PERFLUORINATED CARBOXYLIC ACIDS IN DIRECTLY FLUORINATED HIGH DENSITY POLYETHYLENE MATERIAL

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EXPERIMENTAL

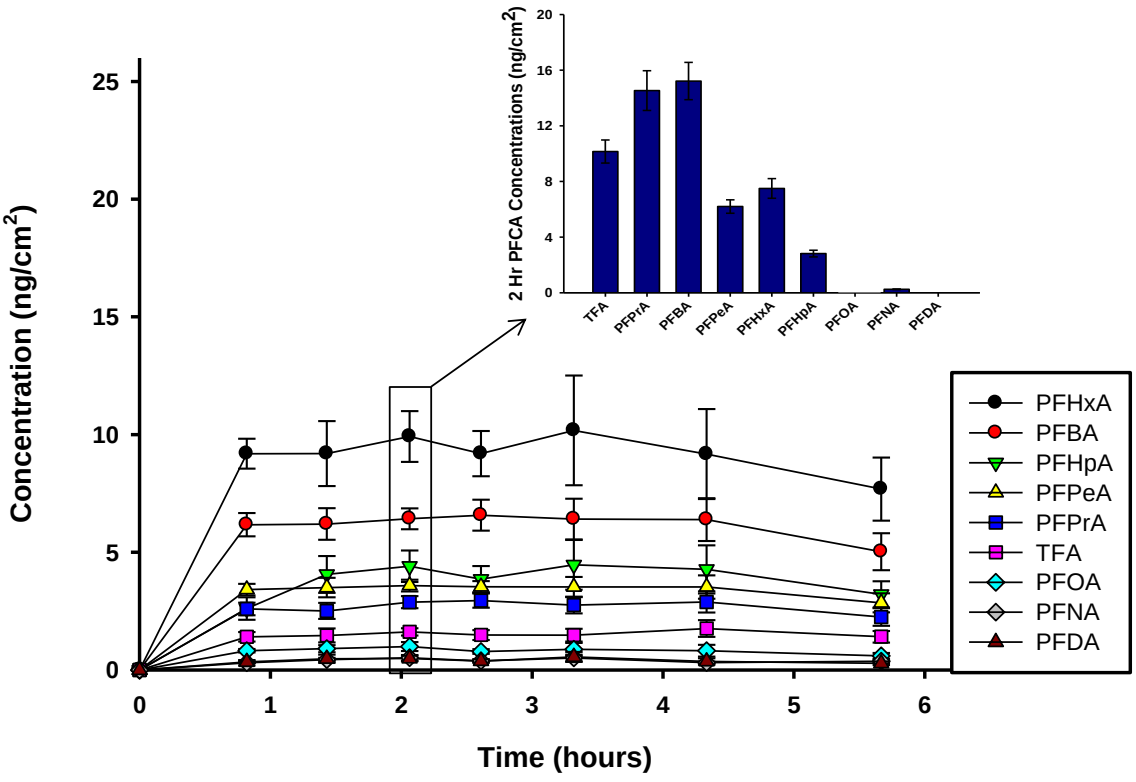
Liquid Chromatography details. Two methods were used to analyze the samples (methods A and B), differentiated by analytes detected (Method A: TFA – PFPeA, Method B: PFHxA – PFDA), internal standard suite used, solvent gradient composition, and flow rate. For both methods, data were obtained using multiple reaction monitoring (MRM) conditions using optimized conditions; the transitions are shown in Table SI 1. Sample analysis was performed using a Waters Acquity LC system, coupled to a Waters Quattro Micro mass spectrometer, and separations were achieved using a Waters XBridge C18 column (4.6 mm x 50 mm, 3.5 μm particle size, Milford, MA, USA), with a 40 μL injection volume. Two methods were used to analyze the samples (methods A and B). Short chain acids ranging from TFA to PFPeA were separated using method A, which had the following solvent gradient with a flow rate of 0.5 mL/min: initial solvent conditions (t=0) were 20:80 methanol:water (10 mM ammonium acetate), increasing to 80:20 over 3 minutes and held for 1 minute (t=4 min), decreasing to the original solvent composition in 30 seconds (t=4.5 min) and equilibrating for 1 min (t=5.5 min). Method B was used to analyze PFHxA to PFDA and had the following solvent gradient at a flow rate of 0.36 mL/min: initial conditions were 60:40 methanol:water (t=0), increasing to 65:35 in 2 minutes (t=2 min), increasing to 70:30 in 1 minutes (t=3 min), increasing to 75:25 in 2 minutes (t=5 min), increasing to 80:20 in 1 minute (t=6 min), reverting to original conditions in 30 seconds (t=6.5) and equilibrating for 3.5 minutes (t=10 min).

TABLE SI 1. Internal standards, multiple reaction monitoring (MRM) transitions, and spike and recovery results for the analytes of interest.

Analyte	Internal Standard	MRM Transition	% Recovery
TFA (C2)	$^{13}C_4$-PFBA	113>69	110 ± 7
PFPrA (C3)	$^{13}C_4$-PFBA	163>119	106 ± 11
PFBA (C4)	$^{13}C_4$-PFBA	213>169	97 ± 10
PFPeA (C5)	$^{13}C_4$-PFBA	263>219	119 ± 10
PFHxA (C6)	$^{13}C_2$-PFHxA	313>269	81 ± 8
PFHpA (C7)	$^{13}C_2$-PFXA	363>319	75 ± 7
PFOA (C8)	$^{13}C_4$-PFOA	412.8>368.9	82 ± 6
PFNA (C9)	$^{13}C_5$-PFNA	462.8>418.97	85 ± 9
PFDA (C10)	$^{13}C_2$-PFDA	512.8>468.9	85 ± 7

Determining optimal PFCA extraction times. To quantify the concentration of perfluorinated carboxylic acids extracted from the bottles, 15 mL sub-samples were taken once PFCA concentrations had reached equilibrium after the completion of the third extraction cycle for each soxhlet apparatus ($T_{avg} \approx 2$ hrs). Optimal times for extracting PFCAs in the bottles using soxhlet extraction are shown in Figure SI 1. Although the concentrations of all PFCAs reached equilibrium after the first extraction cycle, samples were taken after the third in order to account for possible variability in the equilibrium time when extracting other fluorinated bottles.

FIGURE SI 1. Concentrations (ng/cm^2) of PFCAs in a F2 bottle extracted over time. The inset shows the PFCA concentration profile for an F2 bottle after a 2 hour extraction time. Future samples were taken at 2 hours. All time points reflect n = 6 samples. Values less than the LOD are reported as zero, and values less than the LOQ are indicated with an asterisk (*).



Quality control. Method detection limits were determined based on three times the standard deviation of the signals arising from the procedural blanks, the values of which are found in Table SI 2. All values calculated to be below the LOD were given a value of zero, while values below the LOQ remained unaltered and are presented in italics. Analyte responses were determined using a calibration range from 0.5 ppb to 300 ppb. The C_2- to C_{10}-PFCAs were quantified by internal calibration using the following

mass-labeled internal standards: $^{13}C_4$-PFBA (TFA, PFPrA, PFBA, PFPeA), $^{13}C_2$-PFHxA (PFHxA, PFHpA), $^{13}C_4$-PFOA (PFOA), $^{13}C_5$-PFNA (PFNA), $^{13}C_2$-PFDA (PFDA). Analyte recovery was evaluated by spiking a mixed standard of C_2-C_{10} PFCAs (target concentration ~ 50 ng/mL) with their corresponding internal standards into three subsamples of an untreated HDPE bottle, extracted as previously described.

TABLE SI 2. Method detection (LOD) and quantification (LOQ) were determined based on the standard deviation of the signals arising from the procedural blanks analyzed on the Waters Acquity LC and Quattro Micro mass spectrometry system. Units are reported as mass per surface area (SA). LOD and LOQ for both Manufacturer A and B are reported to account for the differences in SA; for manufacturer A, both sides of the bottle are fluorinated giving a total SA of 1148 cm^2, whereas for manufacturer B, only one side is fluorinated, and the SA is 574 cm^2. Sample concentrations less than the LOD were reported as having a value of zero, and concentrations less than the LOQ remained unaltered but were marked with an asterisk.

Analyte	**Manufacturer A**		**Manufacturer B**	
	LOD (ng/cm^2)	LOQ (ng/cm^2)	LOD (ng/cm^2)	LOQ (ng/cm^2)
TFA	0.53	1.8	1.05	3.5
PFPrA	0.17	0.57	0.34	1.1
PFBA	0.20	0.67	0.40	1.3
PFPeA	0.10	0.34	0.20	0.68
PFHxA	0.68	2.3	1.4	4.5
PFHpA	0.079	0.26	0.16	0.52
PFOA	3.7	12	7.4	24
PFNA	0.014	0.047	0.03	0.09
PFDA	0.24	0.79	0.47	1.6