Perfluoroalkylated Substances in the Environment :

What are they? Where do they come from? Where do they go?
What do we know about them?

$F(CF_2)_n$ - X

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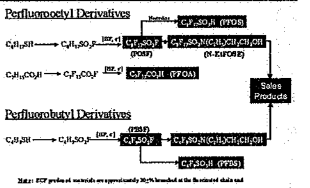
Abstract

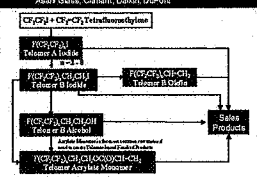
Perfluoroalkylated substances (PFAS) are specialty materials utilized in a wide variety of end-use applications which take advantage of the unique properties of the perfluoroalkyl functionality. These substances are manufactured by different processes and have functionality differences that influence their performance, toxicological and environmental behavior. To start, this paper will begin by reviewing the "classes" of PFAS and then proceed to discuss how these substances are used, their routes into the environment via these uses and provide an overview of what is known about their environmental toxicology and fate. Although only a limited number of essential physicochemical data are available, thus hampering a complete assessment of the environmental fate of PFAS, it has become clear that PFAS behave differently from other non-polar organic microcontaminants. Some PFAS have been identified in environmental media in urbanised areas with and without production sites nearby. For example, perfluorooctane sulfonate (PFOS) has been detected globally in a wide array of organisms as well as in non-exposed and exposed human populations. In general, PFAS acute and chronic ecotoxicity to aquatic organisms is moderate to low. Acute toxicity to rodents is also low. While no human health effects or increased cancer risk have been observed for PFAS, PFOS has been shown to effect development and reproduction while perfluorooctanoic acid (PFOA) has been found to be weakly carcinogenic in repeated-dose rat studies. This review will show the importance of filling in the current environmental fate and effects information gaps for PFAS. As such, areas for future research will be suggested.

Perfluoroalkylated Substances : What are they?

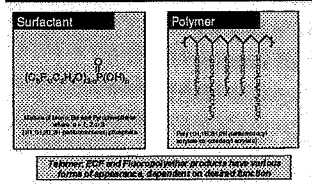
Electrochemical Fluorination
3M, Miteni



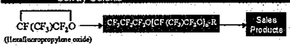
Telomerisation
Asahi Glass, Clariant, Daikin, DuPont



2 Major Sales Product Forms (Examples)



Perfluoropolyethers
Solvay-Solexis



Telomer Production Mass Balance - Draft

- Global Telomer A equivalents produced in 2000-2002
  - approximately 5- 6.5 Million kg/yr
- Regional Product Distribution : North America - 40%; Europe - 30%; Asia Pacific - 30%
- Polymers : 80% of total product manufacture
- Preliminary Data Analysis

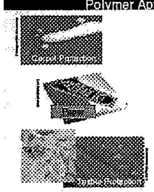
	C4	C6	C8	C ≥ 10	Total
n=	2	3	4	5+	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Polymer	99%	45%	85%	88%	80%
Non-Polymer	1%	55%	15%	12%	20%

Telomer A = $F(CF_2CF_2)_nI$ (n=2-8)

Perfluoroalkylated Substances: Surfactant Applications

As a Surfactant
- wetting and leveling
- 100 - 500 ppm
- Coatings
- Electronics
- Herbicides
- Metal Finishing
- Oil wells
- Polymerisation

Perfluoroalkylated Substances Polymer Applications



As a Polymer
- Water & Oil Repellency
- Stain & Soil Release
- 4000± ppm on weight of substrate
- Leather
- Textiles
- Carpeting
- Coatings

Perfluoroalkylated Substances : Where do they go?

Use & Emissions of PFAS in the Netherlands

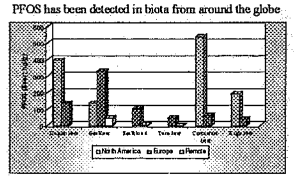
Type of industry	Use of PFAS (tonnes/year)	Form	Emissions (tonnes/year)
Carpet	15	Polymers	10 (worst case)
Paper & Board	60-105 (not in NL)	Polymers & Surfactants	
Textile	N.A.	Polymers	100% of the applied polymers
Leather	20-Oct	Polymers	
Fire-fighting foams (mobile)	0.13-0.81	Surfactant	0.13-0.81 (worst case)
Fire-fighting foams (stationary)	1.0-3.0	Surfactant	1.0-3.0 (worst case)
Specialty surfactants	N.A.	Surfactant	-
Polymerisation aid	> 1	Surfactant	-

Potential Environmental Routes of Entry

	Intermediates	Surfactants	Polymers
Air	Particle adsorbed or vapor phase?	Fugitive emissions from WWTP?	
Soil	Air Deposition Soil - Landfill Land applied sludge	Landfill Land applied sludge	Landfill Land applied sludge
Sediment	WWTP Air Deposition direct discharge	WWTP direct discharge	Direct discharge - point source
Water	WWTP & Septic direct discharge surface presence?	WWTP & Septic direct discharge surface presence?	WWTP & Septic
Examples	$C_8F_{17}CH_2CH_2OH$ $C_4F_9SO_2N(CH_3)CH_2CH_2OH$	Phosphates Ethoxylates Sulfonates	Acrylates Urethanes

Occurrence in the Environment

PFOS has been detected in biota from around the globe



Occurrence in the Environment

PFOS has been detected in humans around the globe.

- **Occupationally exposed**
  - PFOS: 0.14 - 2.19 ppm (3M)
  - PFOA: 0.1 - 6.8 ppm (3M, DuPont)
- **General public**
  - PFOS: 17 - 53 ppb (3M, U.S. only)
  - PFOA: 3 - 17 ppb (3M, U.S. only)
    - not detected in Japan at LOD of 3ppb

(*Organohalogen Compounds*, 55, 319-322, 2002)

Perfluoroalkylated Substances : What do we know about them?

Behaviour in the Environment
not easily predictable

- PFAS substances are complex product mixtures
- Partitioning is not solely controlled by hydrophilic and hydrophobic interactions
  - K_{ow}-based QSARs are not applicable
  - Some PFAS may escape from the water phase
    - semi-volatile vapor pressure and high hydrophobicity may lead to potential for long-range air transport
    - examples: $C_6F_{13}CH_2CH_2OH$, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$
- Adsorption
  - has been observed for PFOS and Telomers
  - PFOA does not strongly adsorb and is expected to stay in water
  - PFOS is expected to end up in water, sediment and organic matter and organisms

Behaviour in the Environment

- Fate
  - Fate of fluorinated organic polymers is unknown
    - polymers are not known to biodegrade (they are not bioavailable)
    - ester bonds may be vulnerable to chemical degradation
  - The perfluoroalkyl chain $F(CF_2)_n$- is not known to be degraded or transformed
  - ECF products degrade to perfluoroalkyl sulfonates and perfluoroalkyl carboxylates
  - Telomer degradation products are not clear and may be multiple
- Bioconcentration Factor (BCF)
  - PFOS ~ 50,000; PFOA ~ 4; $C_8F_{17}CH_2CH_2OH$ ~ ~1,000

Environmental Effects

Representative Environmental Effects Data

	Substance	Acute / Chronic	Trophic Level	Species	Results (mg/L)
ECF	PFOS $C_8F_{17}SO_3H$	Acute	Fish	Fathead minnow	96h NOEC = 3.3
			Invertebrates	Daphnids	48h EC50 = 27
			Algae	Selenastrum capricornutum	96h EC50, growth rate = 126
		Chronic	Fish	Fathead minnow	42d NOEC = 0.30
			Invertebrates	Daphnids	28d NOEC reproduction = 7
			Invertebrates	Mysid shrimp (marine)	35d NOEC reproduction = 0.25
	PFOA $C_7F_{15}COOH$	Acute	Fish	Fathead minnow	96h LC50 = 300
			Bacteria	Photobacterium ph.	30 min EC50 = 117
			Algae	Selenastrum capricornutum	96h EC50, growth rate = 3.8
		Chronic	Fish	Fathead minnow	30d NOEC = >100
			Algae	Selenastrum capricornutum	14d EC50 = 43
	N-EtFOSA $C_8F_{17}SO_2NHCH_2CH_2OH$	Acute	Fish	Fathead minnow	96h LC50 = 206
			Invertebrates	Daphnids	48h EC50 = 14.5
	PFBS $C_4F_9SO_3H$	Acute	Fish	Fathead minnow	96h LC50 = 4.8
			Invertebrates	Daphnids	48h EC50 = 11
Telomer	8-2 Telomer B Alcohol $C_8F_{17}CH_2CH_2OH$	Acute	Fish	Danio rerio	96h NOEC = 0.18
			Invertebrates	Daphnids	48h NOEC = 0.18
			Algae	Scenedesmus subspicatus	72h NOEC = 0.20
			Earthworm	OECD 207	NOEC = 32 mg/kg dw
			Nematode		NOEC > 1000 mg/kg dw

Environmental Effects Data Telomer-based Products

	Acute Fish mg/L	Acute Daphnid mg/L	Acute Algae mg/L
Telomer Phosphate Surfactant	96 hr LC_{50} > 1,000 rainbow trout	48 hr EC_{50} > 1,000	NOEC > 100
Telomer Ethoxylate Surfactant	96 hr LC_{50} = 100-140 rainbow trout	48 hr EC_{50} = 72	
Telomer [illegible] Polymer*	[illegible]	[illegible]	[illegible]
Telomer Acrylate* Polymer	[illegible]	[illegible]	[illegible]

* [illegible]

Conclusions & Future Efforts

- Many data are still lacking to complete an accurate environmental assessment
  - product mixtures complicate the ability to obtain data
  - predictive models do not have sufficient real data to be useful
- Industrial companies and consortia are working to develop additional data
- Global regulatory agencies are interested and actively seeking additional information
- PFOS is a PBT chemical and is globally distributed

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