting photolysis half-life was identified as dissolved organic matter, where increasing concentrations slowed the photolysis of 6:2 FTAB. Under realistic environmental conditions, the half-life of 6:2 FTAB in sunlit surface waters is of the order of 1 to 9 days. It was found to react rapidly with •CO$_3^-$, as well as •OH, due to it bearing an electron-rich N-substituted nitrogen atom. Since the steady-state concentrations of •CO$_3^-$ are much higher in natural waters than •OH,[18] the indirect photolysis of 6:2 FTAB will be mediated primarily by reactions with •CO$_3^-$. 

Mechanistically, this investigation identified eight fluorinated products of 6:2 FTAB photolysis. This include the little studied 6:2 FTAA and 6:2 FTSAm, as well as known the known fluorotelomer species 6:2 FTSA, 6:2 FTOH, and 6:2 FTUCA. As well, the production of three PFCAs, PFHpA, PFHxA, and PFPeA, was observed. Combined, these products accounted for 51 to 68 mol % of photolyzed 6:2 FTAB, and provided the means to propose an overall mechanism for 6:2 FTAB photolysis. The primary sulfonamide, 6:2 FTSAm was the major product detected in all solutions, representing the initial N-dealkylation reaction. The major distinction between solutions was observed between direct and indirect photolysis settings, where 6:2 FTAA was dominant under direct photolysis conditions. This
is likely due to its increased reactivity with oxidizing radicals in indirect photolysis solutions. All the non-PFCA products detected in this experiment are known or suspected environmental precursors to PFCAs. Thus, though PFCAs accounted for 1.0 to 2.3 mol % of products, their yield is expected to increase as the precursors degrade. Ultimately this investigation found that though 6:2 FTAB is a less-persistent alternative to surfactants such as PFOS, it appears to be a source of similarly persistent PFCAs to the environment.
Chapter Four

References


Chapter Five

Appendices
Appendix A - Supporting Information for Chapter Two

5.1 Materials and Methods

5.1.1 GC-MS method

All samples detected by GC-MS were injected and analyzed in duplicate. Analysis of 6:2 FTOH was done using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert XL EI/Cl MSD in positive chemical ionization with methane as a reagent gas. Both 6:2 FTOH (m/z 365.0) and its internal standard, $^{13}$C$_4$-6:2 FTOH (m/z 369.0), were detected by selected ion monitoring with a dwell time of 50 ms. Splitless 1 µL injections were done via an autosampler. An Agilent DB-1701 column (30 m × 0.25 mm × 0.15 µm) was used for chromatography. The oven program was as follows: an initial temperature of 50°C was held for 2 minutes, then ramped to 150°C at a rate of 12°C per minute, and finally raised to 250°C at a rate of 30°C per minute. Helium was used as a carrier gas at a flow rate of 1.2 mL per minute. The inlet temperature was 250°C and the MSD transfer line was 280°C.

5.1.2 Statistical Analysis

The multiple linear regression that was performed assumes a normal distribution of data for its analysis. The true distribution is illustrated in Figure 5.2. The distribution does not cohere entirely with a typical normal distribution, which may limit the scope of the regression performed on the data. However, transformations of the data were unsuccessful in producing a normalized dataset. Non-parametric multiple linear regression was conducted (using the R software package (version 3.2.3) with the loess function) and
indicated that of the three components (bicarbonate, DOM, and nitrate), that only DOM was a significant contributor to the model at p < 0.1 level of confidence.

5.1.3 Spectroradiometry and Comparison to Toronto Sunlight

Spectroradiometric measurements were taken using 10 ms integration time and 20 scans were averaged to produce spectra. Figure 5.1 illustrates two spectra taken inside the solar simulator and beneath our quartz sample cover. As a comparison, spectral irradiance on two representative days in Toronto, ON, Canada is shown. The irradiance was calculated using the “Quick TUV Calculator” from the National Centre for Atmospheric Research (available: http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/). The parameters were: Lat: 43.662°, Long: -79.399°, overhead ozone column was 300 Dobson units, the surface albedo was 0.1, and the ground elevation was 0 km. The June data was from June 30, 2015 at 12 PM EST, and the November data was from November 18, 2015 at 3 PM EST. The integrated spectral irradiance in W/m² is shown for each trace. The simulator appears to output radiation closely matching that of summertime intense sunlight, but it is slightly attenuated by our quartz sample cover.
5.2 Tables and Figures

![Spectroradiometric spectra of the solar simulator with and without a quartz sample cover. Solar radiation spectra from June and November shown in dashed traces](image)

Figure 5.1: Spectroradiometric spectra of the solar simulator with and without a quartz sample cover. Solar radiation spectra from June and November shown in dashed traces

Table 5.1: MS parameters for each analyte. * indicates the quantifying transition, where applicable

<table>
<thead>
<tr>
<th>Analyte</th>
<th>ESI Mode</th>
<th>MRM Transition(s)</th>
<th>Declustering Potential (V)</th>
<th>Collision Energy (V)</th>
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<td>+</td>
<td>571.2&gt;440.0</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571.2&gt;104.1*</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>6:2 FTAA</td>
<td>+</td>
<td>513.0&gt;440.0*</td>
<td>90</td>
<td>28</td>
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<tr>
<td></td>
<td></td>
<td>513.0&gt;58.1</td>
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<td>-28</td>
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<td>-28</td>
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<td>-28</td>
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<td>Analyte</td>
<td>Percent recovery</td>
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<td>LOQ (ng/mL)</td>
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<td>-10</td>
<td>-10</td>
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<td>5:3 FTCA</td>
<td>- 341.0&gt;236.9</td>
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<td>-12</td>
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<td>PFHpA</td>
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<td>PFBA</td>
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<tr>
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<td>- 216.9&gt;171.9</td>
<td>-30</td>
<td>-11</td>
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</table>

Table 5.2: Average percent recoveries (from SFW C, F, and G, and DI; ± standard deviation) and limits of detection and quantification for each analyte.
Figure 5.2: Histogram of half-life values (in hrs)

Table 5.3: Output of multiple linear regression for half-life as a function of bicarbonate, DOM, and nitrate concentrations

<table>
<thead>
<tr>
<th></th>
<th>Standardized Coefficient (b*) (± standard error)</th>
<th>Raw Coefficient (b) (± standard error)</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept (c)</td>
<td>n/a</td>
<td>45.5 ± 11.8</td>
<td>0.00222</td>
</tr>
<tr>
<td>HCO₃⁻ (b₁)</td>
<td>-0.156 ± 0.180</td>
<td>-0.03727 ± 0.0431</td>
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<td>DOM (b₂)</td>
<td>0.757 ± 0.180</td>
<td>0.8138 ± 0.194</td>
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<td>NO₃⁻ (b₃)</td>
<td>-0.0892 ± 0.180</td>
<td>-0.1198 ± 0.242</td>
<td>0.630</td>
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Table 5.4: Molar % of all identified products by indirect and direct photolysis. Averages of all trials ± standard deviations, are reported; n.d. indicates non-detection

<table>
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<tr>
<th></th>
<th>C (n=2)</th>
<th>F (n=3)</th>
<th>G (n=3)</th>
<th>DI (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:2 FTAA</td>
<td>0.22 ± 0.2</td>
<td>0.011 ± 0.014</td>
<td>n.d.</td>
<td>2.6 ± 0.9</td>
</tr>
<tr>
<td>6:2 FTSAm</td>
<td>53 ± 24</td>
<td>61 ± 6</td>
<td>45 ± 9</td>
<td>47.1 ± 1.5</td>
</tr>
<tr>
<td>6:2 FTSA</td>
<td>4.0 ± 0.3</td>
<td>5.2 ± 1.2</td>
<td>5.9 ± 1.4</td>
<td>0.62 ± 0.10</td>
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<tr>
<td>6:2 FTUCA</td>
<td>0.12 ± 0.03</td>
<td>0.052 ± 0.014</td>
<td>0.056 ± 0.008</td>
<td>0.03 ± 0.2</td>
</tr>
<tr>
<td>PFHpA</td>
<td>1.1 ± 0.5</td>
<td>1.3 ± 0.3</td>
<td>0.52 ± 0.04</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td>PFHxA</td>
<td>0.3 ± 0.2</td>
<td>0.5 ± 0.3</td>
<td>0.08 ± 0.03</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>PFPeA</td>
<td>0.47 ± 0.09</td>
<td>0.49 ± 0.12</td>
<td>0.37 ± 0.07</td>
<td>0.048 ± 0.008</td>
</tr>
<tr>
<td>∑ products</td>
<td>59 ± 24</td>
<td>68 ± 5</td>
<td>53 ± 8</td>
<td>51 ± 2</td>
</tr>
</tbody>
</table>
Figure 5.3: Temporal production of fluorinated products: SFW C. Error bars are standard deviations.

Figure 5.4: Temporal production of fluorinated products: SFW F. Error bars are standard deviations.
Figure 5.5: Temporal production of fluorinated products: SFW G. Error bars are standard deviations

Figure 5.6: Temporal production of fluorinated products: DI. Error bars are standard deviations
Figure 5.7: Final product distribution, as shown in Figure 2.4, but without 6:2 FTSAm, to show minor products (n=3 for F and G, n=2 for C and DI). Error bars are standard deviations.

Figure 5.8: OECD LRTP tool output for 6:2 FTSAm with a water half-life of 17280 hrs.
Figure 5.9: OECD LRTP tool output for 6:2 FTSA, with a water half-life of 200 hrs.