Supporting Information

Additional Experimental Details

Aqueous-phase concentrations of PFOS, PFOA, PFHS, PFHA, PFBS, and PFBA were quantified using HPLC-ES-MS. The samples were placed into 750 μL polypropylene autosampler vials and sealed with a PTFE septum crimp cap. 20 μL of collected or diluted sample was injected onto an Agilent 1100 LC for separation on a Betasil C18 column (Thermo-Electron) of dimensions 2.1 mm ID, 100 mm length and 5 μm particle size. A 2 mM aqueous ammonium acetate/methanol mobile phase at a flow rate of 0.75 mL min^{-1} was used with an initial 70:30 water/methanol composition, which was linearly increased to 5:95 water/methanol to separate the surfactants. HPLC effluents were analyzed with an Agilent Ion Trap MS in the negative ion mode for the PFOS molecular ion (m/z = 499), PFHS molecular ion (m/z = 399), the PFBS molecular ion (m/z = 299), the decarboxylated PFOA ion (m/z = 369), the decarboxylated PFHA ion (m/z = 269) and the decarboxylated PFBA molecular ion (m/z = 169). The alkyl sulfate esters were also identified by MS in negative ion mode for octyl sulfate molecular ion (OS, m/z = 209), decyl sulfate molecular ion (DS, m/z = 237) and dodecyl sulfate molecular ion (DDS, m/z = 265). The nebulizer gas pressure was 40 PSI, the drying gas flow rate was 9 L min^{-1} and the drying gas temperature was 325 $^{\circ}$C. The capillary voltage was set at + 3500 V and the skimmer voltage was – 15 V. Quantification was completed by first producing a calibration curve using 8 concentrations between 1 ppb and 250 ppb fitted to a quadratic with X^{-1} weighting. The calibration standards were prepared by 3M. If the sample was initially greater than this range, serial dilutions were made. A number of quality controls were completed to ensure the stability of the HPLC-MS analytical system. Before and after the calibration curve, after quality controls, and after every 5th sample injection, water and methanol blank were

completed to ensure low background PFC levels. After every 10^{th} sample, 2 calibration standards were run as quality control to ensure the initial calibration was still true.

The methylene blue active substances (MBAS) test was used to quantify the total anionic surfactant concentration in solution. The MBAS test is only active for strongly ionized aqueous species. Since the diluted AFFF samples were circum-neutral pH (7.0 – 8.0), the MBAS test should respond to the alkyl sulfate esters, perfluorinated carboxylates and perfluorinated sulfonates ($pK_a < 1.0$) in aqueous AFFF sample dilutions. A 1 mL aliquot of diluted and/or sonicated AFFF solution was mixed with 25 mL of 30 ppm acidic methylene blue solution. The AFFF-MB solution was extracted 3 times with 10 mL of chloroform and these extracts were combined and washed with 25 mL of acidic (H_2SO_4) water. The MB extracted into the chloroform was analyzed by UV-Vis adsorption at 652 nm (ε = 66,000 M^{-1}). A five point calibration curve was made using a linear alkyl benzyl sulfate standard over the range of 50 to 200 μg. The methylene blue would ionpair with anionic surfactants in solution.

A Dionex DX-500 Ion Chromatograph was used for the analysis of fluoride and sulfate. 0.5 mL Sample aliquots were transferred from the reactor to 0.5 ml disposable PolyVial sample vials, sealed with PolyVial filter caps and loaded onto an AS-40 autosampler. The 0.5 ml sample was injected and anions were separated on an IonPac AS11-HC anion exchange column and quantified by conductivity measurement. Linear calibration curves were generated using standard solutions of sodium fluoride and sodium sulfate at concentrations over the range of 1 to 200 mM.

Total organic carbon was determined (TOC, OI Analytical Aurora Model 1030) with an autosampler (OI Analytical Model 1096). 1 mL sample aliquot was drawn into the reactor and inorganic carbon was removed by acidification with a 5% H_3PO_4 solution and helium sparging.

TOC is analyzed using the thermal persulfate method to oxidize the organic carbon to CO_2, which is quantified with an infrared detector. The thermal persulfate method does not oxidize aqueous PFOS or PFOA to a detectable level, thus persulfate TOC measurements are only valid for non-fluorinated organics. Linear calibration curves were generated using potassium hydrogen phtlalate as a carbon standard over a concentration range of 1 to 20 ppmC.

Additional Experimental Results

Figure S1. Sonochemical time-dependent concentrations of organic species in a 1/250 dilution of FC-600. Ultrasonic conditions are f = 505 kHz, PD = 188 W L^{-1}, I = 3 W cm^{-2}, 10° C, argon. **A)** MBAS (○), AS (∇) and PFOS (◊) in μM. $[PFOS]_i$ = 26.2 μM, $[MBAS]_i$ = , and $[AS^-]_i$ = . **A)** TOC in ppmC, $[TOC]_i$ = 272 ppmC. .

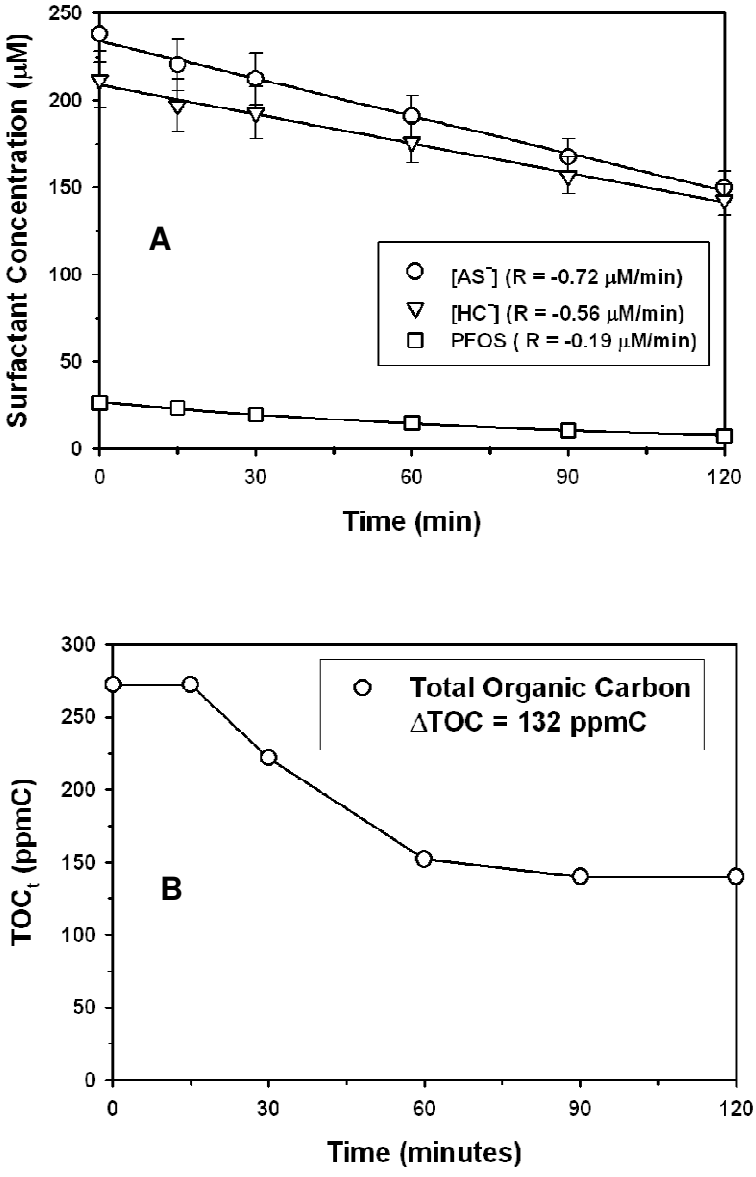

Table 1. FC groundwater concentrations at military AFFF training sites.

Training Site	Total FtOS (ppb) $CF_3(CF_2)_n(CH_2)_2SO_3^-$	Total PFS (ppb) $CF_3(CF_2)_nSO_3^-$	Total PFC (ppb) $CF_3(CF_2)_nCO_2^-$
NAS Fallon	n.d.[7]	1,680 (edge) 206 (100 m)	7,090±160 (edge)[3] 540±20 (100 m)
Tyndall AFB	14,600 (5 m)[7] 4,600 (25 m)	3,500 (5 m)[7] 700 (25 m)	298 (5 m)[3] 124±8 (25 m)
Wurtsmith AFB	96 (18m)[7] 70 (183 m) 9.8 (540 m)	214±13 (18 m)[5] 86±18 (183 m) 13±1 (540 m)	110 (18 m)[5] 19 (183 m) n.d. (540 m)

Notes: In parenthesis is distance from burn pit training area. FtS = fluorotelomer sulfonates, PFS = perfluoroalkylsulfonates, PFC = perfluoroalkylcarboxylates.