Table 1. Target Analyte Acronym, Structure, Molecular Weight, Ions Monitored by PCI- and NCI-MS, and Mean Environmental Concentrations (pg m^{-3}) at Two Sampling Locations for n Samples^b

				Ions Monit	Ions Monitored (m/z) Environmental Concentrations (pg m ⁻³)		
Analyte	Acronym	Structure	Molecular Weight (amu)	PCI	NCI	Toronto (n=4)	Long Point (n=2)
N-methyl perfluorooctane sulfonamidoethanol	NMeFOSE	CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CF ₃ CF ₄ CF ₅ CH ₂ CH ₃ CH ₃	557	558, 540	494, 483, 400	101 (86-123)	35 (34,36)
N-ethyl perfluorooctane sulfonamidoethanol	NEtFOSE	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₃ CF ₂ CF ₃ CF ₂ CF ₃ CH ₂ -CH ₃ CH ₂ -CH ₃	571	572, 554, 540	508, 483, 400	205 (51-393)	76 (68,85)
N-ethyl perfluorooctane sulfonamide	NEtFOSA	CF ₃ CF ₂ CF ₂ CF ₂ CF ₃ CF ₃ NH CH ₂ -CH ₃	527	528	526, 483, 400	14 (n=2)	n.a.
perfluorooctane-1- sulfonyl fluoride	PFOSF	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₃ F	502	^a 503, 419, 169	^a 400, 362, 350	a	a
1-hydroxyethane-2- perfluorobutane		CF ₂ CF ₂ CH ₂ CH ₂ OH	264	265, 227	184, 204	n.d.	n.d.
I-hydroxyethane-2- perfluorohexane	6:2 FTOH	CF ₃ CF ₂ CF ₂ CH ₂ CH ₂ OH	364	365, 327, 393	284, 304, 314	87 (30-196)	29 (41,16)
1-hydroxyethane-2- perfluorooctanol	8:2 FTOH	CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ CH ₂ OH	464	465, 427, 493	384, 404, 414	55 (9-123)	32 (40,25)
1-hydroxyethane-2- perfluorodecanol	10:2 FTOH	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ CH ₂ OH	564	565, 527, 593	484, 504, 514	29 (7-46)	(20,15)
pentadecafluoro-1- octanol (internal standard)	PDFO	CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ OH	400	401, 381	360, 340		

^a Ions were obtained by direct probe mass-spectrometry. PFOSF was not amenable to the GC conditions used and was not monitored in environmental samples by the developed method. ^b The range of environmental concentrations is shown below the mean for both sites. Abbreviations: n.d., not detected; n.a., not applicable. No attempt was made to detect NEtFOSA at Long Point.

degradation. Many such compounds find use in surface treatment of paper and textiles;^{18,19} as surfactants;¹⁹ as insecticides, such as *N*-ethyl perfluorooctane sulfonamide (NEtFOSA; Sulfluramid);^{20,21} and as intermediates in the synthesis of other fluorinated organics.²²

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Synthesis of many higher-molecular-weight fluoroorganics, such as PFOS, proceeds via the intermediate, perfluorooctane-sulfonyl fluoride (PFOSF). Other PFOSF derived products include *N*-methyl perfluorooctane sulfonamidoethanol (NMeFOSE), and *N*-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE), both of which are incorporated as higher-molecular-weight derivatives into surface treatment formulations for paper and textile products to impart oil and water repellency. It is expected that PFOSF, NMeFOSE, NEtFOSE, and NEtFOSA will ultimately degrade to PFOS under environmental or biological conditions, and as a result, they were the focus of the method development presented herein. Although PFOS-based products are voluntarily being phased out by their primary manufacturer because of concerns

about their environmental persistence,²⁴ similar compounds with long perfluorinated tails continue to be produced for comparable applications. Such compounds include fluorotelomer alcohols (FTOHs). FTOHs are primary alcohols, characterized by two nonfluorinated carbons adjacent to the hydroxyl function, and will be referred to herein as 4:2, 6:2, 8:2, and 10:2 FTOH, on the basis of the ratio of perfluorinated to nonfluorinated carbons. The telomerization process used in their manufacture results in only even-numbered carbon chain lengths.²⁵

We report here a quantitative, sensitive, and compound-specific method for the analysis of some fluorinated neutral compounds (Table 1) by gas chromatography/chemical ionization mass spectrometry (GC/CI-MS). The applicability of this method to ambient atmospheric monitoring is described through breakthrough experiments using composite sampling media and through environmental sampling at distinct rural and urban locations.

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EXPERIMENTAL SECTION

Chemicals, Standards, and Sampling Media. HPLC grade methanol (99.93%), HPLC grade ethyl acetate (99.8%), pentadecafluoro-1-octanol (PDFO, 98%), and PFOSF standard (98%), were purchased from Aldrich Chemical Co. (Milwaukee, WI). NEtFOSA standard (95%) was purchased from Lancaster Synthesis (Pelham,

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