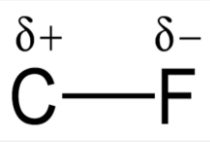
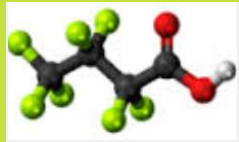


INTRODUCTION TO POLY- AND PERFLUOROALKYL SUBSTANCES (PFAS)

Jennifer Guelfo, PhD
State Agencies Liaison, Brown SRP
May 23, 2016



5/25/2016

1

ACKNOWLEDGEMENTS



National Institute of
Environmental Health Sciences
Superfund Research Program



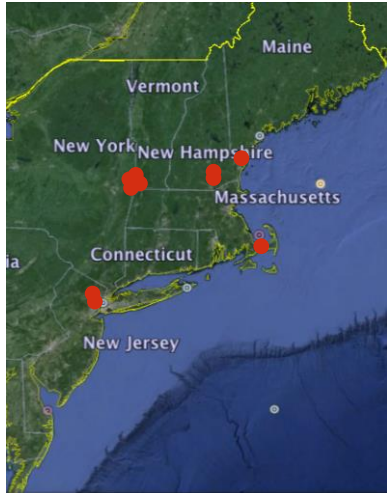
TOXICANT EXPOSURES IN RHODE ISLAND:
Past, Present, and Future



BROWN

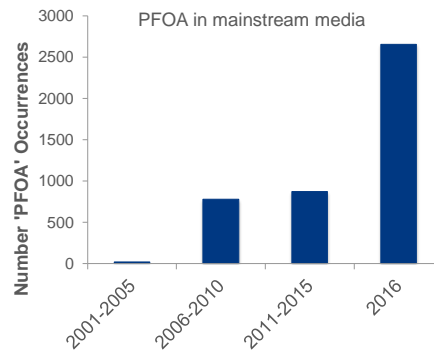
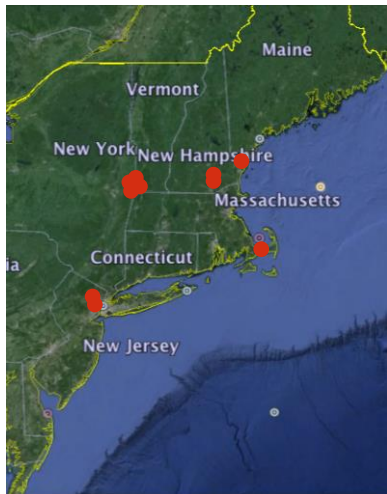
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INTRODUCTION: PFAS IN THE NEWS



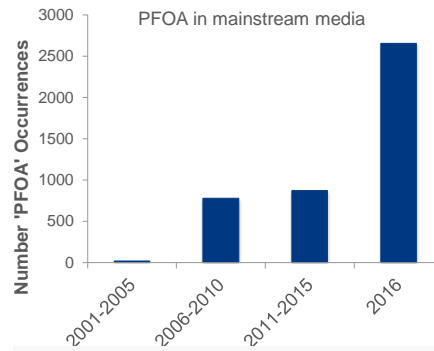
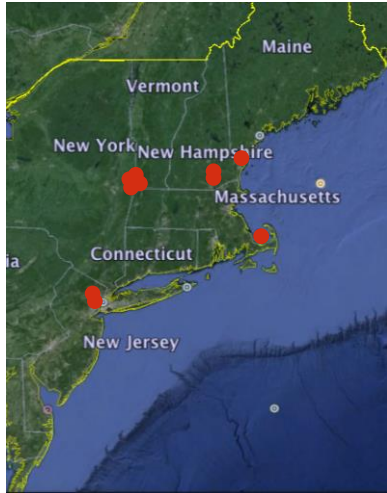
3

INTRODUCTION: PFAS IN THE NEWS



4

INTRODUCTION: PFAS IN THE NEWS



Non-Stick Cookware Kills Another Parrot!

June 1st, 2012



5

INTRODUCTION: THE WORLD OF PFAS¹

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

Non-Polymers

Perfluoroalkyl Substances

Table 2

Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines

- (Aliphatic) perfluorocarbons (PFCs)
- Perfluoroalkyl acids
- Perfluoroalkane sulfonyl fluorides
- Perfluoroalkane sulfonamides
- Perfluoroalkyl iodides
- Perfluoroalkyl aldehydes

Polyfluoroalkyl Substances

Table 3

Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines

- Perfluoroalkane sulfonamido derivatives
- Fluorotelomer-based compounds
- Semifluorinated n-alkanes and alkenes

Polymers

Table 4

Fluoropolymers

Carbon-only polymer backbone with fluorines directly attached

Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers

Variable composition non-fluorinated polymer backbone with fluorinated side chains

- Fluorinated acrylate and methacrylate polymers
- Fluorinated urethane polymers
- Fluorinated oxetane polymers

¹Buck, Robert C., et al. *Integrated environmental assessment and management* 7.4 (2011): 513-541.

INTRODUCTION: THE WORLD OF PFAS¹

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)	
Non-Polymers Perfluoroalkyl Substances Table 2 Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines <ul style="list-style-type: none"> ▪ (Aliphatic) perfluorocarbons (PFCs) ▪ Perfluoroalkyl acids ▪ Perfluoroalkane sulfonyl fluorides ▪ Perfluoroalkane sulfonamides ▪ Perfluoroalkyl iodides ▪ Perfluoroalkyl aldehydes 	Polymers Table 4 Fluoropolymers Carbon-only polymer backbone with fluorines directly attached Perfluoropolyethers Carbon and oxygen polymer backbone with fluorines directly attached to carbon Side-chain Fluorinated Polymers Variable composition non-fluorinated polymer backbone with fluorinated side chains <ul style="list-style-type: none"> ▪ Fluorinated acrylate and methacrylate polymers ▪ Fluorinated urethane polymers ▪ Fluorinated oxetane polymers
Polyfluoroalkyl Substances Table 3 Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines <ul style="list-style-type: none"> ▪ Perfluoroalkane sulfonamido derivatives ▪ Fluorotelomer-based compounds ▪ Semifluorinated n-alkanes and alkenes 	

¹Buck, Robert C., et al. *Integrated environmental assessment and management* 7.4 (2011): 513-541.

INTRODUCTION: THE WORLD OF PFAS¹

Ex: PFOA, PFOS

Ex: 6:2 FtS

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)	
Non-Polymers Perfluoroalkyl Substances Table 2 Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines <ul style="list-style-type: none"> ▪ (Aliphatic) perfluorocarbons (PFCs) ▪ Perfluoroalkyl acids ▪ Perfluoroalkane sulfonyl fluorides ▪ Perfluoroalkane sulfonamides ▪ Perfluoroalkyl iodides ▪ Perfluoroalkyl aldehydes 	Polymers Table 4 Fluoropolymers Carbon-only polymer backbone with fluorines directly attached Perfluoropolyethers Carbon and oxygen polymer backbone with fluorines directly attached to carbon Side-chain Fluorinated Polymers Variable composition non-fluorinated polymer backbone with fluorinated side chains <ul style="list-style-type: none"> ▪ Fluorinated acrylate and methacrylate polymers ▪ Fluorinated urethane polymers ▪ Fluorinated oxetane polymers
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¹Buck, Robert C., et al. *Integrated environmental assessment and management* 7.4 (2011): 513-541.

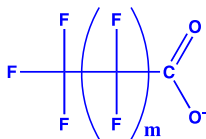
OVERVIEW

- Terminology
- Manufacturing Processes
- Chemistry
- Uses
- Environmental Distribution
- Key Points

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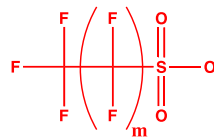
PFAS TERMINOLOGY & STRUCTURE

Perfluoroalkyl carboxylates:



Examples:
 m=2 PFBA
 m=4 PFHxA
 m=6 PFOA

Perfluoroalkane sulfonates:



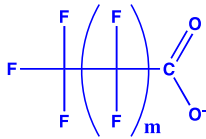
Examples:
 m=3 PFBS
 m=5 PFHxS
 m=7 PFOS

Per = fully fluorinated alkyl tail.

10

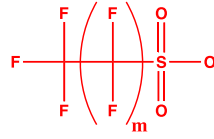
PFAS TERMINOLOGY & STRUCTURE

Perfluoroalkyl carboxylates:



Examples:
 m=2 PFBA
 m=4 PFHxA
m=6 PFOA

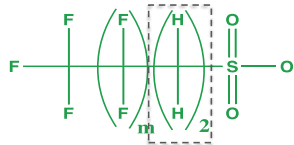
Perfluoroalkane sulfonates:



Examples:
 m=3 PFBS
 m=5 PFHxS
m=7 PFOS

Poly = partially fluorinated alkyl tail.

Polyfluoroalkyl substances:

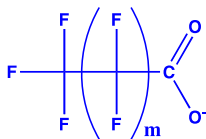


m=5 6:2 FtS
 m=7 8:2 FtS

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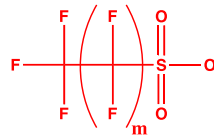
PFAS TERMINOLOGY & STRUCTURE

Perfluoroalkyl carboxylates:



Examples:
 m=2 PFBA
 m=4 PFHxA
m=6 PFOA

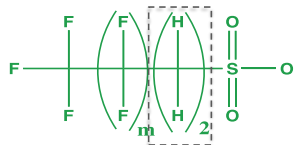
Perfluoroalkane sulfonates:



Examples:
 m=3 PFBS
 m=5 PFHxS
m=7 PFOS

Per + Poly =
Per & polyfluoro alkyl substances (PFAS)

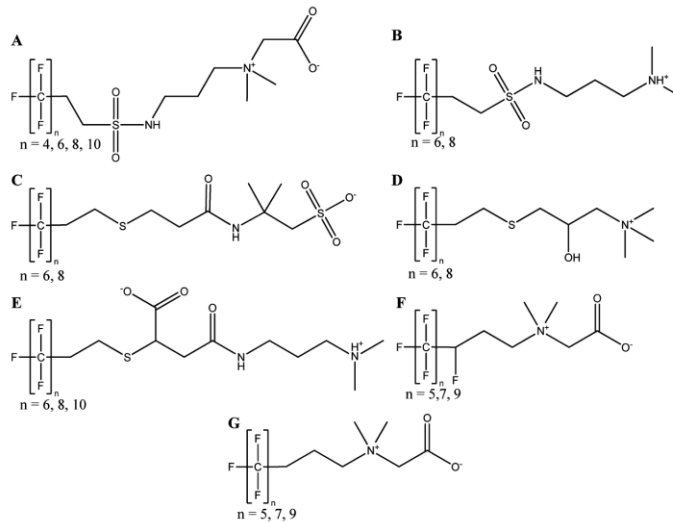
Polyfluoroalkyl substances:



m=5 6:2 FtS
 m=7 8:2 FtS

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PFAS TERMINOLOGY & STRUCTURE²



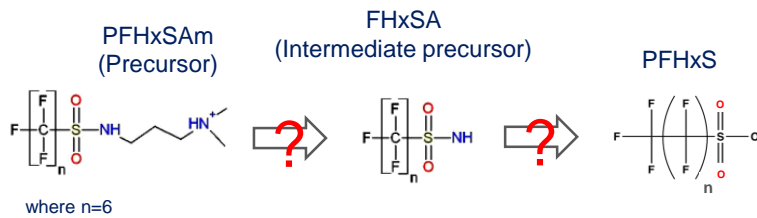
²Place, Benjamin J., and Jennifer A. Field. *ES&T* 46.13 (2012): 7120-7127.

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PFAS TERMINOLOGY

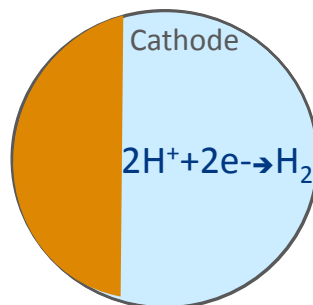
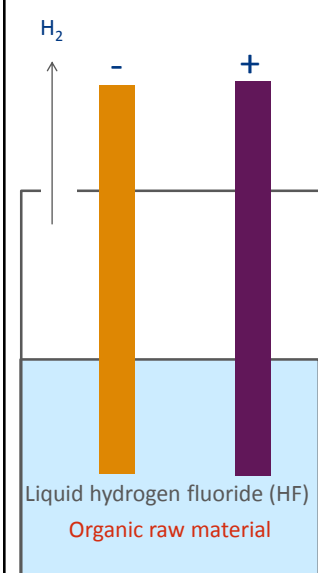
What is a precursor?

Polyfluoroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids



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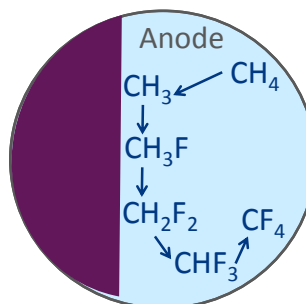
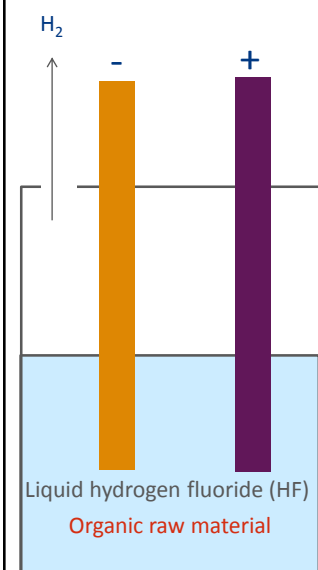
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)^{1,3}



³Kissa, Erik, ed. *Fluorinated surfactants and repellents*. Vol. 97. CRC Press, 2001.

15

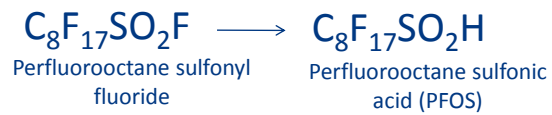
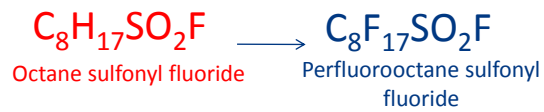
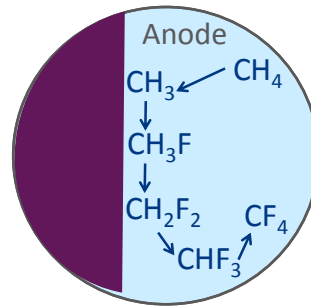
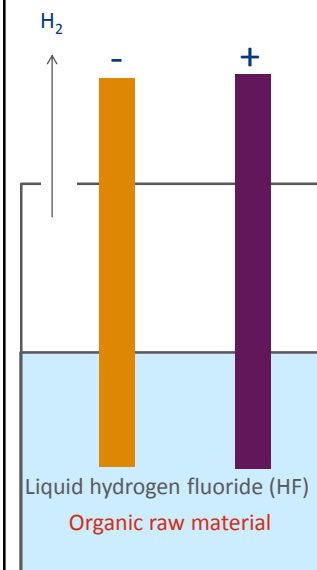
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)^{1,3}



³Kissa, Erik, ed. *Fluorinated surfactants and repellents*. Vol. 97. CRC Press, 2001.

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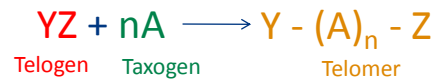
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)^{1,3}



³Kissa, Erik, ed. *Fluorinated surfactants and repellents*. Vol. 97. CRC Press, 2001.

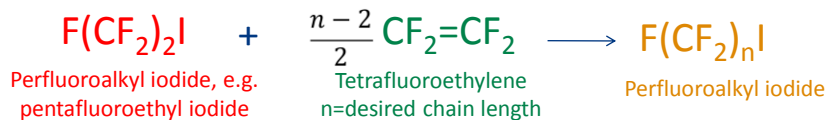
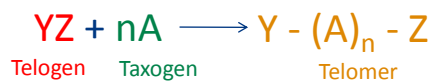
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MANUFACTURING: TELOMERIZATION^{1,3}



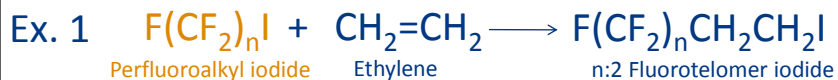
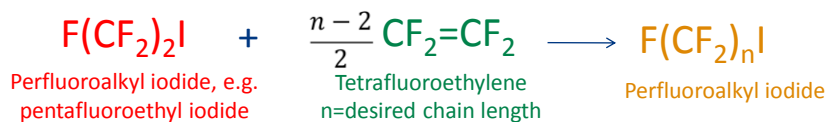
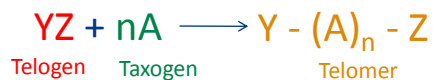
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MANUFACTURING: TELOMERIZATION^{1,3}



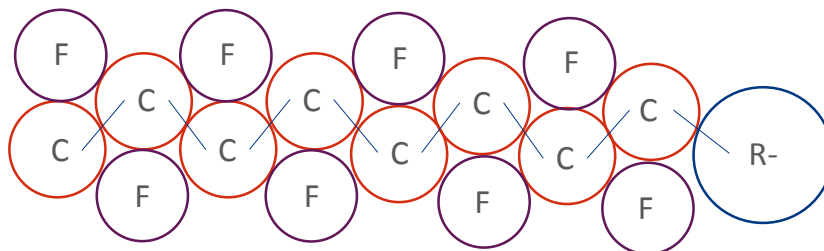
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MANUFACTURING: TELOMERIZATION^{1,3}



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CHEMISTRY³



Chemical properties:

- F highly electronegative
- F not polarizable
- F shields C
- C-F bond strength
- Weak intermolecular interactions

PFAS characteristics:

- Chemically stable
- Thermally stable
- Hydrophobic/lipophobic
- Surfactant properties
- Recalcitrant in environment

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USES: OVERVIEW

Key Uses:

- Fluoropolymer manufacturing (e.g. polytetrafluoroethylene)
- Firefighting foams (e.g. aqueous film-forming foams)



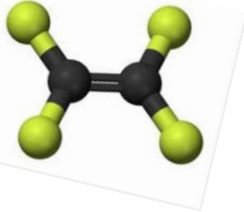
Other Uses:

- Electroplating
- Paper coating
- Stain/water repellants
- Textiles
- Electronics
- Insecticides/ herbicides
- Adhesives, paints, varnish
- Others too numerous to list

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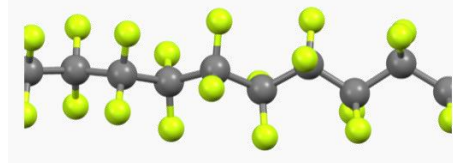
USES: A CLOSER LOOK AT PTFE

Tetrafluoroethylene (TFE)



Emulsion
polymerization →

Polytetrafluoroethylene (PTFE)

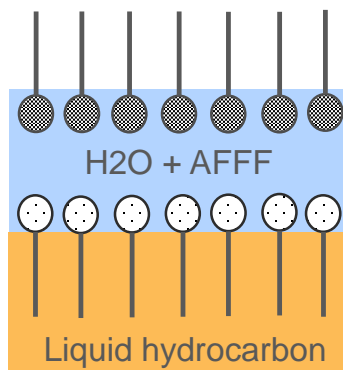


Emulsion polymerization and PFCAs

- PFOA/PFNA the primary PFCAs used
- Used as 'polymerization aids' in emulsion polymerization
- Solubilize TFE monomers
- Generates fine powder and dispersed PTFEs
- Used primarily to coat metals and fabrics
- PFOA/PFNA 'removed' by heat treatment of product

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APPLICATIONS: A CLOSER LOOK AT AFFF^{4,5}



- PFAS (fluorocarbon surfactant)
- Hydrocarbon surfactant

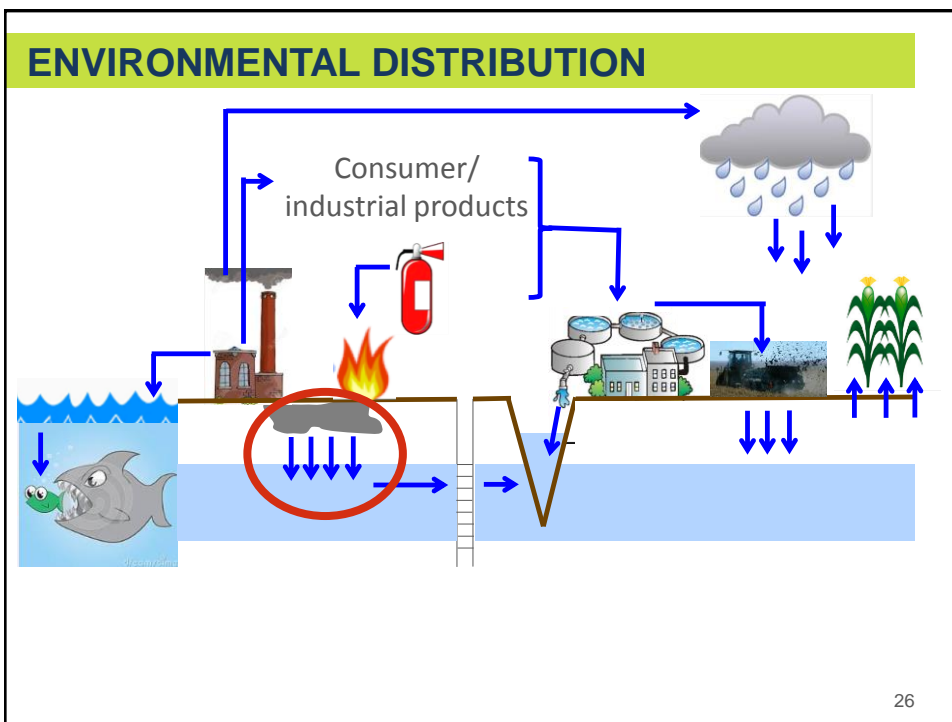
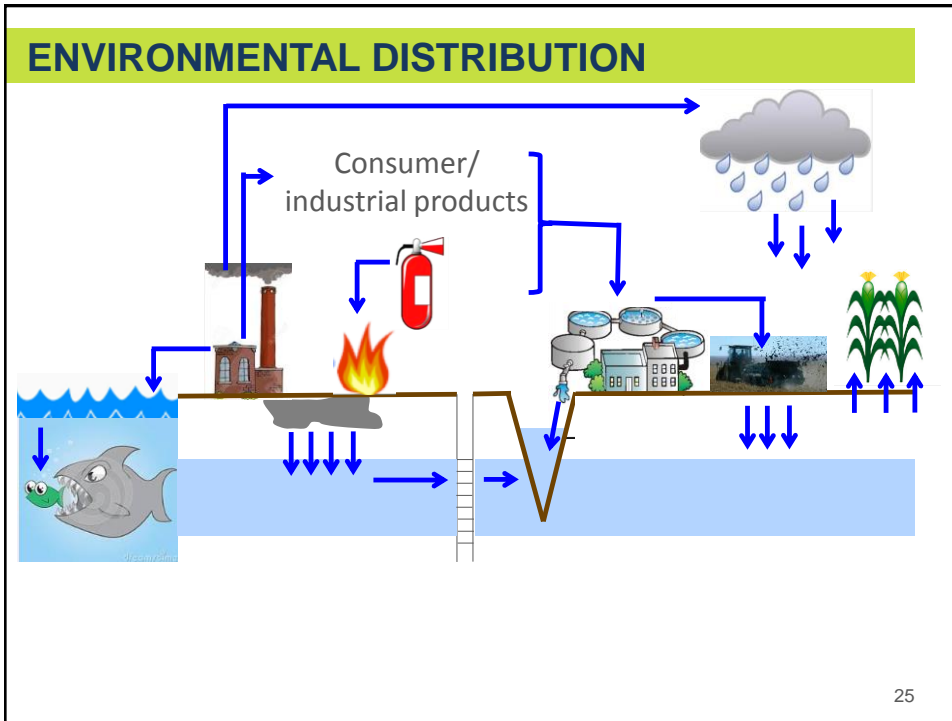
AFFF and PFAS:

- 3M, 1980's-2000:
 - ~7-13 g/L PFCAs + PFSAs
 - 4.9-11.4 g/L PFOS
 - 0.5-1.4 g/L PFHxS
 - Negligible precursors
- 3M, National Foam, Buckeye, Chemguard, Ansul, 2000's-present:
 - Negligible PFCAs + PFSAs
 - Primarily precursors

⁴Moody, Cheryl A., and Jennifer A. Field. ES&T. 34.18 (2000): 3864-3870.

⁵Houtz, Erika F., et al. ES&T 47.15 (2013): 8187-8195.

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TAKE HOME MESSAGE

PFAS are diverse

- Perfluorinated
- Polyfluorinated

Unique chemistry/properties

- Dual phobicity
- Some are surfactants
- Many are recalcitrant

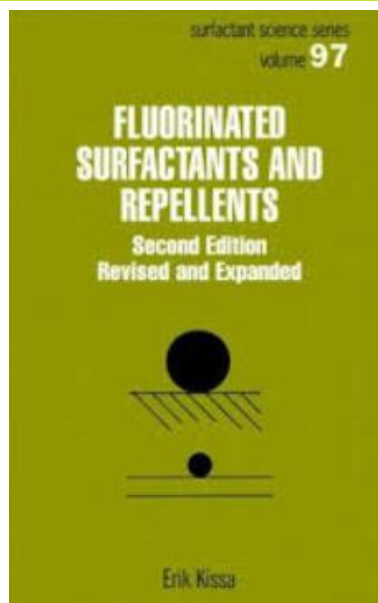
Key Uses

- Fluoropolymer manufacturing
- Aqueous film-forming foams



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RESOURCES



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Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

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(Submitted: 2 May 2011; Returned for Revision 26 May 2011; Accepted 5 July 2011)

ABSTRACT

The primary aim of this article is to provide an overview of perfluoroalkyl and polyfluoroalkyl substances (PFAS) detected in the environment, wildlife, and humans, and recommend clear, specific, and descriptive terminology, names, and acronyms for PFAS. The overarching objective is to assist and harmonize communication on PFAS by offering terminology for use by the global scientific, regulatory, and industrial communities. A particular emphasis is placed on long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives to the use of the long-chain perfluoroalkyl acids or their precursors. First, we define PFAS, classify them into various families, and recommend a pragmatic set of common names and acronyms for both the families and their individual members. Terminology related to fluorinated polymers is an important aspect of our classification. Second, we provide a brief description of the 2 main production processes, electrochemical fluorination and telomerization, used for introducing perfluoroalkyl moieties into organic compounds, and we specify the types of byproducts (isomers and homologues) likely to arise in these processes. Third, we show how the principal families of PFAS are interrelated as industrial, environmental, or metabolic precursors or transformation products of one another. We pay particular attention to those PFAS that have the potential to be converted, by abiotic or biotic environmental processes, to human metabolites, into long-chain perfluoroalkyl carboxylic or sulfonic acids, which are currently the focus of regulatory action. The Supplemental Data lists 42 families and subfamilies of PFAS and 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as Chemical Abstracts Service registry numbers. *Integr Environ Assess Manag* 2011 7(5):513–541. © 2011 SETAC.

Keywords: Perfluoroalkyl; Polyfluoroalkyl; Terminology; Acronyms; PFAS

INTRODUCTION

"Fluorinated substances" is a general, nonspecific name that describes a mixture of organic and inorganic substances that contain at least 1 F atom, with nearly different physical, chemical, and biological properties (Buck et al. 1994). Synonyms include "fluorocarbon(s)" and "fluorinated chemical(s)." A subset of fluorinated substances is the highly fluorinated aliphatic substance that contains 1 or more fluorine atoms (present in the form of C–F bonds) and is referred to as "perfluoroalkyl and polyfluoroalkyl substances" and denoted by the acronym PFAS, justification for the choice of which is provided below.

All Supplemental Data may be found in the online version of this article.
*To whom correspondence may be addressed. E-mail: kissa@vito.be
Published online 24 July 2011 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/ieam.918

Since 1950, PFASs and surfactants and polymers made with the aid of PFASs have been widely used in numerous industrial and commercial applications (Eaton 2003). The C–F bond is extremely strong and stable (Eaton 1994). The chemical and thermal stability of a perfluoroalkyl moiety, in addition to its hydrophobic and lipophobic nature, lead to highly useful and enduring properties in surfactants and polymers into which the perfluoroalkyl moiety is incorporated (Eaton 1994, 2003). Common applications include textile finishes and repellents and grease-proof, food-contact paper (Eaton and Fisher 1994). Surfactant applications that take advantage of the superhydrophobic aqueous surface tension-lowering properties include processing aids for fluoropolymer manufacturing, coatings, and aqueous film-forming foams (AFFFs) used to extinguish fires involving highly flammable liquids (Eaton 1994, Taylor 1979, Kissa 2003). Numerous additional applications have been described (3M Company 1999, Kissa 2003).

As a consequence of the widespread use of PFASs and their resulting emissions, a broad range of these substances have been detected in the environment, wildlife, and humans. The global extent of such contamination was first demonstrated

Critical Review

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