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Supplementary material

Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6 : 2 fluorotelomermercaptoalkylamido sulfonate (6 : 2 FTSAS)

Barbara Weiner,[A, B,1] *Leo W. Y. Yeung,*[A,1] *Erin B. Marchington,*[A] *Lisa A. D'Agostino*[A] *and Scott A. Mabury*[A,C]

[A]Department of Chemistry, University of Toronto, 80 St George Street, Toronto, ON, M5S 3H6, Canada.

[B]Present address: Department of Environmental Engineering, Helmholtz-Centre for Environmental Research, Permoserstrasse 15, D-04318 Leipzig, Germany.

[C]Corresponding author. Email: smabury@chem.utoronto.ca

[1]Joint first authors.

A list of analytical standards for PFAS quantification

Mass labelled standards ($^{13}C_4$-perfluorobutanoate (PFBA), $^{13}C_2$-perfluorohexanoate (PFHxA), $^{13}C_4$-perfluorooctanoate (PFOA), $^{13}C_5$-perfluoronoanoate (PFNA), $^{13}C_4$-perfluorodecanoate (PFDA), $^{13}C_2$-perfluoroundecanoate (PFUnDA), $^{13}C_2$-perfluorododecanoate (PFDoDA), $^{18}O_2$- perfluorohexane sulfonate (PFHxS), $^{13}C_4$-perfluorooctane sulfonate (PFOS), d^3-*N*-methyl perfluorooctanesulfonamidoacetate (d^3 MeFOSAA), d^5-*N*-ethyl perfluorooctanesulfonamidoacetate (d^5 EtFOSAA), $^{13}C_2$-6 : 2 fluorotelomer unsaturated acid (FTUCA) and native standards (4 : 2 fluorotelomer sulfonate (FTSA), 6 : 2 FTSA, 8 : 2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, perfluorotridecanoate (PFTriDA), perfluorotetradecanoate PFTeDA, perfluorobutane sulfonate (PFBS), PFHxS, PFOS, perfluorodecane sulfonate (PFDS), perfluorooctanesulfonamidoacetate (FOSAA), MeFOSAA, EtFOSAA) were donated by Wellington Laboratories (Guelph, ON).

Synthesis of 6 : 2 FTSAS

6 : 2 FTSH (118 µL, 0.50 mmol, 1.0 equivalent) was added under inert atmosphere to $NaBH_4$ (60 mg, 22.2 mmol, 44 equivalent) in MeOH (2.0 mL). The mixture was heated under reflux to 65 °C for 15 min. A suspension of 2-acrylamido-2-methyl-1-propanesulfonic acid (115 mg, 0.75 mmol, 1.5 equivalent) in MeOH (4.0 mL) was added, and the mixture heated to reflux for 6 h and stirred overnight at room temperature. TLC control showed that 6 : 2 FTSH was still present. Therefore, additional $NaBH_4$ was added, and the mixture heated to reflux for 6 h until all thiol was consumed. The solvent was evaporated in vacuum, and the crude product purified by column chromatography with fluorinated silica gel (MeOH : H_2O 80 : 20 > MeOH > THF) to yield a white solid.

Verification of synthesis yielded spectral results as follows: for ^{1}H NMR (400 MHz, CD_3OD) δ = 1.38 (s, 6H, CH_3), 2.30 (t, J = 7.4 Hz, 2H, CH_2), 2.37 (dd, J = 18.9 Hz. J = 7.4 Hz, 2H, CH_2), 2.64 (dd, J = 17.1, J = 7.9, 2H, CH_2), 2.66 (t, J = 7.4 Hz, 2H; CH_2), 3.07 (s, 2H; CH_2); for ^{19}F NMR (377 MHz MHz, CD_3OD) δ = –81.5 (t, J = 10.0 Hz, 3F, CF_3), –114.4 (dtt, J = 32.6 Hz, J = 18.7 Hz, J = 3.8 Hz, 2F, CF_2), –122.0 (m_c, 2F, CF_2), –123.0 (m_c, 2F, CF_2), –123.4 – –123.6 (m, 2F, CF_2), –126.4 (m_c, 2F, CF_2); for ^{13}C NMR (101 MHz, CD_3OD) δ = 23.6 (CH_2), 27.2 (CH_3), 33.1 (C), 38.5 (CH_2), 53.5 (CH_2), 60.4 (CH_2), 173.2 (CO); and, for HR–(ESI)–MS: calc. for $C_{15}H_{17}NO_4F_{13}S_2$ 586.0396, found 586.0376.

^{19}F NMR analysis

The ^{19}F NMR spectra were recorded on a 500-MHz Varian Unity (Plus) spectrometer equipped with a 5-mm NaloracFH ^{19}F proton decoupling probe tuned to 470.3 MHz for ^{19}F resonance. The chemical shifts were recorded relative to the internal standard 4′-(trifluoromethoxy)-acetanilide (TFMA, δ = –58.08 ppm). The spectral window was set from 40 to –300 ppm. The minimum recycling delay time (D_1) value was set to 5.0 s. Samples were run with 500 transients, which resulted in a total experiment time of ~50 min.

AFFF samples were prepared by mixing 300 μL of foam, 200 μL of TFMA (0.8 mg mL^{-1} in acetonitrile) and 150 μL of D_2O in an NMR tube. Samples 5, 10, 7 and 14 were diluted 2× with H_2O because of their high viscosity. Standards of pure 6 : 2 FTSA, 6 : 2 FTSAS and PFOS were prepared from a saturated solution of the respective analyte in MeOH (300 μL), TFMA, (200 μL of 0.8 mg mL^{-1}), D_2O (150 μL) or CD_3OD (150 μL).

LC-MS/MS analysis

The analytes in the AFFF samples were identified using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS Sciex) in ESI- coupled to an Agilent 1100 HPLC system. The chromatographic separation was achieved using a Gemini NX C18 column (4.6 × 50 mm, 3 μm, 110 Å) (Phenomenex, Torrance, CA, USA). AFFF samples were analysed in two batches using the same HPLC method. The aqueous stock solutions were diluted with 50 % MeOH (dilutions ranging from 20 to 200×) and injected (25 μL). The gradient method used a flow rate of 0.5 mL min^{-1} with HPLC grade MeOH and water with 10 mM ammonium acetate as mobile phase. The initial solvent composition at t = 0 min was 65 : 35 MeOH : H_2O, which changed over 3 min to MeOH : H_2O 95 : 5 (t = 3 min), and held for 2 min (t = 5 min), before returning to MeOH : H_2O 65 : 35 in 0.5 min (t = 5.5 min) and being held for 2.5 min (t = 8 min). In batch one, PFCAs (C4-C16) and PFSAs (C4-C10) were monitored. In batch two, 4 : 2, 6 : 2, 8 : 2 FTSAs and FTSAS, 6 : 2 FTSAS-sulfoxide (FTSAS-SO) and sulfone (FTSAS-SO_2), FOSAA, MeFOSAA and EtFOSAA were monitored.

Table S1. MS Parameter for FTSASs and related compounds

Analyte	MRM transition	DP (V)	CE (V)
4 : 2 FTSAS	485.8 > 135.0	–100	–60
6 : 2 FTSAS	585.8 > 135.0	–105	–58
8 : 2 FTSAS	685.8 > 135.0	–100	–36
6 : 2 FTSAS-SO	602.1 > 256.0	–76	–60
6 : 2 FTSAS-SO_2	618.0 > 272.0	–66	–30

As no mass labelled standards were available at the time of the experiment, FTSAs and FTSAS were quantified using external calibration. Because of the lack of native standards, 4 : 2 and 8 : 2 FTSAS were quantified using 6 : 2 FTSAS as surrogate standard. 6 : 2 FTSAS-sulfoxide was monitored and integrated areas were recorded. It was not quantified because of a lack of a standard. As the response of the sulfoxide seemed to be higher than for the 6 : 2 FTSAS, the FTSAS could not be used as surrogate standard.

For the analysis of aqueous analytes during the biodegradation experiment, two HPLC-MS/MS methods were employed. For the analysis of PFCAs (C4-C7), FTUCAs and FTCAs, samples in MeOH were diluted with 50 % water and 25 μL injected using the following gradient method at a flow rate of 0.5 mL min^{-1} with HPLC grade MeOH and water with 10 mM ammonium acetate as mobile phase. The initial solvent composition at t = 0 min was 80 : 20 MeOH : H_2O, which changed over 3 min to MeOH : H_2O 90 : 10 (t = 3 min), and held for 2 min (t = 5 min), before returning to MeOH : H_2O 80 : 20 in 0.5 min (t = 5.5 min) and holding for 1.5 min (t = 7 min).

For the analysis of 6 : 2 FTSA and FTSAS, samples were diluted with 50 % water, and 35 μL injected using the following program: initial solvent composition at t = 0 min was 65 : 35 MeOH : H_2O, which changed over 3 min to MeOH : H_2O 95 : 5 (t = 3 min), and held for 2 min (t = 5 min), before returning to MeOH : H_2O 65 : 35 in 0.5 min (t = 5.5 min) and holding for 2.5 min (t = 8 min).

Multiple instrument blanks were run after each sample to avoid contamination of the instrument. Samples were run in duplicate or triplicate. Values for the limits of quantification (LOQ) for the target analytes (PFBA, C7-C14, 16 PFCAs and PFHxS) were calculated based on the lowest concentration in the calibration curve having a signal to noise ratio greater than 10.

For the biodegradation experiment, C5–7 PFCAs and FTUCAs were quantified using internal calibration. PFPeA and PFHpA were quantified using $^{13}C_2$-PFHxA as surrogate internal standard, 4 : 2 FTUCA, 6 : 2, 3 : 3 and 5 : 3 FTCAs were quantified by $^{13}C_2$-6 : 2 FTUCA as surrogate standard as no mass labelled standards for these analytes were available during the course of the experiment. Quantification of 6 : 2 FTSA and FTSAS was performed by matrix matched external calibration as no internal standards were available at the time of the experiment. Because PFBA was observed in the control blanks with areas comparable or higher than in the experimental bottles, PFBA was not quantified during the biodegradation experiment. One positive control bottle, spiked with active sludge, media and 6 : 2 FTUCA (1000 ng mL^{-1}), was analysed during the course of

the experiment (days 0, 8, 22 and 42) to check the reduction of the initial dose to ensure that the sludge was still active. C4-C6 PFCAs and 5 : 3 FTCA were detected as metabolites in this bottle.

GC-MS analysis

Analysis of 6 : 2 FTOH and 6 : 2 FTSH was performed using a Hewlett-Packard 6890 GC coupled to a 5973 inert MS (Agilent Technologies, Wilmington, DE) in chemical ionisation (CI) mode. Quantification was performed in single ion monitoring (SIM) mode. Chromatographic separation was achieved using an RTX-1701/w Integra-Guard column (30 m × 0.25 mm × 0.25 μm) (Restek, USA) using the following oven program: the initial oven temperature was 40 °C and remained for 2 min, followed by a ramp to 100 °C at 16 °C min^{-1} and hold for 5 min, then heating to 240 °C at 15 °C min^{-1} and hold for 1 min. The total run time was 21.08 min. The carrier gas was helium at a flow rate of 1.54 mL min^{-1}. Injections of 1 μL were performed in pulsed splitless mode.

Quantification of 6 : 2 FTOH and FTSH was by external calibration. Standard solutions in ethyl acetate ranged from 10–1500 ng mL^{-1}. The resulting calibration curves for each analyte were linear and had an R^2 value typically >0.99. An instrumental blank was run after every set of 8 samples (one time point) in which analytes were not detected above the LOQ.

TOF-CIC analysis

Concentration of total fluorine was determined using ion chromatography (IC) coupled to a combustion process. In brief, the sample was set on a ceramic boat, and the sample together with the boat was pushed into a combustion furnace (AQF-100) at 900–1000 °C, where argon and oxygen were the carrier and combustion gases. The organofluorine and inorganic fluorine in the sample was combusted into hydrogen fluoride (HF) in the furnace with a supply of water. The HF produced was transferred into the absorption unit (GA-100), where the HF dissolved into H^+ and F^- in the absorption solution (water spiked with internal standard). The concentration of F^- was analysed using an ion chromatograph. The mobile phase of the IC started at 2 mM potassium hydroxide (KOH), held for 1 min, then the concentration ramped to 40 mM at 9 min, was held until 12 min, and immediately returned to 2 mM until 18 min.

The limit of quantification (LOQ) of total fluorine was evaluated for each sample, based on several criteria including the signal to noise ratio (S/N) > 10, the maximum blank level, the lowest point of the external calibration curve, and the sample volume. The external calibration curve comprised of a series of calibration standards at 2, 20, 100, 200, 1000, 2000 ng F mL^{-1}, and the injection volume was 1.0 mL. The calibration curve exhibited good linearity with R^2 > 0.9999. Quantification was based on the response of the external standards that bracketed the concentrations found in the samples. Methanesulfonic acid (CH_3SO_3H) was added to the absorption solution as an internal standard to correct for any changes in the volume of the absorption solution during the combustion process. All solutions for the combustion ion chromatography were prepared in

Milli-Q water (18MΩ cm), and the fluoride concentration in the Milli-Q water was found to be 0.0655 ng F mL^{-1}.

Extraction procedure

XAD cartridges

The XAD-2 resin and glass wool of each cartridge was transferred into a 15-mL polypropylene tube (BD Biosciences, Franklin Lakes, NJ) and extracted twice with ethyl acetate (2 × 2 mL). The combined fractions were transferred into autosampler vials for analysis of 6 : 2 FTOH and 6 : 2 FTSH by GC-MS. The vials were stored at –20 °C until analysis.

Aqueous phase

All water samples were extracted using the ion-pair method developed by Hansen et al.[1] To 1.0 mL of aqueous sample, 2 mL of TBAS solution (0.5 M, pH 10) and 3 mL of MTBE were added in a 15-mL polypropylene tube. After shaking vigorously for 5 min, the vials were centrifuged at 6000 rpm for 5 min (VWR Clinical 200, Mississauga, ON), and the MTBE layer transferred to a clean polypropylene tube. The aqueous residue was extracted again with 3 mL of MTBE and shaking for 5 min, followed by centrifugation. The combined MTBE extracts were concentrated under nitrogen to dryness, reconstituted in 0.5 mL of HPLC grade MeOH and vortexed for 30 s. The tubes were stored at –20 °C until analysis by LC-MS/MS.

Biodegradation experimental setup

The mineral medium contained 0.40 g of KH_2PO_4, 1.60 g of K_2HPO_4, 1.55 g of NH_4Cl, 0.17 g of $MgCl_2{\cdot}6H_2O$, 0.09 g of $CaCl_2{\cdot}2H_2O$ and 4 g of glucose per litre of HPLC grade water (pH 7.0). After autoclaving, 1.0 mL of Pfennig's vitamins and 5.0 mL of Wolfe's minerals were added by filtration through a 0.25-µm filter. Pfennig's vitamins were composed of 50 mg of *p*-aminobenzoic acid, 50 mg of Vitamin B-12, 10 mg of biotin and 100 mg of thiamine per litre of HPLC grade water. Wolfe's mineral solution contained 1.5 g of nitriloacetic acid, 5.1 g of $MgCl_2{\cdot}6H_2O$, 0.81 g of $MnCl_2{\cdot}4H_2O$, 1.0 g of NaCl, 0.1 g of $CaCl_2{\cdot}6H_2O$, 0.004 g of $CuCl_2$, 0.08 g of $ZnCl_2$, 0.05 g of $AlCl_3$ and 0.04 g $Na_2MoO_4{\cdot}2H_2O$ per litre of HPLC grade water. The medium was autoclaved for 1 h at 121 °C in a Steris SG-120 Scientific Gravity Steriliser.

Mixed liquor (a mixture of raw wastewater and sewage sludge) was collected from Ashbridges Bay WWTP (Toronto, ON). Prior to use, the mixed liquor was aerated with in-house air. The mixed liquor was shaken before use, 50 mL of liquor were transferred with disposable pipettes into polypropylene tubes and centrifuged at 6000 rpm for 25 min. After removal of the supernatant, the biosolids were washed twice with autoclaved mineral media (2 × 30 mL), the supernatants discarded, and the residue resuspended in 75 % of the total volume of media used in the biodegradation experiments. Sterile controls were autoclaved for 1 h at 121 °C.

The degradation setup (in 500-mL polypropylene bottles (Nalgene R, VWR International Ltd, Toronto, ON), sealed with in-house drilled cap and septum to fit 100 mg ORBO Amberlight XAD-2 cartridges

(Supelco, Sigma–Aldrich, Oakville, ON)) included the following: (1) sludge control bottles (n = 2) containing active sludge in media to monitor potential fluorochemical contamination in WWTP sludge; (2) sterile control bottles (n = 2) containing autoclaved sludge in media, 6 : 2 FTSAS (2000 ng mL^{-1}), NaN_3 (300 mg) and $HgCl_2$ (300 mg) in order to observe non-microbial degradation; (3) a positive control bottle (n = 1) containing active sludge in media and 6 : 2 FTUCA (1000 ng mL^{-1}) to verify viability of the microorganisms and (4) experimental bottles (n = 3) containing active sludge in mineral media and 6 : 2 FTSAS (2500 ng mL^{-1}). All bottles were continuously purged with air for 42 days.

The XAD cartridge was exchanged and the resin extracted with ethyl acetate at t = 1, 2, 4, 6, 24, 51, 72, 95, 122, 144, 193, 265, 337, 532 and 1004 h, and the samples were analysed using a GC-MS. The aqueous phase (1 mL) was sampled at t = 1, 2, 4, 6, 24, 51, 72, 95, 122, 144, 193, 265, 337, 532 and 1004 h, and stored at –20 °C until further ion pair extraction.

Spike recovery analysis

A spike and recovery (n = 6) was performed for the extraction efficiency of the XAD-cartridges with ethyl acetate for 6 : 2 FTOH and 6 : 2 FTSH. 6 : 2 FTOH (42 μL of a 0.95-mg mL^{-1} solution in ethyl acetate) and 12 μL of 6 : 2 FTSH (3.45 mg mL^{-1} ethyl acetate) were spiked into 400 mL of sterile sludge and media containing 0.4 mL of Pfennig's vitamins and 2.0 mL of Wolfe's minerals to obtain a final concentration of 100 μg L^{-1} of the analytes. Double XAD-2-cartridges were placed on top of the purge and trap bottles, and the bottles were purged for 1 day. Each cartridge was extracted separately as described above. For calculation of the recoveries, the quantified amounts were summed up over both cartridges: 125 % ± 12 for 6 : 2 FTOH and 26 % ± 20 for 6 : 2 FTSH.

A recovery experiment (n = 3) was performed for 6 : 2 FTSA, 6 : 2 FTSAS, PFCAs, FTCAs and FTUCAs. 50 mL sterile sludge in media containing 50 μL of Pfennig's vitamins and 250 μL of Wolfe's minerals were spiked with each 10 μL of a 50-mg L^{-1} stock solution in MeOH of PFBA, PFPeA, PFHxA, PFHpA, 6 : 2 FTUCA, 6 : 2 FTCA, 6 : 2 FTSA and 6 : 2 FTSAS to obtain a concentration of 10 μg L^{-1} of all analytes per bottle. The bottles were shaken, closed and left to stand for 1 day. The resultant recoveries using the ion pair extraction ranged from 101–126 %.

Table S2. MSDS information of the AFFF samples

na, not available. NdMAP-PFOSA, *N*-[3-(Dimethylamino)propyl] perfluorooctane sulfonamide, *N*′-oxide; CAS number 178094-69-4

Sample ID	Location used, date	AFFF manufacturer, MSDS date	AFFF product name	Listed fluorochemicals
1	Toronto, 2004	Hazard Control Tech., 1997	F-500	no
2	Cobourg, 2005	Angus Fire, na	n.a.	no
3	Maxville, 2005	Angus Fire, 2004	Tridol S 3 %	yes
4	Greater Toronto Area Airport, 2005	Ansul, 2002	Anslite 3 % AFFF - DC-3	yes
5[A]	Thorold, 2007	Angus Fire, 2000; Angus Fire, 1997	Niagara 1-3, Forexpan	Niagara 1-3: fluorosurfactants <5 %; Forexpan: no
6	London, 2007	Hazard Control Technologies, Inc., 2003	F-500	no
7	Trenton, 2007	n.a.	n.a.	n.a.
8	Thorold, 2007[B]	Angus Fire, 2000	Niagara 1-3	fluorosurfactants < 5 %
9	Thorold, 2007[B]	Angus Fire, 2007	Hi Combat A (TM)	No
10	Thorold, 2007[B]	3M, 2005	ATC-603 Light water ATC3	N-DMAP PFOSA potassium salt: 1–5 %; fluoroaliphatic polymer: 1–5 %; residual organic fluorochemicals: 0–1 %
11	Eastern Ontario, 2008	Ansul, 2006	Ansul Anulite ARC	fluorosurfactants
12	3M AFFF[C]	3M, 1999	FC-203FC Light water Brand AFFF	amphoteric fluoroalkylamide 1–5 %, residual fluorochemicals <1 %, PFOS salts 0.5–1.5 %

[A]Foam 5 is a foam mixture of Niagara 1-3 and Forexpam.

[B]Samples 8–10 were collected on a later date than sample 5 from the same fire location.

[C]Commercial products

Table S3. Limits of quantification (LOQs) for PFAS analysis in the AFFF sample (μg mL^{-1}) and in the biodegradation study (ng mL^{-1})

Analyte	Type of calibration	Internal standard	Surrogate Stanadrd	LOQ
PFBA	internal	13C4 PFBA		0.1
PFPeA	internal	13C5 PFPeA		0.05
PFHxA	internal	13C2 PFHxA		0.05
PFHpA	internal	13C4 PFHpA		0.1
PFOA	internal	13C4 PFOA		0.05
PFNA	internal	13C5 PFNA		0.05
PFDA	internal	13C2 PFDA		0.05
PFUnDA	internal	13C2 PFUnDA		0.1
PFDoDA	internal	13C2 PFDoDA		0.1
PFTrDA	internal	13C2 PFDoDA		0.1
PFTeDA	internal	13C2 PFDoDA		0.1
6 : 2 FTUCA	internal	13C2 6 : 2 FTUCA		0.1
6 : 2 FTCA	internal	13C2 6 : 2 FTCA		1
5 : 3 FTCA	external			1
PFBS	external			0.05
PFHxS	internal	18O2 PFHxS		0.2
PFOS	internal	13C4 PFOS		0.05
PFNS	internal	13C4 PFOS		
PFDS	internal	13C4 PFOS		0.05
4 : 2 FTSA	external			0.05
6 : 2 FTSA	external			0.05
8 : 2 FTSA	external			0.05
4 : 2 FTSAS[A]	external		6 : 2 FTSAS	0.05
6 : 2 FTSAS	external			0.05
8 : 2 FTSAS[A]	external		6 : 2 FTSAS	0.05

[A]As no native and mass labelled standards were available for 4 : 2 and 8 : 2 FTSAS, these analytes were quantified based on the calibration of 6 : 2 FTSAS, and thus share the same values for LOQs.

Table S4. PFAS concentrations (μg mL^{-1}) in foam concentrates

Blank cells are compounds below LOQ (Table S3); samples showing a detectable signal are marked with an asterisk

Foam	1	2	3	4	5	6	7	8	9	10	11	12
PFBS		250.1 ± 11.3			7.17 ± 0.36					10.1 ± .96		335 ± 12.0
PFHxS		1300 ± 59.0			20.0 ± 1.03				237 ± 17.1	30.3 ± 1.37		1200 ± 0.20
PFOS		12000 ± 358			348 ± 1.61	0.22 ± 0.03	20.0 ± 2.94		58.9 ± 1.77	1200 ± 38.8		8700 ± 488
PFDS		16.7 ± 0.20										
PFBA		51.9 ± 3.24			4.13 ± 0.27		4.27 ± 0.04			17.2 ± 2.17		66.8 ± 2.97
PFPeA		60.6 ± 1.59			4.05 ± 0.18					9.27 ± 1.08		96.4 ± 6.28
PFHxA		143 ± 2.92			21.2 ± 0.59		3.72 ± 0.16			50.3 ± 1.50		299 ± 1.28
PFHpA		40.9 ± 3.17	9.22 ± 1.63		9.85 ± 0.02				12.8 ± 0.43	24.0 ± 0.71		89.1 ± 1.40
PFOA		132 ± 0.65		3.16 ± 0.15	17.8 ± 0.52		3.08 ± 0.09	3.45 ± 0.36		68.6 ± 7.04		245 ± 1.19
PFNA					0.55 ± 0.03	0.08 ± 0.0	0.78 ± 0.01	3.19 ± 1.08				
PFDA												
PFUnDA							0.99 ± 0.01					
PFDoDA							1.52 ± 0.05					
6 : 2 FTSA	36.4 ± 5.3		61.4 ± 6.71	96.0 ± 20.2	26.5 ± 4.16		0.64 ± 0.28	152 ± 26.0			2.11 ± 0.25	
8 : 2 FTSA	27.8 ± 0.13			35.7 ± 1.3	5.77 ± 0.52		29.5 ± 3.05					
4 : 2 FTSAS	38.4 ± 6.4		32.6 ± 6.58	27.8 ± 5.2							8.95 ± 2.26	
6 : 2 FTSAS	3800 ± 104	204 ± 38.2	7100 ± 954	1500 ± 5.9	68.4 ± 10.8		1.30 ± 0.73	5000 ± 535	12.4 ± 2.81		2100 ± 241	
8 : 2 FTSAS	103 ± 7.4		49.6 ± 7.05					6.03 ± 0.21			168 ± 15.5	
6 : 2 FTSAS-SO	*	*	*	*	*		*	*	*		*	

Table S5. Total fluorine (TF), total organofluorine (TOF), known PFAS, unknown, inorganic fluorine (IF) concentrations (μg F mL^{-1}) in AFFF samples

TOF = TF – IF; unknown = TOF – known PFAS; known PFAS: quantifiable PFAS, including PFCAs (C4–14), PFSAs (C4, 6, 8–10), FTSA and FTSAS (4 : 2, 6 : 2, 8 : 2), FOSAA, MeFOSAA, EtFOSAA and FTUCAs (4 : 2, 6 : 2, 8 : 2, 10 : 2, 3 : 3, 5 : 3, 7 : 3)

Foam	1	2	3	4	5	6	7	8	9	10	11	12
TF	5230	18000	8710	16300	6700	475	14300	12200	991	6600	4500	14400
TOF	5190	17800	8670	16300	6660	441	14230	12200	968	6500	4460	14200
known PFAS	1717	8550	3087	743	328	0.20	42	2220	199	936	969	7100
unknown	3473	9250	5583	15557	6332	441	14188	9980	769	5564	3491	7100
IF	38.8	244	36.9	40.5	42.7	34.3	13.8	23.3	23.3	98.3	38.8	174

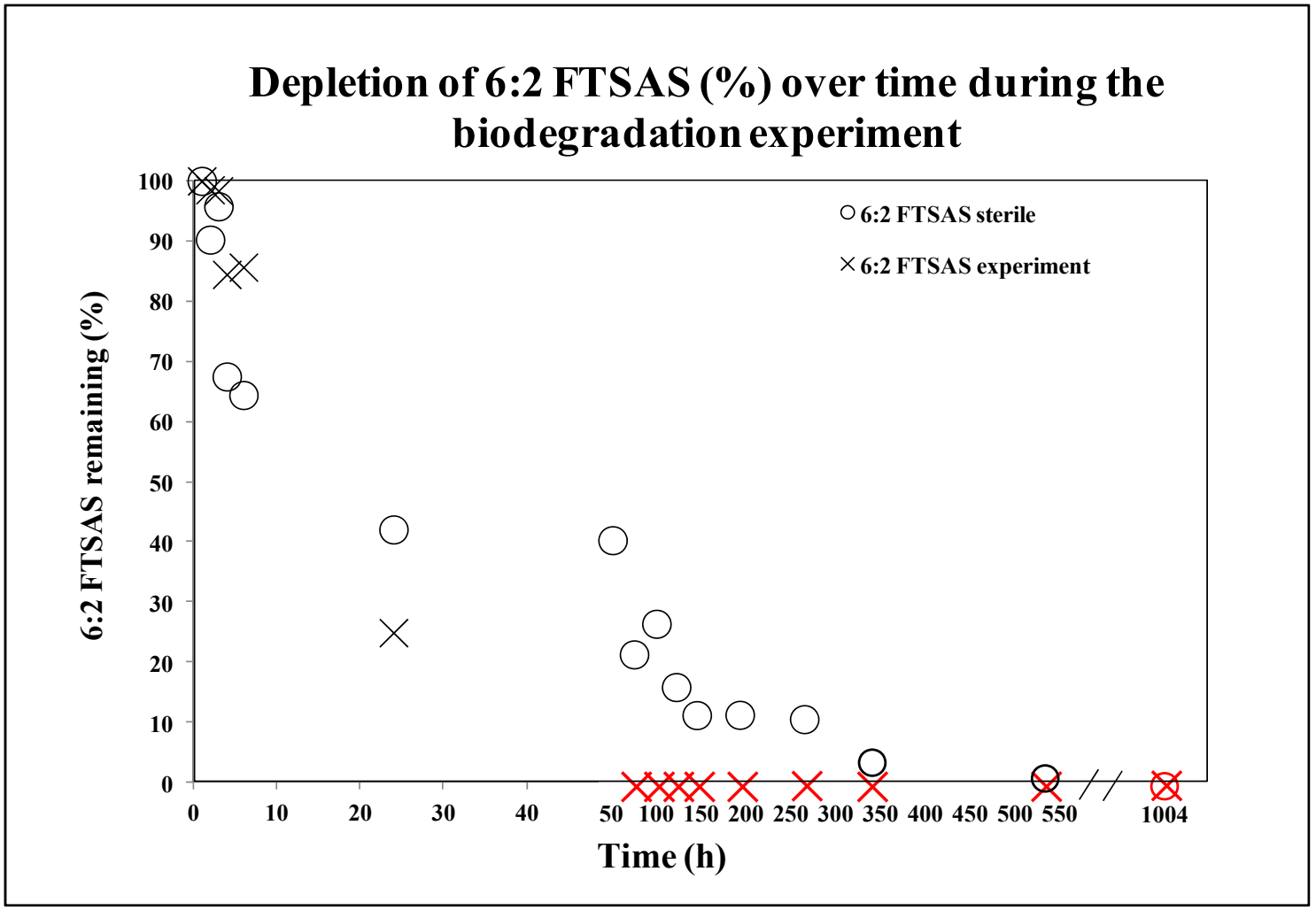

Fig. S1. Graph showing the percentage of 6 : 2 FTSAS depletion over 42 days. (Red symbol indicates sample below LOQ.)

References

[1] K. J. Hansen, L. A. Clemen, M. E. Ellefson, H. O. Johnson, Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ. Sci. Technol.* **2001**, *35*, 766. doi:10.1021/es001489z