

1 **SUPPORTING INFORMATION**

2 **External Liquid Calibration Method for Iodide Chemical Ionization Mass**
3 **Spectrometry Enables Quantification of Gas-Phase Per- and Polyfluoroalkyl**
4 **Substances (PFAS) Dynamics in Indoor Air**

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29 Section S1. Safety Considerations

30 Given the known adverse health effects associated with PFAS, proper care must be taken when
31 working with these compounds. In the case of many novel PFAS, there is little to no toxicological
32 information available, further underscoring the need to take caution when working with this
33 chemical class. All popcorn prepared for I-HR-ToF-CIMS sampling was promptly discarded
34 following preparation. Additionally, the microwave used in these experiments is not used to
35 prepare any food intended for human consumption.

36 To minimize risk of exposure, all solutions were created in a fume hood and with vials having a
37 pierceable septa. Gas-tight Hamilton syringes and our closed calibration system (i.e., CAMILS)
38 further limited the probability of contamination and exposure. Lastly, careful consideration was
39 given to the quantities of each compound used for analysis, with prepared concentrations limited
40 to 1000 ng mL⁻¹, and sample volumes limited to 2 mL.

41 Section S2. Instrumental Parameters for I-HR-ToF-CIMS

42 For all calibrations, instrument pressures and voltages were held constant to allow for
43 reproducibility, with setpoints seen in Table S1. Furthermore, the microchannel plate (MCP)
44 detector voltage was adjusted at the beginning of each experiment to provide a single ion signal of
45 2.5 mV·ns to account for detector drift over time. Generally, our I-HR-ToF-CIMS provides a mass
46 resolution of 2,500.

47 **Table S1. I-HR-ToF-CIMS Operating Parameters**

Component	Setpoint	Component	Setpoint
Ion-Molecule Reactor (IMR) Pressure	80.0 mbar	Short Segmented Quadrupole (SSQ) Pressure	2.00 mbar
IMR Temperature	60 °C	RF Ampl. 1	0.147 V

IMR Voltage	0 V	RF1	291000000 Hz
Nozzle	-3.5 V	RF Ampl. 2	3 V
Q1 Entr. Pl.	-2.3 V	RF2	410000000 Hz
Q1 Front	-1.25 V	U+low	645 V
Q1 Back	-1.88 V	U+high	45 V
Lens Skimmer	-4 V	U-low	55 V
Skimmer	3 V	U-high	652 V
Q2 Front	4.6 V	Lens	2900 V
Q2 Back	5.5 V	Drift	3000 V
Skimmer 2	11 V	Refl. Grid	650 V
Reference	34 V	Refl. Backplane	705.299 V
Ion-Lens 2	135 V	Hardmirror	0 V
Delf. Flange	49 V	Post Acc	2900 V
Deflector	52 V	MCP	2290-2360 V [†]

48 [†]Adjusted daily to maintain a single ion signal of 2.5 mV.ns.

49 Section S3. Standard Preparation

50 Standards of neat 1H,1H,2H,2H-Perfluoro-1-hexanol (4:2 FTOH, >97.0%) and 1H,1H,2H,2H-
 51 Perfluoro-1-octanol (6:2 FTOH, >98.0%) were purchased from TSI, Inc. Neat 1H,1H,2H,2H-
 52 Perfluoro-1-decanol (8:2 FTOH, 97%) and a 50- $\mu\text{g mL}^{-1}$ standard of 1H,1H,2H,2H-Perfluoro-1-
 53 dodecanol (10:2 FTOH, 98.4%) in methanol were purchased from Sigma-Aldrich and Cambridge
 54 Isotope Laboratories, respectively.

55 For PFAA calibrations, 100- $\mu\text{g mL}^{-1}$ standards of perfluoro-n-octanoic acid (PFOA, 100.0%)
 56 and perfluoro-n-butanoic acid (PFBA, 100.0%) in methanol were purchased from AccuStandard,
 57 Inc. A 50- $\mu\text{g mL}^{-1}$ standard of hexafluoropropylene oxide-dimer acid (HFPO-DA, GenX, >98%)
 58 in methanol was purchased from Wellington Laboratories.

59 For the additional compounds tested, a 50- $\mu\text{g mL}^{-1}$ standard of N-ethyl-
 60 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluorooctane-1-sulfonamide (N-EtFOSA, 100%) was
 61 purchased from Wellington Laboratories. Neat standards of 1H,1H,10H,10H-Perfluoro-1,10-
 62 decanediol (1:8:1 FTdiOH, 96%) and 2H-Perfluoro-5-methyl-3,6-dioxanonane (E2, 97%) were
 63 purchased from Synquest Laboratories and VWR, respectively.

64 Nominal standards of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 1:8:1 FtdiOH and E2 were prepared at
 65 50 $\mu\text{g mL}^{-1}$ in Optima LC-MS Grade Methanol (Thermo Scientific). These standards, along with
 66 the 10:2 FTOH, PFOA, PFBA, HFPO-DA, and N-EtFOSA standards were then diluted to 100 and
 67 1000 ng mL^{-1} in HPLC grade ethyl acetate (Sigma-Aldrich) using volumetric glassware and gas-
 68 tight Hamilton syringes. All standards were prepared in triplicate immediately prior to calibration
 69 and transferred to amber glass screw top vials (2 mL vial, PTFE caps, silicone septa; Agilent
 70 Technologies).

71 Section S4. Calculation of Mixing Ratios in pptv and Sensitivity Determination

72 After each injection, a well-defined peak in the time-series for the associated m/Q was observed,
 73 listed in Table S2. Mass errors are also reported for each compound. Though deprotonated PFAAs
 74 were observed and fitted, no calibrations are presented, as linearity was poor and deviations among
 75 replicate injections were high.

76 **Table S2.** Monitored m/Q and Mass Errors for Detected PFAS Compounds

Abbreviation	Formula	m/Q	Mass Error (ΔmDa)
4:2 FTOH / I ⁻	C ₆ H ₅ F ₉ OI ⁻	390.92	0.6
6:2 FTOH / I ⁻	C ₈ H ₅ F ₁₃ OI ⁻	490.92	1.9
8:2 FTOH / I ⁻	C ₁₀ H ₅ F ₁₇ OI ⁻	590.91	1.2
10:2 FTOH / I ⁻	C ₁₂ H ₅ F ₂₁ OI ⁻	690.91	2.0

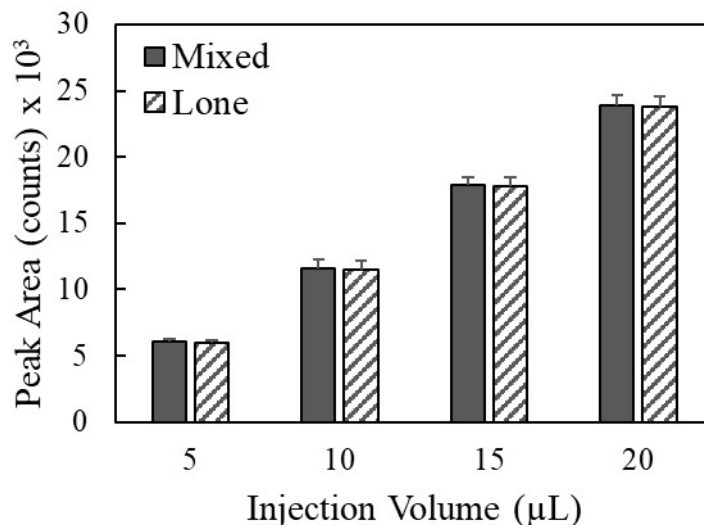
PFBA / I ⁻	C ₄ HF ₇ O ₂ I ⁻	340.89	2.4
PFBA ⁻	C ₄ F ₇ O ₂ ⁻	212.98	3.9
PFOA / I ⁻	C ₈ HF ₁₅ O ₂ I ⁻	540.88	0.4
PFOA ⁻	C ₈ F ₁₅ O ₂ ⁻	412.97	4.1
HFPO-DA / I ⁻	C ₆ HF ₁₁ O ₃ I ⁻	456.88	1.4
HFPO-DA ⁻	C ₆ F ₁₁ O ₃ ⁻	328.97	4.8
N-EtFOSA / I ⁻	C ₁₀ H ₆ F ₁₇ NO ₂ SI ⁻	653.89	7.9
1:8:1 FtdiOH / I ⁻	C ₁₀ H ₆ F ₁₆ O ₂ I ⁻	588.92	2.4
E2 / I ⁻	C ₈ HF ₁₇ O ₂ I ⁻	578.88	0.4

77

78 The average count rate for each injection was determined by integrating the desorption peak and
79 dividing the resulting area by the peak width in seconds. The volume of air sampled during each
80 injection was calculated as the product of the inlet flow rate and the peak width in seconds. The
81 moles of each PFAS analyte were then calculated from the injection volume and concentration,
82 and the ideal gas law allowed for conversion of volume of air to moles of air. Molar mixing ratios
83 of PFAS to air allowed for determination of concentrations in pptv.

84 **Section S5. Ionization Efficiency with Mixed Standard Injections**

85 To evaluate whether significant competition for ionization occurs in the presence of multiple
86 analytes, two calibrations were performed for 6:2 FTOH. The first was performed using a solution
87 of mixed 4:2, 6:2, 8:2 and 10:2 FTOH at 500 ng mL⁻¹, while the second was performed using 500
88 ng mL⁻¹ of only 6:2 FTOH. As seen in Figure S1, there was no significant reduction in peak area
89 resulting from a mixed standard injection.



90

91 **Figure S1.** Peak areas for 500 ng mL⁻¹ injections of 6:2 FTOH in a mixed standard and injections
 92 of 500 ng mL⁻¹ 6:2 FTOH alone.

93 **Section S6. Determination of Optimal Calibration Conditions**

94 To determine the optimal conditions for calibration, solutions of 6:2 FTOH were prepared
 95 individually in methanol, acetonitrile, and ethyl acetate, and sensitivities determined for each under
 96 humidified (50% relative humidity, RH) and dry (<1% RH) conditions (Table S3).

97 **Table S3.** Relative sensitivities of 6:2 FTOH for varying solvents and humidity levels.

Solvent	Relative Sensitivity [†] (%)	
	Humidified Air (50% RH)	Dry Air (<1% RH)
Acetonitrile	26	49
Methanol	42	70
Ethyl Acetate	58	100

98 [†]All sensitivities normalized relative to that of ethyl acetate as a solvent with dry air conditions.

99 As evidenced in Table S3, solutions prepared in ethyl acetate using dry air as a carrier gas
 100 provided the highest sensitivity. However, to better approximate typical indoor conditions for air
 101 sampling, all calibrations were performed at 50% RH, as the typical RH in our laboratory is 47-

102 53%. Given the strong effect of RH on instrument sensitivity, it is critical that the conditions used
103 during the calibration match ambient conditions during sampling to ensure an accurate result.

104 **Section S7. Extractive GC-MS Analysis of FTOHs**

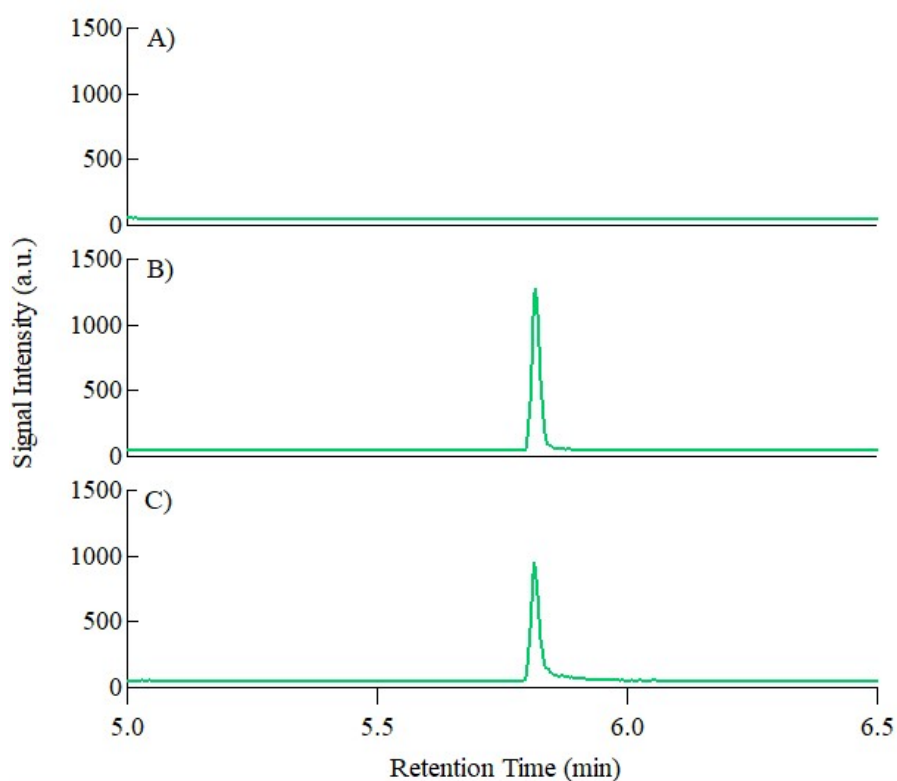
105 **Section S7.1. Extractive GC-MS Procedures**

106 The rain jacket used for the I-HR-ToF-CIMS experiments was extracted and analyzed following
107 a modified version of the protocol developed by Eichler et al.¹ for cloth strips and clothing. Briefly,
108 10 cm² of jacket material were extracted 3 times using 3 mL of a 3:1 (v/v) hexane/methanol
109 mixture. Extracts were filtered with nylon syringe filters and dried to a final volume of 300 μ L.
110 For popcorn bag analysis, three unpopped microwave popcorn bags of the same brand and type
111 used for the I-HR-ToF-CIMS experiments were also extracted following this protocol, with a few
112 exceptions, which are detailed herein. Each bag was cut open at the top and the kernels and grease
113 were poured out and disposed of. The bags were then opened completely by tearing them open
114 along the center and bottom seams. Any remaining grease was removed by repeated wiping of the
115 interior bag surface with Kimwipes. The interior bag surface was considered clean once the
116 Kimwipes came away with no yellow coloration. A 10 cm² piece (~110 mg) was cut from each of
117 the three bags using scissors cleaned with methanol and used for extraction. The material was
118 extracted twice by sonication in 4 mL of methanol, followed by clean-up of the combined extract
119 using approximately 20 mg of ENVI-Carb (SupelcleanTM ENVI-CarbTM SPE Bulk Packing,
120 Supelco, Bellefonte, PA). After centrifugation and evaporation to ~5 mL under a gentle stream of
121 nitrogen, samples were filtered with methanol-rinsed nylon syringe filters (13 mm diameter, 0.22-
122 μ m pore size; VWR, Radnor, PA). Evaporation resumed until the three samples reached a final
123 volume of 500 μ L, and 300 μ L aliquots were transferred to polypropylene autosampler vials (300
124 μ L, Thermo Scientific, Fisher Scientific, Pittsburgh, PA) for analysis.

125 The samples were analyzed for eight volatile PFAS analytes using gas chromatography-mass
126 spectrometry (GC/MS). Details of the GC/MS method can be found in Eichler et al.¹ Peak
127 identification was performed via Agilent Enhanced ChemStation (Version F.01.03.2357) software
128 to confirm the presence of 6:2 FTOH in the microwave popcorn bags and of 8:2 and 10:2 FTOH
129 in the rain jacket.

130 Section S7.2. Extractive GC-MS Results

131 To further verify that the signals detected at m/Q 490.92, 590.91, and 690.91 using the I-HR-
132 ToF-CIMS were, in fact, 6:2, 8:2, and 10:2 FTOH, extraction of the rain jacket and microwave
133 popcorn bags for analysis by GC/MS was performed.

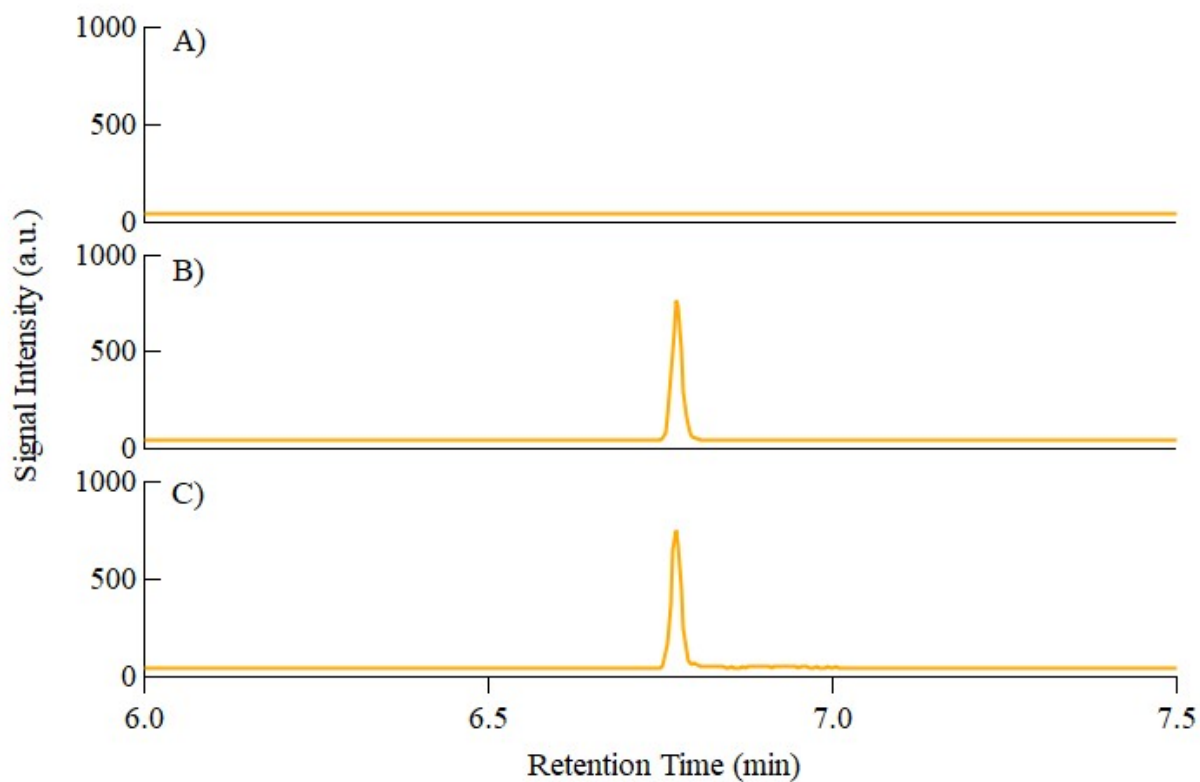


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135 **Figure S2.** EICs for 6:2 FTOH (m/Q 344; RT=5.8 min) in a method blank sample (Panel A), an
136 extracted popcorn bag sample (Panel B), and an authentic standard of 6:2 FTOH (Panel C).

137 As shown in Figure S2, the presence of 6:2 FTOH in the microwave popcorn bags was confirmed
138 by the detection of m/Q 344 in the bag extract at a retention time of approximately 5.8 minutes.

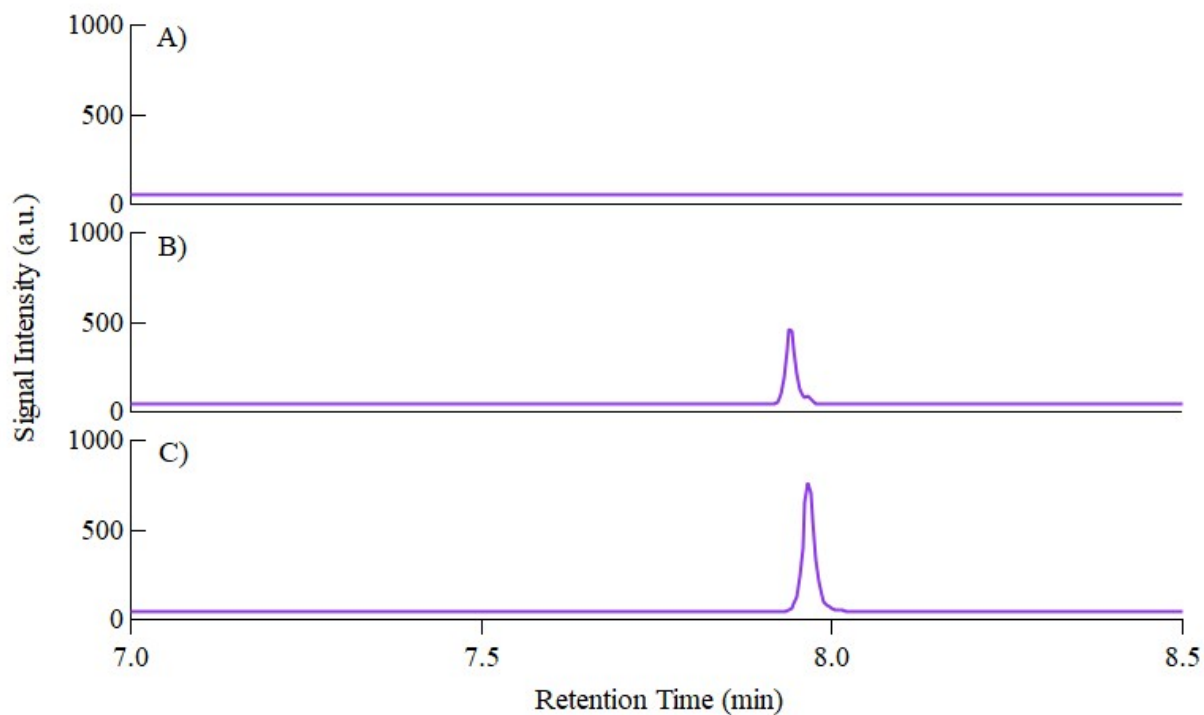
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142 **Figure S3.** EICs for 8:2 FTOH (m/Q 405; RT=6.7 min) in a method blank sample (Panel A), an
143 extracted rain jacket sample (Panel B), and an authentic standard of 8:2 FTOH (Panel C).



144

145 **Figure S4.** EICs for 10:2 FTOH (m/Q 505; RT=7.9 min) in a method blank sample (Panel A), an
146 extracted rain jacket sample (Panel B), and an authentic standard of 10:2 FTOH (Panel C).

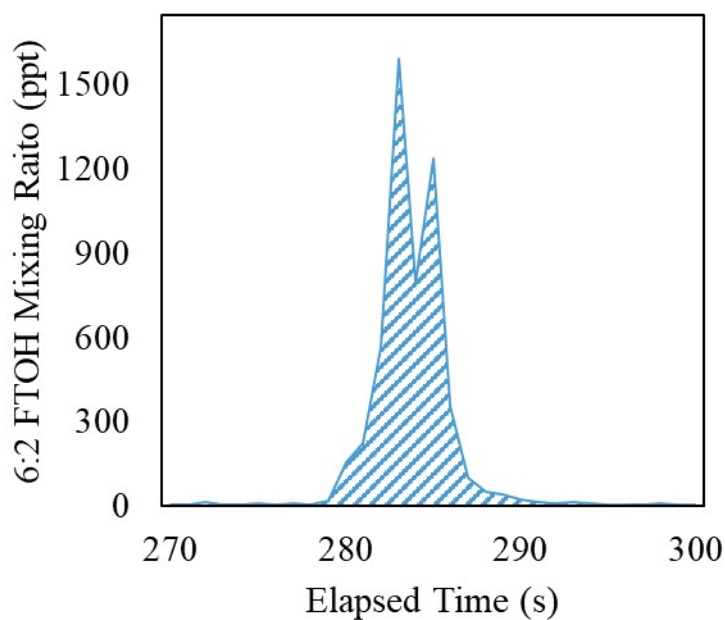
147 As shown in Figures S3 and S4, the presence of 8:2 and 10:2 FTOH in the rain jacket were
148 confirmed by the detection of m/Q 405 and 505 in the jacket extract at retention times of
149 approximately 6.7 and 7.9 minutes, respectively. We acknowledge that there is an apparent
150 retention time shift between the 10:2 FTOH peak in the jacket extract (Figure S4, Panel B)
151 compared to that in the authentic standard (Figure S4, Panel C). We hypothesize that this is due to
152 a matrix effect caused by the use of hexane in combination with methanol for the extraction of the
153 jacket material, and that this effect is seen for 10:2 FTOH but not for 8:2 FTOH due to the
154 comparatively higher octanol-water partition coefficient of 10:2 FTOH.¹

155 **Section S8. The Effect of Integration Time vs Averaging Time**

156 The authors note that the determined sensitivity is not dependent on integration time, so long as
157 background count rates are much lower than the injection count rate and integration time is held
158 constant across injections. If, for example, the integration time were doubled for each peak, the
159 average count rate would then be half of the previous value. At the same time, the volume of carrier
160 gas would double, leading to a mixing ratio that is half of the previous value. As such, there would
161 be no change to the measured sensitivity.

162 Alternatively, when making quantitative measurements of a sample, the frequency of averaging
163 is an important factor in determination of the limits of detection and quantification. In essence, a
164 longer averaging time allows for greater certainty that the measured signal is truly distinguishable
165 from noise, translating into lower limits of detection and quantification with longer averaging
166 times. Generally, 120-s averaging allows for ~90% reduction in LOD and LOQ as compared to
167 3-s averaging. In the event of a highly dynamic system, shorter averaging times may be necessary
168 to capture the variability in concentration, albeit with increased LOD/LOQ.

169 Section S9. Further Popcorn Experiments



170

171 **Figure S5.** Signal of 6:2 FTOH from a microwave popcorn bag sampled at ~2 cm from the I-HR-
172 ToF-CIMS inlet immediately after popping. The bag was held in front of the IMR inlet and lightly
173 squeezed, allowing the contents to escape from the ventilation slit in the top of the bag. Performed
174 with 1-s averaging. $t=0$ represents the microwave start time.

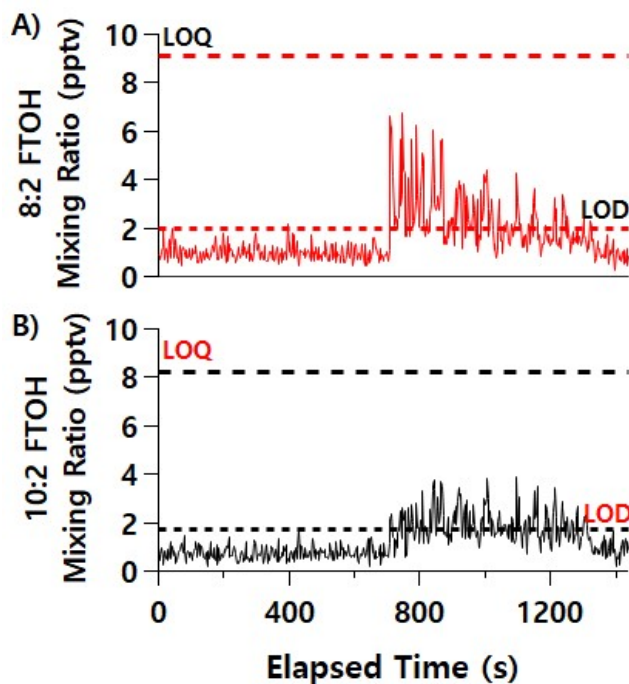
175 For each brand, the popcorn bag was immediately removed from the microwave and squeezed
176 approximately 2 cm from I-HR-ToF-CIMS inlet. Only the same brand that produced observable
177 6:2 FTOH when cooking showed 6:2 FTOH when squeezed in front of the inlet. No other FTOHs
178 or PFAAs were detected from that brand, nor were any target PFAS signals observed for the other
179 brands when squeezed directly in front of the inlet.

180 Notably, the concentrations observed in Figure S5 are roughly 2 orders of magnitude greater
181 than those measured at 2 m from the closed microwave, with instantaneous mixing ratios of 6:2
182 FTOH reaching as high as 1590 pptv when the bag was squeezed (compared to peak 6:2 FTOH
183 concentrations of 31.6 ± 4.5 pptv as sampled at 2 m). When integrated, a single squeeze at 2 cm
184 from the inlet produced a peak corresponding to 2.9 ng of 6:2 FTOH emitted (shaded area in Figure
185 S5). Compared to prior studies with integrated PUF-XAD sampling,² we did not sample the
186 headspace for an extended period of time.

187 **Section S10. Non-Quantitative Detection of FTOH Concentrations Influenced by Rain** 188 **Jacket Emissions**

189 Figure S6 shows concentrations of 8:2 and 10:2 FTOH measured when a person entered the
190 laboratory while wearing a commercially-available rain jacket and approached the I-HR-ToF-
191 CIMS. The instrument was first allowed to sample laboratory air while a researcher wore the rain
192 jacket in a separate room. After ~10 minutes to allow the rain jacket to equilibrate with body

193 temperature, the researcher then entered the laboratory and approached the I-HR-ToF-CIMS and
194 stood ~1 m from the instrument inlet for ~10 minutes before leaving the laboratory.
195



196

197 **Figure S6.** Time series of 8:2 FTOH (Panel A) and 10:2 FTOH (Panel B) concentrations as
198 measured by I-HR-ToF-CIMS. Laboratory air was sampled prior to and as researcher wearing a
199 rain jacket approached and stood ~1m from the instrument at $t \approx 700$ s. For 8:2 FTOH, 3-s LOD
200 and LOQ are indicated with red dashed lines at 2.0 and 9.1 pptv, respectively. For 10:2 FTOH, 3-
201 s LOD and LOQ are indicated with black dashed lines at 1.7 and 8.3 pptv, respectively.

202 As shown in Figure S6, the concentrations of 8:2 and 10:2 FTOH generated from wearing a
203 single rain-jacket caused concentrations to rise above LOD values, but concentrations remained
204 below the LOQ for both compounds. In this case, detection of these two FTOHs was possible, but
205 quantification was not. Subsequently, the same rain jacket was sampled much closer to the inlet to
206 reduce dilution and provide a quantitative demonstration of source detection, as shown in Figure
207 4 of the main text.

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