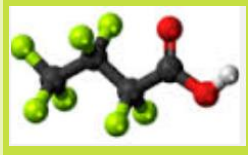
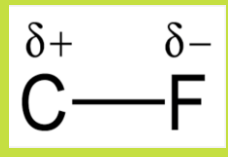
INTRODUCTION TO POLY- AND PERFLUOROALKYL SUBSTANCES (PFAS)

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





ACKNOWLEDGEMENTS

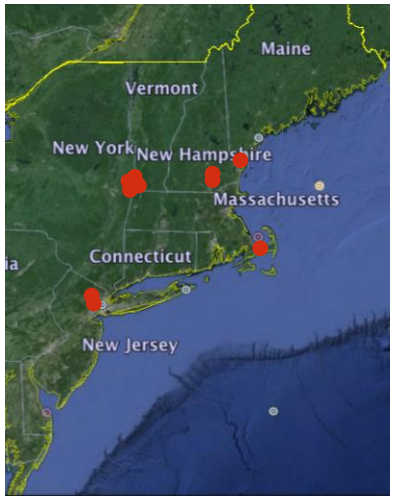
NEWMOA

NIH National Institute of Environmental Health Sciences
Superfund Research Program

Toxicant Exposures in Rhode Island:
Past, Present, and Future

BROWN

INTRODUCTION: PFAS IN THE NEWS



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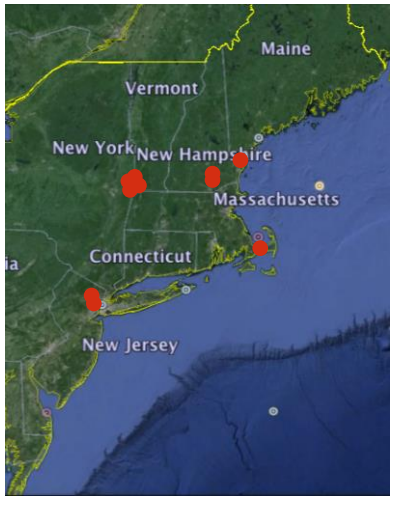
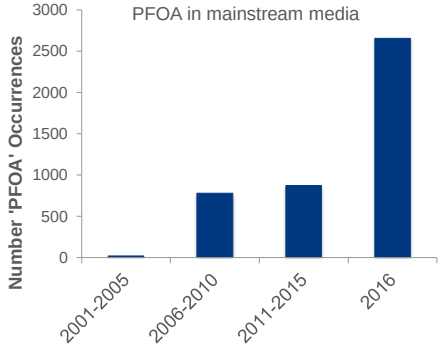
INTRODUCTION: PFAS IN THE NEWS





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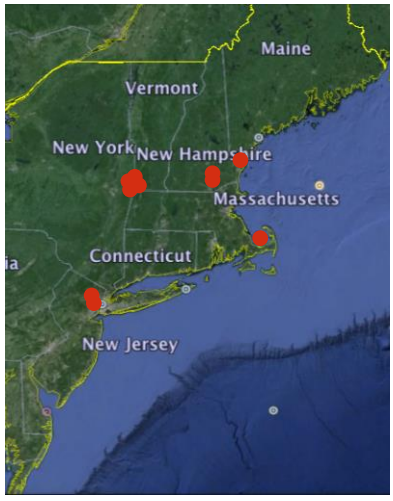
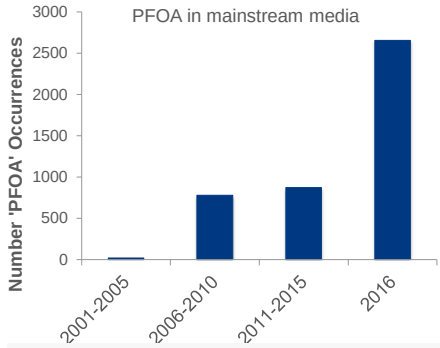
INTRODUCTION: PFAS IN THE NEWS





Non-Stick Cookware Kills Another Parrot!

June 1st, 2012

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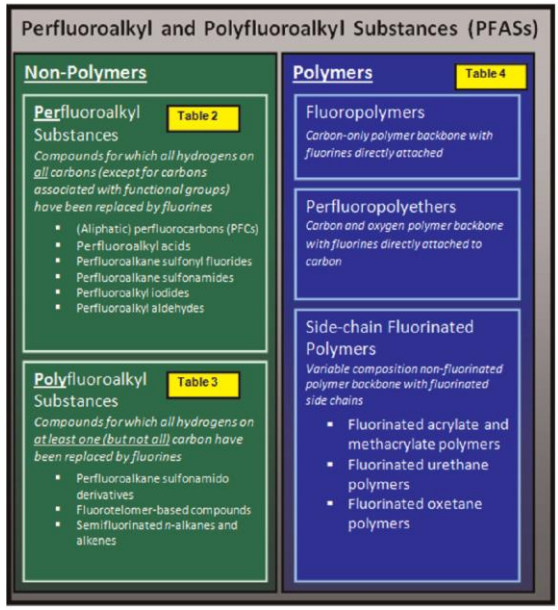
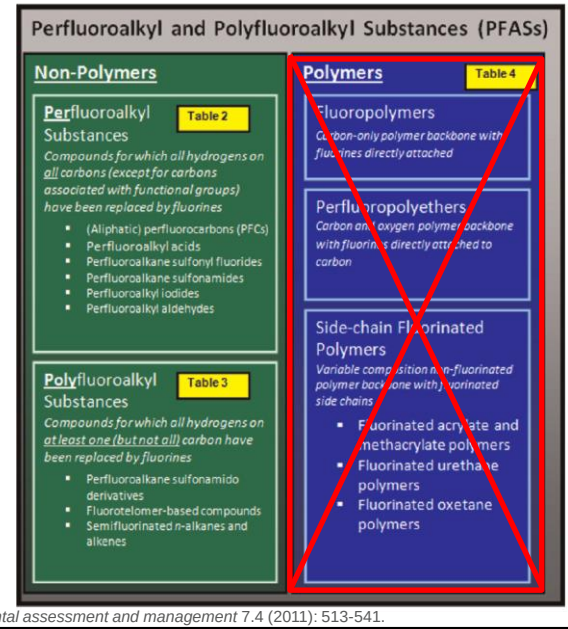
INTRODUCTION: THE WORLD OF PFAS[1]



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

INTRODUCTION: THE WORLD OF PFAS[1]

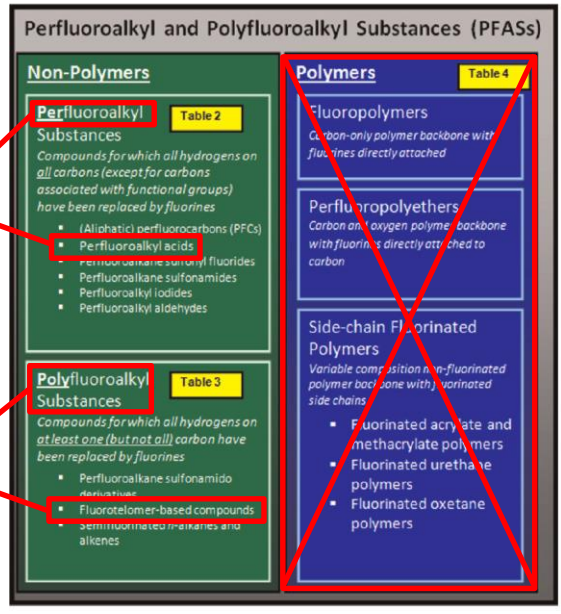


[1]Buck, Robert C., et al. *Integrated environmental assessment and management* 7.4 (2011): 513-541.

INTRODUCTION: THE WORLD OF PFAS[1]

Ex: PFOA, PFOS

Ex: 6:2 FtS



[1]Buck, 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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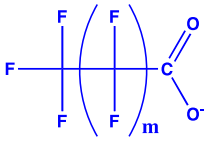
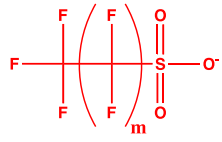
PFAS TERMINOLOGY & STRUCTURE

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.

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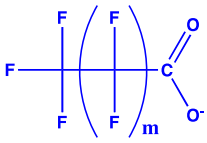
PFAS TERMINOLOGY & STRUCTURE

Perfluoroalkyl carboxylates:



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m=4 PFHxA
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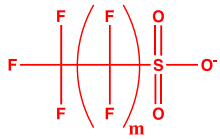
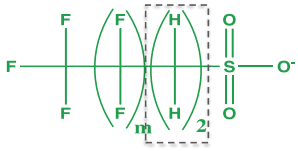
Perfluoroalkane sulfonates:



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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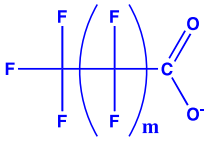
PFAS TERMINOLOGY & STRUCTURE

Perfluoroalkyl carboxylates:



Examples:
m=2 PFBA
m=4 PFHxA
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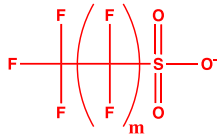
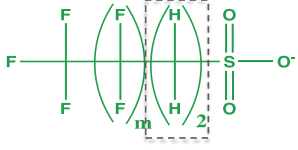
Perfluoroalkane sulfonates:



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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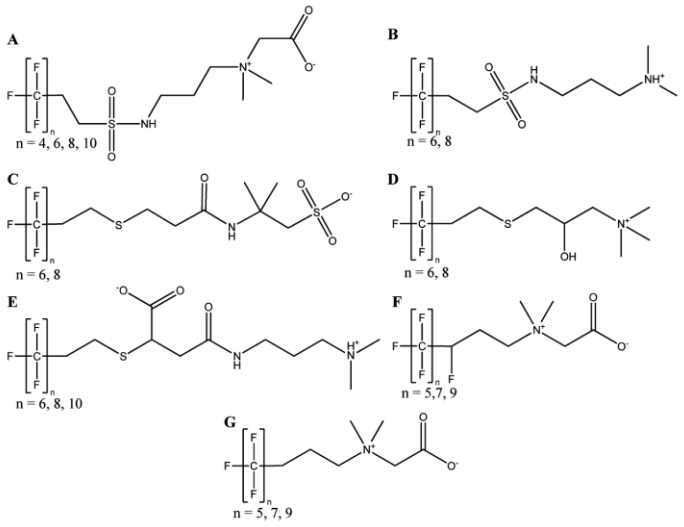
PFAS TERMINOLOGY & STRUCTURE[2]



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

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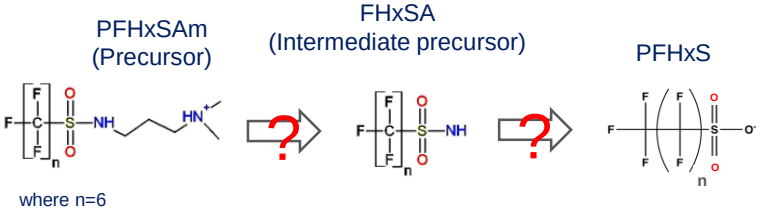
PFAS TERMINOLOGY

What is a precursor?

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



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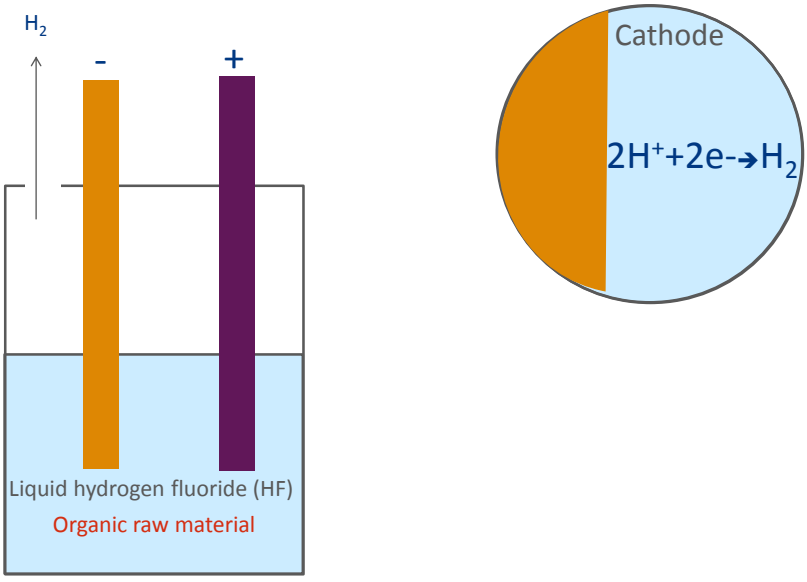
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)[1,3]



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

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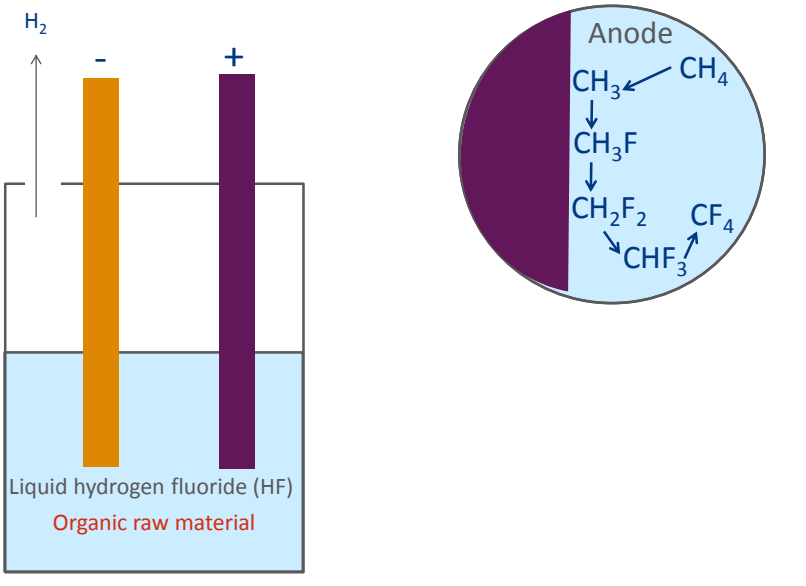
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)[1,3]



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

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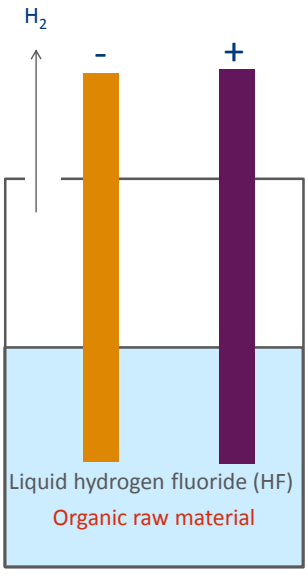
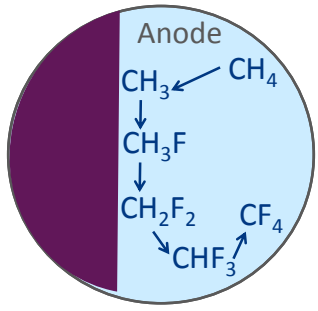
MANUFACTURING: ELECTROCHEMICAL FLUORINATION (ECF)[1,3]





$C_8H_{17}SO_2F \longrightarrow C_8F_{17}SO_2F$

Octane sulfonyl fluoride → Perfluorooctane sulfonyl fluoride

$C_8F_{17}SO_2F \longrightarrow C_8F_{17}SO_2H$

Perfluorooctane sulfonyl fluoride → Perfluorooctane sulfonic acid (PFOS)

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

MANUFACTURING: TELOMERIZATION[1,3]

$$YZ + nA \longrightarrow Y - (A)_n - Z$$

Telogen + Taxogen → Telomer

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MANUFACTURING: TELOMERIZATION[1,3]

$$YZ + nA \longrightarrow Y\text{-}(A)_n\text{-}Z$$

Telogen — Taxogen — Telomer

$$F(CF_2)_2I + \frac{n-2}{2}\,CF_2{=}CF_2 \longrightarrow F(CF_2)_nI$$

Perfluoroalkyl iodide, e.g. pentafluoroethyl iodide — Tetrafluoroethylene, n=desired chain length — Perfluoroalkyl iodide

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MANUFACTURING: TELOMERIZATION[1,3]

$$YZ + nA \longrightarrow Y\text{-}(A)_n\text{-}Z$$

Telogen — Taxogen — Telomer

$$F(CF_2)_2I + \frac{n-2}{2}\,CF_2{=}CF_2 \longrightarrow F(CF_2)_nI$$

Perfluoroalkyl iodide, e.g. pentafluoroethyl iodide — Tetrafluoroethylene, n=desired chain length — Perfluoroalkyl iodide

Ex. 1 $F(CF_2)_nI + CH_2{=}CH_2 \longrightarrow F(CF_2)_nCH_2CH_2I$

Perfluoroalkyl iodide — Ethylene — n:2 Fluorotelomer iodide

Ex. 2 $F(CF_2)_nI \xrightarrow{\text{Oleum, heat, pressure}} CF_3(CF_2)_{n-1}CF_2OOH + \tfrac{1}{2}I_2$

Perfluoroalkyl iodide — Perfluoroalkyl carboxylic acid

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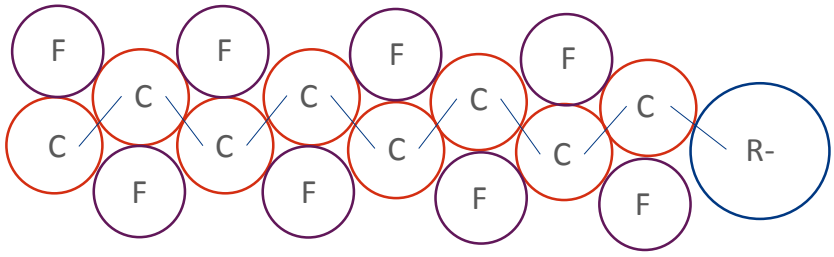
CHEMISTRY[3]



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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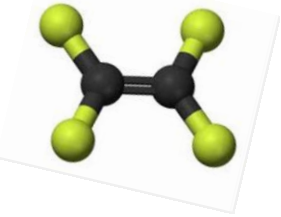
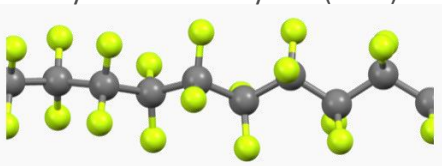
USES: A CLOSER LOOK AT PTFE

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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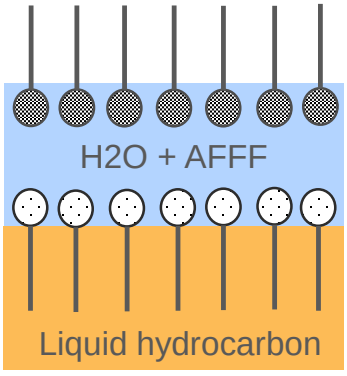
APPLICATIONS: A CLOSER LOOK AT AFFF[4,5]



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

[4]Moody, Cheryl A., and Jennifer A. Field. ES&T. 34.18 (2000): 3864-3870.
[5]Houtz, Erika F., et al. ES&T 47.15 (2013): 8187-8195.

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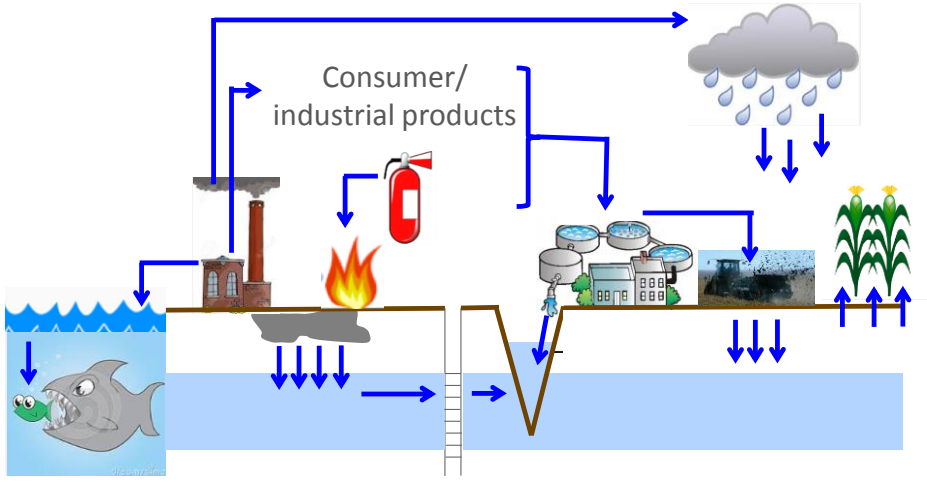
ENVIRONMENTAL DISTRIBUTION



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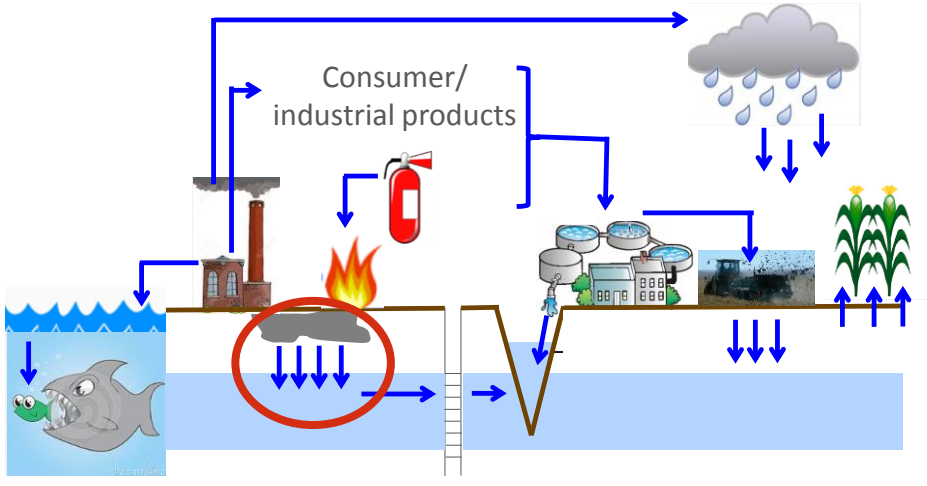
ENVIRONMENTAL DISTRIBUTION



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TAKE HOME MESSAGE

PFAS are diverse
- *Per*fluorinated
- *Poly*fluorinated

Unique chemistry/properties
- Dual phobicity
- Some are surfactants
- Many are recalcitrant

Key Uses
- Fluoropolymer manufacturing
- Aqueous film-forming foams

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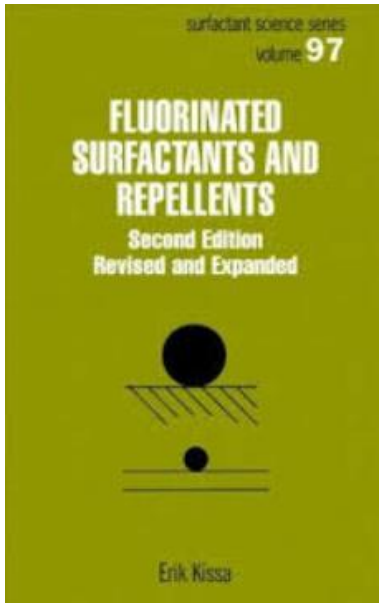
RESOURCES



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

Critical Review

ABSTRACT

INTRODUCTION

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