

## Temporal Study of Perfluorinated Alkyl Surfactants in Niagara River Sediments (1980-2002)

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### Introduction

Perfluoroalkyl compounds are an emerging class of contaminants widely distributed in the environment<sup>1</sup>. They are persistent, bio-accumulative and potentially toxic and carcinogenic. Manufacturers have used these chemicals in soil and stain-resistant coatings for fabrics, carpets and leather and in grease and oil-repellent coatings for paper products. Industrial uses include fire-fighting foams, mining and oil well surfactants, photographic film and insecticides<sup>2</sup>.

Fluorinated compounds have been manufactured for over 50 years. A large number of scientific papers have reported the concentration of perfluorinated compounds in surface waters<sup>3</sup>, human blood<sup>4</sup>, tissues of wildlife<sup>1</sup> (fish, birds, polar bears, bald eagles etc.) sediments and house dust<sup>5</sup>.

The Great Lakes region is strongly industrialized on both the American and Canadian sides of the lakes. The Niagara River, origination from Lake Erie, is the main source to Lake Ontario contributing over 80% of the total tributary flow and approximately 50% of fine-grained sediments entering the lake. This paper presents a 22-year (1980-2002) temporal study of perfluorinated alkyl surfactants in the suspended sediment collected at Niagara-on-the-Lake in the Niagara River.

### Materials and Methods

**Collection:** Suspended sediment samples were collected in April and/or May using a submersible pump connected to an intake line and Westphalia centrifuge assembly connected to a Goulden Large Sample Extractor<sup>6</sup> (GLSE). After collection the suspended sediment samples were freeze-dried.

**Sample preparation:** After the addition of surrogate standard (PFOA (M+4)), 0.25M sodium carbonate and 0.5 M tetrabutylammonium hydrogen sulphate (ion pairing reagent), the sediment samples (~5g) were extracted twice with 5ml aliquots of methyl-tert-butyl- ether (MTBE). MTBE extracts were separated from the aqueous layer using a centrifuge, transferred, combined and then evaporated to approximately 0.5 ml. After the addition of 0.5ml of 1,1,1,3,3,3-Hexafluoro-2-propanol, the final extracts were filtered through 0.2µm nylon syringe filters and evaporated to dryness. The sample extracts were reconstituted with 0.5ml methanol and stored in the dark at 4°C until instrumental analysis.

**Instrumental Analysis:** Suspended sediment sample extracts were analyzed using an Agilent 1100<sup>TM</sup> LC coupled to an Applied Biosystems/Sciex 4000QTrap<sup>TM</sup> triplequadrupole mass spectrometer. The target analytes were chromatographically separated on a 4mm x 2.0mm Phenomenex Security Guard<sup>TM</sup> C18 guard column and 50mm x 2.1mm x 4µm Genesis C18 analytical column (Chromatographic Specialties, Brockville, ON) using a water/methanol (+10mM ammonium acetate) gradient at 250µl/min in a 8min run. The mass spectrometer was operated in negative electrospray ionization (ESI) MRM mode. Typical instrument settings were used: nebulizer gas (N<sub>2</sub>) -45psi, turbo gas (N<sub>2</sub>) -60psi at 400°C, curtain gas (N<sub>2</sub>) -10psi; interface heater -100°C, needle voltage -4.5kV. Q1 and Q3 resolution were set at unit mass resolution. MRM transitions were optimized for each target compound.

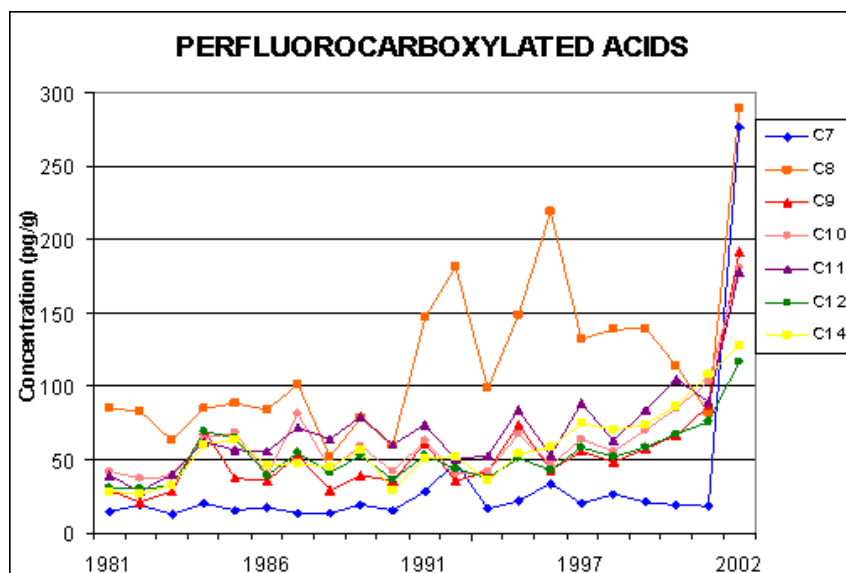
The MRM transitions used for quantification were  $[M - H]^- \rightarrow [FSO_3]^-$  for perfluorinated sulfonates and  $[M - H]^- \rightarrow [M - COOH]^-$  for perfluorinated carboxylates. Quantification was done using internal standard methods. Labelled PFOA and PFDA (M+2) were added to extracts before injection in order to compensate for matrix effects and instrument variability. Labelled PFOA (M+4) was added to each blank, spike and sample before extraction.

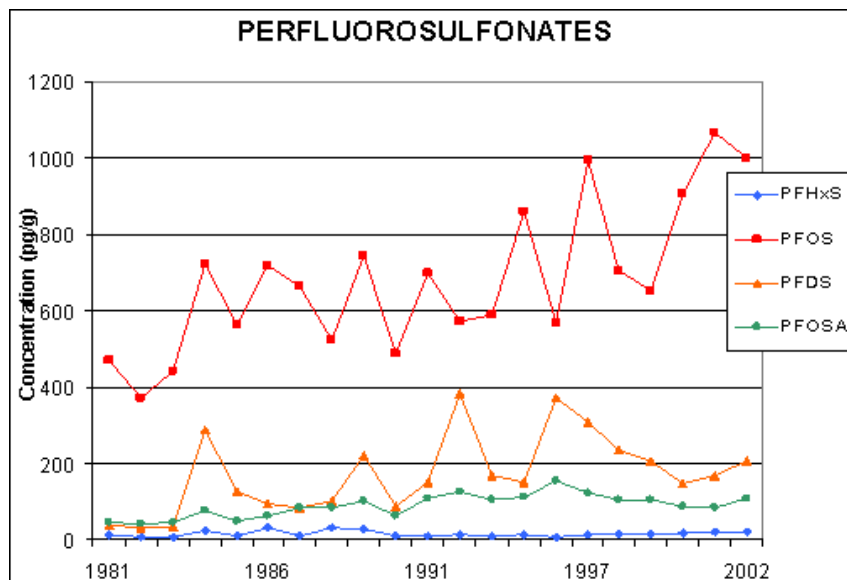
### Results and Discussion

Sediment samples collected at the Niagara-on-the-Lake station were analyzed for seven perfluorocarboxylates (Perfluoroheptanoic acid (C7), Perfluorooctanoic acid (C8), Perfluorononanoic acid (C9), Perfluorodecanoic acid (C10), Perfluoroundecanoic acid (C11), Perfluorododecanoic acid (C12), Perfluorotetradecanoic acid (C14)), three perfluorosulfonates (Perfluorohexanesulfonate (PFHxS), Perfluorooctanesulfonate (PFOS), Perfluorodecane sulfonate (PFDS)) and Perfluorooctanesulfonylamide (PFOSA).

Sediments samples were extracted and analyzed along with blanks, spikes and duplicates. The recoveries for the surrogate standard PFOA (M+4) were between 50 and 80%.

Figure 1 presents the temporal trends of these compounds during 1981-2002. The concentrations for perfluorocarboxylated acids were between 10 and 300 pg/g with the highest values for PFOA. Perfluorosulfonate concentrations were between 5 and 1100 pg/g. The concentrations of PFHxS, PFDS and PFOSA were much less than those of PFOS ranging from 5 to 400 pg/g. PFOS concentrations increased during the period of study from less than 400 pg/g in 1980s to more than 1000 pg/g in 2002. There is a general trend toward increasing concentration for all fluorinated organic compounds monitored. Data for the 1980 sample were omitted from these graphs because of the relatively high concentrations (1100 pg/g for PFOS and 210 pg/g for PFOA) which made trend analysis more difficult. Similar results for the 1980 samples were obtained for PCDDs/ PCDFs, DLPCBs and PBDEs.





**Figure 1:** Concentrations of Perfluorocarboxylates and Perfluorosulfonates in Niagara River suspended sediment over the period 1981-2002.

### Conclusions

Perfluorinated alkyl surfactants are present to varying degrees in Niagara River suspended sediments. Potential sources of perfluorinated alkyl surfactants in the Niagara River suspended sediments may originate from hazardous waste disposal sites (Hyde Park Dump that discharges in Niagara River through the Bloody Run Creek and Pettit Flume on Tonawanda Island) as well as transient sources through the particulate matter transport.

During the period of this study (1981 -2002) there was an increase in the concentration of perfluorinated alkyl surfactants in the suspended sediment which was very similar to the trends in PBDEs already reported for the same location<sup>6</sup>.

### References

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