

A Method to Measure Total Gaseous Fluorine

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KEYWORDS Fluorine, gas, total elemental measurement, in situ, mass balance, per- and polyfluoroalkyl substances (PFAS), greenhouse gas, fluorosurfactant

SYNOPSIS New method allows first characterization of gaseous total fluorine and shows unknown fluorine in fluorosurfactant headspace and ambient samples

1 **ABSTRACT:** Total fluorine (TF) analysis is a powerful tool for the characterization of organofluorine
2 contaminants in the environment. Organofluorine compounds are known primarily with respect to the
3 notorious subgroup of poly- and perfluoroalkyl substances (PFAS) and as potent greenhouse gases that
4 can impact climate. The use of targeted methods for every organofluorine compound in the environment
5 is not feasible. While methods are available for TF analysis of condensed phase samples, no technique
6 exists for gas phase TF measurements (TF_g). Herein we demonstrate an in-situ instrumental method for
7 TF_g via platinum catalyzed thermolysis at 1000 °C in the presence of propane. TF_g is fully converted into
8 HF and subsequently quantified by existing techniques for F⁻. The method was validated using nine orga-
9 nofluorine compounds with differing functional groups. We characterized TF_g and compared to common
10 speciated measurements in the headspace of four commercial fluorosurfactants and outdoor air. Most TF_g
11 (65%-99.8%) in the fluorosurfactant headspace was unknown. In outdoor air, >50% of TF_g was unknown.
12 These high quantities of unknown organofluorine indicate a measurement gap in the gas phase, which
13 could have important implications for atmospheric sources and burdens of PFAS and fluorinated green-
14 house gases.

15 Introduction

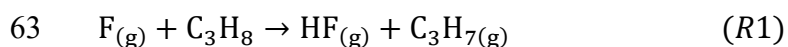
16 Many organic fluorine (OF) compounds are known for their general environmental persistence, with
17 the recent spotlight on a subclass known as per- and polyfluoroalkyl substances (PFAS).¹ As the number
18 of discovered PFAS compounds continue to increase, establishing a total fluorine budget has proven both
19 more useful and feasible to accomplish compared to developing targeted methodologies for over 4700
20 known PFAS chemicals in the environment.² There are a number of existing methods to measure total
21 fluorine (TF) in aqueous and solid matrices, often with operationally defined fractions³ such as extractable
22 OF (EOF), or adsorbable OF. Generally, these are destructive methods that measure inorganic fluoride (F⁻
23) after sample mineralization. Currently, the most widely utilized method for TF analysis is combustion
24 ion chromatography (CIC),^{4,5} particularly in the context of PFAS analysis.⁶⁻⁸ A major advantage of CIC
25 is its low detection limits and its applicability to both liquid and solid samples. Other less frequently used
26 techniques include continuum source molecular absorption spectroscopy,⁹ ¹⁹F nuclear magnetic reso-
27 nance,¹⁰ and inductively coupled plasma – mass spectrometry.¹¹ While there are drawbacks to each afore-
28 mentioned technique,⁵ they represent an ample selection of analytical tools for TF analysis of solid and
29 aqueous environmental matrices. However, no method currently exists for TF_g measurements. Attempts
30 have been made to circumvent this issue via sampling of particulates¹² and/or gaseous adsorption to pol-
31 yurethane foam and activated charcoal,¹³ followed by extraction and analysis of the resulting condensed
32 phase samples. These sampling techniques are selective by nature, often failing to capture the most vola-
33 tile OF fraction (e.g., CFCs). A true TF_g measurement currently does not exist with modern analytical
34 sampling techniques. Considering that targeted measurements of OF compounds are often for those that
35 are volatile,¹⁴ establishing a TF_g budget could provide crucial insight into overlooked fluorinated gases.

36 In the context of PFAS, the importance of TF mass balance in the condensed phase has been repeat-
37 edly demonstrated. Recent publications established fluorine mass balance for a variety of matrices (e.g.,
38 surface water, sediment, fish, sampled atmospheric particle, aqueous film forming foam) and found that
39 targeted PFAS analysis (between 19-50 analyzed species) typically account for a small portion of EOF

40 (<1%-16%),^{6,12,13,15} while cases where targeted PFAS accounts for 100% of EOF are rarely observed.⁷
41 During spill events, quantifying TF_g may be of an even higher importance to TF in the condensed phase,
42 given that inhalation is the most rapid human exposure pathway.¹⁶

43 Another potential application of a TF_g measurement is for halogenated greenhouse gases
44 (HG HGs). The total radiative forcing (RF) from greenhouse gases is estimated from the sum contributions
45 of CO₂, CH₄, N₂O, and HG HGs. Despite the low atmospheric abundance of HG HGs, they contribute
46 significantly (18% of total RF)¹⁷ to the total RF due to their high radiative efficiencies. Currently, the RF
47 of HG HGs is determined from the sum contributions of monitored long-lived gases, where the atmos-
48 pheric abundance of each compound must be periodically measured.¹⁷ In addition, some HG HGs are rel-
49 atively short-lived and thus are not well mixed in the atmosphere, making their RF estimations more
50 challenging. Ambient atmospheric TF_g could be used to constrain the completeness of existing HG HG
51 measurements, lowering the uncertainty. In addition, the existence of any unmonitored or unknown spe-
52 cies can be uncovered. More importantly, quantifying the number of F-containing bonds that are directly
53 responsible for greenhouse gas effects of atmospheric halogenated species¹⁸ may be a fundamentally ef-
54 fective approach for climate policy compared to monitoring individual species to estimate RF.

55 Methods for continuous, in-situ measurement of total elements in air have been recently developed
56 (e.g., total carbon, total reactive nitrogen, and total gaseous chlorine (TCl_g))¹⁹⁻²⁴ based on the principle of
57 passing air continuously over a heated metal catalyst to convert all chemicals containing that element into
58 a molecule that can be easily measured. For TCl_g, chlorine-containing gases are catalytically thermolyzed
59 using platinum (Pt) at 825 °C into HCl in the presence of propane. Following the same approach, the
60 development of a method for the in-situ and continuous measurement of TF_g is described in this work.
61 Similar to TCl_g thermolysis, we postulate that F atoms are formed during TF_g thermolysis, which form
62 HF upon H abstraction from propane (R1) or any of its thermolysis products.



64 The main objectives of this work are: (i) method validation of the TF_g approach, and the application of
65 the new method to measure (ii) the headspace of commercial fluorosurfactants and (iii) outdoor air.

66 **Materials and Methods**

67 *Chemicals*

68 Chemicals for method validation (i.e., conversion efficiency) were purchased from Synquest (FL,
69 USA): 1H,1H,2H-perfluoro-1-octene (97%), perfluorooctyl iodide (98%), pentafluorophenol (99%), 4-
70 chlorobenzo trifluoride (98%), methyl nonafluorobutyl ether (99%), 2-(trifluoromethyl)-3-ethoxydode-
71 cafluorohexane (99%), perfluoro(2-methyl)-3-pentanone (98%), 1,1,1,3,3,3-hexafluoro-2-propanol
72 (99%), pentafluoropropionic acid (PFPrA, 99%). Nitrogen (grade 4.8) and propane (C₃H₈, 12.7% in ni-
73 trogen, v/v) were purchased from Linde (ON, Canada). Ultrapure Milli-Q water (18.2 MΩ·cm) was ob-
74 tained from an in-house system (Direct 8; EMD Millipore, ON, Canada). A custom made zero air gener-
75 ator was used for method validation and fluorosurfactant experiments.²⁵

76 *Total Fluorine Instrumentation*

77 The TF_g instrumentation configuration is similar to that previously described for TCl_g.¹⁹ A detailed
78 description is provided in the supporting information (SI; Section S1). Briefly, the main components of
79 the TF_g instrument consists of a Pt catalyst mesh, a quartz glass flow tube, and a split-tube furnace. A
80 constant flow of 2 L min⁻¹ of sample gas is combined with 50 mL min⁻¹ propane and introduced to the
81 furnace to quantitatively convert TF_g to HF, which is subsequently collected in water using a perfluoroal-
82 koxy alkane (PFA) impinger. Quantification of the impinger solution was conducted using an ion selective
83 electrode (ISE) for F⁻ or an ion chromatograph coupled to a conductivity detector (IC-CD) for F⁻ and Cl⁻
84 (Section S2). All tubing and fittings for handling gas flow were made of PFA. Gas flows were measured
85 using a DryCal Definer 220 (Mesa Labs, CO, USA). The optimal furnace temperature for TF_g conversion
86 was determined through the measurement of the conversion efficiency of methyl nonafluorobutyl ether at
87 temperatures between 850–1000 °C.

89 Method validation used a similar approach as previously described for TCI_g^{19} (setup shown in
90 Figure S1). Permeation devices (PDs) of 9 OF compounds were prepared by pipetting approximately 200
91 μL of each compound into 50 mm PFA tubes (3 mm i.d., 1 mm wall thickness) sealed at either one or both
92 ends with porous polytetrafluoroethylene (PTFE) (3.17 mm o.d.). In the first case, the other end was
93 sealed by annealing. At a constant temperature, PDs emit a consistent mass of the contained compound
94 as a gas over time. The PDs were placed within a temperature-controlled aluminum block.²⁶ Mass emis-
95 sion rates of each PD were determined gravimetrically with at least 3 measurements on an Accuris (ON,
96 Canada) analytical balance (± 0.0001 g) over at least 3 days, with least squares regression $R^2 > 0.99$.
97 Emission rate uncertainties were determined from one standard deviation of the regression slope. A stable
98 carrier gas flow of dry N_2 set by a critical orifice was used to deliver compounds for validation experi-
99 ments. Blanks were obtained by introducing zero air only. ISE was used to quantify the impinger solution.
100 Percent conversion efficiency (CE) was calculated for each compound as:

$$101 \quad CE (\%) = \frac{\text{Measured } \text{TF}_g}{\text{Expected } \text{TF}_g} \times 100\% \quad (1)$$

102 where the expected TF_g was calculated from the PD emission rate.

103 *Commercial Fluorosurfactants Headspace*

104 The headspace of four fluorosurfactants (Masurf FS-1520, Zonyl FSE, Zonyl FS-62, FC-203FC
105 AFFF) was sampled using the TF_g instrument, ORBO Amberlite 609 XAD-2 sorbent (400/200 mg; Mil-
106 lipore Sigma, ON, Canada) for neutral volatile PFAS, and an impinger filled with 15-20 mL Milli-Q water
107 for perfluorinated alkyl acids (PFAAs) (Figure S3). Fluoride from the TF_g instrument was quantified using
108 ISE. The aqueous impinger samples were quantified using UPLC-MS/MS, while XADs extracts were
109 quantified using both GC-MS and UPLC-MS/MS. Detailed descriptions of experimental setup, chemicals,
110 instrumentation, analytical procedures, and quality control are in Section S3 of the SI.

111 *Outdoor Air Measurement*

112 Outdoor air was sampled by impinger collection at 30-minute intervals from 09:30 to 17:30 eastern
113 daylight time on 20 February 2023 from a rooftop at York University, Toronto, Canada (43.7738° N,
114 79.5071° W, 220 m above sea level). A polyethersulfone filter (0.45 µm, Foxx Life Sciences, NH, USA)
115 was placed at the inlet to remove particulates. Impinger solutions were quantified using IC-CD.

116 **Results and Discussion**

117 *Method Validation*

118 Methyl nonafluorobutyl ether reached complete conversion at temperatures >950 °C at 2 L min⁻¹
119 sampling rate, with a maximum of 102.5 ± 4.3% at 1000 °C (Figure S5). Therefore, subsequent validation
120 experiments and measurements were made with this optimal furnace temperature of 1000 °C.

121 Complete TF_g conversion (96% – 103%) of 8 compounds with a range of functional groups was
122 achieved (Figure S6). PFPrA had an average of 85% conversion from three measurements of 71%, 81%,
123 and 103% taken in chronological order, suggesting that the initially low conversion was caused by sorp-
124 tion losses of the acid on the unheated quartz surface at the front end of the flow tube, and that complete
125 conversion was eventually achieved with a desorption lag time, which is a commonly observed in the
126 sampling of strong acids.^{27,28} A similar effect was noted during previous TCl_g validation measurements
127 for HCl.¹⁹

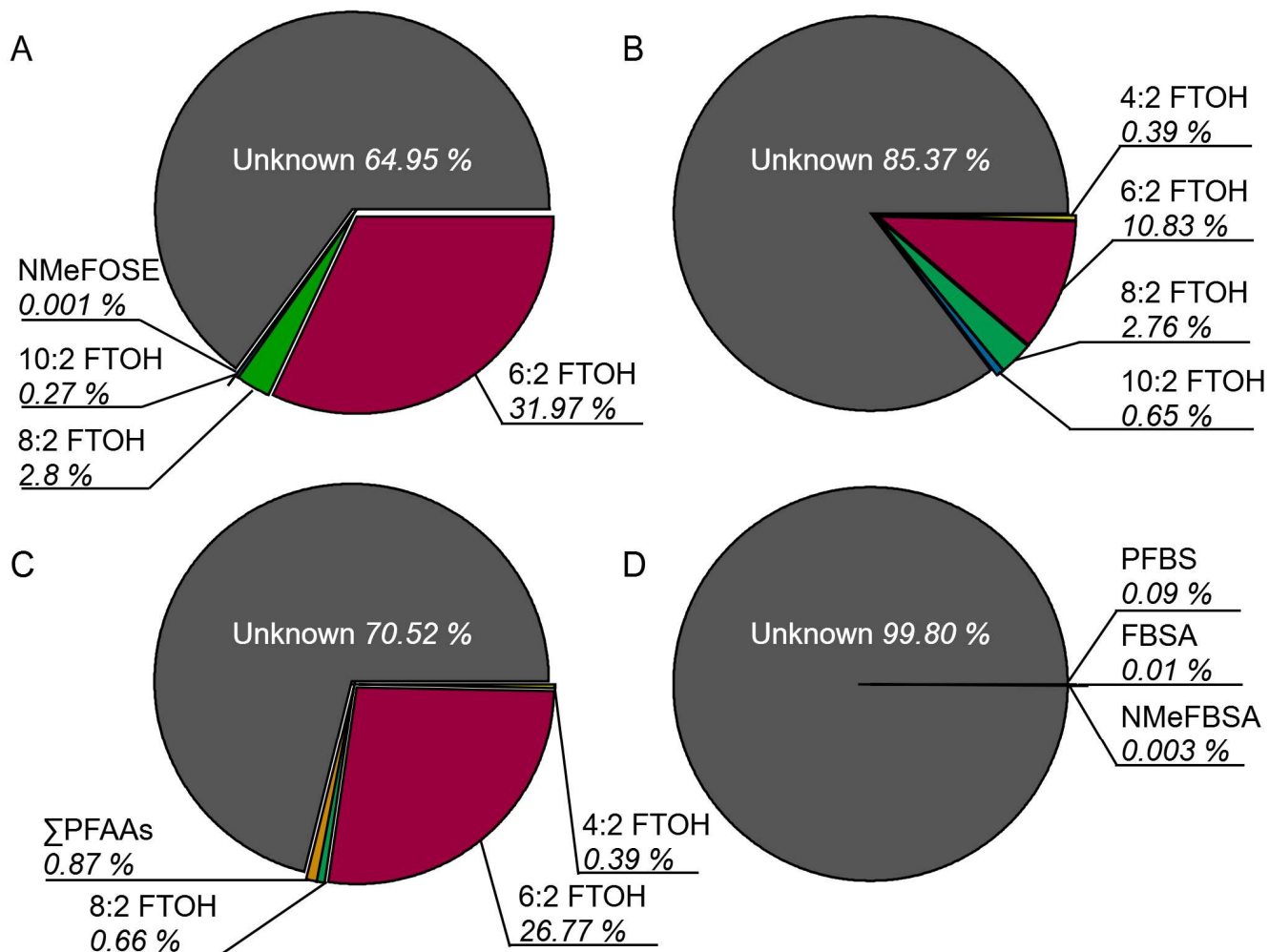
128 This method is the first to demonstrate the capability of TF_g analysis. Quantitative conversion of
129 TF_g to HF and the continuous flow design enables its coupling with any HF detection method, with a wide
130 range of potential applications. Two applications are described in the sections that follow.

131 *Commercial Fluorosurfactant Headspace Measurement*

132 We tested the headspace of four fluorosurfactants for TF_g along with speciated PFAS that are most
133 commonly measured in the gas phase.²⁹ This allows us to assess the potential fraction of gaseous PFAS

134 not captured by typical methods. Headspace TF_g mixing ratios of all analyzed fluorosurfactants were >1.5
135 ppmv F (Figure S7). Measured mixing ratios of individual PFAS species can be found in Table S6.

136 As anticipated, the largest headspace TF_g fraction for all four analyzed fluorosurfactants is un-
137 known (Figure 1; 65%-99.8%). Many volatile chemicals are known precursors to fluorosurfactants (e.g.,
138 fluorotelomer iodides)³⁰ that may be present as residuals in commercial products and are not typically
139 included in targeted methods. Among our targeted measurements, 6:2 FTOH was the most abundant spe-
140 cies detected for all fluorosurfactants (11-32%) except AFFF, followed by 8:2 FTOH (0.7-2.8%) and 10:2
141 or 4:2 FTOH (0.3-0.7%). This is consistent with findings from Riedel et al.,³¹ where the relative FTOH
142 headspace abundances in a suite of FS brand fluorosurfactants displayed the same pattern. Riedel et al.
143 also found very little FTOH in Arctic 3 AFFF. We detected select perfluorosulfonamide compounds from
144 Masurf FS-1520 and AFFF in miniscule proportions (0.001-0.003%). A suite of PFAAs were detected
145 from Zonyl FS-62 comprising 0.9% of the headspace TF_g , with PFHxA in the greatest abundance (Figure
146 S8). This is consistent with the known composition of FS-62 (Table S7), which consists of 13-21%
147 fluorotelomer sulfonic acids along with 1-3% acetic acid in water, thus facilitating gas phase partitioning
148 of PFAAs through low aqueous pH.



149

150 **Figure 1.** TF_g (grey) and speciated (coloured) compositions measured in the headspace of four commercial fluorosurfactants: (a) Masurf FS-1520, (b) Zonyl FSE, (c) Zonyl FS-62, and (d) AFFF (FC-203FC).
 151
 152 Fractions represent headspace concentrations normalized to mixing ratios of F.

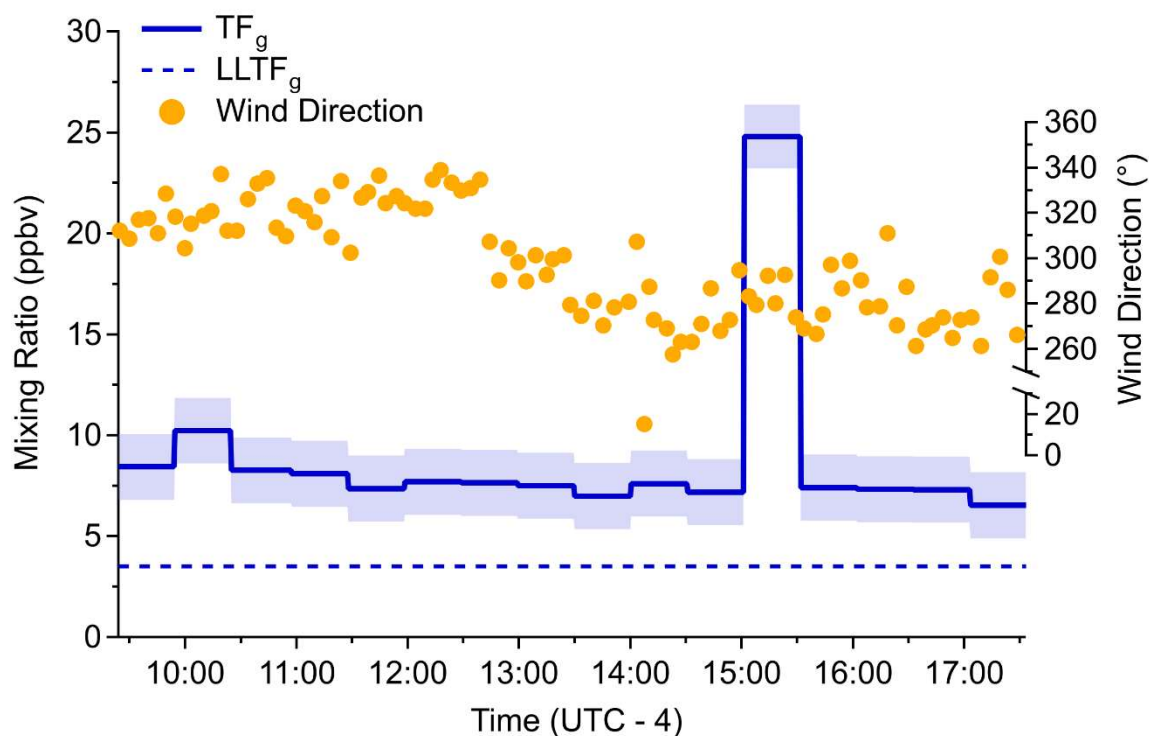
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154 We noted during our experiments that measured headspace TF_g of Masurf FS-1520 decreased by
 155 an order of magnitude after 6 months of storage. This may be due to evaporative loss or permeation loss
 156 of volatile PFAS through polypropylene container walls. Therefore, we only qualitatively consider differ-
 157 ences in TF_g mixing ratios between each surfactant since our observed levels could be considered a lower
 158 limit of TF_g. Zonyl FS-62 appeared to produce a greater headspace emission of TF_g (10.2 ppmv F) com-
 159 pared to the other three surfactants, which all had similar emissions (1.5-2.4 ppmv F).

160 The TF_g composition of AFFF was almost entirely unknown (99.8%). This result contrasts previ-
161 ous findings from Roth et al.,³² where PFOA was detected in very high concentrations in AFFF (C306-
162 MS-C) headspace (>10000 µg/m³ or >8 ppmv F) along with other analytes such as PFHxA (100-200
163 µg/m³) and 6:2 FTOH (40 µg/m³) that were also targeted, but not observed in our study. Large variabilities
164 in AFFF composition have been observed between different manufacturers and production times,³³ so
165 agreement is not necessarily expected. In addition, Roth et al. agitated their AFFF sample, which would
166 aid the headspace release of PFAS compounds, especially the PFAA surfactants. Unknown gas phase
167 PFAS emissions is concerning as the historical use and environmental release of AFFF in North America
168 is known to be extensive.^{34,35} Much work had been done previously to characterize PFAS in condensed
169 phase environmental media (e.g., groundwater) from historical AFFF release sites. These studies typically
170 find that over 50% of any analyzed TF fraction (e.g., EOF, total oxidizable precursor) is unaccounted
171 for.^{7,36} Much of the known/unknown precursors have been estimated to act as PFAS contamination sources
172 for decades or centuries through slow biotransformation into PFAAs.^{36,37} These results demonstrate that
173 use of fluorosurfactants could lead to emission of previously unrecognized PFAS into the atmosphere.

174 *Outdoor Air Measurement*

175 The instrument was deployed to analyze outdoor ambient air (Figure 2), alongside the associated
176 TCl_g measurement (Figure S9) to provide a comparison to previous measurements¹⁹ as well as a source
177 of complementary information.



178

179 **Figure 2.** TF_g (blue solid line), $LLTF_g$ (dashed blue line), and wind direction (orange points; 0° is north)
 180 time series from Feb 20, 9:30 AM to 5:30 PM local time. Shaded areas represent measurement standard
 181 deviation in recovered F^- , calculated from IC-CD calibration regression statistics.

182 Background mixing ratios of TF_g and TCl_g should theoretically be representative of long-lived
 183 (LL) GHGs. Therefore, the expected $LLTF_g$ and $LLTCl_g$ background can be calculated using the sum of
 184 the reported mixing ratios of GHGs from the latest reports³⁸ (Table S8). Calculated global backgrounds
 185 of $LLTF_g$ and $LLTCl_g$ were 3.5 and 3.3 ppbv respectively. In comparison, we observed TF_g background
 186 in ambient air more than twice the expected $LLTF_g$, between 6.5 – 8.4 ppbv. In contrast, ambient TCl_g
 187 ranged between 2.1 – 4.3 ppbv, which is in reasonable agreement with the expected $LLTCl_g$ value and
 188 consistent with previous ambient TCl_g measurements.¹⁹ These results suggest that large quantities of fluor-
 189 inated species exist at the sampling location which are also non-chlorinated. These species may be moni-
 190 tored GHG compounds originating from a local point or diffuse regional sources that have not under-
 191 gone full dilution in the atmosphere, or unmonitored gases with F-containing bonds. Note that campus
 192 fume hoods do not act as a point source to the sampling site (Section S6).

193 A TF_g/TCl_g plume was detected from 15:00 – 15:30. Given that the peak was detected for both
194 TF_g and TCl_g, it is possible that the corresponding plume contains compounds with both Cl and F, such
195 as a chlorofluorocarbon (CFC). To ascertain this possibility, the measured Cl:F ratio of 4 can be used for
196 suspect screening. According to the list of monitored LLHGHGs (Table S1), the highest Cl:F ratio is 3,
197 implying the plume was likely comprised of multiple monitored compounds, or different halogenated
198 species altogether. Some potential facilities as point sources were identified (Figure S10) using the wind
199 direction, reported emissions, and potential for PFAS use in their industrial activities. To further investi-
200 gate the chemical makeup of the plume requires additional molecular information and is beyond the scope
201 of the current work.

202 This short measurement campaign demonstrates the utility of TF_g (coupled with TCl_g) measure-
203 ments for monitoring ambient TF_g and that known HGHGs cannot account for observed levels. Further
204 study is necessary to elucidate sources and longer-term temporal variations.²⁴

205 *Implications*

206 The importance of TF analysis for establishing a fluorine mass balance is now widely recog-
207 nized,³⁹ and the method for TF_g analysis presented here serves as the final phase of matter that can now
208 be effectively targeted for TF and is the final piece of the TF puzzle. Measurements of fluorosurfactant
209 headspace and ambient air both show the importance of missing TF_g in the gas phase. Emissions of un-
210 known fluorinated chemicals to the atmosphere could contribute to the global transport of PFAS, as well
211 as impact climate. Further study is necessary to understand the spatial and temporal distribution of TF_g,
212 as well as its speciation, sources, and fate.

213

214 **ASSOCIATED CONTENT**

215 **Supporting Information.** Detailed descriptions and additional information on instrumentation, experi-
216 mental setup, QA/QC, method optimization/validation, environmental sample analysis results

217 This material is available free of charge via the Internet at <http://pubs.acs.org>.

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221 Acknowledgement

222 We acknowledge funding for this work from Environment and Climate Change Canada and Natural Sci-
223 ences and Engineering Research Council. R. Ye acknowledges funding from Ontario Graduate Scholar-
224 ship. We thank Mark Gordon for assistance with plume height and dispersion calculations.

225

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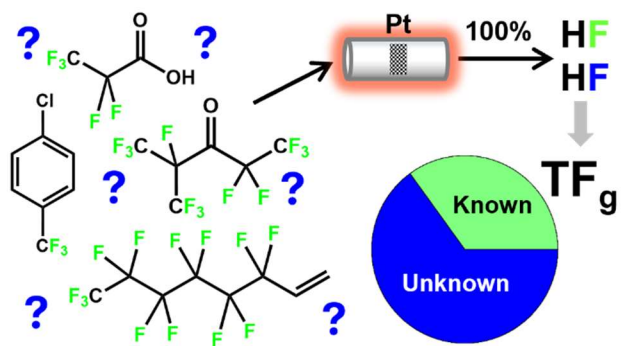
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