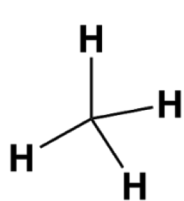


Kathleen A Durkin

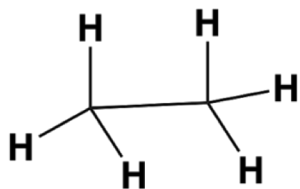
A Primer on The Chemistry of PFAS

Conference: The Problem of PFAS Contamination: How Can
We Make Rapid Progress to Address it?
December 13, 2019

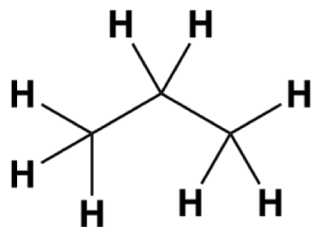
PFAS = Per and poly Fluoro Alkyl Substances



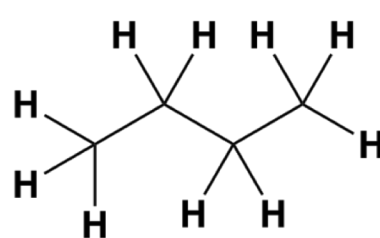
Methane (CH_4)



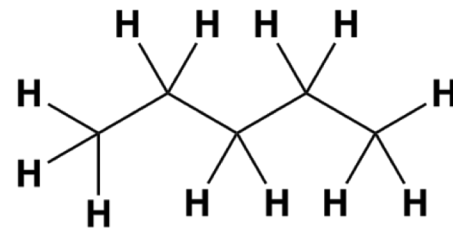
Ethane (C_2H_6)



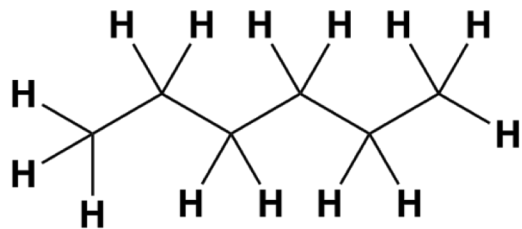
Propane (C_3H_8)



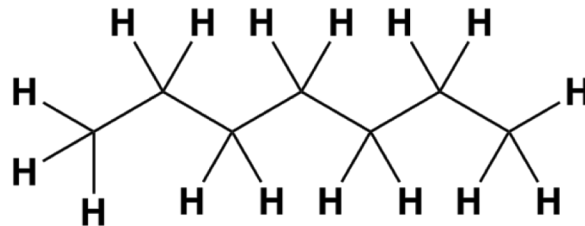
Butane (C_4H_{10})



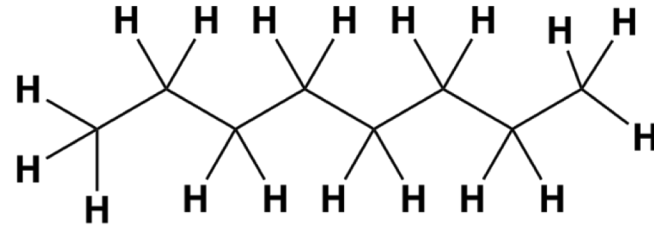
Pentane (C_5H_{12})



Hexane (C_6H_{14})

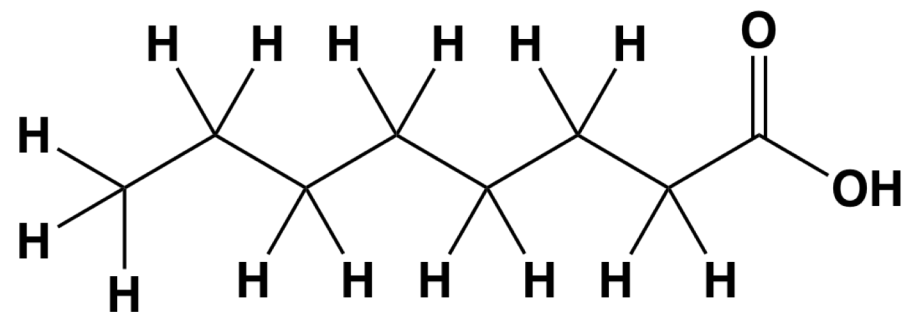


Heptane (C_7H_{16})

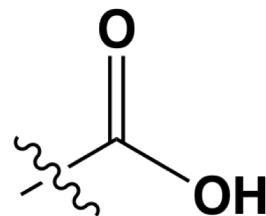


Octane (C_8H_{18})

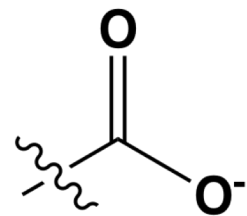
PFAS = Per and poly Fluoro Alkyl Substances



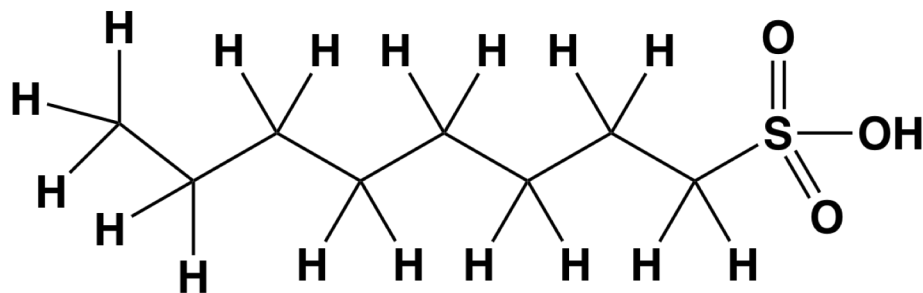
Octanoic acid



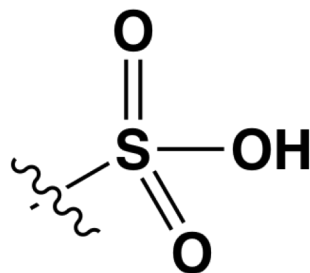
Carboxylic acid



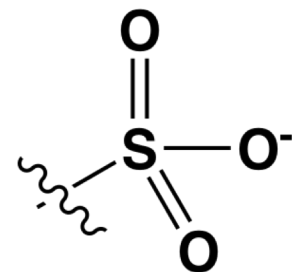
Carboxylate ion



Octane sulfonic acid

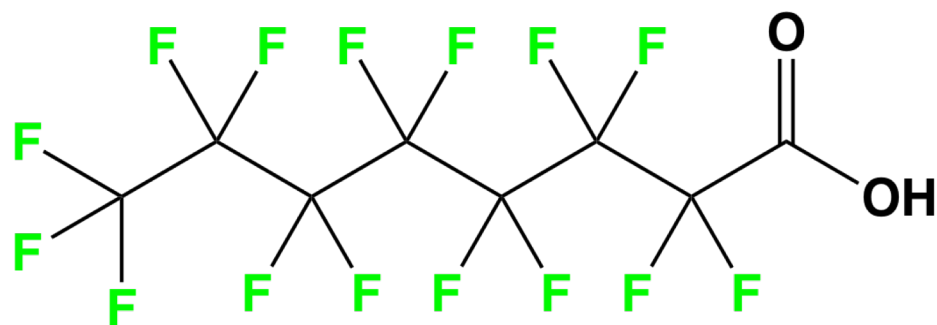


Sulfonic acid

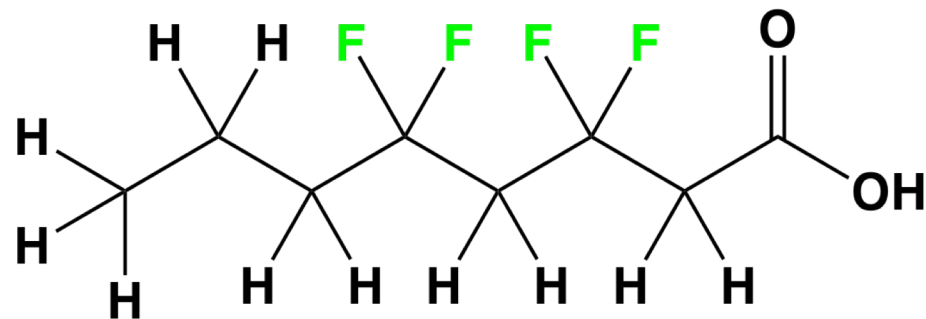


Sulfonate ion

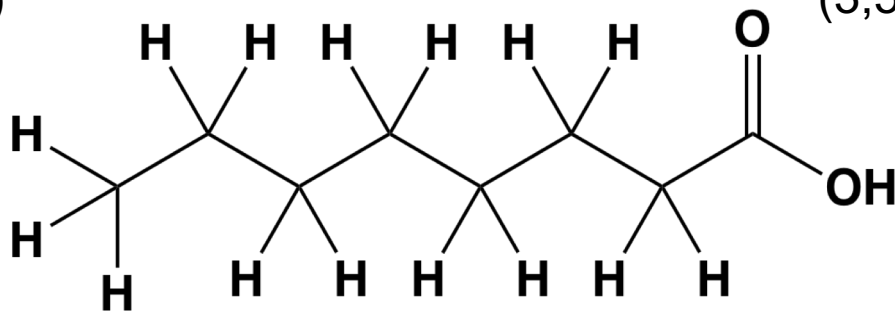
PFAS = Per and poly Fluoro Alkyl Substances



Perfluorooctanoic acid
(PFOA)



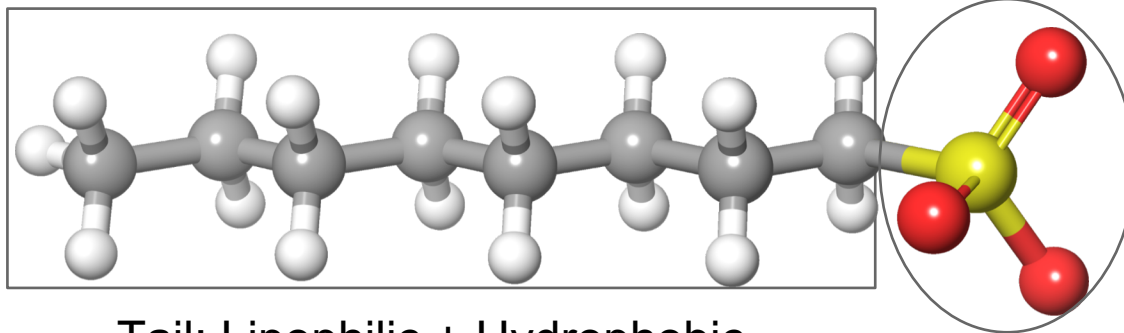
Polyfluorooctanoic acid
(3,5-tetra-fluorooctanoic acid)



Octanoic acid

PFAS Heads and Tails

(Octane
sulfonate)

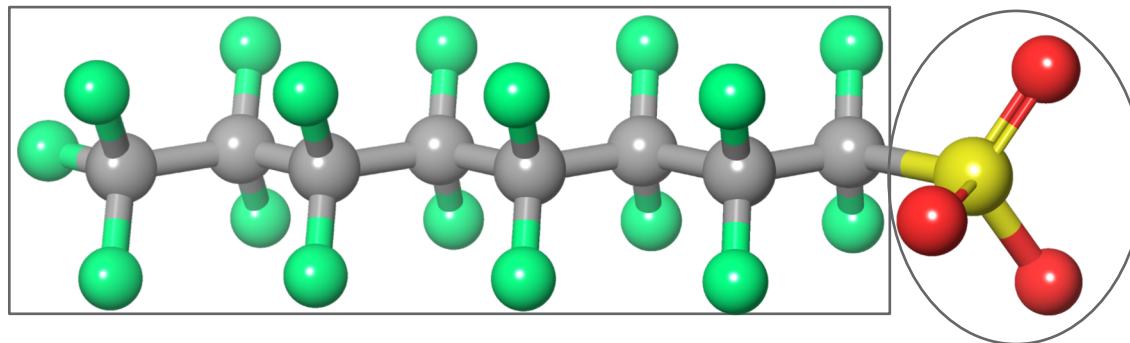


Tail: Lipophilic + Hydrophobic

Head:

- Anionic
- Polar
- Hydrophilic

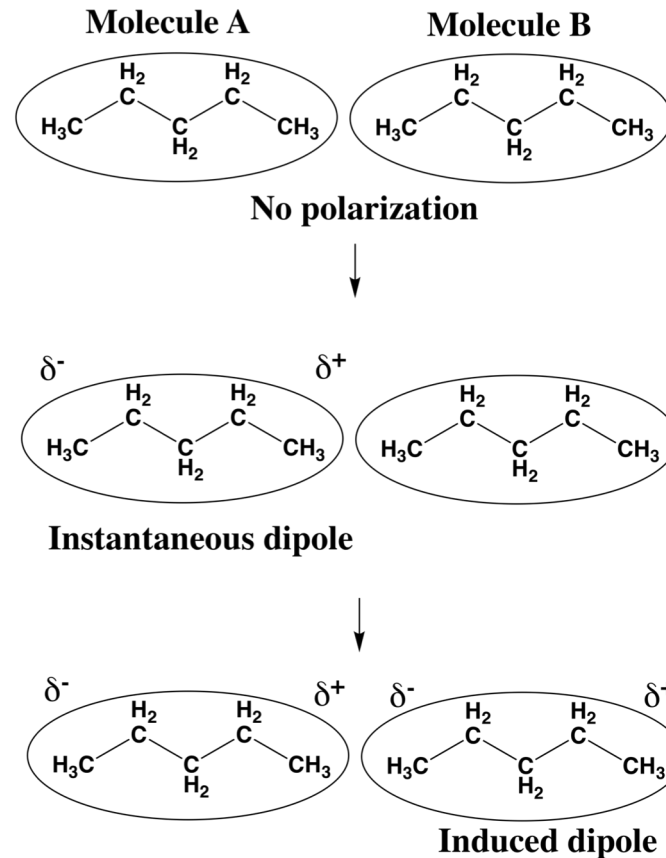
(PFOS)



Tail: Lipophobic + Hydrophobic

F=green
H=white
C=grey
S=yellow
O=red

Polarizability?



Perspective on Fluorocarbon
Chemistry, DM Lemal, J. Org.
Chem. 2004, 69, 1, 1-11.

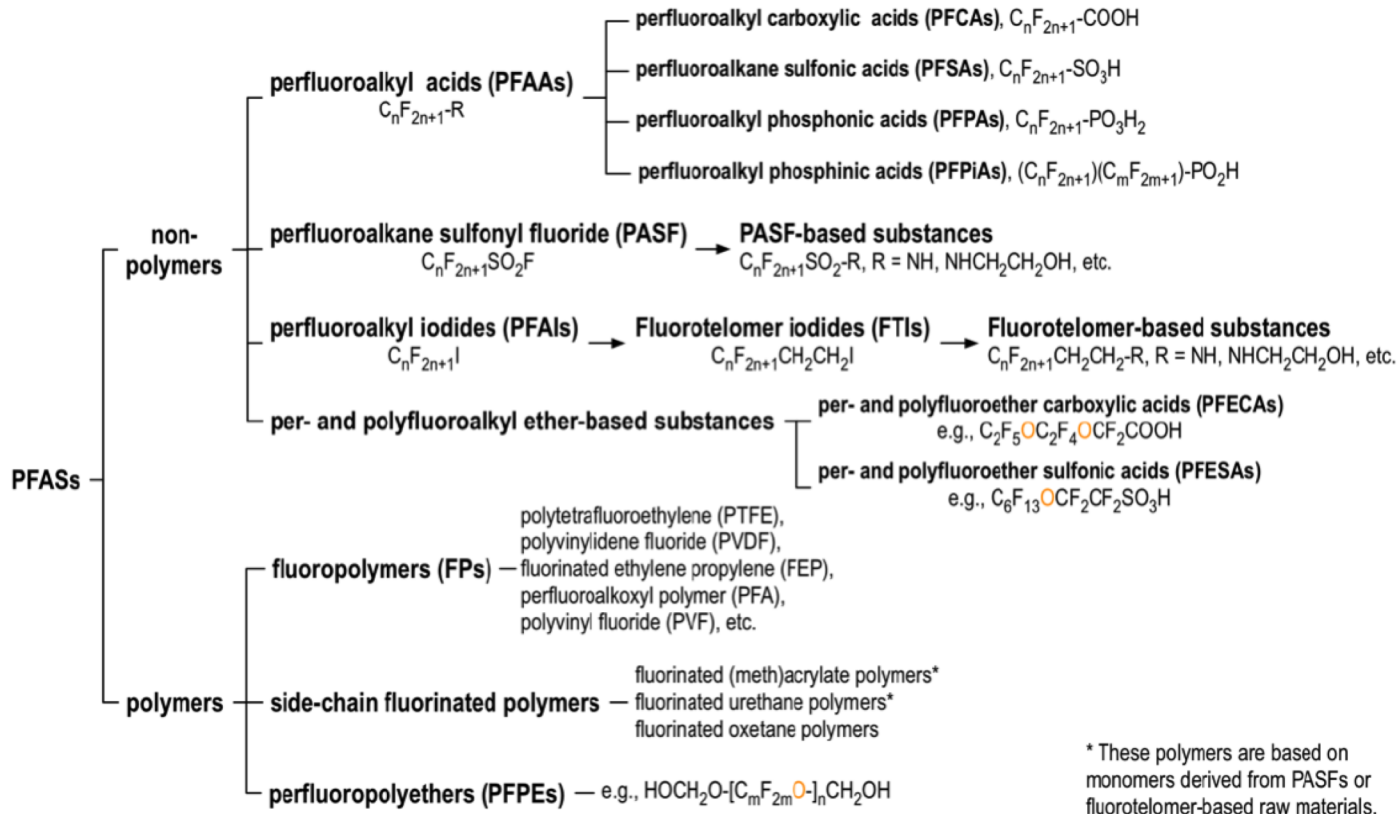
- F is most electronegative element
- C-F is strongest organic covalent bond
- Small VDW radius; can replace H
- C-F bond is not **polarizable**
- C-H bond is **polarizable**

PFAS relative to hydrocarbon analog:

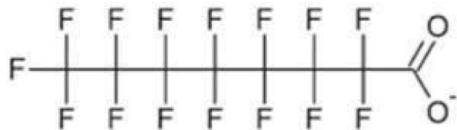
- Stronger acidity
- Greater chemical and thermal stability
- Lower molecular interaction energies

Perspective on Fluorocarbon Chemistry, DM Lemal, J. Org. Chem. 2004, 69, 1, 1-11
<https://pubs.acs.org/doi/10.1021/jo0302556>

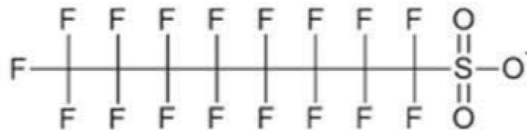
>6000 PFAS
currently on
the global
market



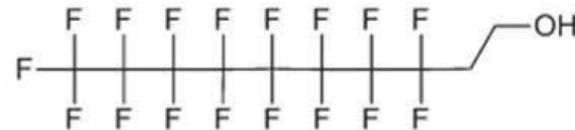
<http://www.oecd.org/chemicalsafety/Working%20Towards%20a%20Global%20Emission%20Inventory%20of%20PFASS.pdf>



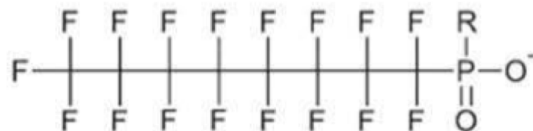
Perfluorocarboxylic acids
(ex. PFOA)



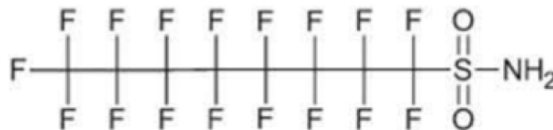
Perfluorosulfonic acids
(ex. PFOS)



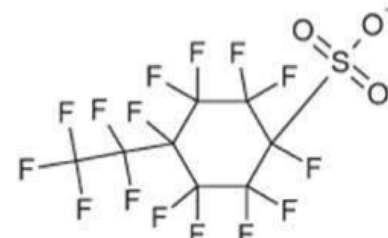
Fluorotelomer alcohol
(ex. 8:2 FTOH)



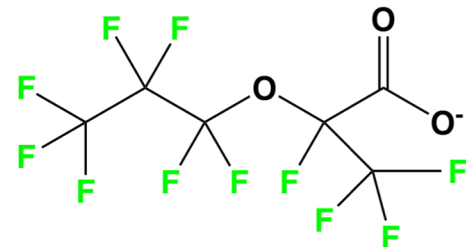
Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPI)



Perfluorosulfonamide
(ex. FOSA)

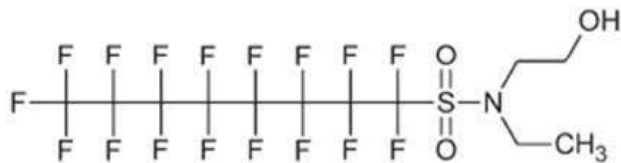


Perfluorinated cyclo sulfonates
(ex. PFECHS)

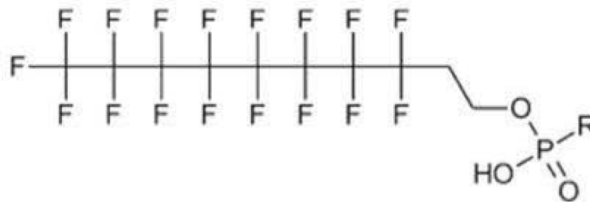


NH₄⁺

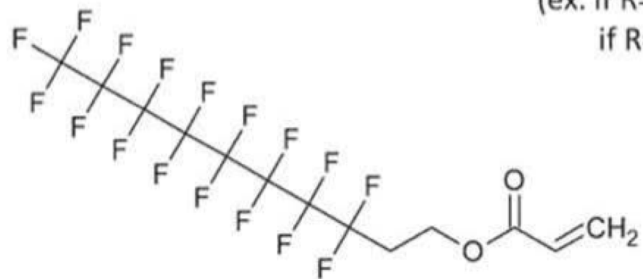
Perfluoropolyether carboxylate (GenX)



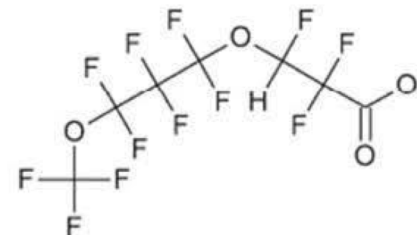
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



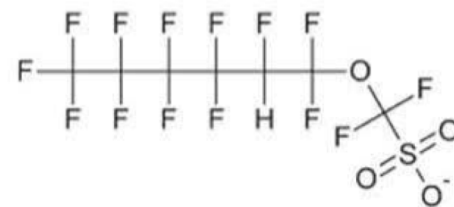
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)

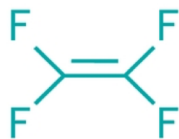


Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)

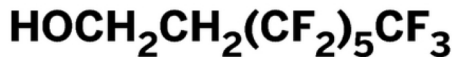
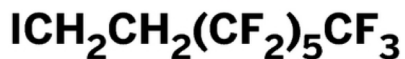
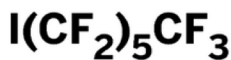


Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

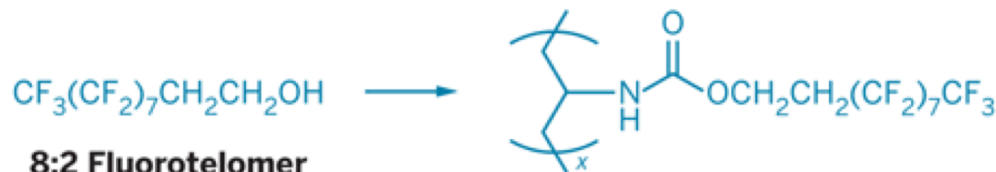
Circle of Chemistry



Tetrafluoroethylene

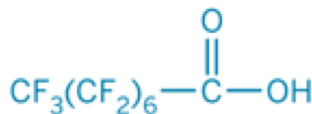


Fluorinated alcohol

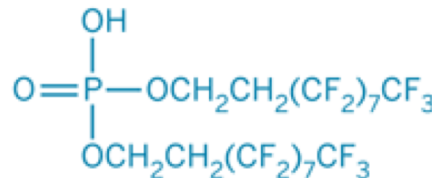


8:2 Fluorotelomer alcohol (FTOH)

Fluorotelomer polyurethane



PFOA



Fluorotelomer phosphate surfactant

Chemical and Bio processes include transformation of Poly \rightarrow Per and other PFAS breakdown products

Chem and Eng News 2010, 2014. Various articles.

Thank You

We are very grateful to OEHHA for
funding on PFAS and related projects.

NIH S10OD023532 for computer
resources.