FLUORINATED SURFACTANTS ~ ENVIRONMENTAL & ANALYTICAL CHEMISTRY

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Introduction

Perfluorinated surfactants (FSs) are recalcitrant and persistent chemicals with wide-usage in industrial and consumer applications. Funded by a Toxic Substances Research Initiative (TSRI) grant (Canadian government) our research team has been investigating perfluorinated anionic surfactants and have shown them to be a new class of persistent organic pollutant of concern to Canada. Electrochemical fluorination (ECF) provides a route to a suite of compounds containing a perfluorinated chain with varying functional groups (e.g. carboxylate/sulfonate); these compounds are produced as mixtures of varying chain lengths and branched impurities. The primary chemical driving most of the current intense interest is perfluorooctane sulfonic acid or PFOS, as noted by several recent articles in Nature and related publications.[1,2,3,4] Relatively high concentrations of PFOS,have been observed worldwide in human blood serum as well as biota.[5] Due to these observations of highly contaminated biota, in conjunction with the extreme persistence of these compounds, the major manufacturer of these compounds (e.g. PFOS, perfluorooctanoic acid or PFOA), the 3M Corporation, has announced a cessation in their production.[6] It is important to note that these compounds have been in commercial use for ~50 years, which has resulted in the widespread occurrence of mg/L concentrations of PFOS in human blood.

This talk will specifically present our work on the following:

1. Basic LC/MS/MS methods for FSs analysis;
2. Identification of novel FSs not previously observed in the environment;
3. BCF/BAF values for a suite of perfluorocarboxylate/sulfonates in rainbow trout;
4. An hypothesis for the role of PFOS-precursors as a means for long-range transport.

ANALYTICAL METHODS

Fluorine NMR

All ^{19}F NMR spectra were obtained on a Varian Unity 500, 3-channel spectrometer operating at 470.297 mHz at 26 °C. The NMR was equipped with a 5-mm Nalorac ^{19}F proton decoupling probe. To zero fill the free induction decays (FID), the Fourier number was set to equal twice the number of data points. All chemical shifts were relative to $CFCl_3$ (0.000 ppm). The NMR spectra were acquired with optimized parameters where the 90^o pulse width was 10.5 sec and the spectral window chosen to incoporate the shift range for target analytes. To optimize S/N in concentrated samples we typically used $Cr(acac)_3$ as a relaxation agent at 4 mg/ml. For quantification, the minimum recycling delay time (D_1) value (equal to approximately 5 times the T_1) was set to the maximum T_1 for the analytes of interest.[7]

GC-CI-MS

Was utilized to analyze volatile fluoro-alcohols in both positive (PCI) and negative (NCI) chemical ionization modes. A Hewlett Packard 5973 Mass Selective Detector, equipped with a chemical ionization source, acquired mass spectral data using methane as the reagent gas (PCI, 1 mL min^{-1}; NCI, 2 mL min^{-1}). Gas chromatographic separation was performed on a 30m DB-Wax column (0.25 mm id, 250 mm film thickness, J&W Scientific, Folsom, CA) using helium as the carrier gas.[8]

LC/MS/MS

The methanol extracts, with the internal standard present, were chromatographed (guard column (Security Guard, C18, Phenomenex, Torrance, CA), and Genesis C8 column, 2.1 mm x 50 mm, 4 µm, (Chromatographic Specialties, Brockville, Ontario)) using high performance liquid chromatography (Model 700, Waters, Milford, MA) with a flow rate of 300 µL/min. The gradient was operated from 40 to 95 % eluent B for 5 min, then held at 95 % eluent B for 10 min, where eluent A is 10 mM aqueous ammonium acetate, and eluent B is 10 mM ammonium acetate in methanol.

All mass spectra were acquired on a Quattro Micro liquid chromatography tandem mass spectrometer equipped with a Z-spray interface (Micromass, Manchester, UK) employing negative electrospray ionization. The capillary voltage was 2.7 kV, and the cone voltage ranged from 14 to 55 V, dependent on the individual compound of interest. The dwell time was 0.2 sec. The source block and desolvation temperatures were 130 and 330 ^{o}C, respectively. The nebulizer and desolvation gas flowrates were 50 and 550 L/hr, respectively. During tandem mass spectrometric analysis, argon was used as the collision gas (5.0 x 10^{-3} mBar) where the collision energy (12 to 45 eV) was varied for optimal performance for each compound. Full scan mode was employed for identification of individual surfactants. For quantification, multiple reaction monitoring (MRM) was used for each perfluorinated surfactant.[9, 10]

Results and Discussion

Although this work is on-going, we have established a basic understanding of the fate, disposition, aquatic toxicity, and persistence of these compounds in the environment.

1. Reverse-phase LC/MS/MS has proven invaluable for monitoring and detecting anionic perfluorinated carboxylates and sulfonate surfactants in environmental samples. Coupled with appropriate sample concentration/cleanup we routinely monitore ppq/ppt levels of FSs in surface waters and in fish. 19F NMR has proven useful in confirming identity, in identifying new ‘pollutants’ and providing a powerful method for ‘total’ FSs. [9]
2. We have discovered a previously unrecognized suite of longer chain perfluoroalkyl carboxylates (C10 through C14) that appear to have a higher bioaccumulation potential than PFOS. [10]
3. BCF values rise ~10x for each additional –CF_2 group in both perfluorocarboxlyates and sulfonates; equal ‘size’ sulfonates have slightly higher BCF values than the corresponding carboxylate. Under field conditions PFOS had a higher apparent ‘BAF’ than our lab studies would suggest and we propose that other fluoro-compounds may be present that can be metablized to yield PFOS.[11,12]
4. We have provided a plausible explanation for the significant question as to the mechanism for the worldwide dispersal of PFOS via our novel hypothesis that volatile FSs precursors are the transporters for PFOS. We have measured sulfonamide-alcohol derivatives of PFOS in Toronto and across North America in the pg/m^3 range and propose that they arise from residual material in surface coatings and/or represent degraded surface bound material (Fig 1). Further measurements and modeling are currently being pursued to strengthen the evidence for our understanding.[8]

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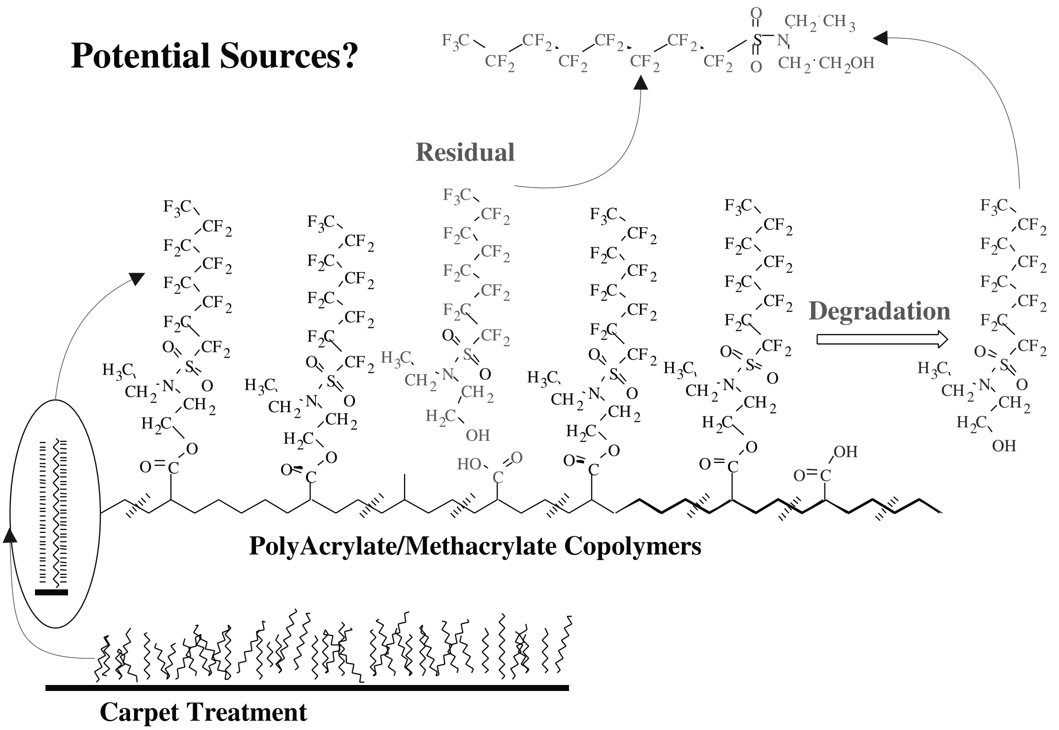

Figure 1. Possible sources for fugitive emissions of volatile PFOS-precursors.

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