FluoroCouncil Briefing to the WA State Departments of Ecology and Health

Per- and Polyfluoroalkyl Substances (PFAS) Chemical Action Plan (CAP)

November 1, 2017

FluoroCouncil
Global Industry Council
for FluoroTechnology

Outline

- Key Messages
- PFAS Chemical Differences
- Overview of Major Comments
- Conclusion

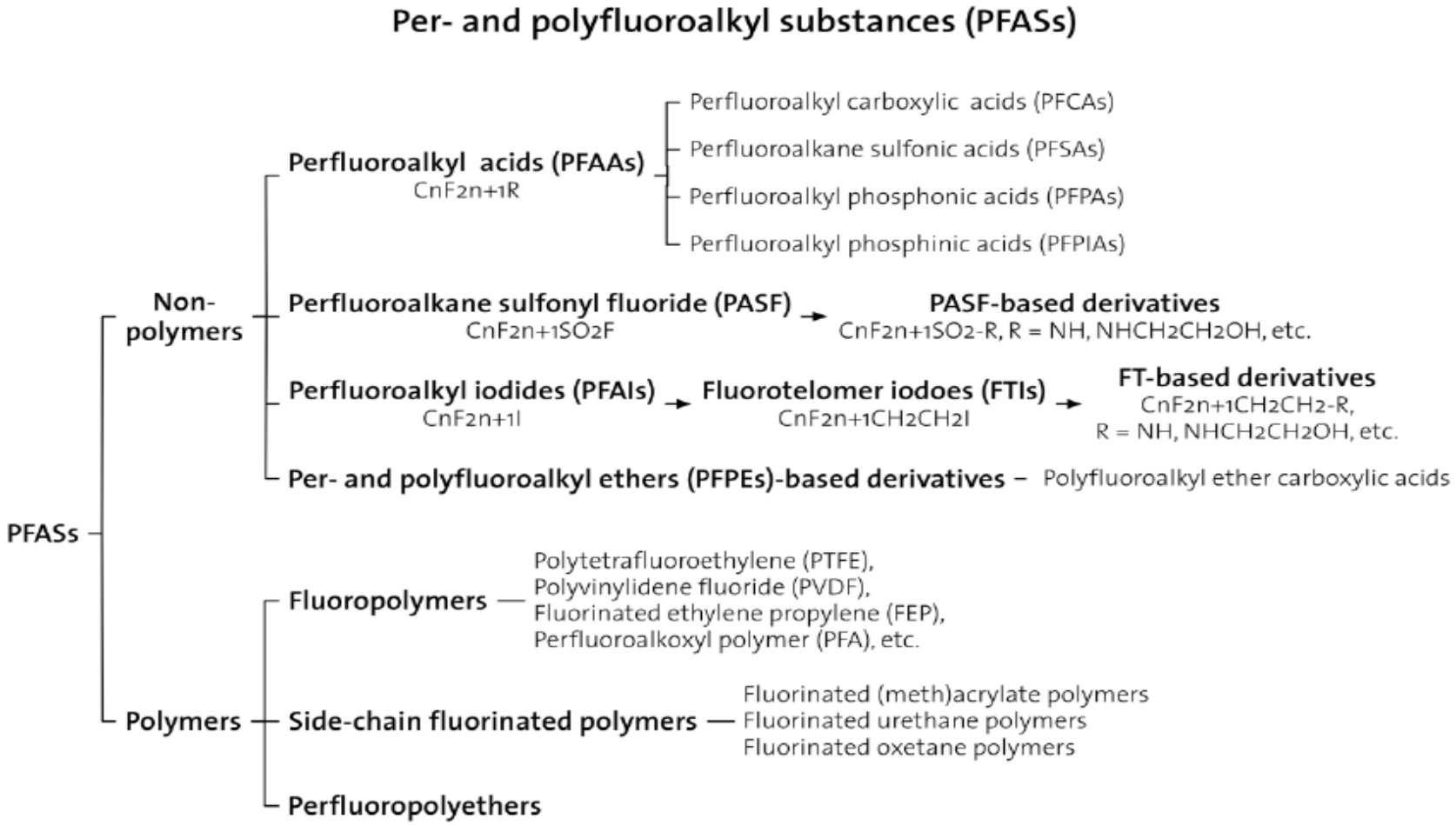
Key Messages

- FluoroCouncil supports development of a science- and risk-based PFAS CAP.
- Long-chain PFAAs are detected in the WA environment and wildlife.
- Contamination continues through use of stockpiled products and import of chemicals and articles containing long-chain PFAAs.
- Short-chain PFAAs, their precursors, and fluoropolymers are not PBTs.
- Short-chain PFAAs are less frequently detected in water/sediment and are not detected in wildlife.

- **The PFAS CAP should focus on long-chain PFAAs as known PBTs found in WA environment.**
- **Short-chain PFAAs, their precursors and fluoropolymers do not present a significant risk to the environment or human health and should not be included in the CAP.**

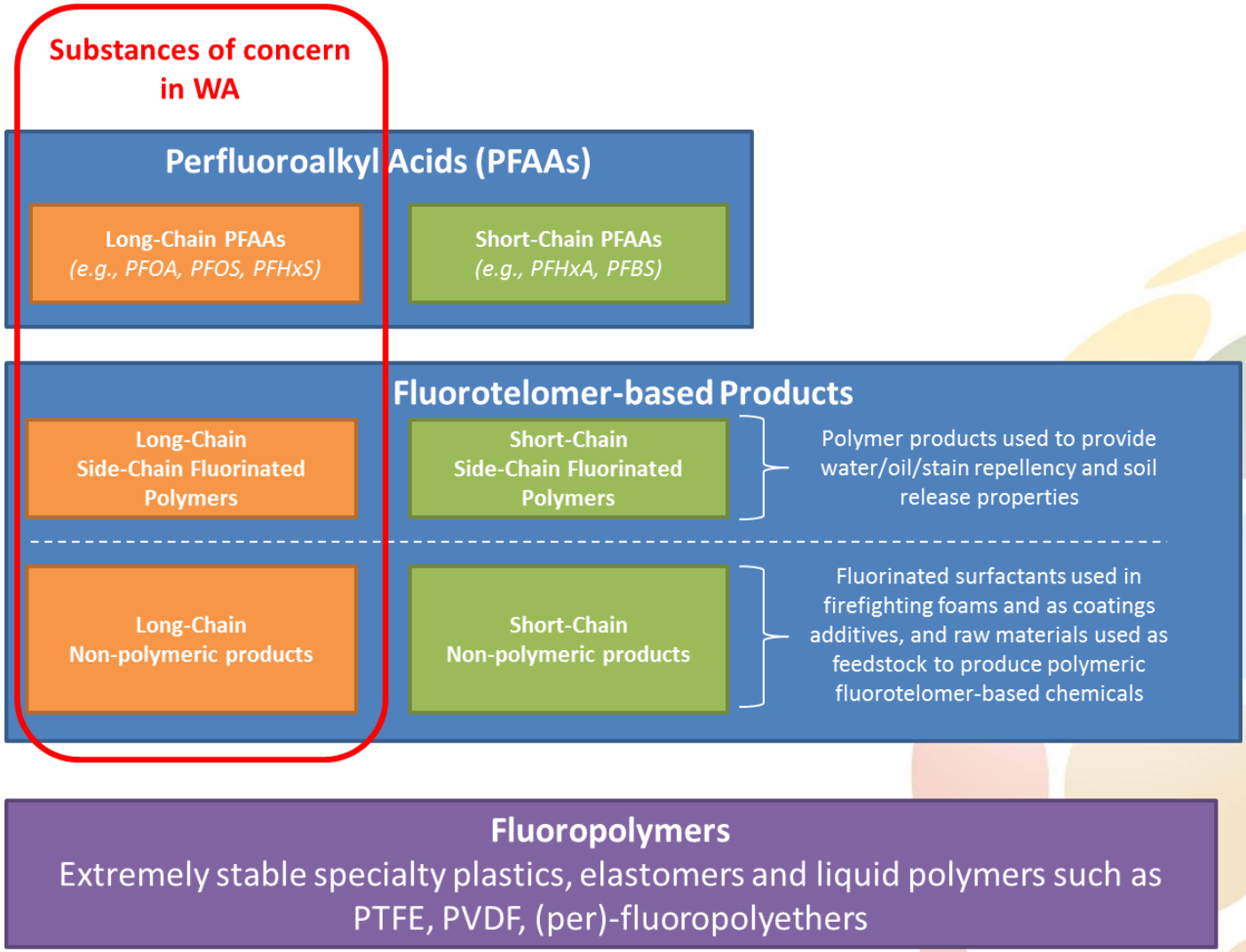
PFAS: A Broad Classification of Diverse Substances

Overview of PFAS



OECD(2013), OECD/UNEP Global PFC Group, Synthesis paper on per-and polyfluorinatedchemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.

PFAS Simplified: Long-chain, Short-chain, Fluoropolymers



What are Long Chain PFAS (OECD)?

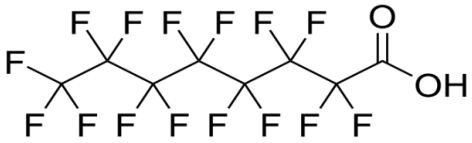
- Perfluorocarboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA);
- Perfluoroalkyl sulfonates (PFSAs) with carbon chain lengths C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS); and
- Precursors* of these substances that may be produced or present in products.

** For definition purposes "precursor" means a substance that has been recognized as having the potential to degrade to perfluorocarboxylic acids with a carbon chain length of C8 and higher (including PFOA) or perfluoroalkyl sulfonates with a carbon chain length of C6 of higher (including PFHxS and PFOS).*

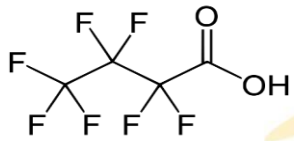
http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/

Structural Differences in PFAS

- **Perfluoroalkyl acids (PFAAs):**
  - Long Chain: Perfluorooctanoic Acid (PFOA)
  - MW = 414.07 g/mol

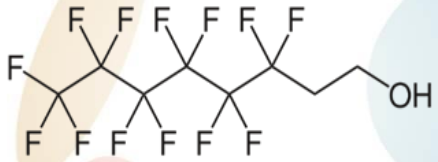


  - Short Chain: Perfluorobutanoic acid (PFBA)
  - MW = 214.04 g/mol



- **Fluorotelomer based products:**
  - Long Chain: Perfluorododecylethanol 12:2 (12:2 FTOH)
  - MW = 664.15 g/mol

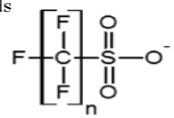
  - Short Chain: Perfluorohexylethanol 6:2 (6:2 FTOH)
  - MW = 364.11 g/mol



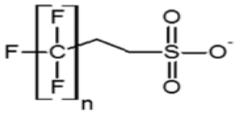
- **Fluoropolymers:**
  - E.g., Polytetrafluoroethylene (PTFE)
  - Polymers can consist of several tens to hundred thousands of monomer units
  - MW from 500k to >10 million

Functional Group Differences

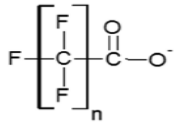
Perfluoroalkyl sulfonic acids
PFSAs
n = 4-10



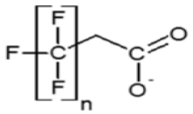
Fluorotelomer sulfonic acids
n:2 FTSAs
n = 4, 6, 8



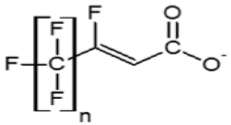
Perfluoroalkyl carboxylic acid
PFCAs
Short Chain
~~n = 4-7~~ **n = 3-6**
Long Chain
~~n = 8-18~~ **n = 7-18**



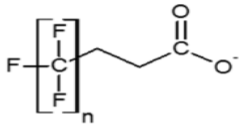
Fluorotelomer carboxylic acids
FTCAs
n:2 FTCA
n = 4, 6, 8, 10



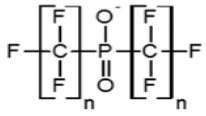
n:2 FTUCAs
n = 4, 6, 8, 10



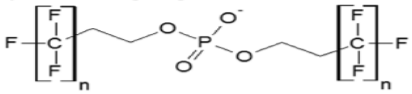
n:3 FTCA
n = 3, 5, 7, 9



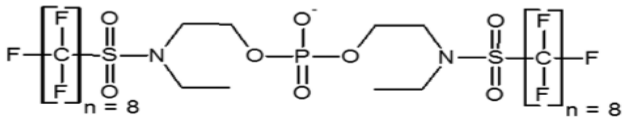
Disubstitued perfluoroalkyl phosphinic acids
PFPIAs
n = 4, 6, 8



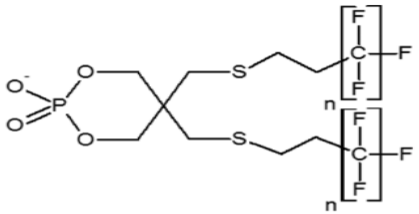
Di-substitued polyfluorinated phosphate esters
DiPAPs
n = 4, 6, 8, 10



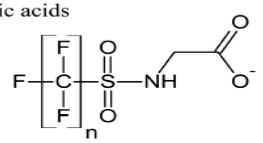
Bis(N-ethyl perfluoroalkylsulfonamidoethane) phosphate
DiSAmPAP



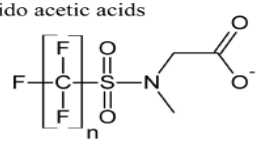
Fluorotelomer mercaptoalkyl phosphate esters
FTMAPs
n = 4, 6, 8, 10



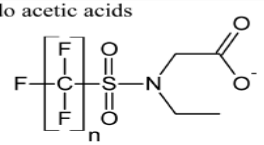
Fluoroalkyl sulfonamido acetic acids
FASAAs
n = 4-8



N-methyl fluoroalkyl sulfonamido acetic acids
MeFASAAs
n = 4-8



N-ethyl fluoroalkyl sulfonamido acetic acids
EtFASAAs
n = 4-8



Lang et al. (2016), Release of Per- and Polyfluoroalkyl Substances (PFASs) from Carpet and Clothing in Model Anaerobic Landfill Reactors.

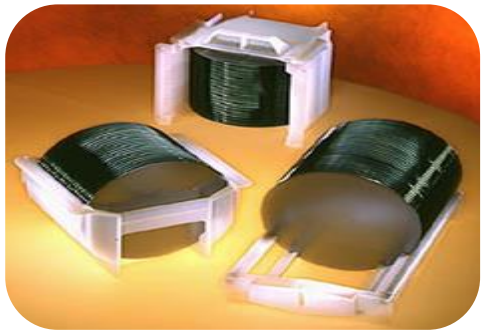
Fluoropolymers are critical to modern life

Electronics: High frequency signal transmission; smudge-resistant touch screens

Membranes in outdoor apparel, providing a breathable barrier against wind and rain

Medical Devices: High dielectric insulators in medical equipment that relies on high frequency signals

Aerospace/Auto: Weight reducing fuel lines; heat/chemical resistant wire coatings



Semiconductor manufacturing: Providing pure environments to transport/store harsh chemicals

Nonstick surfaces in cookware and small appliances

Fluorotelomer-based Products are critical to modern life

Healthcare: Garments/Drapes that Protect Against Disease Transmission

First Responder Gear Treatments and Bulletproof Vests that Maintain Performance in Extreme Conditions

Oil/Grease Resistant Food Packaging that is Recyclable, Increases Shelf-Life, Reduces Packaging

Textiles/Carpet with Water/Oil Repellency, Stain Resistance and Soil Release and Longer Useful Life

Class B (Flammable Liquid) Fire Fighting Foam with Shorter Extinguishing Time and Burnback Resistance

PFAS: A Broad Classification of Diverse Substances

- The category of “PFAS” includes a broad variety of substances that differ in:
  - Structure
  - Property
  - Use
  - Hazard Profile
  - Risk
- An accurate, substance-specific evaluation is needed

Overview of FluoroCouncil's Major Comments on CAP Chapters

Major Comments

The PFAS CAP should focus on long-chain perfluoroalkyl acids (long-chain PFAAs: long-chain PFCAs and long-chain PFSAs)

1. Long-chain PFAAs are the concern facing WA.

2. The goal of CAP regulations is to reduce and phase-out PBT uses, releases and exposures in WA that pose a risk: Only long-chain PFAAs are PBTs.

3. Discussing “PFAS” as a single broad class is technically inaccurate and dilutes the impact that WA could have to truly address their concerns.

Long-chain PFAAs are the concern facing WA

Long-chain PFAAs found in WA Environment, Products

- Long-chain PFAAs (namely PFOS, PFOA) have been found in WA waters, wildlife, localized drinking water at elevated levels
  - 2016 Ecology study (long-chain PFAAs were widespread in biota, surface waters)*
  - Military installation sampling (PFOS, PFOA found at elevated levels)
  - UCMR3 data (PFOS/PFOA detected at three locations, one at elevated levels)
- Long-chain PFAAs (including PFOA, PFNA) have been found in children's products tested in WA

*Mathieu C and M McCall. Survey of Per- and Poly-fluoralkyl Substances (PFASs) in Rivers and Lakes, 2017. Washington Department of Ecology, Olympia, WA. Available at: https://fortress.wa.gov/ecy/publications/documents/1703021.pdf

Addressing Sources of Long-Chain PFAAs

- **Contamination Sources**
  - Use of older AFFF formulations^
  - Older manufacturing processes
  - Products treated with legacy long-chains

- **Regulatory Gaps – Imports, Global Emissions**
  - Production/use/trade of long-chain PFAAs (PFOA, PFOS, PFHxS), precursors, and treated articles continues outside the U.S. by non-Stewardship Program companies
  - EPA's TSCA SNUR does not restrict PFOA in key imported articles and is limited by its ability to regulate ongoing uses

^ Legacy AFFF sources may impact drinking water with PFOS, PFHxS, PFOA detected at highest frequency and concentrations (Anderson et al. Chemosphere 2016, DOI: 10.1016/j.chemosphere.2016.01.014)

Existing and Proposed Regulations for Various Long-chain PFAAs in Selected Countries/Regions

Country/Region	PFHxS	PFOS	PFSA Higher Homologs	PFOA	PFNA	PFCA Higher Homologs
Canada		•		•	•	•
USA	•	•	•	✦	✦	✦
EU-REACH*		•		•^	✦	✦
Russia		✧				
Australia	•	•	•	•	•	•
China		✧				
Japan		•				
Korea		•		•		
Stockholm Convention	✦	•^		✦		

Table Legend:

* PFHxS, PFOA, PFNA and longer-chain PFCAs have been identified as SVHCs

^ Includes articles

• Regulation in place

✦ Proposed regulation

✧ Regulation in place excluding Acceptable Purpose and Specific Exemptions (Stockholm Convention)

Adopted from OECD Environment, Health and Safety Publications Series on Risk Management No. 29 "RISK REDUCTION APPROACHES FOR PFASs – A CROSS-COUNTRY ANALYSIS", 2015 http://www.oecd.org/chemicalsafety/risk-management/Risk_Reduction_Approaches%20for%20PFASS.pdf

Short-chain PFAS and Fluoropolymers: Not Major Sources of Long-chain PFAAs

- Major manufacturers in U.S., Europe, Japan have discontinued the manufacture and use of long-chain PFAAs and their precursors.
  - PFOA is no longer used as polymerization aid in manufacture of fluoropolymers
  - Long-chain fluorotelomer-based products substituted with short-chains

- Short-chain PFAAs and short-chain fluorotelomer-based products are not material sources of or precursors for long-chain PFAAs.
  - i.e., ppb levels (e.g., EU REACH PFOA restriction – 25 ppb)
- Fluoropolymers manufactured in the U.S., Europe, Japan are not sources of or precursors for long-chain PFAAs.

Conclusion

- WA CAP should focus on long-chain PFAAs - addressing environmental contamination and identifying, eliminating ongoing sources
- Other PFAS (short-chains, fluoropolymers) do not contribute to long-chain levels

All PFAS are not PBTs

WA CAP Regulations Address PBTs

- Regulations that govern the CAP program recognize the unique risk concerns associated with PBTs.
- WAC § 173-333-100 - The goal of CAP regulations is to "reduce and phase-out PBT uses, releases and exposures" in WA
- WAC § 173-333-300 – "The purpose of evaluating a chemical on Persistence, Bioaccumulation and Toxicity is to identify chemicals that remain in the environmental for long periods of time **and** bioaccumulate to levels that pose threats to human health and the environment" [emphasis added]
  - Only PFOS and its salts on WA PBT List

Consideration of non-PBTs is limited

- WAC §173-333-420 – CAP contents
  - CAP **policy options** for addressing PBTs can include “use of available substitutes” for PBTs
  - CAP **recommendations** can include switching to and encouraging the development of safer substitutes for PBTs

Specific Short-chain PFAS substances do not meet Stockholm Convention POPs criteria

Table 1.1: Summary of POP criteria for specific short-chain perfluorinated substances

Fluorochemical	Environmental Source	Stockholm Convention POP Criteria					Conclusion
		Persistence	Bioaccumulation	Long-range Environmental Transport	Toxicity		
					Ecotoxicity	Toxicity to Humans	
Methacrylate Polymer	Commercial product	Meets criteria	Does not meet criteria	Does not meet criteria	Does not meet criteria	Does not meet criteria	Does not meet POP criteria (meets 1 of 4)
6:2 FTOH	Manufacturing intermediate	Parent does not meet criteria*	Does not meet criteria	Meets criteria based on atmospheric transport**	Does not meet criteria	Does not meet criteria	Does not meet POP criteria (meets 1 of 4)
6:2 FTAC	Manufacturing intermediate	Parent unlikely to meet criteria*	Does not meet criteria	Unlikely to meet criteria	Does not meet criteria	Does not meet criteria	Does not meet POP criteria (meets 1 of 4)
6:2 FTMAC	Manufacturing intermediate	Parent unlikely to meet criteria*	Does not meet criteria	Does not meet criteria	Does not meet criteria	Does not meet criteria	Does not meet POP criteria (meets 1 of 4)
PFHxA/ PFHx	Degradation product	Meets criteria	Does not meet criteria	Indeterminate	Does not meet criteria	Does not meet criteria	Does not meet POP criteria (meets 1 of 4)

* Parent chemical forms PFHxA as a terminal degradation product

** Additional information is necessary to determine if concentrations in remote environments are of "potential concern" according to Annex D 1 (D) (i).

Ramboll Environ, "Assessment of POP Criteria for Specific Short-chain Perfluorinated Alkyl Substances" 2016. Available at https://fluorocouncil.com/Assessment-of-POP-Criteria-for-Specific-Short-Chain-Perfluorinated-Alkyl-Substances

Short-chain PFAAs are well studied

- Rich database on short-chain PFAAs (with focus on PFHxA as primary degradation product)
- Studies conducted include:
  - testing for cancer
  - reproductive/developmental toxicity
  - systemic toxicity
  - bioaccumulation
  - ecological endpoints
  - environmental fate and transport

- Relevant studies available at www.fluorocouncil.com/resources/research

PFHxA*: Toxicity Summary

- Does not represent a reproductive, developmental or neurobehavioral hazard
- Not carcinogenic
- Not mutagenic
- Does not bioaccumulate in fish
- Quickly eliminated from living organisms
- Not an endocrine disruptor (SETAC NA poster/publication in prep)

* PFHxA is an impurity/degradation product

GreenScreen® Hazard Ratings

GreenScreen® Hazard Ratings for Perfluorohexanoic Acid

Group I Human					Group II and II* Human									Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						single	repeated*	single	repeated*										
L	*L*	*L*	*M*	DG	M	H	*M*	DG	L	*L*	DG	*vH*	*vH*	M	L	vH	L	*M*	*M*

Note: Hazard levels (Very High (vH), High (H), Moderate (M), Low (L), Very Low (vL)) in *italics* reflect estimated values, authoritative B lists, screening lists, weak analogues, and lower confidence. Hazard levels in **BOLD** font are

GreenScreen® Hazard Ratings for Acetic Acid

Group I Human					Group II and II* Human									Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						single	repeated*	single	repeated*										
L	L	DG	L	DG	M	M	L	L	L	M	M	vH	vH	M	L	vL	*vL*	M	M

Note: Hazard levels (Very High (vH), High (H), Moderate (M), Low (L), Very Low (vL)) in *italics* reflect estimated (modeled) values, authoritative B lists, screening lists, weak analogues, and lower confidence. Hazard levels in **BOLD** font are used with good quality data, authoritative A lists, or strong analogues. Group II Human Health endpoints differ from Group II* Human Health endpoints in that they have four hazard scores (i.e., vH, H, M and L) instead of three (i.e., H, M and L), and are based on single exposures instead of repeated exposures. Please see Appendix A for a glossary of hazard acronyms.

http://www.theic2.org/hazard-assessment

PFHx Toxicity Profile

Impurity/Degradation product - Perfluorohexanoate (PFHx)

Repeated-Dose Mammalian (Oral)

- 2-year chronic (rat) [5]
  - NOAEL M 15 mg/kg/day; F 30 mg/kg/day
  - Not carcinogenic
- 90-day sub chronic (rat) [1, 2]
  - NOAEL 100 mg/kg/day
  - Target: body weight
- One-Generation Reproduction (rat) [1]
  - NOAEL 100 mg/kg/day
  - No effects on reproductive parameters
- Repro/Development (mouse) [6]
  - NOAEL 100 mg/kg/day
- Development (rat) [1]
  - NOAEL 100 mg/kg/day
- Pharmacokinetics (rat, mouse, monkey) [3]
  - Single and repeated dose studies completed: rapid elimination for both genders in all species

Summary

- Not damaging to DNA, not genotoxic or mutagenic
- Not a selective developmental or reproductive toxicant
- Not carcinogenic [5]
- Rapid bioelimination, not bioaccumulative [4]
- Not expected to be harmful to human health or the environment at environmentally relevant concentrations

(1) Loveless et al., *Toxicology,* **2009**, 264(1-2),32-44
(2) Chengelis et al., *Repro Tox,* **2009,** 24(3-4), 342-351
(3) Gannon et al., *Toxicology,* **2011**, 283(1): 55-62
(4) Conder et al., *Environ Sci Technol,* **2008**, 42(4): 995-1003
(5) Klaunig JE et al., *Toxicol Pathol*., **2015,** 43(2):209-20
(6) Mukerji et al., *Toxicology Reports,* **2015**, 2: 130-143

Elimination Half-life Studies in Plasma - Perfluoroalkyl acids (PFAAs)

Elimination $t_{1/2}$ (Days)	short-chain			long-chain		
	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
Rat	0.3	0.2	0.2 – 0.05	7	5	25
Monkey	2	4	1	100	21	45
# Fluorinated Carbons	3	4	5	6	7	8

- **BIG difference between "long" and "short" chain PFAAs**
- **Short chain PFAAs eliminate rapidly and significantly less toxic**

Gannon et al., *Toxicology* **2011,** *283*, (1), 55-62.
Chengelis et al., *Repro Tox* **2009** (27), 400-406.

Fluoropolymers are not toxic

- High molecular weight polymers
- Extremely stable
- Too large to be bioavailable or toxic
- Insoluble in water and not mobile
- Do not degrade in the environment into PFAAs
- Therefore, present no significant risk to human health or the environment
- As a result, regulators do not require the development of significant toxicity data on fluoropolymers

Conclusion

- Only long-chain PFAAs are PBTs and thus, within the scope of the CAP program
- Other PFAS (short-chain PFAAs, fluoropolymers) are not PBTs and thus, should not be included in the CAP

Discussing PFAS as a single class is technically inaccurate

“PFAS” is a broad, diverse family of chemistry

- PFAS chemistries are complex and broad
- Alleged 3,000+ chemicals in the PFAS category
- No scientifically sound rational for treating them all the same
  - Vary in physical properties
  - Vary in chemical properties
  - Vary in hazard profiles
  - Chemical structure, size and functional group all imparts unique characteristics
- See our detailed comments for numerous instances where the use of “PFAS” in CAP chapters was inaccurate and incorrect

Conclusion

- The term “PFAS” is too broad
- The CAP chapters are technically flawed due to treating PFAS as a single common class of chemicals

Recommendations

- The PFAS CAP should focus on long-chain PFAAs as known PBTs found in WA environment.
  - Develop a clear problem statement and use a science-based decision logic to evaluate
  - Develop scientifically-based recommendations that will specifically and directly address the stated problem
- Short-chain PFAA, their precursors and fluoropolymers do not present a significant risk to the environment or human health and should not be included in the CAP.

Contact

Jessica Bowman

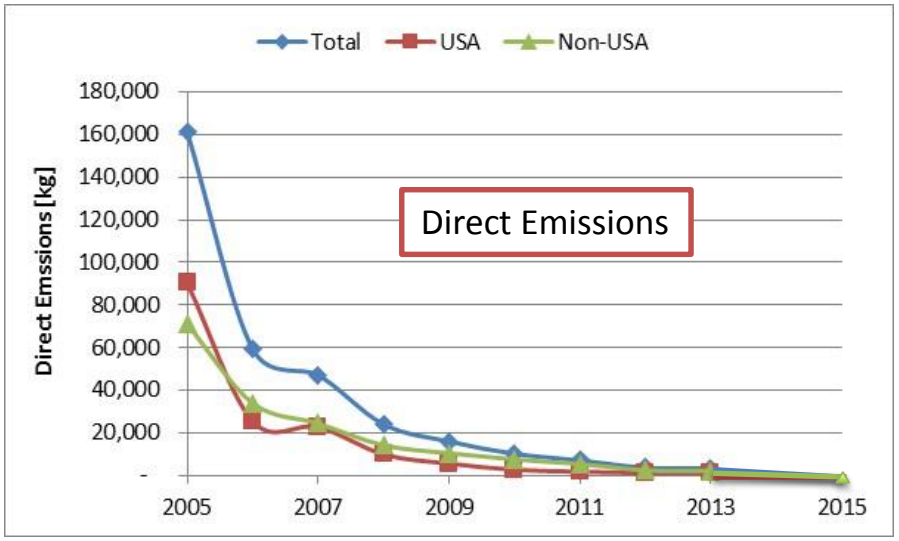
Jessica_bowman@fluorocouncil.org

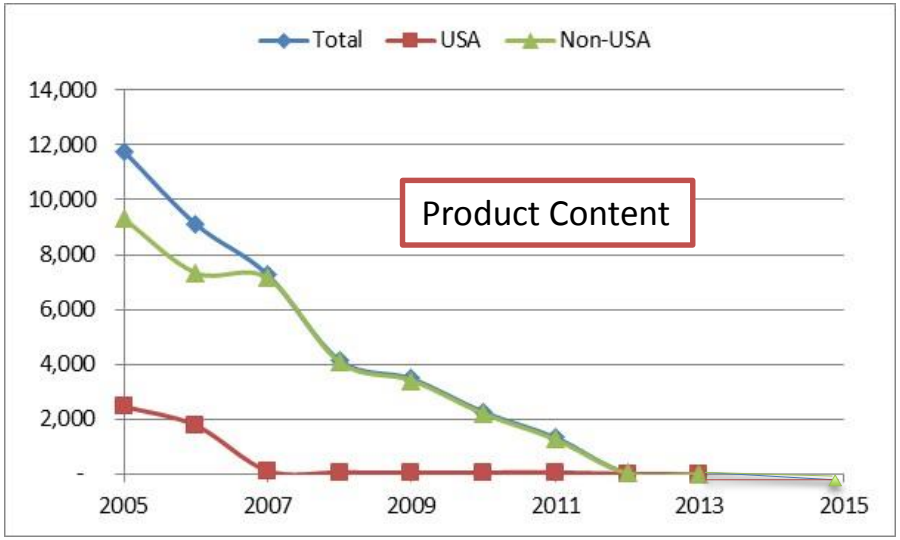
+1-202-249-6737

www.fluorocouncil.org

Backup Slides

US EPA PFOA Stewardship Program





- Global and voluntary partnership between U.S. EPA and industry aimed to reduce human and environmental exposure to PFOA, its precursors and higher homologues

✓ **All companies met the goal in 2015 or earlier:** https://www.epa.gov/sites/production/files/2017-02/documents/2016_pfoa_stewardship_summary_table_0.pdf

✓ **Led to virtual elimination of those chemicals from facility emissions to all media and product content**

- Source: "EPA Summary Tables" https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/20102015-pfoa-stewardship-program-2014-annual-progress
- Baseline = Year 2000 or other

Historic PFCA Emission Sources

- Manufacture of PFOA in the U.S. ceased in 2013. Use of PFOA and related long-chains to produce fluoropolymers ceased by 2016 in North America pursuant to the U.S. EPA 2010/15 PFOA Stewardship Program.

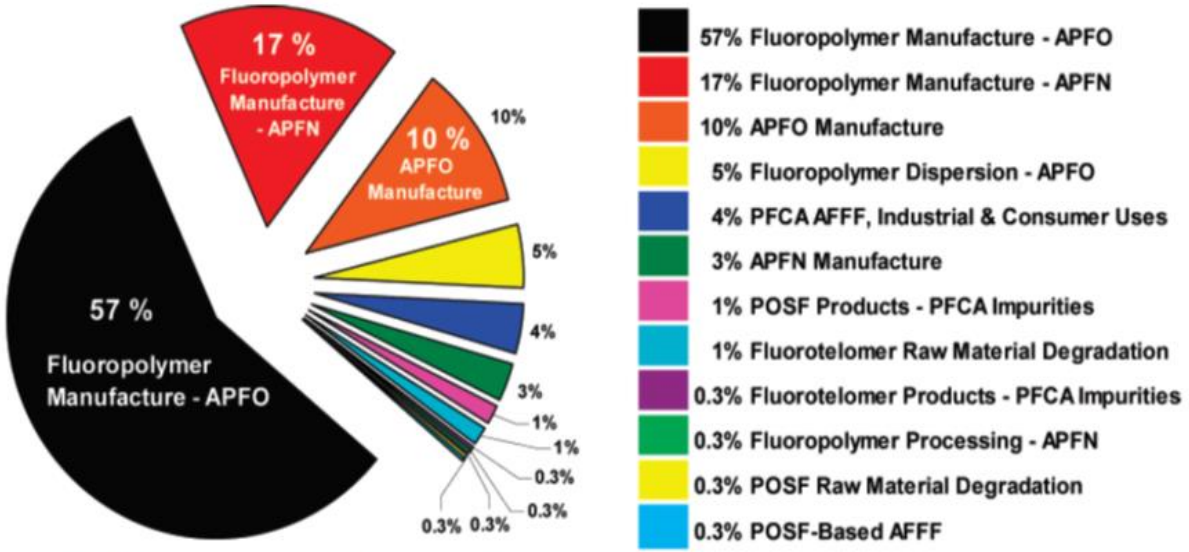


FIGURE 3. Percent of total historical global PFCA emissions by source.

Prevedouros et al., Environmental Science & Technology 40 (2006) 32-44