

Fluorinated compounds - sources, environmental levels and transformation

Perfluoroalkyl Compounds in Surficial Sediment from Canadian Great Lake Tributaries

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Introduction:

A screening-level survey of recently deposited sediments was undertaken for Canadian tributaries to the Great Lakes over a five year period ending in 2005. The geographical scope of the program was from the Quebec provincial border on Lake Ontario in the east to the Canadian/American border on Lake Superior in the northwest. A total of 431 tributaries were sampled and analyzed for 52 organic compounds. A subset of these samples (N=103) were analyzed for a suite of new and emerging POPs including perfluoroalkyl sulfonates, perfluoroalkyl carboxylates, polybrominated diphenyl ethers, PCDDs/Fs and DLPCBs. Perfluoroalkyl sulfonates and perfluoroalkyl carboxylates are chemicals which belong to a class of compounds known as perfluoroalkylated surfactants (PFAS). They are composed mainly of carbon-fluorine bonds, have high chemical stability and impart oil and water repellency to surfaces. They are commonly used as an industrial polymer (Teflon™), paper coatings in food packaging, stain repellents and fire fighting foams.

Methods:

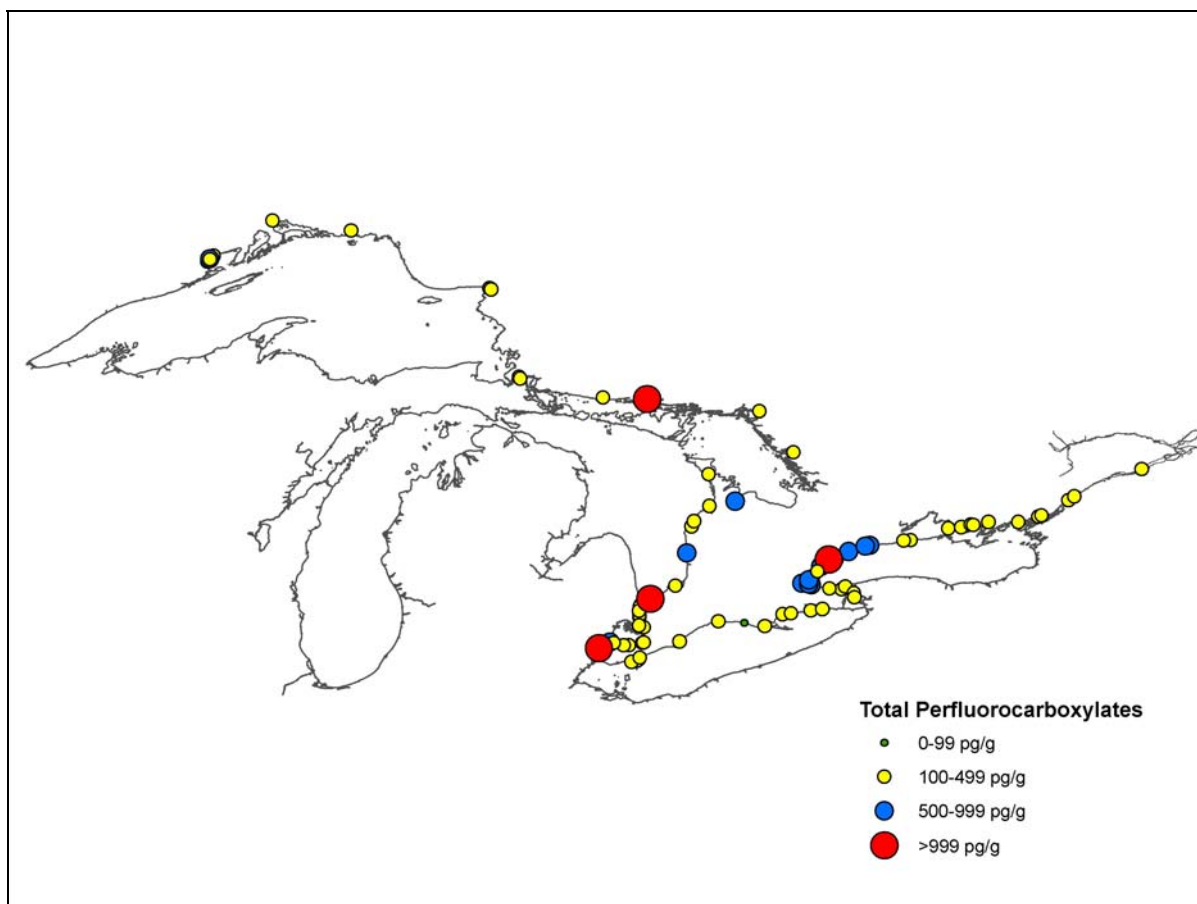
The sampling program was based on the *Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants*, developed by the United States Geological Survey (USGS) for the U.S. National Water-Quality Assessment Program (NAWQA; Shelton and Capel, 1994). In the NAWQA program, downstream locations in watersheds are selected to provide a coarse-scale network of sites. At these "integrator" sites, large-scale problems that may not be detected in smaller basins have a reasonable chance of being detected. A number of sub-samples are combined so that one sample is obtained that is representative of the overall conditions of that tributary. Sampling was conducted in the late summer-fall at one or more depositional sites upstream of the mouth of each tributary. Only the very fine grained surface deposits, to a maximum depth of 2 cm were collected. Samples were obtained using either a stainless steel spoon or an all-stainless steel Wildco Petite Ponar. The surface sediments were collected and combined in a glass bowl then sieved through a 2-mm stainless sieve. The samples were further homogenized by mixing for two minutes before being transferred to sample jars.

In brief, the sample preparation for the perfluorinated compounds consisted of the addition of a surrogate standard (PFOA (M+4)), 0.25 M sodium carbonate and 0.5 M tetrabutylammonium hydrogen sulphate followed by an extraction with methyl-tert-butyl-ether (MTBE). The organic fraction was evaporated to 0.5 mL, spiked with 0.5mL 1,1,1,3,3,3-hexafluoro-2-propanol then brought to dryness. Samples were brought up to a final volume of 0.5mL in methanol. The analyses of the perfluorinated compounds were done using an Agilent 1100™ LC equipped with a 4 mm x 2.0 mm Phenomenex Security Guard™ C18 guard column and a 50mm x 2.1 mm x 4µm Jones Genesis C18 analytical column (Chromatographic Specialties, Brockville, ON) with a 80:20 water/methanol gradient at 250µl/min. Coupled to this was an Applied Biosystems/Sciex 4000 Qtrap™ triple quadrupole mass spectrometer operated in negative electrospray ionization (ESI) MRM mode with nebulizer gas (N₂) 45psi, turbo gas (N₂) 60 psi at 400C, curtain gas (N₂) 10 psi, interface heater 100°C. MRM transition ions are listed in table 1.

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Table 1: Transition Ions monitored for PFAS analysis

| Compound | Chain length | Acronym | MRM Transition Ions | |
|-----------------------------|--------------|---------|---------------------|---------------|
| | | | Parent (m/z) | Product (m/z) |
| Perfluorohexane sulfonate | 6 | PFHxS | 399 | 99 |
| Perfluorooctane sulfonate | 8 | PFOS | 499 | 99 |
| Perfluorooctane sulfonamide | 8 | PFOSA | 498 | 78 |
| Perfluorodecasulfonate | 10 | PFDS | 599 | 99 |
| Perfluoroheptanoic acid | 7 | PFHpA | 363 | 319 |
| Perfluorooctanoic acid | 8 | PFOA | 413 | 369 |
| Perfluorononanoic acid | 9 | PFNA | 463 | 419 |
| Perfluorodecanoic acid | 10 | PFDA | 513 | 469 |
| Perfluoroundecanoic acid | 11 | PFUA | 563 | 519 |
| Perfluorododecanoic acid | 12 | PFDoA | 613 | 569 |



Results and Discussion:

Perfluorocarboxylated acids (PFCA) were detected in all of the tributary sediments analyzed with average total values (sum of C7-C15) ranging from 253 pg/g and 315 pg/g for Lake Erie and Lake Superior, respectively, to 545 pg/g and 600 pg/g for Lake Ontario and Lake Huron, respectively. The highest mean concentration of a PFCA in surficial sediments was for PFOA which showed a west to east concentration gradient across the Great Lakes. Mean concentrations were 38 pg/g in Lake Superior (n=11), 88 pg/g in Lake Huron tributaries (n=14), 101 pg/g (n=31) in Lake Erie and a maximum average concentration of 130 pg/g in Lake Ontario (n=47). While this gradient held true for PFOA, there was no similar pattern for the other PFCAs. Total perfluorocarboxylates (sum of C2-C15) ranged from 83-3115 pg/g.

Perfluorosulfonate compounds were not found in every tributary analyzed. While PFOSA was the most common, detected in all but two samples, the highest concentrations were found for both PFOS and PFDS. Concentrations for PFDS were the highest of the sulfonate compounds ranging from <0.2-3110 pg/g, followed by PFOS which had a range of <0.6-1272 ng/g. Mean concentrations for all of the lakes tributaries sampled were 24 pg/L, 32 pg/L, 158 pg/L and 173 pg/L for PFOSA, PFHxS, PFDS and PFOS respectively. While high levels of PFOS accompanied with significant levels of PFDS and PFHxS often reflect an influence from released fire fighting foam (AFFF) the Lake Ontario tributaries often had much higher PFDS concentrations than PFOS. For example, Chedoke Creek in Hamilton showed 3110 pg/g PFDS but had only 277 pg/g PFOS. This difference likely indicates a significant source other than AFFF.

Telomer acids (6:2, 8:2, 10:2) both saturated and unsaturated were also monitored. The saturated acids were never found above the detection limit of 100 pg/g while the unsaturated acids were found infrequently above the detection limit of 0.8 pg/g. Of the unsaturated telomer acids 6:2 and 8:2 were detected 12% and 6% respectively in the tributaries across the four Great Lakes. The 10:2 unsaturated acid was not found in any of the Lake Erie or Lake Ontario tributaries but found at a frequency of 22% in the tributaries across Lake Huron and Lake Superior. There was no pattern to the detection frequency between the three unsaturated acids as each acid was detected on its own, in at least one tributary.

While the highest values for PFAS were found near large urban areas, not all large urban tributaries contained high concentrations of PFAS. The highest values of total perfluorocarboxylates and total perfluorosulfonates were found in the tributaries of large centres such as, Toronto, Hamilton, Burlington (Lake Ontario) Sarnia (Lake Huron) and Windsor. However none of the six tributaries in Thunder Bay and Sault Ste Marie (Lake Superior) had elevated levels PFAS. It is also noteworthy that none of the tested tributaries to Lake Erie had elevated concentrations which may be a reflection of its rural character. Contrary to these observations, Marsh Creek, a tributary in the small community of Picton Ontario which drains into the Bay of Quinte (Lake Ontario) had the highest levels of perfluorocarboxylates and the second highest levels of perfluorosulfonate.

The results of this survey provide information about recently deposited sediment quality, and can be used to help identify if Canadian watersheds are sources of pollutants to the Great Lakes.

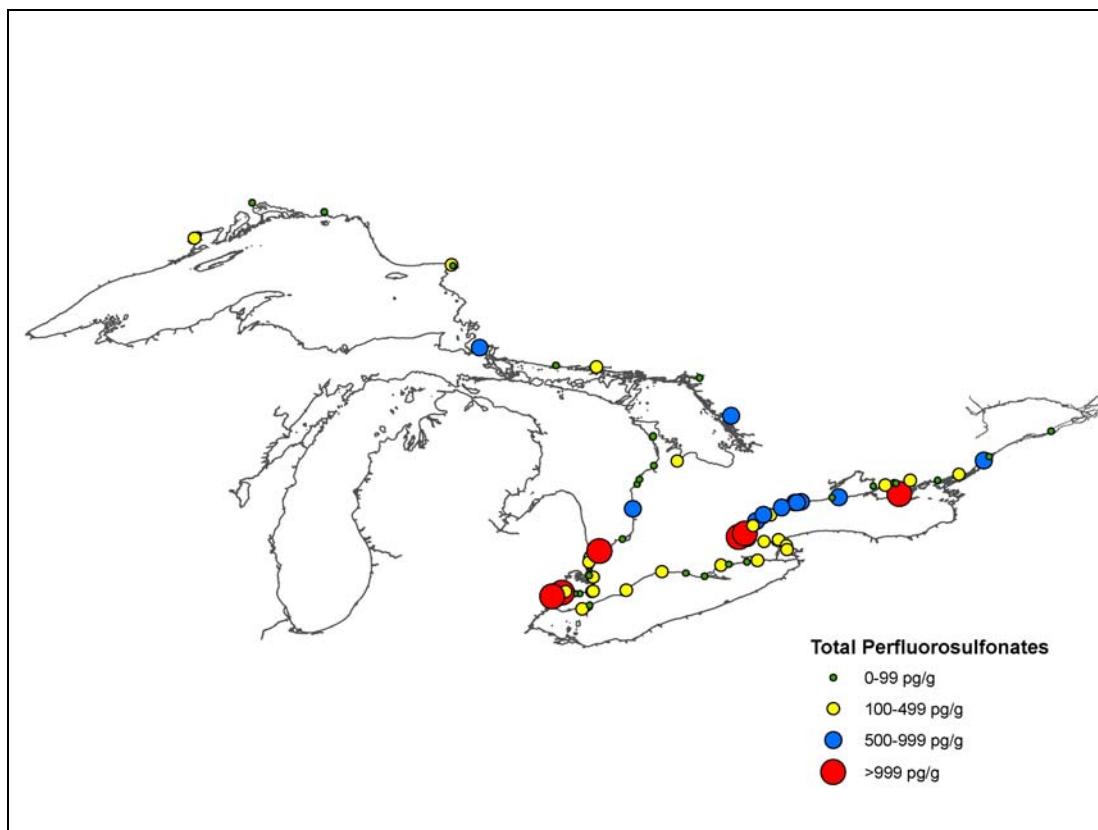


Figure 2: Levels of perfluorooctane sulfonate in Canadian tributaries to the Great Lakes

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