

Employing Liquid Chromatography/Tandem Mass Spectrometry for the Determination of Perfluorinated Surfactants in Biota and Aqueous Samples.

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Introduction. Perfluorinated surfactants are employed in a variety of industrial and commercial applications including lubricants, paints, food-packaging, and fire-fighting foams (1). Recently, perfluorinated surfactants, such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), have received attention due in part to their persistence in the environment. In June 2000, a fire alarm malfunctioned at L. B. Pearson International Airport, Toronto, Ontario, and released 22,000 L of fire-fighting foam that contained perfluorinated surfactants into Etobicoke Creek, a tributary of Lake Ontario. Liquid chromatography/tandem mass spectrometry methodologies were developed and employed to monitor the residence time and long term fate of two classes of anionic perfluorinated surfactants released into Etobicoke Creek.

Materials and Methods. Perfluoroalkanesulfonate and perfluorocarboxylate homologues were extracted from fish liver tissue and aqueous samples (2, 3), and then the extracts were chromatographed using high performance liquid chromatography with a flow rate of 300 L/min. Mass spectra were acquired with negative electrospray ionization and a triple quadrupole instrument (Quattro LC Micromass, U. K.). The capillary voltage was 2.7 kV, and the cone voltage ranged from 14 to 55 V, depending on the compound of interest. During analysis, the collision energy (12 to 45 eV) was adjusted for optimal performance. For quantification, multiple reaction monitoring was used for each perfluorinated surfactant; for example, the transition of PFOS anion (m/z 499) to m/z 99 (FSO_3^-) was monitored. As an example, the instrumental detection limit for PFOS was 4 pg. Concurrently, similar methodology was demonstrated with a modified quadrupole/time-of-flight mass spectrometer (Q-Tof-2, Micromass, U. K.).

Results and Discussion. Fish were collected from Spring Creek and Etobicoke Creek twice over an eight-month period. The fish were identified as *Notropus cornutus*, Common shiner, and weighed from 3 to 8 g. Total perfluoroalkanesulfonate (4, 6, and 8 carbons) concentrations in fish liver tissue samples ranged from 2.00 to 72.9 g/g. A range of perfluorocarboxylate homologues (5 to 14 carbons) were detected in fish liver tissues at concentrations ranging from 0.070 to 1.02 g/g. The presence of higher chain perfluorocarboxylates (i.e., perfluorodecanoic acid) in fish liver tissues is of interest because perfluorocarboxylic acids are known peroxisome proliferators (4).

In addition to fish samples, surface water was collected from Etobicoke Creek at six different locations over 153 days. In the suite of aqueous samples (54 total), perfluoroalkanesulfonates (6 and 8 carbons) were detected in surface water with total concentrations ranging from non-detect (nd) to 2260 g/L. Other perfluoroalkanesulfonate homologues observed in surface water samples, but not quantified, included perfluoroheptanesulfonate and perfluorobutanesulfonate. Perfluorooctanoate concentrations (nd to 11.3 g/L) were lower than those concentrations determined for perfluoroalkanesulfonates. Lower chain perfluorocarboxylate homologues, including perfluoroheptanoic acid, perfluorohexanoic acid, and perfluoropentanoic acid were observed qualitatively. The surface water samples collected 153 days after the accidental spill into the creek had detectable concentrations of perfluorinated surfactants.

The observation of a suite of homologues perfluoroalkanesulfonate and perfluorocarboxylate homologues in fish and surface water samples contaminated with fire-fighting foams (i.e., aqueous film forming foams, AFFFs) is consistent with previous reports of AFFF-contaminated groundwater (5).

Perfluorooctanesulfonate was the predominant perfluorinated compound detected in fish liver tissue and surface water samples collected from Etobicoke Creek (Figure 1). Fire-fighting foam thought to be similar in composition to the one released at L. B. Pearson International Airport was analyzed by the developed methodologies, and PFOS was the predominant perfluorinated surfactant (Figure 1).

Interestingly, control fish and surface water collected upstream of the airport and spill had detectable concentrations of perfluorinated surfactants. These background concentrations may be indicative of the widespread contamination of perfluoroalkanesulfonates and perfluorocarboxylates. Clearly, additional research is needed to assess perfluorinated surfactants in natural environments.

References.

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Figure 1. PFHxS, PFOS, and PFOA distribution in fish liver tissue, surface water, and a commercially available fire-fighting foam.

