Details of the Analytical Procedures and Reactor Configurations.

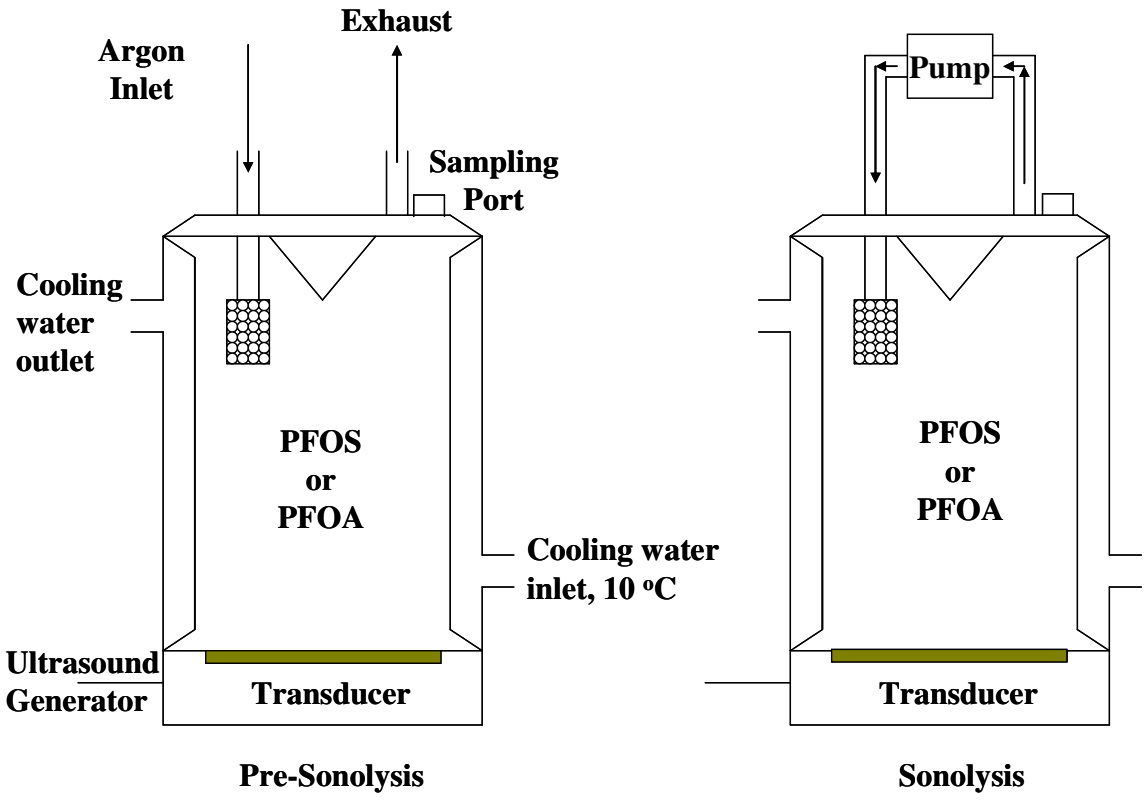
HPLC-MS of the Initial Perfluorinated Surfactants and Shorter Chains:

Analysis for initial PF surfactant and possible shorter-chain products was completed by HPLC-MS. Sample aliquots (700 μL) were withdrawn from the reactor using disposable plastic syringes. The samples were placed into 750 μL polypropylene autosampler vials and sealed with a PTFE septum crimp cap. For reactions with intial concentrations greater than 250 ppb, serial dilutions to achieve a concentration below 200 ppb were completed prior to analysis. 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. An 0.01 M aqueous ammonium acetate : methanol mobile phase at a flow rate of 0.75 mL min^{-1} was used with an initial composition of 70:30 aqueous: methanol. The LC method consisted of an initial ramp to 29:71 over the first minute, then ramping to 25:75 over the next three minutes, followed by a 0.5 minute ramp to 95:5 with a hold at 95:5 for 2 minutes to wash the column and then ramping back down to 30:70 over 0.5 minutes and finishing with a 4 minute post-time to allow the pressure to equilibrate. Chromatographically separated samples were analyzed by an Agilent Ion Trap in negative mode monitoring for the perfluorooctanesulfonate molecular ion (m/z = 499) and the decarboxylated perfluorooctanoate (m/z = 369). The nebulizer gas pressure was 40 PSI, drying gas flow rate and temperature were 9 L min^{-1} and 325 ºC, the capillary voltage was set at + 3500 V and the skimmer voltage was – 15 V. Quantification was completed by producing a calibration curve using 8 concentrations between 1 ppb and 200 ppb fitted to a quadratic with X^{-1} weighting. Kinetic experiments were analyzed starting with the final timepoint (lowest concentration) first. Quality control duplicates of one of the calibration points were run after every two kinetic experiment analyses to verify that the calibration curve was still valid. A water and a methanol blank were run before and after the calibration curve, every kinetic sample set and the duplicate quality controls.

Ion Chromatography of Fluoride, Sulfate and other Ions:

PFOS and PFOA were analyzed for in all experiments by an HPLC-MSD-Ion Trap (Agilent). Fluoride and sulfate were analyzed by ion chromatography (Dionex) were completed using 618 kHz, 250 W L^{-1} and 6.4 W cm^{-2} on a closed system where the produced gas was resparged into solution to retain all products. The reactor configuration is in Figure S1. PFOS and PFOA were sonicated separately at initial concentrations of approximately 10 μM. A Dionex DX-500 Ion chromatography was used for the analysis of fluoride, sulfate and other possible product ions. 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, sodium sulfate and sodium formate at concentrations varying from 1 to 200 mM.

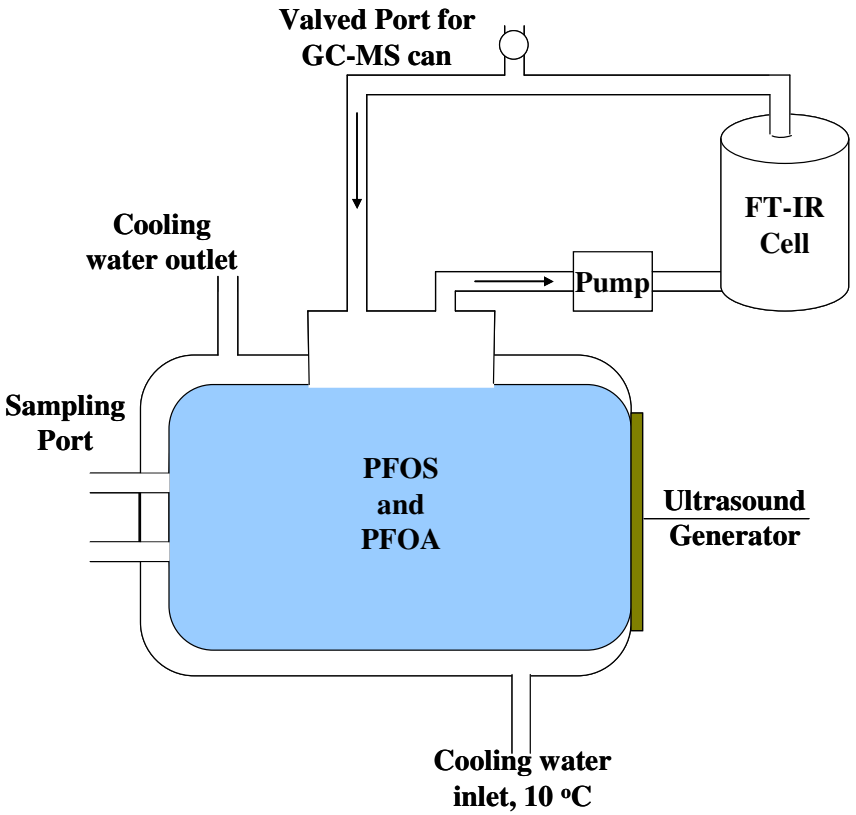
Figure S1.



FT-IR and GC-MS for Trace Fluorinated Gases:

Trace gas analyses by GC-MS (Agilent) and FT-IR (Midac) were sonicated at 500 kHz, 150 W L^{-1} and 2.9 W cm^2 on a closed system where the headspace was recirculated but not resparged through a 300 mL multiple reflection FT-IR cell with an in-line valved port for GC-MS sampling. The reactor configuration is in Figure S2. PFOS and PFOA were sonicated simultaneously at a total initial concentration of 20 µM (10 µM each). Multiple different analyses were used to identify any trace poly-fluorinated gases created during ultrasonic irradiation. The sonochemical reactor was sealed from outside atmosphere and any gases formed were recirculated with a peristaltic pump through a 300 mL gas reservoir was inserted into the recirculation line and were NOT sparged back into solution to allow for accumulation of the trace gases. At varying points during the reaction, an approximately 250 mL volume evacuated can, < 1 torr, was attached to a valved Tee in the recirulating line and subsequently opened to collect the gas content of the headspace once evacuated sonicated was stopped (i.e. only one can was collected per experiment). The contents of the can were analyzed by GC-MS at the 3M Environmental Laboratory. Alternatively, the reservoir was replaced with a multiple reflection FT-IR cell (Midac, Titan) and used for the real-time analysis of the gas-phase fluorocarbons CHF_3 and CH_2F_2.

Figure S2.



Flow-Through Analysis for CO and CO_2:

The experiments where CO and CO_2 were measured during sonication were completed using 354 kHz, 250 W L^{-1} and 6.4 W cm^{-2} using a continuously sparged (100 to 125 mL min^{-1}) open system where the product gas was evacuated (≈ 100 mL min^{-1}) into a high-vacuum chamber through a stainless-steel membrane inlet to be analyzed by EI-MS (Balzers). The reactor configuration is in Figure S3. PFOS and PFOA were sonicated separately at initial concentrations of 100 μM. Gas analysis on a continuously sparged open system was used to monitor the production of CO and CO_2. An open system was utilized to limit sonolytic secondary oxidation or reduction of these gas products. The system was sparged normally with argon at a flow rate of 100 to 150 mL min^{-1}. After the sparge gas exited the reactor, it passed by a membrane inlet (Aqualine) where a portion of the gas was pulled into the vacuum chamber (Pfeiffer-Vacuum, 5 x 10^{-6} torr) through a capillary. The gas was then ionized by high-energy (80 eV) electrons and analyzed by a quadrupole mass spectrometer (Balzer's Prisma). Quantification was completed by normalizing to total gas content assuming that all monitored species had similar ionization cross-sections. Similar analyses were completed on sonicated MilliQ water as a control, under which conditions no gas products were observed.

Figure S3.

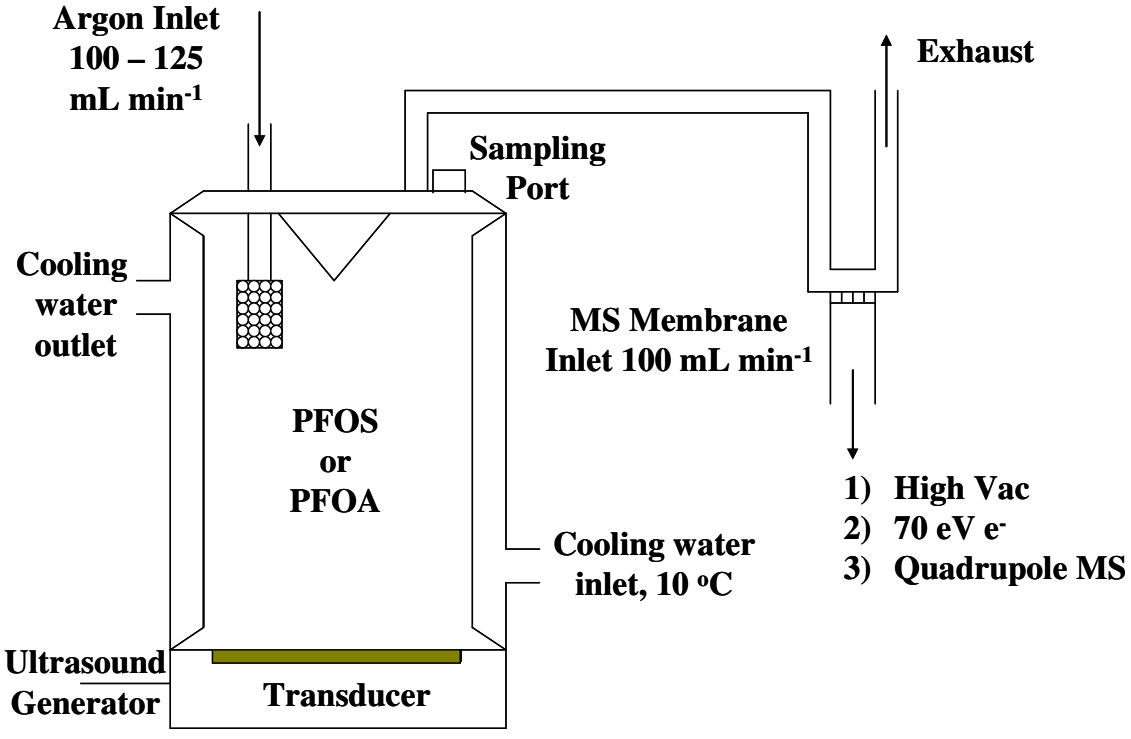


Table S1. Gas-phase products of PFOX sonolysis as determined by GC-MS.

Compound	Measured Conc. (PPMV)	Number of Fluorines	Mole Fraction - F
Unknown C7 Fluoroalkenes (13)	3.5	12	1.76E-03
Unknown C5 Fluoroalkenes (9)	1.23	8	4.12E-04
Hexafluoropropene	1.6	6	4.02E-04
Unknown C6 Fluoroalkenes (6)	0.8	10	3.35E-04
Trifluoromethane	2.4	3	3.01E-04
Difluoromethane	3.3	2	2.76E-04
Unknown C4 Fluoroalkenes (4)	0.72	6	1.81E-04
Methyl fluoride	3.5	1	1.46E-04
Tetrafluoroethylene	0.86	4	1.44E-04
1,1-Difluoroethene	1.6	2	1.34E-04
Pentafluoroethane	0.57	5	1.19E-04
Unknown C8 Fluoroalkenes (2)	0.13	14	7.62E-05

Octafluoro-2-butene	0.14	8	4.69E-05
Unknown C3 Fluoroalkenes (5)	0.28	4	4.69E-05
2H-Heptafluoropropane	0.14	7	4.10E-05
1,1-Difluoroethane	0.45	2	3.77E-05
1-Propene, 1,1,3,3,3-pentafluoro-	0.12	5	2.51E-05
1,1,1-Trifluoroethane	0.18	3	2.26E-05
1,3-Butadiene, 1,1,2,3,4,4-hexafluoro-	0.086	6	2.16E-05
Ethene, trifluoro-	0.14	3	1.76E-05
1,1,1,2-Tetrafluoroethane	0.1	4	1.67E-05
2-Butyne, 1,1,1,4,4,4-hexafluoro	0.04	6	1.00E-05
Fluoroethane	0.2	1	8.37E-06
1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene	0.018	8	6.03E-06
Ethene, fluoro-	0.11	1	4.60E-06
3,3,3-Trifluoropropene	0.028	3	3.52E-06
2,2-Difluoropropane	0.04	2	3.35E-06

Ethene, 1,2-difluoro-	0.02	2	1.67E-06
2-Fluoropropene	0.01	1	4.19E-07
Total F from all Gases			4.60E-03

The species and concentrations listed in the table are from a 300 mL can taken after 120 minutes of sonication at 500 kHz and 150 W L^{-1} of a solution of initial PFOS and PFOA concentration of 10 µM. Mole fractions are determined by assuming a gas density of 22.4 L $mole^{-1}$. It should be noted that the headspace gases were not resparged into solution, so this is not representative of a specific timepoint but gases that had accumulated over time. For the unknown fluorinated alkenes the number of fluorines was taken to be the number on the perfluorinated species minus two (the number in parentheses is the number of different species detected). This assumption was made from the speciation of the C3 and C4 fluoroolefins: the totally fluorinated species was dominant, yet there was large number of low-level partially fluorinated species detected. The species are listed from greatest to least mole fraction of fluorine.