PERFLUOROALKYL CONTAMINANTS IN WINDOW FILM: URBAN/RURAL, INDOOR/OUTDOOR, AND SUMMER/WINTER GRADIENTS

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Introduction

Per- and polyfluoroalkyl contaminants (PFCs) have been detected throughout the world, from the arctic to indoor air and human blood [1-4]. Potential sources are numerous as these chemicals and their derivatives are used in a variety of industrial and commercial applications such as carpet, leather, and floor treatments, microwave popcorn bags, insecticides, fire fighting foams, paints, cosmetics, and nonstick cookware [5,6]. In recent studies, neutral PFCs were much greater in indoor compared with outdoor air [3,7,8], although no such difference was found for ionic compounds [8]. As such, confusion still exists on principle sources and exposure routes to both the environment and humans.

Window film has been previously identified as a simple and effective passive sampler of air concentrations of a variety of contaminants such as polychlorinated biphenyls and polybrominated diphenyl ethers [9,10]. Window film is easy to collect and analyze and can be used as a time-integrated sampler of contaminant concentrations in air [9]. However, prior to this study the use of window film to measure PFCs had not been assessed.

The objective of this study was to evaluate ionic PFCs in window film along urban/rural, indoor/outdoor, and summer/winter gradients in Toronto, Ontario, Canada, in order to evaluate locations and seasons of relatively elevated concentrations and to gain an understanding of the relative importance of possible sources.

Materials and Methods

Window film was collected from 2 downtown, 1 industrial, 2 suburban, and 2 rural locations in Toronto, Ontario, Canada. At each location, a sample was taken both indoors and outdoors, and during winter (February to March) and summer (July and August) of 2007. Windows of two carpet stores (indoor and outdoor) were also sampled during the summer. At each location, the window was first cleaned with laboratory Kimwipes using methanol as a solvent. After 28 days, the windows were (re)sampled by wiping the windows with precleaned methanol wetted laboratory Kimwipes. Therefore, each sample represents four weeks of film accumulation. The sample Kimwipes were stored in 50 mL polyethylene centrifuge tubes. Field blank samples were taken with each sample by waving precleaned laboratory Kimwipes in the air for 2 minutes.

The samples and field blanks were extracted with a modification of the Hansen et al. [11] ion pairing method. Briefly, extractions were performed in the 50 mL polyethylene centrifuge tubes. The samples were spiked with a $^{13}C_4$-PFOA control standard and then HPLC water, Na_2CO_3, tetrabutylammonium hydrogensulfate (ion-paring agent), and methyl-*tert*-butyl ether (MTBE) were added to the tubes. The tubes were shaken vigorously for 5 minutes and centrifuged to separate the supernatant (MTBE). The MTBE supernatant was then transferred to a clean polyethylene centrifuge tube. The extraction was repeated 2 times. MTBE extracts were then evaporated to dryness, the residue reconstituted in methanol, and the methanol filtered through 0.2 µm nylon syringe filters. Aliquots of the final methanol extracts, internal standards in methanol, and water (50% of final concentration) were mixed and analyzed by reversed phase liquid chromatography tandem quadrupole mass spectrometry (HPLC-MS/MS) [12]. The following PFCs were quantified: perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), perfluorooctane sulfonamide (PFOSA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotetradecanoic acid (PFTeA),

6:2-fluorotelomer unsaturated carboxylic acid (6:2-FTUCA), 8:2-fluorotelomer unsaturated carboxylic acid (8:2-FTUCA), and 10:2-fluorotelomer unsaturated carboxylic acid (10:2-FTUCA).

Results and Discussion

No PFCs were detected in any of the field or analytical method blank samples. In contrast, PFCs were found in all of the film samples. The percent recovery of $^{13}C_4$-PFOA was 88.4 ± 7.5 (mean ± sd) and ranged from 75 to 109%.

An urban/rural gradient was previously observed for PCBs, PAHs, organochlorine pesticides, and PBDEs in film collected from outdoor windows in Toronto, Canada [9,13]. In this study, no such apparent urban/rural gradient was observed in the outdoor window film, with total PFC concentrations ranging from 0.08 – 0.76 pg/cm^2 and 0.09 – 0.94 pg/cm^2 in the winter and summer, respectively (Figure 1). With the exception of the two rural sites, PFC concentrations changed between the winter and summer although there was no consistent direction of the change. The relative proportions of chemicals were similar among the outdoor sites in both the winter and summer, with dominant contributions from PFOA, PFOS, and PFNA. This pattern suggests similar and diffuse sources of the PFCs to the outdoor film at all of the study sites.

For indoor window film samples, no urban/rural gradient was observed, similar to the outdoor samples, and concentrations of total PFCs ranged from 0.05 – 2.5 pg/cm^2 and 0.15 – 5.6 pg/cm^2 in the winter and summer, respectively (Figure 2). For the most part, concentrations were greater on indoor compared with outdoor windows with an indoor:outdoor ratio of up to 1000 (PFDS at the industrial site). In both the summer and winter, the rural 1 site had the highest concentrations of total PFCs, followed by the industrial site, and the downtown 1 and suburban 2 had the lowest concentrations. Although the relative proportion of chemicals varied highly among sites, the pattern did not change between seasons. These results provide evidence that each indoor location has its own PFC concentration signature, especially at sites of elevated concentrations, and suggest point sources of different types are responsible for the indoor contamination. Concentrations were generally higher in the summer compared with the winter season, the reason for which has yet to be determined.

The PFC concentrations in the film collected from the interior windows of two carpet stores were elevated (∑PFC concentrations = 16 and 7 pg/cm^2) and had a different compound profile compared to the other indoor window samples collected (Figure 3). In contrast, the film collected from the exterior windows at the carpet stores were almost 100 times lower than indoor films (∑PFC concentrations = 0.17 and 0.09 pg/cm^2) and had a similar concentration and compound profile compared with the other outdoor locations. Our previous work provided evidence that new carpet installation does not lead to increased window film concentrations after 28 days (Gewurtz et al. unpublished data), which may be due to the removal of residuals from carpet protectors by major manufacturers and new technologies based on lower carbon number polyfluorinated side chains [14]. Thus we hypothesize that the elevated PFC concentrations in the interior window film at the carpet stores are reflective of past use.

Further studies are currently underway to evaluate possible point sources of PFCs to indoor window film (e.g. floor wax) and to examine variability in concentrations in windows both within and among rooms of the same building.

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Figure 1: PFC concentrations in outdoor window film (pg/cm^2) collected during the winter (February - March) and summer (July - August) along an urban/rural gradient in Toronto, ON, Canada

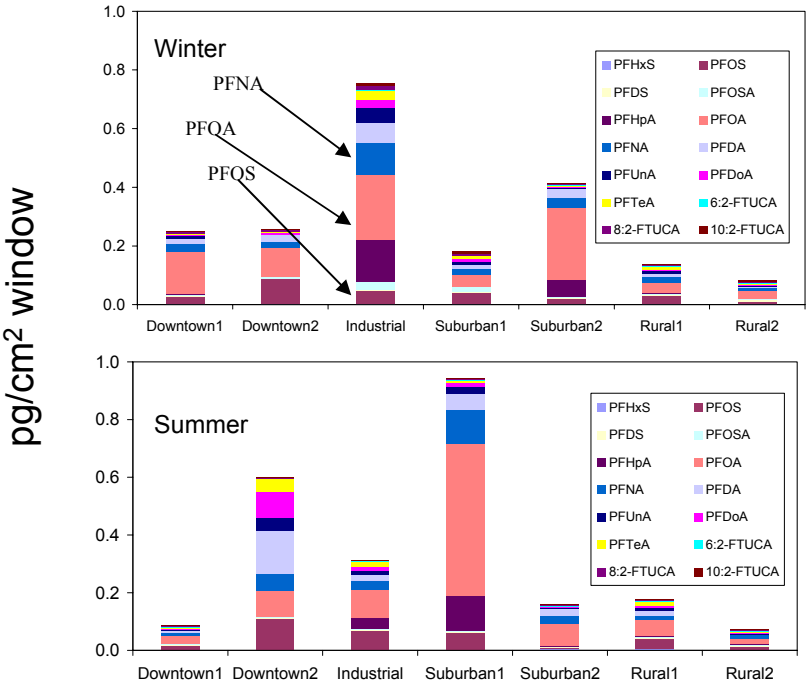

Figure 2: PFC concentrations in indoor window film (pg/cm^2) collected during the winter (February - March) and summer (July - August) along an urban/rural gradient in Toronto, ON, Canada

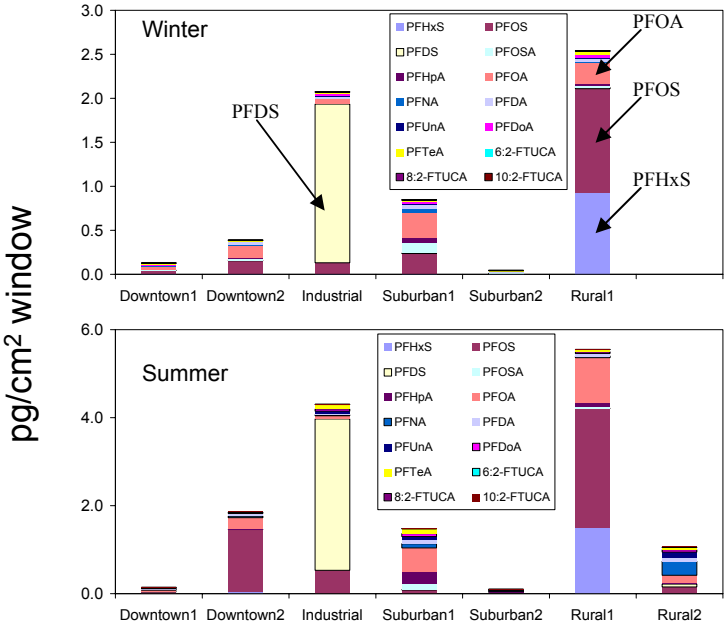

Figure 3: PFC concentrations in indoor and outdoor window film samples collected during the summer for the purpose of comparing carpet stores to the other locations