Supporting Information

Paints: A Source of Volatile PFAS in Air – Potential Implications for Inhalation Exposure

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Materials. High performance LC (HPLC) grade water (>99%) and methanol for nonvolatile PFAS analysis (>99%) were purchased from Fisher Scientific (Hampton, NH). Methanol for volatile PFAS analysis (≥99.5%) and ammonium acetate for nonvolatile PFAS analysis (≥97%) were purchased from VWR (Radnor, PA). Deuterated methanol (99.8%) for ^{19}F NMR was purchased from Cambridge Isotope Laboratories (Tewksbury, MA). Deuterated TFE (d_3-TFE) was purchased from Sigma Aldrich (St. Louis, MO).

GC-MS Analysis. Extracts (10 µL) were injected in splitless mode with an inlet temperature of 280 °C. A 4 mm i.d. single taper Topaz inlet liner with 15 mg deactivated quartz wool (Restek, Bellefonte, PA) was used. Helium was used as the carrier gas in a constant flow mode of 1 mL/min. Separations were performed using a deactivated, fused silica tubing capillary column (Agilent, 5 m × 0.53 mm i.d.) connected to an Rxi-624Sil MS capillary column (Restek, 30 m ×0.25 mm i.d., 1.40 µm film thickness). The GC oven temperature program was as follows: 50 °C for 2 min, ramped to 188 °C at a rate of 5 °C/min, then ramped to 300 °C at a rate of 15 °C/min. The Agilent 6890 GC was connected to an Agilent 5973N MS that was operated in positive chemical ionization mode in selected ion monitoring mode with methane as the reagent gas at a flow rate of 1 mL/min.

Analyte concentrations were determined by a calibration curve with a minimum of 6 points with 1/x weighted linear regression or quadratic regression. Standards were prepared in the range of 1 – 2000 pg/µL for FTOHs, FOSAs, and FOSEs, 1-1000 pg/µL for 8:2 FTAc and 10:2 FTAc, and 0.005 – 10 pg/µL for 4:2- and 6:2 FTAcs and FTMAcs. Continuing calibration verification of 1, 10, and 100 pg/µL were analyzed after five paint samples and concentrations were expected to fall within +/- 30%. Method blanks and solvent blanks were analyzed to monitor potential carryover introduced during the experimental procedure. Additionally, an injection of 100 pg/uL of eight

mass-labeled surrogate standards followed every paint injection to monitor the thermal transformation of nonvolatile PFAS.

Method accuracy and precision for volatile PFAS were determined by spiking three replicates of a blank (PS-08) paint (20 mg in 1500 µL methanol) to give a final concentration of 83 pg/µL of target FTOHs, perfluoroalkyl sulfonamides (FOSAs), and perfluoroctane sulfonamidoethanols (FOSEs) and 4.2 pg/µL of fluorotelomer acrylates (FTACs) and fluorotelomer methacrylates (FTMAcs). Whole method LOD and LOQ were determined using the method of Vial and Jardy.[1] Nine blank (PS-08) paint samples were spiked with target FTOH, FOSA, and FOSE to give concentrations ranging from 0.2 – 620 pg/µL and FTAc and FTMAc concentrations ranging from 0.05 – 83 pg/µL. Samples were then treated by the same procedure for liquid paint by GC-MS analysis. The LOD was calculated based on linear regression with 1/x weighting and method LOQ was calculated by multiplying LOD by 3.3. The LOD and LOQ were increased above false positive levels. Hydrogen abstraction of mass labeled 8:2 FTOH resulted in the largest false positives when compared to other mass labeled FTOH standards.[2] This resulted in an increased LOD and LOQ for 8:2 FTOH (Table S4).

LC-qTOF Analysis. Chromatographic separations were achieved using an Agilent 1260 HPLC (Santa Clara, CA). Aliquots of 100 µL were injected onto a Zorbax Eclipse XDB-C8 (Agilent, 4.6 × 20 mm, 3.5 µm) guard column fitted with a Zorbax Eclipse Plus analytical column (Agilent, 4.6 × 75 mm, 3.5 µm) as modified after Backe et al (2013).[3] The aqueous mobile phase (A) was 20 mM ammonium acetate (Fisher Scientific, Hampton, NH) in 3% v/v HPLC-grade methanol in HPLC-grade water and the organic mobile phase (B) was HPLC-grade methanol. An AB SCIEX X500R qTOF-MS/MS system (Framingham, MA) was operated in negative mode (ESI-) and positive mode (ESI +) in electrospray ionization. Data were collected under SWATH® data-

independent acquisition for both TOF-MS and MS/MS modes. Both PFBA and MPFBA were analyzed in MS/MS mode to reduce background interferences. Over the entirety of the data acquisition period, precursor ion data (TOF-MS) were collected over an *m/z* range of 100 Daltons (Da; TOF start mass) to 1250 Da (TOF stop). The accumulation time was 200 ms and the ion spray voltage was -4500 V. The source and gas parameters were: 550 °C source temperature, 60 psi ion source gasses, 35 psi curtain gas, and 10 psi collision gas. The declustering potential was -20 V with 0 V spread and the collision energy was -5 V with 0 V spread. Product ion scan (TOF-MS/MS) data were collected over an *m/z* range from 50 Da (TOF start mass) to 1200 Da (TOF stop). The accumulation time for each SWATH® window was 50 ms. Identification and quantification of target PFAS was described in Schwichtenberg et al (2020).[4]

Calibration curves were weighted 1/x or $1/x^2$ and made with a minimum of 5 points over the range. In negative mode the calibration range was 200-100,000 ng/L except for FTCAs which ranged from 200 - 50,000 ng/L. The mass labeled surrogates used for quantification of each target PFAS are listed in Table S1. For negative mode analyses, values for a third-party reference standard (Absolute Standards, Hamden, CT) containing carboxylates (C6-14), sulfonates (C4, 6, 8), MeFOSAA, and EtFOSAA were required to fall within 70-130 % of the expected values. In positive mode, the calibration curves ranged from 200-100,000 ng/L for the five positive mode standards (PFSxSaAm, 6:2 FTSAB, N-Tamp-FHxSA, 5:3 FTB, and 5:1:2 FTB) and the d3-prometon surrogate (Table S1). For both negative and positive mode, continuing calibration verification standards consisting of the two lowest calibration points were analyzed every 10 samples and required to fall within 70-130 % of the expected value.

Suspect Screening and Semi-Quantification. Mass spectral features were integrated with an XIC width of 0.02 Da, baseline subtraction over 2 min, and a Gaussian smoothing width of 1.0.

Only peaks with a signal-to-noise ratio >25 were considered for compound matching. The NIST "Suspect List of Possible Per- and Polyfluoroalkyl Substances (PFAS)" version 1.5 was used for identifying suspects. After removing molecules >1250 Da, duplicates, and target PFAS, the list was further sorted using the added RDKit function and filtering by the NumHDonors and NumHAcceptors (ESI- and ESI+, respectively). The negative and positive mode lists overlap with each other, so if an analyte is found in both modes, the one with the higher area count was used. Unver negative mode, all imported molecular formula were screened as $[M-H]^-$, while under positive mode, imported molecular formula were screened for M^+ when there is a permanent charge on the molecule or for $[M+1]^+$ if the molecule is neutral.

Mass spectral features were considered matches when associated with a compound on the NIST list[1] with <5 ppm mass error, <10% isotope ratio difference, and <70% spectral library match based on the SCIEX OS purity algorithm (or a higher library score with only the precursor ion matching upon visual inspection). Mass spectral features were considered library matches when associated with a compound on the NIST list with <10 ppm mass error, <20% isotope ratio difference, and >70% spectral library match, as well as visual confirmation of at least one matching fragment. Since MS/MS spectral matching gives higher confidence in identification, library matches were allowed to have a wider range of acceptable values for mass error and isotope ratio difference. Broadly, a library match would be considered to have a confidence level of 2a. All structural isomers were reported when several fit the NIST match criteria and a single isomer could not be definitively identified. If a feature was associated with a NIST list PFAS as a library match and co-occurred with a homologous series consisting of other Level 1 and 2a matches and the retention time was appropriate (e.g., increasing retention time with increasing chain length and retention time difference between homologs within a PFAS class), all other

isomer matches for that feature were discarded and the suspect was considered a Level 3d match.[2] Other circumstantial evidence was also used to select isomers including if a feature was matched with fluorotelomer (FT)- and electrofluorination (ECF)-derived compounds, the presence or absence of peak branching was used as an indication of which match was more likely (branching from ECF and linear only from FT). However, if the peak area was low (<104), the absence of branching could not be used to rule out a FT isomer match. All branched isomers were integrated when present and reported as a single area or semiquantitative concentration. Compound matching also considered other class members; for example, the presence of odd-numbered homologues (e.g., C5, C7,…) was used as evidence for the ECF-derived matches, as FT-derived compounds are typically present in even-numbered homologues

^{19}F NMR Analysis. The NMR experiments were conducted using a Bruker 800 MHz Avance IIIHD NMR spectrometer equipped with a 5 mm TCI cryoprobe tuned to ^{19}F. Data were collected with a calibrated 90 degree pulse of 11 us, a spectral window of 237.2 ppm, 65536 complex points, and a 15 s recycle delay. Experiments were collected in automation using a refrigerated SampleCase and IconNMR software (Bruker, Billerica, MA). Spectra were referenced to $CFCl_3$ by adjusting the TFE resonance to 76.76 ppm.[5] Initial experiments using 20 mg of paint diluted in 1500 µL of *d*-methanol resulted in low fluorine signals. The mass of paint was then increased to 30 mg and the volume of *d*-methanol decreased to 600 µL to increase signal.

Whole method LOD and LOQ were determined using the method of Vial and Jardy.[1] Seven standard of TFE with concentrations ranging from 50 to 1500 ng/L were prepared in D_2O. The LOD was calculated based on linear regression with 1/x weighting and method LOQ was calculated by multiplying LOD by 3.3. The values for LOD and LOQ (19 and 64 µM, respectively) were then

estimated for paint analysis by including the mass (30 mg) and dilution (600 μL) used for ^{19}F NMR analysis of paint samples, resulting in an LOQ of 1.2 μmol F/g.

TD-GC/MS Analysis. For TD-GC/MS analysis, the tubes were then desorbed by a thermal desorption system (TD100-xr, Markes International). The flow path in the TD was set to 220 °C, the purge flow was 50 mL/min, and desorption was performed for 12 min at 320 °C with 50 mL/min flow. The flow path was split 10:1, allowing for a tenth of the sample to be analyzed and the rest to be recollected into the TD tube. Volatile PFAS were then focused in a cold trap (Markes International) and desorbed from 25 °C to 335 °C at a rate of 100 °C/min. Separations were performed using a DB-VRX capillary column (Agilent, 60 m × 0.25 mm i.d. × 1.4 μm film thickness). The GC oven temperature program was as follows: 35 °C for 5 min, ramped to 230 °C at a rate of 10 °C/min, and held for 10 min. The Agilent 7890B GC was connected to an Agilent 5977A MS that was operated in positive chemical ionization mode in selected ion monitoring mode. Calibration standards were prepared to concentrations ranging from 0.0005 to 250 ng (on TD tube).

While the flow rate was higher than typical flow rate for emission studies, the goal was to collect the air from the painted box as close to the chosen time point as possible; therefore, maximum flow rate for the air sampler was used. Breakthrough experiment was performed by spiking a TD tube with 200 ng of 6:2 FTOH and 50ng MFHET. A second tube was also spiked with 50 ng MFHET. The two TD tubes were connected and 5.7 L of office air (<LOQ 6:2 FTOH) was collected at the 4 L/min. flow rate through the tubes. The 6:2 FTOH was <LOQ in the second TD tube indicating no breakthrough at the chosen flow rate.

Whole method LOD and LOQ were determined using the method of Vial and Jardy.[1] Eight TD tubes were spiked with a range of masses of 6:2 FTOH (0.0001–0.1ng on TD tube). The LOD

was calculated based on linear regression with 1/x weighting and method LOQ was calculated by multiplying LOD by 3.3. The calculated LOQ was compared with the lowest calibration mass in the calibration curves, to account for the presence of signals corresponding to neutral PFAS in the background, and the higher number was chosen as the LOQ for 6:2 FTOH. The LOQ for 6:2 FTOH was calculated to be 0.05 ng (0.00005 μg, on TD tube) and with the final sampling volume (8.7 L), the method LOQ for 6:2 FTOH was 0.0057 ng/L (5.7×10^{-6} μg/L).

Confirmatory Analysis by programmable temperature vaporizing (PTV) GC-HRMS. Two paint samples that were positive for volatile PFAS (PS-24 and PS-30) were sent to the laboratory of Dr. Heather Stapleton at Duke University for analysis 6:2 FTOH. Briefly, an aliquot (0.5 g) of paint was diluted in ethyl acetate and spiked with $^{13}C_2$-6:2 FTOH and $^{13}C_2$-8:2 FTOH mass-labeled standards, further diluted 1:10, centrifuged, and filtered. The paint samples were injected (1 μL) into a programmable temperature vaporizing (PTV) inlet with an initial temperature of 80 °C that was ramped at 15 °C/sec to 250 °C and analyzed by Q Exactive GC hybrid quadrupole-Orbitrap GC−MS/MS system (ThermoScientific) operated in PCI mode.

Optimization of Paint Dilution Parameters

In order to determine the optimal mass of paint, different masses were chosen and treated with the experimental procedure for GC-MS analysis. Briefly, samples of 20, 25, 30, and 35 mg of PS-10 were diluted in 1.5 mL methanol and placed in a centrifuge for 10 minutes at 2000 *g*. After centrifugation, samples that had particulate matter suspended in solution were not chosen. A mass of 20 mg of paint was chosen unless such mass decreased the elution flow of SAX SPE. Two paints (PS-24 and -32) required a decreased mass of 10 mg that did not decrease SPE elution flow.

Table S1. List of target volatile PFAS analytes. Surrogate standards are sold in methanol except for d_3-6:2 FTAc and d_5-6:2 FTMAc, which are sold in ethyl acetate.

	Analyte	Acronym	Neutral Molecular Formula	Quantifier Ion (*m/z*)	Qualifier Ion (*m/z*)	Surrogate Standard
Group 1	4:2 fluorotelomer alcohol	4:2 FTOH	$C_6H_5OF_9$	265	227	MFBET
	6:2 fluorotelomer alcohol	6:2 FTOH	$C_8H_5OF_{13}$	365	327	MFHET
	8:2 fluorotelomer alcohol	8:2 FTOH	$C_{10}H_5OF_{17}$	465	427	M2FOET
	10:2 fluorotelomer alcohol	10:2 FTOH	$C_{12}H_5OF_{21}$	565	527	MFDET
	12:2 fluorotelomer alcohol	12:2 FTOH	$C_{14}H_5OF_{25}$	665	627	MFDET
	N-methyl perfluoroalkane sulfonamide	MeFOSA	$C_9H_4NO_2SF_{17}$	514	-	d_3-N-MeFOSA-M
	N-ethyl perfluoro-1-octane sulfonamide	EtFOSA	$C_{10}H_6NO_2SF_{17}$	528	-	d_5-N-EtFOSA-M
	N-methyl perfluorooctane sulfonamidoethanol	MeFOSE	$C_{11}H_8NO_3SF_{17}$	540	558	d_7-N-MeFOSE-M
	N-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	$C_{12}H_{10}NO_3SF_{17}$	554	572	d_9-N-EtFOSE-M
Group 2	4:2 fluorotelomer acrylate	4:2 FTAc	$C_9H_7F_9O_2$	319	-	d_3-6:2 FTAc
	6:2 fluorotelomer acrylate	6:2 FTAc	$C_{11}H_7F_{13}O_2$	419	-	d_3-6:2 FTAc
	8:2 fluorotelomer acrylate	8:2 FTAc	$C_{13}H_7F_{17}O_2$	519	-	d_3-6:2 FTAc
	10:2 fluorotelomer acrylate	10:2 FTAc	$C_{15}H_7F_{21}O_2$	619	-	d_3-6:2 FTAc
	6:2 Fluorotelomer methylacrylate	6:2 FTMAc	$C_{12}H_9F_{13}O_2$	433	461	d_5-6:2 FTMAc
	8:2 Fluorotelomer methylacrylate	8:2 FTMAc	$C_{14}H_9F_{17}O_2$	533	561	d_5-6:2 FTMAc

Table S2. List of suspect volatile PFAS analytes.

Analyte	Acronym	Neutral Molecular Formula	Quantifier Ion (*m/z*)	Qualifier Ion (*m/z*)	Surrogate Standard
14:2 fluorotelomer alcohol	14:2 FTOH	$C_{16}H_5OF_{29}$	765	727	MFDET
N-methyl perfluoropropane sulfonamidoethanol	MeFPrSE	$C_6H_8NO_3SF_7$	290	308	d_7-N-MeFOSE-M
N-methyl perfluorobutane sulfonamidoethanol	MeFBSE	$C_7H_8NO_3SF_9$	340	358	d_7-N-MeFOSE-M
N-methyl perfluoropentane sulfonamidoethanol	MeFPeSE	$C_8H_8NO_3SF_{11}$	390	408	d_7-N-MeFOSE-M
N-methyl perfluorohexane sulfonamidoethanol	MeFHxSE	$C_9H_8NO_3SF_{13}$	440	458	d_7-N-MeFOSE-M
N-methyl perfluoroheptane sulfonamidoethanol	MeFHpSE	$C_{10}H_8NO_3SF_{15}$	490	508	d_7-N-MeFOSE-M
N-ethyl perfluoroethane sulfonamidoethanol	EtFEtSE	$C_6H_{10}NO_3SF_5$	254	272	d_9-N-EtFOSE-M
N-ethyl perfluoropropane sulfonamidoethanol	EtFPrSE	$C_7H_{10}NO_3SF_7$	304	322	d_9-N-EtFOSE-M
N-ethyl perfluorobutane sulfonamidoethanol	EtFBSE	$C_8H_{10}NO_3SF_9$	354	372	d_9-N-EtFOSE-M
N-ethyl perfluoropentane sulfonamidoethanol	EtFPeSE	$C_9H_{10}NO_3SF_{11}$	404	422	d_9-N-EtFOSE-M
N-ethyl perfluorohexane sulfonamidoethanol	EtFHxSE	$C_{10}H_{10}NO_3SF_{13}$	454	472	d_9-N-EtFOSE-M
N-ethyl perfluoroheptane sulfonamidoethanol	EtFHpSE	$C_{11}H_{10}NO_3SF_{15}$	504	522	d_9-N-EtFOSE-M
4:2 fluorotelomer iodide	4:2 FTI	$C_6H_4F_9I$	355	403	d_5-6:2 FTMAc
6:2 fluorotelomer iodide	6:2 FTI	$C_8H_4F_{13}I$	455	503	d_5-6:2 FTMAc
8:2 fluorotelomer iodide	8:2 FTI	$C_{10}H_4F_{17}I$	555	603	d_5-6:2 FTMAc
10:2 fluorotelomer iodide	10:2 FTI	$C_{12}H_4F_{21}I$	655	703	d_5-6:2 FTMAc
Perfluorobutyl iodide	PFBI	C_4F_9I	219	327	d_5-6:2 FTMAc
Perfluorohexyl iodide	PFHxI	$C_6F_{13}I$	319	427	d_5-6:2 FTMAc
Perfluorooctyl iodide	PFOI	$C_8F_{17}I$	419	527	d_5-6:2 FTMAc
Perfluorodecyl iodide	PFDI	$C_{10}F_{21}I$	519	627	d_5-6:2 FTMAc
6:2 fluorotelomer olefin	6:2 FTO	$C_8H_3F_{13}$	327	-	d_5-6:2 FTMAc
8:2 fluorotelomer olefin	8:2 FTO	$C_{10}H_3F_{17}$	427	-	d_5-6:2 FTMAc
10:2 fluorotelomer olefin	10:2 FTO	$C_{12}H_3F_{21}$	527	-	d_5-6:2 FTMAc
12:2 fluorotelomer olefin	12:2 FTO	$C_{14}H_3F_{25}$	627	-	d_5-6:2 FTMAc

Table S3. List of target nonvolatile PFAS analytes.[1]

Analyte	Acronym	Neutral Molecular Formula	Surrogate Standard
Perfluoro-n-butanoic acid	PFBA[2]	$C_4HO_2F_7$	MPFBA
Perfluoro-n-petnanoic acid	PFPeA	$C_5HO_2F_9$	M3PFPeA
Perfluoro-n-hexanoic acid	PFHxA	$C_6HO_2F_{11}$	M2PFHxA
Perfluoro-n-heptanoic acid	PFHpA	$C_7HO_2F_{13}$	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	$C_8HO_2F_{15}$	M4PFOA
Perfluoro-n-nonanoic acid	PFNA	$C_9HO_2F_{17}$	M5PFNA
Perfluoro-n-decanoic acid	PFDA	$C_{10}HO_2F_{19}$	MPFDA
Perfluoro-n-undecanoic acid	PFUdA	$C_{11}HO_2F_{21}$	MPFUdA
Perfluoro-n-dodecanoic acid	PFDoA	$C_{12}HO_2F_{23}$	MPFDoA
Perfluoro-n-tridecanoic acid	PFTrDA	$C_{13}HO_2F_{25}$	MPFDoA
Perfluoro-n-tetradecanoic acid	PFTeDA	$C_{14}HO_2F_{27}$	M2PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	$C_{16}HO_2F_{31}$	M2PFHxDA
Perfluoropropane sulfonate	PFPrS	$C_3HO_3SF_7$	M3PFBS
Perfluorobutane sulfonate	PFBS	$C_4HO_3SF_9$	M3PFBS
Perfluoropentane sulfonate	PFPeS	$C_5HO_3SF_{11}$	M3PFBS
Perfluorohexane sulfonate	PFHxS	$C_6HO_3SF_{13}$	MPFHxS
Perfluoroheptane sulfonate	PFHpS	$C_7HO_3SF_{15}$	MPFHxS
Perfluorooctane sulfonate	PFOS	$C_8HO_3SF_{17}$	MPFOS
Perfluorononane sulfonate	PFNS	$C_9HO_3SF_{19}$	MPFOS
Perfluorodecane sulfonate	PFDS	$C_{10}HO_3SF_{21}$	MPFOS
Perfluorododecane sulfonate	PFDoS	$C_{12}HO_3SF_{25}$	MPFOS
8-chloro-perfluorooctane sulfonate	Cl-PFOS	$C_8HClF_{16}SO_3$	MPFOS
Perfluoroethylcyclohexane sulfonate	PFEtCHxS	$C_8HO_3SF_{15}$	MPFHxS
Perfluorobutane sulfonamide	FBSA	$C_4H_2O_2NSF_9$	M8FOSA
Perfluorohexane sulfonamide	FHxSA	$C_6H_2O_2NSF_{13}$	M8FOSA
Perfluorooctane sulfonamide	FOSA	$C_8H_2O_2NSF_{17}$	M8FOSA
N-methylperfluoro-1-octane sulfonamide	MeFOSA	$C_9H_4O_2NSF_{17}$	d-N-MeFOSA-M
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	$C_{10}H_6O_2NSF_{17}$	d-N-EtFOSA-M
Perfluorooctane sulfonamido acetic acid	FOSAA	$C_{10}H_4O_4NSF_{17}$	d_3-N-MeFOSAA
N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	$C_{11}H_6O_4NSF_{17}$	d_3-N-MeFOSAA
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	$C_{12}H_8O_4NSF_{17}$	d5-N-EtFOSAA
4:2 fluorotelomer sulfonate	4:2 FTS	$C_6H_5O_3SF_9$	M2-4:2FTS
6:2 fluorotelomer sulfonate	6:2 FTS	$C_8H_5O_3SF_{13}$	M2-6:2FTS
8:2 fluorotelomer sulfonate	8:2 FTS	$C_{10}H_5O_3S_{F17}$	M2-8:2FTS

Analyte	Acronym	Neutral Molecular Formula	Surrogate Standard
10:2 fluorotelomer sulfonate	10:2 FTS	$C_{12}H_5O_3SF_{21}$	M2-8:2FTS
6:2 fluorotelomer carboxylic acid	6:2 FTCA	$C_8H_3O_2F_{13}$	M6:2FTA
8:2 fluorotelomer carboxylic acid	8:2 FTCA	$C_{10}H_3O_2F_{17}$	M8:2FTA
10:2 fluorotelomer carboxylic acid	10:2 FTCA	$C_{12}H_3O_2F_{21}$	M10:2FTA
3:3 fluorotelomer carboxylic acid	3:3 FTCA	$C_6H_5O_2F_7$	M6:2FTA
5:3 fluorotelomer carboxylic acid	5:3 FTCA	$C_8H_5O_2F_{11}$	M8:2FTA
7:3 fluorotelomer carboxylic acid	7:3 FTCA	$C_{10}H_5O_2F_{15}$	M10:2FTA
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	$C_8H_2O_2F_{12}$	M6:2FTUA
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	$C_{10}H_2O_2F_{16}$	M8:2FTUA
Dodecafluoro-3H-4,8-dioxanoate	ADONA	$C_7H_2O_4F_{12}$	M5PFNA
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	$C_8HF_{16}ClSO_4$	MPFOS
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11-PF3OUdS	$C_{10}HF_{20}ClSO_4$	MPFOS
hexafluoropropylene oxide-dimer acid	HFPO-DA	$C_6HF_{11}O_3$	MHFPO-DA
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2 diPAP	$C_{16}H_9F_{26}O_4P$	M4 8:2 diPAP
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2 diPAP	$C_{20}H_9F_{34}O_4P$	M4 8:2 diPAP
Bis-[2-(N-ethyleperflurooctane-1-sulfonamido)ethyl] phosphate	diSAmPAP	$C_{24}H_{19}F_{34}N_2O_8PS_2$	M4 8:2 diPAP
N-(3-dimethylaminopropan-1-yl)-perfluoro-1-hexanesulfonamide	PFHxSaAm	$C_{11}H_{13}F_{13}N_2O_2S$	d_3-prometon
1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3- [[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-	6:2 FtSaB	$C_{15}H_{19}F_{13}N_2O_4S$	d_3-prometon
N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium	N-TAmP-FHxSA	$C_{12}H_{15}F_{13}N_2O_2S$	d_3-prometon
2-[(4,4,5,5,6,6,7,7,8,8,8-Undecafluorooctyl)dimethylammonio]acetate	5:3 FTB	$C_{12}H_{14}F_{11}NO_2$	d_3-prometon
2-[(3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluorooctyl)dimethylammonio]acetate	5:1:2 FTB	$C_{12}H_{13}F_{12}NO_2$	d_3-prometon

[1][M-H]$^-$ adducts were used for quantification

[2]MRM transitions of 213 → 169 and 217 → 172 were used for quantification of PFBA and MPFBA, respectively, to reduce background.

Table S4. Paint specifications including paint and coating firm, brand, finish or base, interior or exterior, and water or oil-based

Paint	Paint and Coating Firm	Brand	Finish or Base	Interior (I) or Exterior (E)	Water (W) or Oil (O) based
PS-05	1	A	Base 1	E	W
PS-06	1	A	Base 2	E	W
PS-08	2	B	Base 1	I	W
PS-10	3	C	Eggshell	I	W
PS-11	1	D	Semi-Gloss	I	W
PS-12	1	E	Satin	I	W
PS-13	1	F	Eggshell	I	W
PS-14	4	G	Base 1	I	W
PS-15	4	H	Base 1	I	W
PS-16	1	D	Eggshell	I	W
PS-17	4	I	Base 1	I	O
PS-19	4	J	Flat	I	W
PS-20	4	J	Flat	I	W
PS-21	4	K	Base 2	I	W
PS-22	4	I	Base 2	I	O
PS-23	4	I	Base 3	I	O
PS-24	2	L	Semi-Gloss	E	W
PS-25	1	E	Semi-Gloss	E	W
PS-26	1	E	Flat	I	W
PS-27	1	E	Eggshell	I	W
PS-28	1	D	Matte	I	W
PS-29	1	M	Matte	I	W
PS-30	1	M	Eggshell	I	W
PS-31	1	M	Semi-Gloss	I	W
PS-32	3	N	Semi-Gloss	E	W

Table S5. Whole method precision (% RSD), whole method accuracy (% average recovery), LOD, and LOQ. The LOQ was calculated by multiplying LOD with 3.3.[a]

Analyte	Whole method precision (% average recovery)	Whole method accuracy (% RSD)	LOD (µg/g)	LOQ (µg/g)
4:2 FTOH	75	3.7	0.21	0.70
6:2 FTOH	75	2.9	0.26	0.86
8:2 FTOH	94	1.9	0.46	1.5
10:2 FTOH	65	1.8	0.32	1.1
12:2 FTOH	97	5.5	0.35	1.1
MeFOSA	68	1.6	0.32	1.1
EtFOSA	78	2.7	0.31	1.0
MeFOSE	70	1.4	0.53	1.7
EtFOSE	78	1.4	0.54	1.8
4:2 FTAc	65	0.64	0.0080	0.026
6:2 FTAc	100	2.0	0.018	0.060
8:2 FTAc	66	3.4	0.080	0.26
10:2 FTAc	89	1.2	0.094	0.10
6:2 FTMAc	100	3.7	0.017	0.057
8:2 FTMAc	130	3.0	0.024	0.080

[a] For LOD and LOQ, blank paint (PS-08) was spiked with 0.012 to 47 µg/g of FTOHs, FOSAs, and FOSEs and 0.0037 to 6.25 µg/g of FTAcs and FTMAcs.

Table S6. Volatile PFAS surrogate standards percent recovery on matrix spike and samples. The recovery of volatile surrogate standard was determined based on the response of each surrogate standard relative to the response of 7:1-FTOH as the internal standard. Data for PS-06, PS-10, and PS-20 (n = 3) are provided as the average ± standard deviation. All paints are interior paints unless otherwise denoted as (E) for exterior.

Sample Name	d_4-4:2 FTOH	$^{13}C_2$-d_2-6:2 FTOH	$^{13}C_2$-8:2 FTOH	$^{13}C_2$-d_2-10:2 FTOH	d_3-N-MeFOSA-M	d_5-N-EtFOSA-M	d_7-N-MeFOSE-M	d_9-N-EtFOSE-M
Method Blank	100	110	97	120	150	160	110	110
PS-05 (E)	89	110	100	150	130	120	120	130
PS-06 (E)	91±4.2	120±5.7	110±5.5	140±10	75±11	43±10	130±16	140±20
PS-07	80	99	95	160	200	200	150	NA
PS-08	91	95	86	130	160	160	120	110
PS-09	92	100	86	110	130	130	110	100
PS-10	87±0.77	100±1.7	100±0.46	110±2.3	160±3.9	140±4.3	130±12	140±13
PS-11	95	110	89	140	170	170	130	110
PS-12	100	120	100	140	170	180	250	120
PS-13	80	91	85	130	160	170	140	120
PS-14	110	120	104	190	180	180	190	140
PS-15	80	99	89	150	200	190	140	150
PS-16	75	97	88	140	180	180	130	120
PS-17	110	110	100	110	150	160	140	160
PS-19	86	93	84	96	120	120	100	120
PS-20	85±5.1	110±10	93±7.9	110±9.2	130±11	130±11	120±17	140±18
PS-21	92	130	110	120	150	150	130	150
PS-22	75	80	77	83	110	120	100	110
PS-23	82	89	86	92	130	130	120	110
PS-24 (E)	89	110	97	92	110	100	140	120
PS-25 (E)	88	93	94	86	81	72	170	81
PS-26	100	99	100	90	100	92	140	110
PS-27	99	99	94	88	110	100	120	89
PS-28	92	98	93	86	110	100	96	89
PS-29	88	97	90	81	100	100	83	80

Sample Name	d_4-4:2 FTOH	$^{13}C_2$-d_2-6:2 FTOH	$^{13}C_2$-8:2 FTOH	$^{13}C_2$-d_2-10:2 FTOH	d_3-N-MeFOSA-M	d_5-N-EtFOSA-M	d_7-N-MeFOSE-M	d_9-N-EtFOSE-M
PS-30	94	110	93	89	85	62	100	88
PS-31	96	100	97	95	63	35	99	92
PS-32 (E)	90	92	91	85	110	100	92	95

Table S7. Whole method precision (% RSD), whole method accuracy (% average recovery), LOD, and LOQ based on liquid paint sample spiked with nonvolatile PFAS. 0.37 µg/g nonvolatile PFAS were spiked for whole method precision and whole method accuracy (n = 4). 0.0075 to 0.075 µg/g nonvolatile PFAS were spiked for LOD (n = 8) and LOQ was calculated by multiplying LOD with 3.3.

Analyte	Whole method precision (% average recovery)	Whole method accuracy (% RSD)	LOD (µg/g)	LOQ (µg/g)
PFBA	120	14	0.002	0.0066
PFPeA	98	21	0.0037	0.012
PFHxA	110	13	0.0032	0.011
PFHpA	100	13	0.0012	0.0040
PFOA	110	14	0.0025	0.0083
PFNA	100	15	0.0023	0.0078
PFDA	100	15	0.002	0.0066
PFUdA	110	17	0.0017	0.0057
PFDoA	110	16	0.0024	0.0079
PFTrDA	98	23	0.0026	0.0087
PFTeDA	110	18	0.0025	0.0082
PFHxDA	100	18	0.0022	0.0073
PFPrS	90	18	0.0030	0.010
PFBS	97	17	0.0021	0.0069
PFPeS	66	14	0.0019	0.0064
PFHxS	97	15	0.0023	0.0078
PFHpS	100	19	0.0023	0.0078
PFOS	95	16	0.0019	0.0064
PFNS	110	16	0.0021	0.0070
PFDS	120	19	0.0021	0.0070
PFDoS	95	16	0.0017	0.0055
Cl-PFOS	120	15	0.0020	0.0067
PFEtCHxS	110	17	0.0022	0.0072
FBSA	120	12	0.004	0.013
FHxSA	78	15	0.0035	0.012
FOSA	120	14	0.0018	0.0059
MeFOSA	110	15	0.0017	0.0055
EtFOSA	110	11	0.0021	0.0070
FOSAA	110	22	0.0021	0.0069
MeFOSAA	87	16	0.0017	0.0056
EtFOSAA	110	11	0.002	0.0066
4:2 FTS	100	17	0.0037	0.012
6:2 FTS	170	23	0.0049	0.016
8:2 FTS	120	13	0.0035	0.012

Analyte	Whole method precision (% average recovery)	Whole method accuracy (% RSD)	LOD (µg/g)	LOQ (µg/g)
10:2 FTS	140	15	0.0033	0.011
3:3 FTCA	210	20	0.0033	0.011
5:3 FTCA	97	12	0.0035	0.012
7:3 FTCA	120	15	0.0033	0.011
6:2 FTCA	100	34	0.0051	0.017
8:2 FTCA	100	10	0.0045	0.015
10:2 FTCA	120	38	0.0037	0.012
6:2 UFTCA	110	14	0.0046	0.015
8:2 UFTCA	120	12	0.0038	0.013
ADONA	100	15	0.0032	0.011
9Cl-PF3ONS	110	18	0.0019	0.0063
11-PF3OUdS	110	16	0.0021	0.0072
HFPO-DA	95	29	0.0043	0.014
6:2 diPAP	76	25	0.0021	0.0068
8:2 diPAP	88	16	0.0030	0.010
diSAmPAP	65	29	0.0033	0.011
PFHxSaAm	98	21	0.0029	0.0087
6:2 FtSaB	82	20	0.0032	0.0096
N-TAmP-FHxSA	99	17	0.0027	0.0081
5:3 FTB	80	14	0.0026	0.0078
5:1:2 FTB	82	18	0.0027	0.0081

Table S8. Parameters used for the exposure assessment by ConsExpo including painting details, area of room, population parameters, and physical and chemical properties of 6:2 FTOH and paint. Application time, population parameters, chemical and physical properties of paint are defined by ConsExpo Paint Fact Sheet.[6]

Parameters	Input
Painting Details	
Air Change Rate	0.5 hr^{-1} [7]
Type of Paint	Water-based wall paint
Amount of Paint	7.57 L (2 gallons)
Application Time	132 minutes [6]
Application Method	Brush or Roller
Area of Room	
Average sized door	21 sq ft [8]
Average sized window	12 sq ft [8]
Wall Surface excluding door and window	351 sq ft
Population Parameters	
Adult Man Body Weight and Inhalation Rate	77.2 kg, 1.62 m^3/hr [6]
Adult Woman Body Weight and Inhalation Rate	64.1 kg, 1.43 m^3/hr [6]
Child Body Weight and Inhalation Rate	24.3 kg, 0.762 m^3/hr [6]
Chemical & Physical Properties of 6:2 FTOH	
Vapor Pressure	130 Pa [16]
Molecular Weight	364 g/mol
Chemical & Physical Properties of Paint	
Mass Transfer Rate	11 m/hr [6]
Molecular Weight of Matrix where Solvent is not the component of interest	120 g/mol [6]

Table S9. FTOH concentrations (pg/µL) resulting from injections of non-volatiles native and mass-labeled (ML) 6:2 diPAP (500 pg/µL), native and mass-labeled 8:2 diPAP (500 pg/µL), and Zonyl® FSO (1:10,000 dilution). Samples were either SAX SPE cleaned or no SPE clean-up step at 280 °C and 130 °C inlet temperatures.

		280 °C inlet		130 °C inlet	
Analyte	FTOH Observed	SAX SPE	Non SAX SPE	SAX SPE	Non SAX SPE
6:2 diPAP	6:2 FTOH	<LOD	64	<LOD	2.5
ML 6:2 diPAP	ML 6:2 FTOH	<LOD	25	<LOD	5.3
8:2 diPAP	8:2 FTOH	<LOD	43	<LOD	1.9
ML 8:2 diPAP	ML 8:2 FTOH	<LOD	36	<LOD	2.5
Zonyl® FSO	4:2 FTOH	7.5	11	8.1	11
	6:2 FTOH	970	1200	869	1300
	8:2 FTOH	630	780	582	780
	10:2 FTOH	200	250	160	250
	12:2 FTOH	58	89	<LOD	95
	14:2 FTOH	<LOD	13	<LOD	17

Table S10: Target analyte concentrations (µg/g) of individual volatile PFAS in 27 paints analyzed by GC-MS. Data for PS-06 and PS-10 (n = 3) were provided in average ± standard deviation. Exterior (E), interior (I), and oil-based* paints are identified.

		4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	4:2 FTAc	6:2 FTAc	8:2 FTAc	10:2 FTAc	6:2 FTMAc	8:2 FTMAc
PS-05	E	<LOQ	**28**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-06	E	<LOQ	**83±3.4**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-07	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-08	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-09	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-10	I	<LOD	**1.1±0.12**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-11	I	<LOD	**1.6**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-12	I	<LOQ	**34**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-13	I	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-14	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-15	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-16	I	<LOD	**0.95**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-17*	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-19	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-20	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-21	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-22*	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-23*	I	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-24	E	<LOD	**12**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-25	E	<LOD	**9.0**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-26	I	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-27	I	<LOD	**5.4**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-28	I	<LOD	**5.0**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

		4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	4:2 FTAc	6:2 FTAc	8:2 FTAc	10:2 FTAc	6:2 FTMAc	8:2 FTMAc
PS-29	I	<LOD	**0.92**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-30	I	<LOD	**1.1**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-31	I	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PS-32	E	<LOD	**3.0**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
LOQ	-	0.70	0.86	1.5	1.1	1.1	1.1	1.0	1.7	1.8	0.026	0.060	0.26	0.31	0.057	0.080

Table S11. Target analyte concentrations (μg/g) of individual nonvolatile PFAS analyzed by LC-qTOF. Data for PS-10 (n = 3) were provided in average ± standard deviation.

	MB	PS-05	PS-06	PS-08	PS-10	PS-11	PS-12	PS-16	PS-24	PS-25	PS-27	PS-28	PS-29	PS-30	PS-32	LOQ
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0066
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.012
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011
PFHpA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0040
PFOA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0083
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0078
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0066
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0057
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0079
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0087
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0082
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0073
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.010
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.072**	<LOD	<LOD	<LOD	0.0069
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0064
PFHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0078
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0078
PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0064
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0070
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0070
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0055
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0067
PFEtCHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0072
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.013

	MB	PS-05	PS-06	PS-08	PS-33	PS-34	PS-35	PS-39	PS-47	PS-48	PS-50	PS-51	PS-52	PS-53	PS-55	LOQ
FHxSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.013
FOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0059
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0055
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	**0.41**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0070
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0069
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0056
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0066
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.012
6:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.016
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.012
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011
5:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.012
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.017
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.015
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.012
6:2 UTFCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.015
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.013
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0063
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0072
HFPO-DA	<LOD	**0.16**	**1.2**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.014
6:2 diPAP	<LOD	**20**	**49**	**0.073**	**24±2.3**	**19**	**58**	**17**	**7.6**	**42**	**12**	**12**	**15**	**12**	**23**	0.0068
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.010
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.011

	MB	PS-05	PS-06	PS-08	PS-33	PS-34	PS-35	PS-39	PS-47	PS-48	PS-50	PS-51	PS-52	PS-53	PS-55	LOQ
PFHxSaAm	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0087
6:2 FtSaB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0096
N-TAmP-FHxSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0081
5:3 FTB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0078
5:1:2 FTB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0081

Table S12. Comparison of 6:2 FTOH concentrations in wet and dry paints (PS-06 and PS-10). Concentrations were done in triplicate and standard deviation is provided (±SD).

Paint	Liquid Paint Concentration (µg/g)	Dry Paint Concentration Measured (µg/g)	Dry Paint Concentration Conversion (µg/g)	% Loss
PS-06	83±7.4	98±24	51±12	39
PS-10	1.1±0.12	1.2±0.11	0.64±0.057	40

Table S13. Inhalation doses for children, women, and men with varying air exchange rates (0.5-1.0 hr^{-1}), vapor pressures (18-880 Pa), and temperatures (15-35 °C). Inhalation doses that exceed the reference dose of 5 µg/kg-day are in bold. The baseline is 25 °C, 0.5 h^{-1}, 130 Pa.

			PS-10	PS-11	PS-12	PS-16	PS-27	PS-28	PS-29	PS-30
Child	Temperature (°C)	15	0.48	0.46	**9.9**	0.28	1.6	1.5	0.27	0.32
		35	0.45	0.44	**9.3**	0.26	1.5	1.4	0.25	0.30
	Air Change Rate (h^{-1})	0.75	0.31	0.45	**9.6**	0.27	1.5	1.4	0.26	0.31
		1.0	0.30	0.44	**9.2**	0.26	1.5	1.4	0.25	0.30
	Vapor Pressure (Pa)	18	0.067	0.065	1.4	0.039	0.22	0.20	0.038	0.045
		880	2.5	2.5	**52**	1.5	**8.3**	**7.7**	1.4	1.7
	**baseline*		0.32	0.47	**9.9**	0.28	1.6	1.5	0.27	0.32
Woman	Temperature (°C)	15	0.23	0.31	**6.8**	0.18	1.1	1.0	0.19	0.23
		35	0.21	0.29	**6.4**	0.17	1.0	0.97	0.18	0.21
	Air Change Rate (h^{-1})	0.75	0.22	0.30	**6.6**	0.18	1.1	1.0	018	0.22
		1.0	0.21	0.29	**6.4**	0.17	1.0	0.97	0.18	0.21
	Vapor Pressure (Pa)	18	0.048	0.044	0.96	0.026	0.16	0.15	0.027	0.032
		880	1.8	1.6	**36**	0.97	**5.9**	**5.5**	1.0	1.2
	**baseline*		0.23	0.31	**6.8**	0.18	1.1	1.0	0.19	0.23
Man	Temperature (°C)	15	0.21	0.29	**6.4**	0.17	1.1	0.97	0.18	0.21
		35	0.20	0.27	**6.0**	0.16	0.98	0.91	0.17	0.20
	Air Change Rate (h^{-1})	0.75	0.21	0.28	**6.2**	0.17	1.0	0.94	0.17	0.21
		1.0	0.20	0.27	**6.0**	0.16	0.98	0.91	0.17	0.20
	Vapor Pressure (Pa)	18	0.030	0.041	0.99	0.026	0.15	0.14	0.025	0.030
		880	1.1	1.5	**34**	0.91	**5.6**	**5.2**	0.95	1.1
	**baseline*		0.21	0.29	**6.4**	0.17	1.1	0.97	0.18	0.21

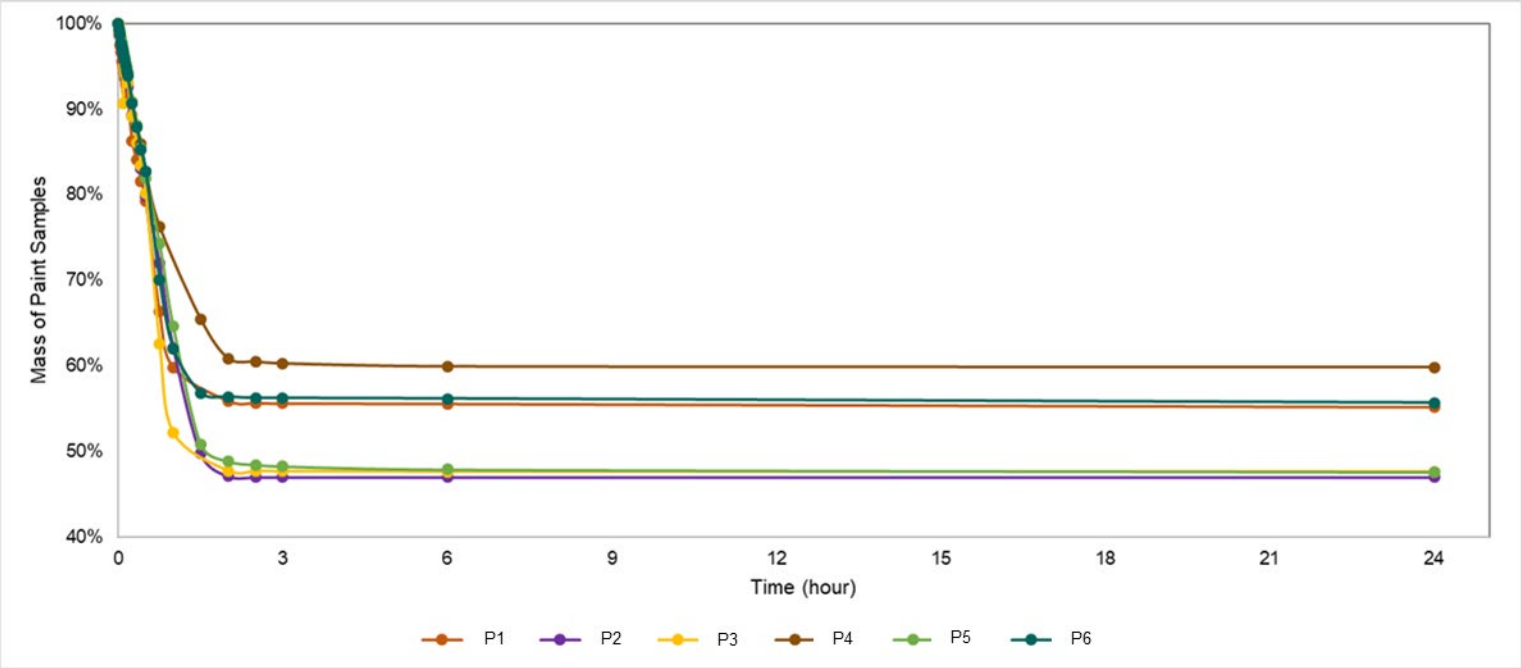

Figure S1. Mass loss observed during a 24-hour period for six paints. Major mass loss occurs within the first 3 hours of a paint drying and loss is minimal afterwards.

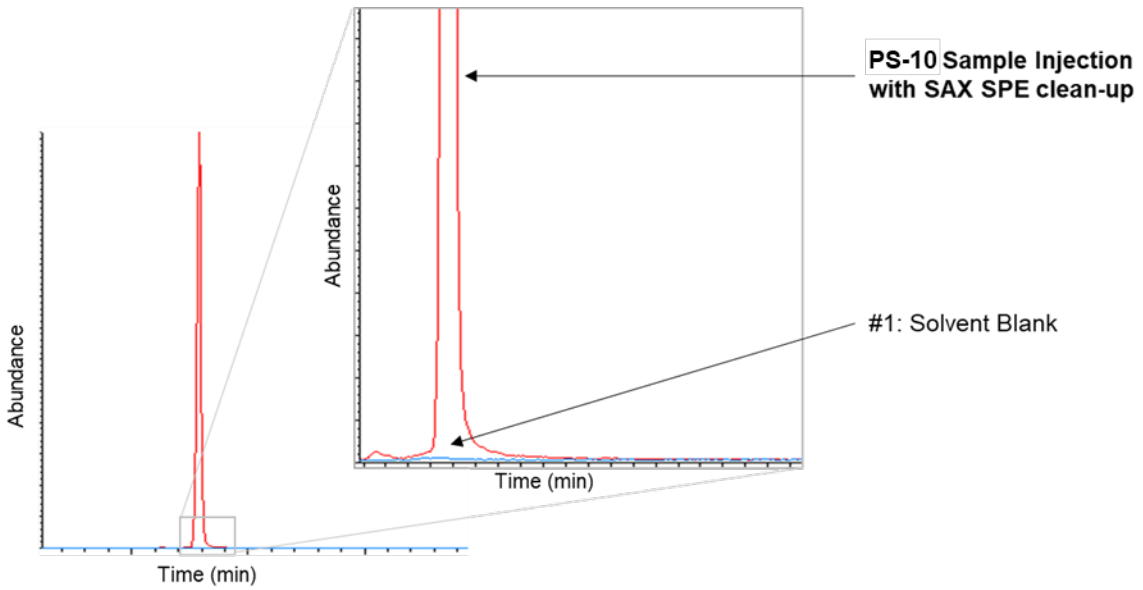

Figure S2. GC-MS extracted ion chromatogram of 6:2 FTOH (red) in PS-10 followed by blank methanol injections that does not show 6:2 FTOH 'carryover', as a result of including SAX SPE in the experimental procedure.

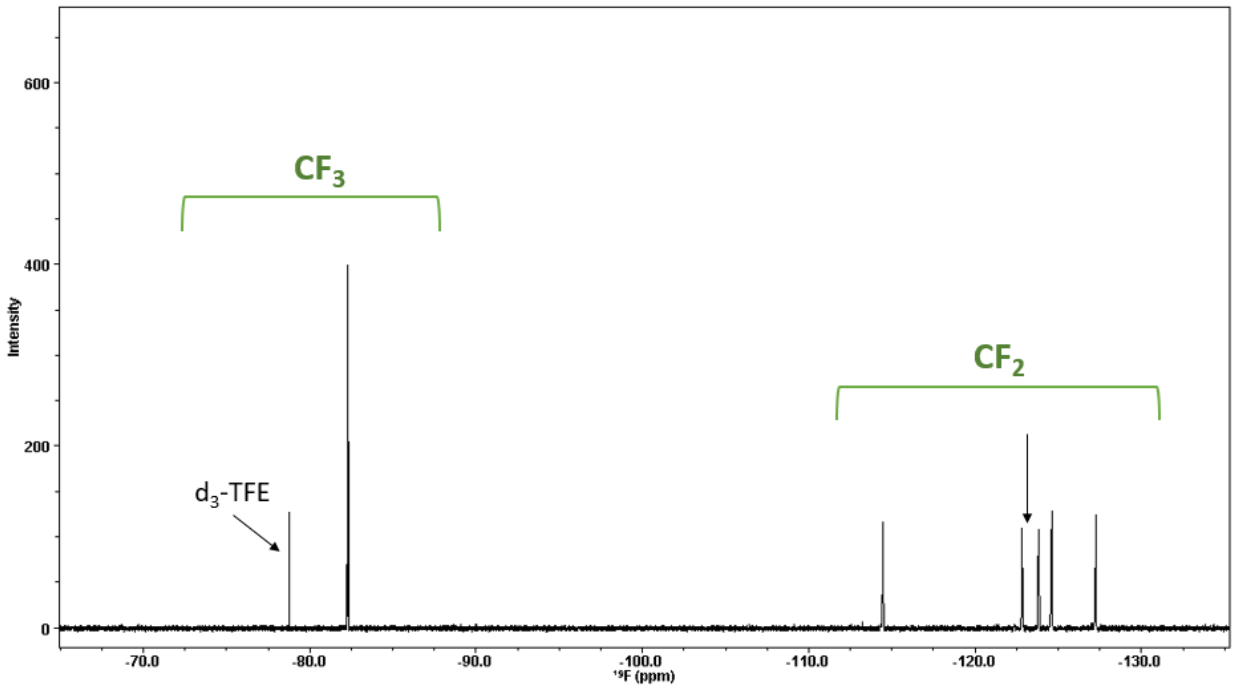

Figure S3. ^{19}F NMR spectrum of PS-11, where five CF_2 signals (-110 to -130 ppm) and one CF_3 signal (-75 to -85 ppm) indicate 6:2 telomer-based PFAS. Arrow signifies where inorganic fluoride would appear if present (-122.91 ppm)

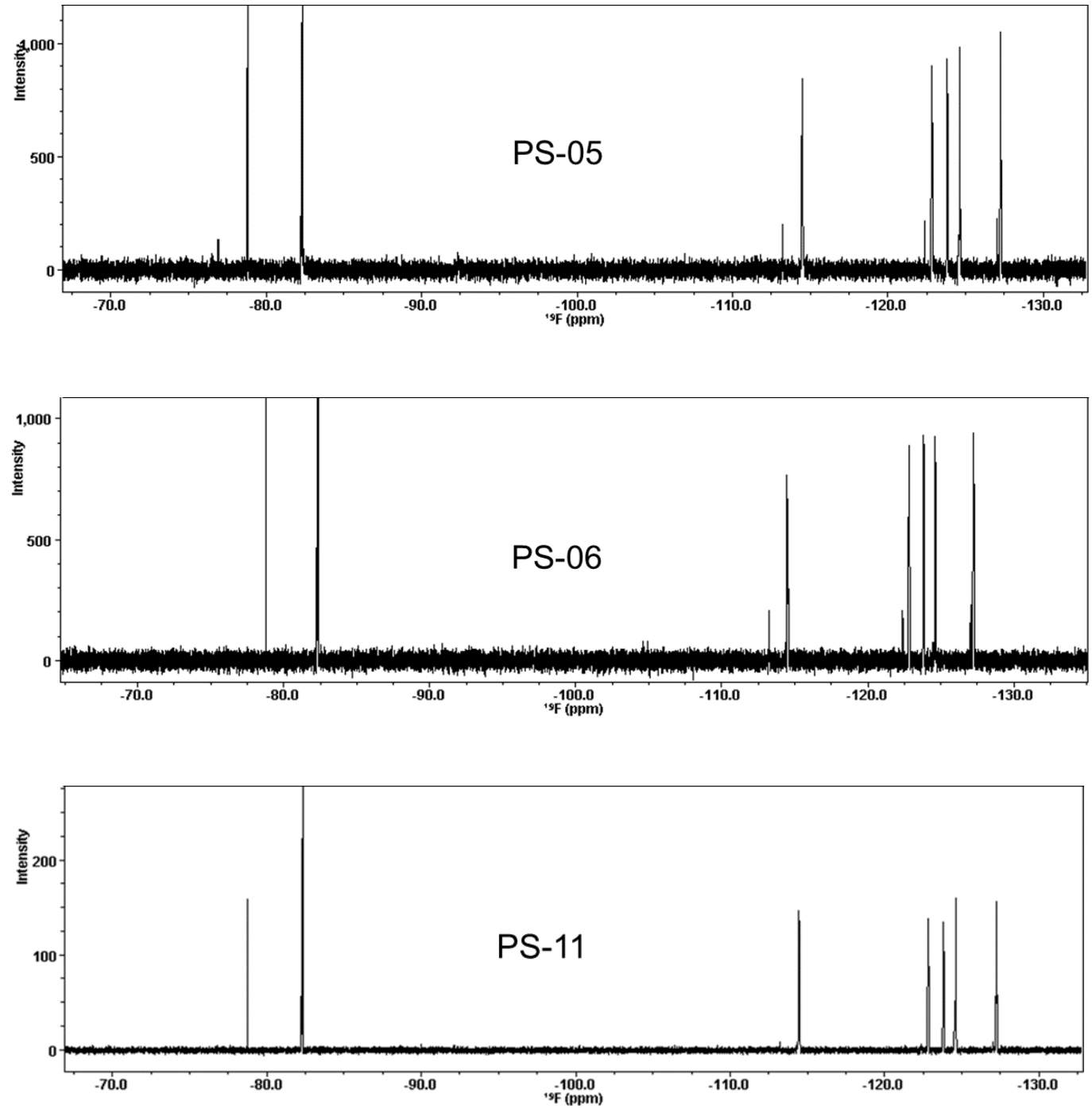

Figure S4. Fluorine NMR spectra of paints 05, 06, and 11. All spectra show 6:2 telomer species as the predominant fluorinated species. However, PS-05 and -06 also display additional fluorine signals that may pertain to other fluorinated species. Inorganic fluorine was not present at -122.91 ppm.

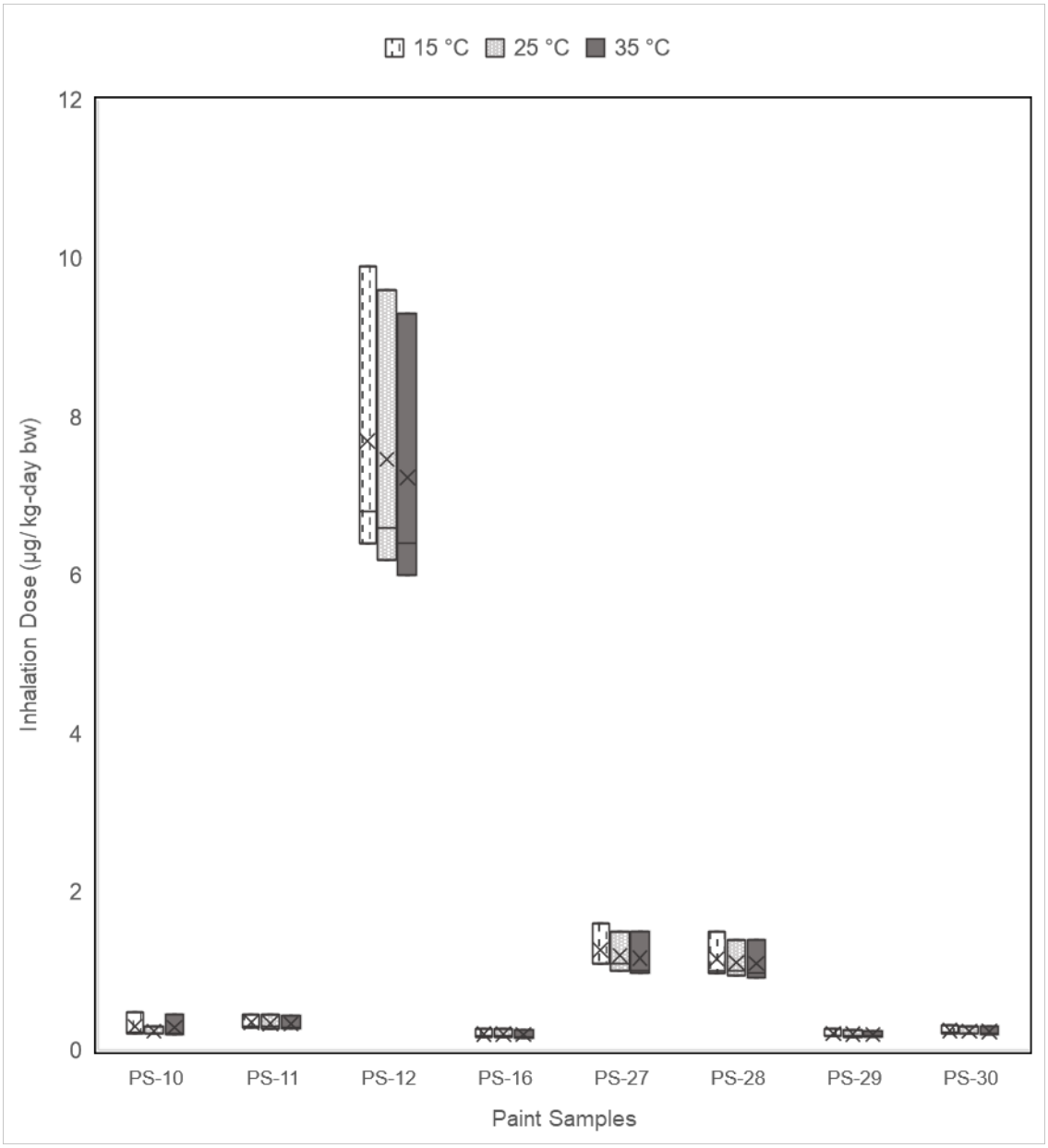

Figure S5. Inhalation doses of 6:2 FTOH resulting from 3 different temperatures (15, 25, and 35 °C) from ConsExpo.

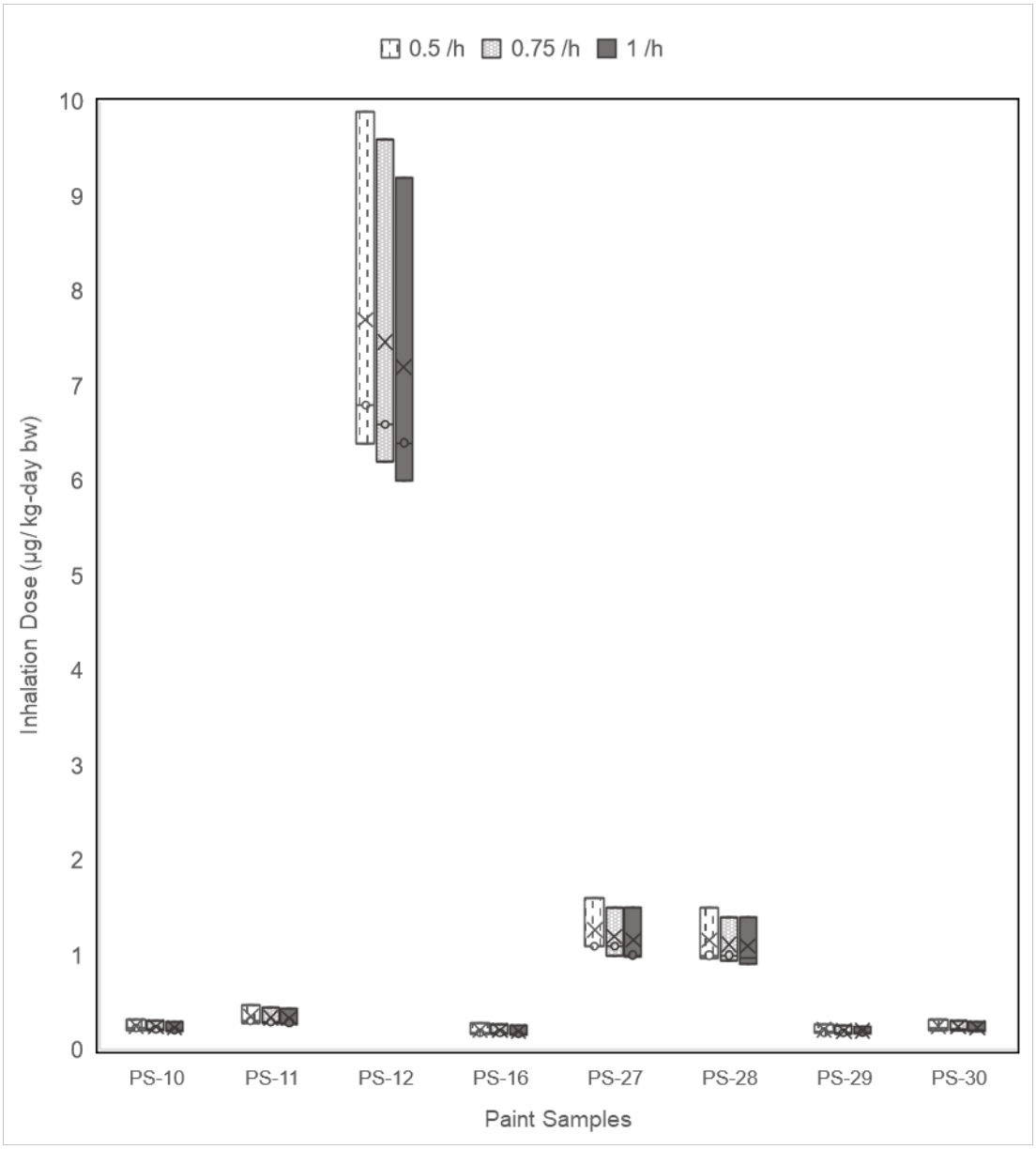

Figure S6. Inhalation doses of 6:2 FTOH resulting from 3 different air exchange rates (0.5, 0.75, 1 h^{-1}) from ConsExpo.

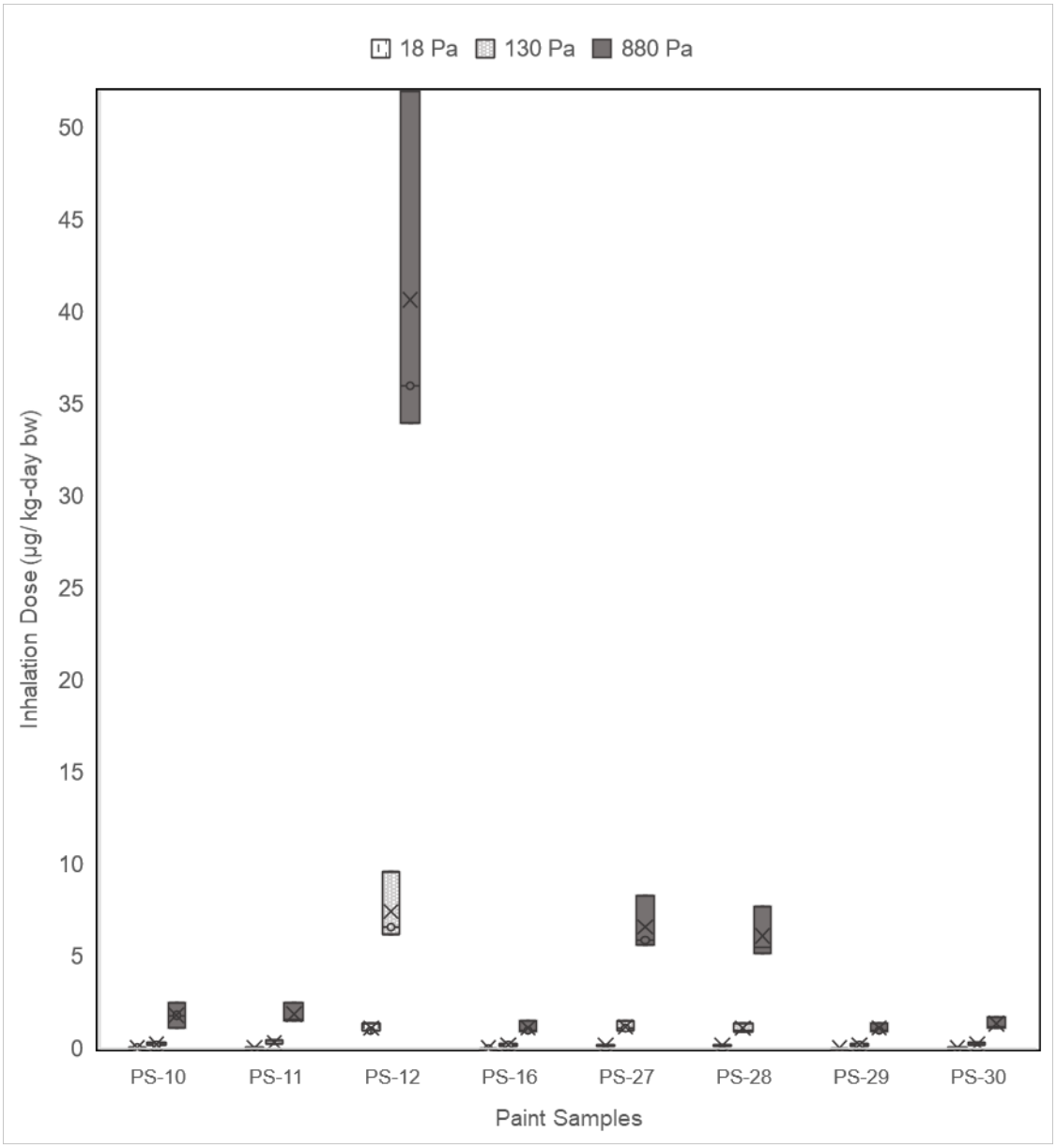

Figure S7. Inhalation doses of 6:2 FTOH resulting from 3 different vapor pressures (18, 130, and 880 Pa) from ConsExpo.

Eq S1. *Total Fluorine Concentration (μmol F g^{-1})*

$$\Sigma[F] = (Area\ total\ - Area\ IS)\ x\ \frac{\left[IS\ \left(\frac{mol}{L}\right)\right] x\ \#\ F\ atoms}{Area\ IS}\ x\ DF\ x\ \frac{L}{g\ of\ Paint} = \frac{\mu mol\ F}{g\ Paint}$$

Eq S2. *Conversion of Dry FTOH Concentration to Account for Drying. An average loss of 52 g for every 100 g of liquid paint was taken from Figure S1.*

$$\frac{\mu g\ FTOH}{g\ dry\ paint}\ x\ \frac{52\ g\ dry\ paint}{100\ g\ liquid\ paint} = \frac{\mu g\ FTOH}{g\ liquid\ paint\ _{(compensating\ for\ drying)}}$$

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