Investigating PFAS in Western Canada

ESAA Webinar

April 2020





What are PFAS?

They are a family of man-made chemicals used in a wide variety of industrial and consumer products and in specialized applications.



Environmental Science & Technology

Article

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Exceptionally High Serum Concentrations of Perfluorohexanesulfonate in a Canadian Family are Linked to Home Carpet Treatment Applications

Sanjay Beesoon, * Stephen J. Genuis, * Jonathan P. Benskin, *, * and Jonathan W. Martin*, *



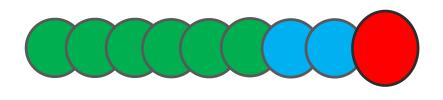
[†]Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, AB, Canada

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Per- vs. Poly- fluoroalkyl



Perfluoroalkyl = fully fluorinated carbon chain



6:2 FTS

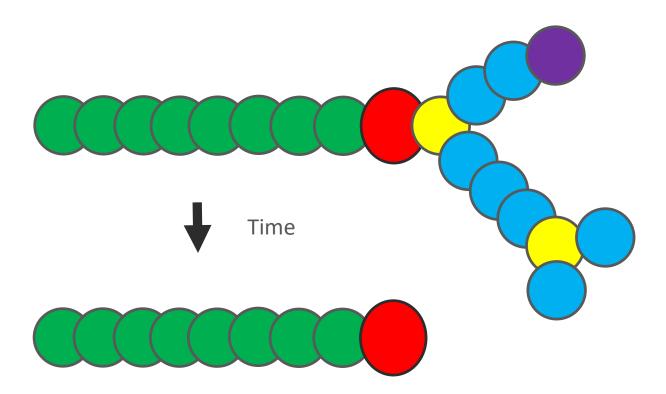
Polyfluoroalkyl = partially fluorinated carbon chain



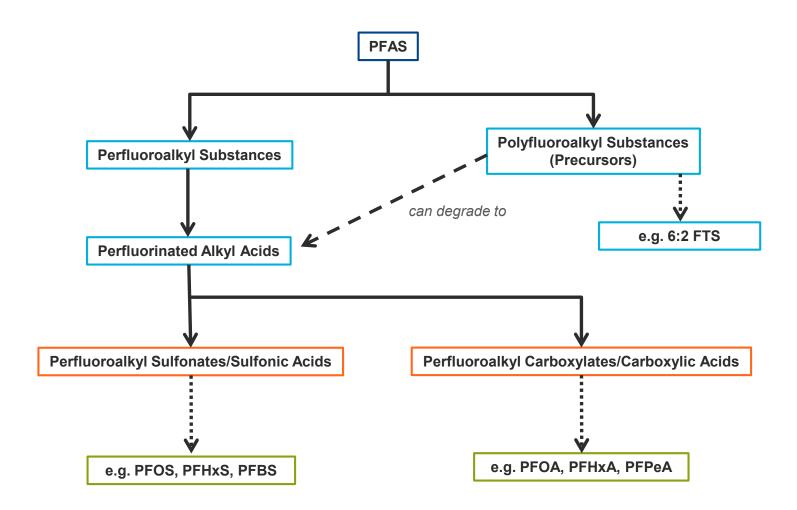
Precursors

"There are known knowns. There are things we know that we know. There are known unknowns. That is to say, there are things that we now know we don't know. "

– Donald Rumsfeld, 2002









What is the concern?

- CEPA listed toxic substances (PFOS, PFOA)
- Stockholm Convention listed (PFOS, PFOA) (PFHxS under review)
- Basel Convention requirements (PFOS in waste)
- Persistent fully fluorinated part doesn't break down in nature
- Bioaccumulative some PFAS accumulate in tissues of higher trophic level biota
- **Toxic** known human and ecological health effects
- Mobile contaminant plumes can be large



Point Sources – Class B Foams

- Firefighting foams containing PFAS have been used in Canada since the 1970s and continue to be used
- Used both in training and emergency response activities





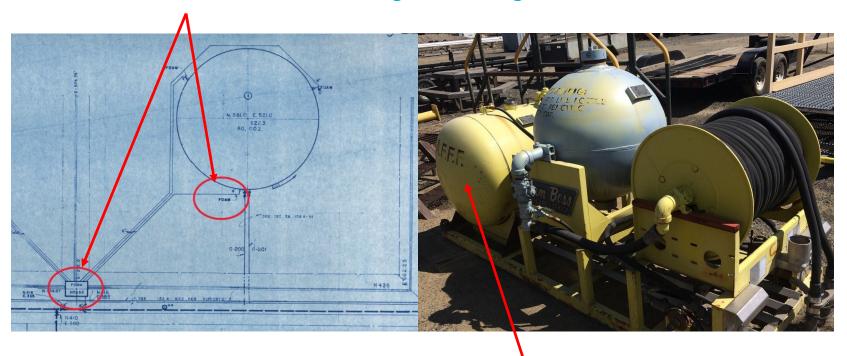
Photo: Global News

Estimate of mass loading from training: 10 kg/year



Point Sources – Class B Foams

Foam infrastructure associated with large fuel storage tank



Historic firefighting equipment (AFFF tank on left)

Estimate of mass loading during fire event: 8 kg/event



Point Sources – Class B Foams

- Prohibition of the manufacture, use, sale, offer for sale or import of PFOS, PFOA and long-chain (C9-C20) PFAS under the Prohibition of Certain Toxic Substances Regulations, 2012.
- PFAS composition in foams may differ by jurisdiction.
- Class A foams not expected to contain PFAS.







Other Sources

- Landfills
- Wastewater treatment facilities
- Wastewater lagoons
- Biosolids application areas
- Food waste compost and paper sludges



Western Canadian Landfill Leachate

PFHxA, PFPeA, PFOA, PFOS predominant PFAS in landfill leachates ^{1,2}

	Analyte	Mean (ppb)	Range (ppb)		
	PFBA	0.227	<mdl-3.260< td=""></mdl-3.260<>		
	PFPeA	0.359	<mdl-3.920< td=""></mdl-3.920<>		
	PFHxA	0.695	<mdl-7.090< td=""></mdl-7.090<>		
C4-C12	PFHpA	0.278	<mdl-2.310< td=""></mdl-2.310<>		
\rightarrow	PFOA	0.439	0.006-3.450		
Perfluoro	PFNA	0.022	<mdl-0.117< td=""></mdl-0.117<>		
Carboxylates	PFDA	0.015	<mdl-0.190< td=""></mdl-0.190<>		
	PFUnA	0.002	<mdl-0.011< td=""></mdl-0.011<>		
	PFDoA	0.003	<mdl-0.032< td=""></mdl-0.032<>		
C4-C8	PFBS	0.114	<mdl-1.370< td=""></mdl-1.370<>		
Perfluoro	PFHxS	0.300	<mdl-3.010< td=""></mdl-3.010<>		
Sulfonates	PFOS	0.279	<mdl-4.840< td=""></mdl-4.840<>		
	PFOSA	0.008	<mdl-0.063< td=""></mdl-0.063<>		
	^a MDL: Method detection limit				

Mass loading of 8-25 kg/year for landfill studied (24 compounds) ^{2,3}

³ Hamid et al (2018) Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills, Env.Poll. (235): 74-84



¹ Belinda Li (2011) *Perfluorinated Compounds in Landfill Leachate and their Effect on the Performance of Sodium Bentonite Landfill Liners*, MASc thesis UBC/UNBC

² Benskin et al (2012) *Per- and Polyfluoroalkyl Substances in Landfill Leachate: Patterns, Time Trends, and Sources*, ES&T (46): 11532-11540

Wastewater

Environment Canada Study (Guerra et al, 2014)

- PFOA, PFOS and PFHxA most frequently detected
- Median final effluent levels of 0.012, 0.005 and 0.009 ug/L, respectively
- Median mass loading of ~2 kg/year (13 PFAS)

SK Water Security Agency Study (in progress)

PFOA and PFOS detected in raw and treated wastewater

Wastewater treatment plants may transform PFAS precursors into "dead-end" PFAS which then do not degrade further in the environment.



Biosolids

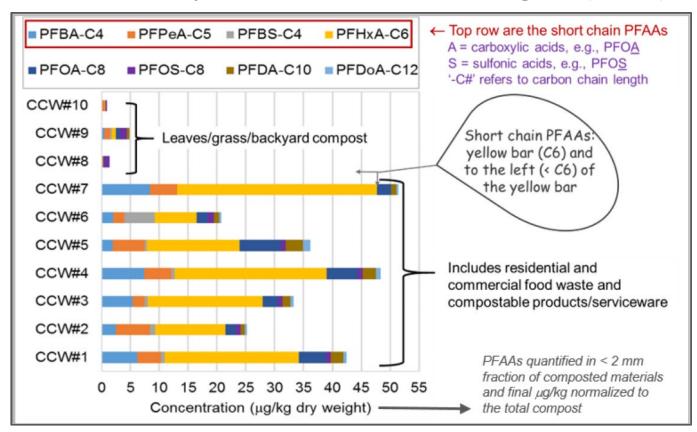
- > 80,000 dry tonnes biosolids produced annually in BC & AB
- Significant proportion applied to agricultural land, subject to provincial regulations and guidelines
- Median Canadian biosolid concentration of ~0.013 ug/g PFOS ¹ (similar to data from one BC WWTP of 0.015 ug/g PFOS)
- Median mass loading of 0.05 kg/year for WWTP studied ¹



¹ Guerra et al (2014) Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment , J.Haz.Mat. 272: 148-154.

Composts and Paper Sludges

Purdue University and Zero Waste Washington (2018)





Other Sources - Metal Plating

• PFAS in products used to suppress volatilization of hexavalent chromium (e.g. Fumetrol), added to plating baths

PERFLUOROALKYL SUBSTANCES IN GROUNDWATER (ug/L)												
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
0.12	0.33	0.38	0.15	ND	ND	ND	ND	ND	0.54	0.03	1.7	ND
0.06	0.36	0.39	0.10	ND	ND	ND	ND	ND	5.7	0.04	8.1	ND
ND	0.51	0.41	0.14	0.06	ND	ND	ND	ND	0.71	0.02	5.4	ND
0.09	0.28	0.14	ND	ND	ND	ND	ND	ND	0.17	ND	1.3	ND
0.10	0.48	0.35	0.19	ND	ND	ND	ND	ND	0.34	ND	2.1	ND
3.0												

Estimated use of 0.5-5 kg PFAS/year at individual facilities



PFAS Manufacturing Timelines (US focus)

PFAS ¹	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)
PFOA		Initial Production	Protective Coatings					
Fluoro- telomers					Initial Production	Firefighting Fo	oams	Predominant form of firefighting foam

Source: ITRC Fact Sheet - History and Use of Per- and Polyfluoroalkyl Substances (PFAS)



How do I look for PFAS at my site?



Society of Contaminated Sites Approved Professionals of BC PFAS Guidance (May 2019)

Guidance for the Assessment and Remediation of Per- and Polyfluoroalkyl Substances in British Columbia

Submitted to:

Society of Contaminated Sites Approved Professionals of British Columbia

May 2019



Interstate Technology and Regulatory Council – PFAS Guidance (April 2020)





Special Considerations – Field Program

- Adaptation of project timelines
- Use of PFAS-free water
- Elimination of suspect PFAS materials in equipment and field supplies
- Use of dedicated/disposable materials and equipment
- Implementation of preferred sampling methods (drilling, groundwater sampling)
- Decontamination of equipment
- Collection of QAQC samples



Special Considerations - Laboratory Methods

- Commercial laboratories employing in-house developed methods. There is no standardized, prescribed method.
- Laboratory results can be affected by:
 - Presence of sediment
 - Contaminant levels
 - Quantification standards used by lab
 - Background levels of PFAS within sampling and laboratory environments



BC Environmental Laboratory Manual

Organics

Revision Date: Sept 15, 2017

Perfluoroalkyl Substances (PFAS) in Soils by LC/MS/MS - PBM

Parameter Perfluoroalkyl Substances (Perfluorobutane Sulfonate (PFBS), Perflourooctane Sulfonate

(PFOS), Perfluorooctanoic Acid (PFOA)) in Soils

Analytical Method Methanol Extraction, Solid Phase Extraction (SPE) Clean-up, LC//MS/MS

Introduction This method is applicable to the quantitative determination of perfluorinated alkyl substances

in soils and solids.

Organics

Revision Date: Sept 15, 2017

Perfluoroalkyl Substances (PFAS) in Water by LC/MS/MS - PBM

Parameter Perfluoroalkyl Substances (Perfluorobutane Sulfonate (PFBS), Perflourooctane Sulfonate

(PFOS), Perfluorooctanoic Acid (PFOA)) in Waters

Analytical Method Solid Phase Extraction (SPE), LC/MS/MS

Introduction This method is applicable to the quantitative determination of perfluorinated alkyl substances

in waters.



Laboratory Methods - Advances

 Total oxidizable precursor (TOP) assay



Article

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Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and David L. Sedlak*

Total organic fluorine analysis – CIC, NAA



Total Oxidizable Precursor Assay

- incomplete oxidation can be an issue
- no regulatory guidance on interpretation of results

MODERATE CONCENTRATION AREA RESULTS (POST- TOP ASSAY) (ug/L)						
Laboratory #	1	2	3	4	%RSD	%RPD
PFBS	0.146	< 0.4	0.162	0.16	56.3	-
PFHxS	1.54	2.3	2.44	1.78	21.1	-
PFHpS	0.172	< 0.4	0.0385	0.02	111.1	-
PFOS	4	1.8	2.65	1.27	49.0	-
PFBA	< 16.1	3.0	3.16	3	103.3	-
PFPeA	6.64	9.2	10	9.6	17.1	-
PFHxA	9.56	7.8	10	7.95	12.6	-
PFHpA	1.18	1.6	1.92	1.64	19.3	-
PFOA	0.436	0.52	0.631	0.555	15.1	-
PFNA	0.02	< 0.4	0.0315	< 0.01	165	-
PFDA	< 0.1	< 0.4	< 0.00461	< 0.02	nc	-
4:2 FTS	< 0.02	-	-	< 0.15	-	nc
6:2 FTS	0.916	< 0.04	-	< 0.25	113.8	-
8:2 FTS	0.038	< 0.04	-	< 0.05	nc	-



They are at my site...now what?

ECCC

 Federal Environmental Quality Guidelines for PFOS – June 2018

Health Canada

- Guidelines for Canadian Drinking Water Quality (PFOS and PFOA only) – December 2018
- Drinking Water Screening Values April 2019 (FTS update)
- Soil Screening Values May 2019 (FTS update)

CCME

 Draft Canadian Soil and Groundwater Quality Guidelines for PFOS - issued for public comment in August 2018



Provincial Regulatory Frameworks

BC - Contaminated Sites Regulation - November 2017

- PFBS: soil (human soil ingestion), groundwater (drinking water)
- PFOA: groundwater (drinking water)
- PFOS: soil (multiple pathways), groundwater (aquatic life and drinking water)

Alberta

 Expect Tier 1 guidelines to be updated after release of CCME PFOS guidelines

Saskatchewan and Manitoba

No updates (will apply CCME)



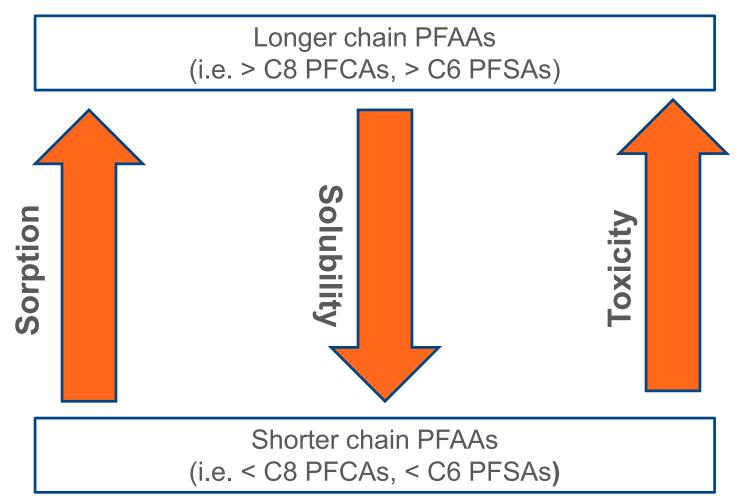
Source versus Background Levels - PFOS

Media	Anthropogenic Background	Source Zone or Source Affected	Environmental Criteria
Groundwater	< 0.02 ug/L	1-1000 ug/L	0.3 - 60 ug/L
Soil	< 0.01 mg/kg	0.1 - 50 mg/kg	0.01 - 150 mg/kg
Surface Water	< 0.02 ug/L	1-100 ug/L	6.8 ug/L
Wastewater Effluent	< 0.02 ug/L ^{1,2}	0.5-1.3 ug/L ^{1,2}	n.a.

¹ — Houtz et al (2016) *Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts.* Wat.Res. 95: 142-149. ² — Guerra et al (2014) *Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment*, J.Haz.Mat. 272: 148-154.



Why should we care about PFAS other than PFOS and PFOA?







Remediation – Field Implemented





Remediation – Field Implemented





Environmental Risk Assessment

 Migration to drinking water supplies, uptake to other media (biota, food)







Human Health TRVs

Health Canada

- PFOS: 6.0E-05 mg/kg-day
- PFOA: 2.1E-05 mg/kg-day
- PFBS: 1.6E-03 mg/kg-day (interim)
- PFBA: 3.0E-03 mg/kg-day (interim)
- PFNA: 2.19E-06 mg/kg-day (interim)
- Other PFAS (6) PFOS or PFOA TRV adopted (interim)

BC Ministry of Environment and Climate Change Strategy

- PFOS: 3E-05 mg/kg-day (HC/ATSDR)
- PFOA: 2E-05 mg/kg-day (ATSDR)
- PFBS: 2E-02 mg/kg-day (Nov 2015 US EPA RSL)

Ontario Ministry of Environment, Climate and Parks

PFOS: 1.8E-06 mg/kg-day (NJDEP, Cal EPA) to 3.1E-06 mg/kg-day (MDH, NHDES)



Ecological Health

Environment and Climate Change Canada: PFOS

- Draft soil guidelines protective of trophic transfers to terrestrial wildlife
- Fish tissue guidelines
- Tissue guidelines for aquatic biota food items
- Bird egg guidelines

SERDP programs underway or recently completed

- Guidance for assessing ecological risks of PFAS at AFFF sites (posted 01/2020)
- TRVs for amphibians (to be completed 09/2021)
- TRVs for birds (PFOS, PFOA and PFAS mixtures)



Thank You!

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