BINATIONAL FRAMEWORK FOR IDENTIFYING SUBSTANCES OF POTENTIAL THREAT TO THE GREAT LAKES BASIN

Test Case: Perfluorooctane Sulfonate (PFOS), its Salts and its Precursors
(Larger Class: Perfluorinated Alkyl (PFA))

I. FEEDERS FOR SUBSTANCE IDENTIFICATION

National Chemical Management Programs

Canada
PFOS has been assessed CEPA toxic under the Canadian Environmental Protection Act (CEPA, 1999) and was added to CEPA 1999 Schedule 1 - List of Toxic Substances in 2006.¹

A key element of the Chemicals Management Plan (CMP) involves taking immediate action on five substance categories including PFOS.² The Canadian Government has proposed to prohibit uses of 50 PFOS substances because there is strong evidence that they pose a risk to the environment or human health.³ PFOS is included in the monitoring plan for the CMP (either Year 1 or Year 2).⁴

United States
PFOS is not included in EPA’s High Production Volume (HPV) Program. 3M, the principal global manufacturer of PFOS, working in partnership with EPA, announced in 2000 that it would voluntarily phase out production by the end of 2002. Following the voluntary phaseout of PFOS by 3M, EPA took prompt regulatory action on March 11, 2002,⁵ and December 9, 2002,⁶ by publishing two significant new use rules (SNURs) under the Toxic Substances Control Act (TSCA) to limit any future manufacture or importation of 88 PFAS chemicals specifically included in that phaseout. Furthermore, on October 9, 2007,⁷ EPA published another SNUR on 183 additional PFAS chemicals. These SNURs recognized the continuation of a few specifically limited, highly technical uses of these chemicals for which alternatives were not available, and which were characterized by very low volume, low exposure, and low releases. Any other uses of these chemicals would require prior notice to and review by the USEPA.

The October 2007 SNUR allowed for one existing use of one PFOS salt as a mist suppressant in chromium plating, especially to promote compliance with a Clean Air Act MACT standard and the OSHA permissible exposure limit (PEL) for hexavalent chromium. The preamble to the final rule noted EPA’s concern about ongoing PFOS releases to wastewater, and the Agency’s interest in ways to minimize and/or prevent these releases.

Great Lakes Monitoring and Surveillance
There are specific PFOS substances (and its salts) common with the Great Lakes Screening Project. These include:⁸

<table>
<thead>
<tr>
<th>CAS #</th>
<th>Chemical Name</th>
</tr>
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<tbody>
<tr>
<td>1691-99-2</td>
<td>1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-</td>
</tr>
<tr>
<td>2795-39-3</td>
<td>1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt</td>
</tr>
<tr>
<td>2991-51-7</td>
<td>Glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-, potassium salt</td>
</tr>
</tbody>
</table>
### Other Sources of Information

**Organization for Economic Co-operation and Development (OECD)**

In 2000, several member countries collected information on the environmental and human health hazards of PFOS to produce a hazard assessment report. The report concluded that PFOS’s persistence, its presence in the environment and in a number of wildlife species, and bioaccumulation potential are a cause for concern.

**European Union**

In 2007 EU measures were adopted introducing legislation across Europe restricting PFOS. The new restrictions became effective June 27, 2008.

The EU also published Directive 2006/122/EC on December 27, 2006, which states that PFOS and related substances shall not be placed on the market according to the following restrictions:

- in concentrations equal to or higher than 0.005% by mass as a substance or constituent of preparations;
- in semi-finished products or products, or parts thereof, at a level of 0.1% by mass; and
- in textiles or other coated materials in which the amount of PFOS will be equal to or higher than 1 µg/m² of the coated material.

**Australia**

In Australia, there has been a voluntary phase-out agreement for PFOS since 2000.

**Norway**

In April 2005, Norway proposed major reductions in emissions of PFOS by 2010.
The Norwegian Pollution Control Authority has adopted new legislation on PFOS in textiles, firefighting foams and impregnating agents. The new law came into force on July 1, 2007. Norway has laid down the same limits for the use of PFOS as the EU.  

**Sweden**

In 2005, Sweden proposed PFOS and 96 PFOS-related substances as candidates for the Stockholm Convention on Persistent Organic Pollutants (POPs). A draft risk management evaluation was prepared for discussion at the third meeting of the POPRC (November 2007) recommending listing PFOS under the Annex A of the Convention in order to eliminate or restrict production and use. It is expected that this recommendation will be put forward for decision at the 4th Conference of the Parties in May 2009.  

**United Nations Economic Commission for Europe (UNECE)**


**States**

The Minnesota Pollution Control Agency and Department of Health have undertaken significant work with respect to perfluorinated compound (PFC) contamination in Minnesota. See [http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html](http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html) and [http://www.pca.state.mn.us/cleanup/pfc/index.html](http://www.pca.state.mn.us/cleanup/pfc/index.html).  

**II. CONSIDERATIONS FOR SUBSTANCE SELECTION**

**Monitoring and Surveillance**

Numerous monitoring and surveillance data are available which demonstrates the presence of PFOS (and related substances (PFA)) in the Great Lakes Basin. For example:

- Furdui *et al.* 2007, “Spatial Distribution of Perfluoroalkyl Contaminants in Lake Trout from the Great Lakes”.  
  - Reports perfluoroalkyl contaminant concentrations in Lake Trout from the Great Lakes.
  - Lowest average concentration of ΣPFC found in samples from Lake Superior (13 ± 1 ng g⁻¹). Highest average concentration found in samples from Lake Erie (152 ± 14 ng g⁻¹). Samples from Lake Ontario (60 ± 5 ng g⁻¹) and Lake Huron (58 ± 10 ng g⁻¹) showed similar average ΣPFC concentrations.
  - The major perfluoroalkyl contaminant observed was perfluorooctane sulfonate (PFOS) with the highest concentration found in samples from Lake Erie (121 ± 14 ng g⁻¹), followed by samples from Lake Ontario (46 ± 5 ng g⁻¹), Lake Huron (39 ± 10 ng g⁻¹), Lake Michigan (16 ± 3 ng g⁻¹), and Lake Superior (5 ± 1 ng g⁻¹).

- Martin *et al.* 2004, “Perfluoroalkyl Contaminants in the Lake Ontario Food Web”.
  - Reports concentrations of PFOS in various organisms from a food web of Lake Ontario.
The highest levels were found in polar bear, with a mean level of 3100 ng/g from seven animals (maximum value > 4000 ng/g). The concentrations of PFOS in polar bear are 5-10 times higher than the concentration of all other perfluoroalkyl substances and were higher than any other previously reported concentrations of persistent organochlorine chemicals in polar bear fat.

- Boulanger et al. 2004, “Detection of perfluorooctane surfactants in Great Lakes water”.
  - Reports concentrations of perfluorooctane surfactants from 16 water samples from Lakes Erie & Ontario.
  - Concentrations of PFOS in the two lakes ranged from 21-70 ng/L.
  - Analysis also showed the presence of PFOS precursors, N-EtFOSAA (range of 4.2-11 ng/L) and FOSA (range of 0.6-1.3 ng/L), in all samples above the LOQ.
  - PFOSulfinate, another precursor, was identified at six of eight locations with a concentration range, when present, of <2.2-17 ng/L.
  - These are the first reported concentrations of perfluorooctane surfactants in Great Lakes water and the first report of PFOS precursors in any water body.

  - Reports concentrations of PFOS in air, water, sediment & biota.
  - Information available at:

Concentrations of PFOS collected in a screening-level survey of recently deposited sediments in Canadian Great Lakes tributaries from 2001 to 2005 indicated relatively low PFOS concentrations that appear to be indicative of land use (i.e., elevated levels are generally found in more populated watersheds) (see figure below).
**Environmental Levels and Trends**
For environmental levels, please see monitoring and surveillance data.

Retrospective analyses of archived lake trout samples from Lake Ontario have identified a 4.25-fold increase (from 43 to 180 ng/g wet weight, whole fish) from 1980 to 2001.²²

A summary of studies of fluorinated surfactants in the Great Lakes environment is presented in Appendix A.

**Source/Use/Release/Exposure Information**
Source/use/release/exposure information available primarily from Environment Canada’s *Perfluorooctane Sulphonate (PFOS), Its Salts and Its Precursors Risk Management Strategy.*²³

**Source/Use**
PFOS, its salts and its precursors are not manufactured in Canada but rather are imported as chemicals or products from the United States for Canadian uses. The principal applications of PFOS and its precursors are for water, oil, soil and grease repellents for use on rugs, carpets, fabric and upholstery, and in food packaging, as well as specialized chemical applications such as firefighting foams, hydraulic fluids, carpet spot removers, mining and oil well surfactants and other specialized chemical formulations. In Canada, in the past, PFOS substances were typically imported as raw chemicals and in products and formulations.

An Environment Canada use pattern survey undertaken in 2000 indicated that, from 1997 to 2000, an estimated 318 tonnes of PFOS substances were used in Canada.

**Release**
PFOS, its salts and its precursors may enter the environment through treated or untreated municipal/industrial wastewater discharges to surface water and through leachates from landfills when products and materials containing these substances are sent for final disposal. PFOS may also be released directly to air, land, and surface water when products containing PFOS are used.

**Exposure**
Exposure in the Canadian environment likely results from the release, transformation, and movement of PFOS and its precursors in effluents and fugitive emissions from manufacturing sites elsewhere in the world, and releases from industrial and municipal wastewater effluents.

**Environmental Benchmarks**
A few states have established environmental quality benchmark criteria. No benchmarks are available from Canada. The United Kingdom has also issued some criteria for PFOS and PFOA in drinking water.

**States**
Minnesota has issued a Health Risk Limit for PFOS (0.3 ug/L) in drinking water, and fish contaminant advisories for several highly impacted bodies of water. Minnesota is also considering
effluent limits for PFCs in wastewater. Two other states, New Jersey and North Carolina, also regulate PFCs in drinking water.

**United Kingdom**
The Health Protection Agency advises that the maximum acceptable concentration of PFOS in drinking water is $0.3 \mu g/L$.24

**Environmental and Health Data**
Information on health data can be found from Health Canada’s State of the Science Report for a Screening Health Assessment for PFOS (July 2006).25

The final ecological screening assessment report concludes that PFOS, its salts and its precursors are considered to meet the criteria set out in section 64(a) of CEPA 1999. The draft 2004 human health screening assessment report concludes that PFOS, its salts and its precursors do not meet the criteria set out in section 64(c) of CEPA 1999.26

**Other Reasons for Concern**
Evidence suggests that PFOS has endocrine disrupting properties in rats.27

**III. PRESENT MANAGEMENT STATUS**

**Canada**
On December 16, 2006, the proposed Perfluorooctane Sulfonate and Its Salts and Certain Other Compounds Regulations were published in the *Canada Gazette*, Part I. The final Regulations were published in Part II of the *Canada Gazette* on June 11, 2008. The Regulations prohibit the manufacturing, use, selling, offering for sale or importing PFOS and its salts and certain other compounds; with some exceptions. More information on this regulation can be found at: [http://gazetteducanada.gc.ca/partII/2008/20080611/html/sor178-e.html](http://gazetteducanada.gc.ca/partII/2008/20080611/html/sor178-e.html).28

**United States**
The SNURs require manufacturers and importers to notify the EPA at least 90 days before new manufacture or import of these substances. This provides the EPA with the necessary time to evaluate the intended new use and prohibit or limit the new activity if necessary. The three SNURs essentially restrict all manufacture and importation, with the exception of PFOS salt used as a mist suppressant in chromium plating.29

EPA Region 5 recently completed a field survey of wastewater at chromium plating facilities in both Chicago and Cleveland to determine the extent of PFC releases to wastewater from this authorized use. The survey results will be summarized and submitted to EPA Office of Air Quality Planning and Standards under the CAA residual risk analysis for the Chromium MACT, in order to inform the rulemaking with respect to the metal finishing source category.

EPA has also engaged the National Association of Surface Finishers, beginning some dialogue on the development of alternative compounds and best management practices to minimize and/or prevent PFOS releases. Future activities are being determined at this time, pending guidance from EPA Region 5.
RECOMMENDATION

To be determined.

APPENDIX A
Fluorinated Surfactants in the Great Lakes Environment - Published Studies


   Summary: This study measured concentrations of perfluorinated surfactants released by a spill in Etobicoke Creek, a tributary of Lake Ontario. Measurements from surface waters and fish livers were taken. The study suggested that perfluorinated surfactants will persist and bioaccumulate following release into the aquatic environment.


   Summary: This study analyzed for perfluorooctane surfactants from sixteen sites in Lake Erie and Ontario. Concentrations of PFOS and PFOA in the two lakes ranged from 21-70 and 27-50 ng/L, respectively. Precursors to these compounds were also measured in both lakes.


   Summary: Trophic transfer of perfluorooctane sulfonate (PFOS) and other related perfluorinated compounds were examined in a Great Lakes benthic food web. Concentrations of perfluorooctane sulfonate were measured in tissue from various organisms including water–algae–zebra mussel–round goby–smallmouth bass. PFOS was most widely detected in benthic organisms at various
trophic levels. This study calculated the bioaccumulation factor in benthic invertebrates to be 1000, while biomagnification factors in larger predators like bald eagles and minks to be 10 to 20 times that of their prey.


Summary: A mass budget was done on eight perfluorooctane surfactants in Lake Ontario. The study showed inflow from Lake Erie as well as waste water treatment plants are the two major sources of perfluorooctane surfactants into Lake Ontario. Outflow through the St. Lawrence River is the major loss mechanism. This study also measured perfluorooctane surfactants on particulate matter in the air.


Summary: This study measured concentrations of perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs) in 4 year-old lake trout in all five Great Lakes. Results showed that the highest average concentrations were found in Lake Erie, followed by Lake Ontario and Huron, with Lake Michigan and Superior having the lowest concentrations respectively. Data also showed the major contributor to the sum concentrations of perfluorinated carboxylates (PFCAs) was from PFOA.


Summary: This study analyzed PFOS, the homologous series of PFCAs, and the PFOS-precursor heptadecafluorooctane sulfonamide (FOSA) in various organisms from a food web of Lake Ontario. The highest mean concentration was found in benthic organisms at the lowest trophic level, since these organisms are foraged on by larger fish, there is potential for biomagnification. Bioaccumulation in larger fish was also shown in this study.

Summary: This study determined concentrations of perfluorooctanesulfonate (PFOS) and several other perfluoroalkyl surfactants (PASs) in nine major water bodies in New York State. Elevated levels of PFOA were found in the Hudson River. PFOS were the most abundant perfluorinated compound in all fish and bird liver samples, and overall average concentrations of PFOS in fish were 8850-fold greater than that in surface water.


REFERENCES


14 Ibid.

15 Ibid.

16 Ibid.


