



Health



Environment



Technology



Sustainability

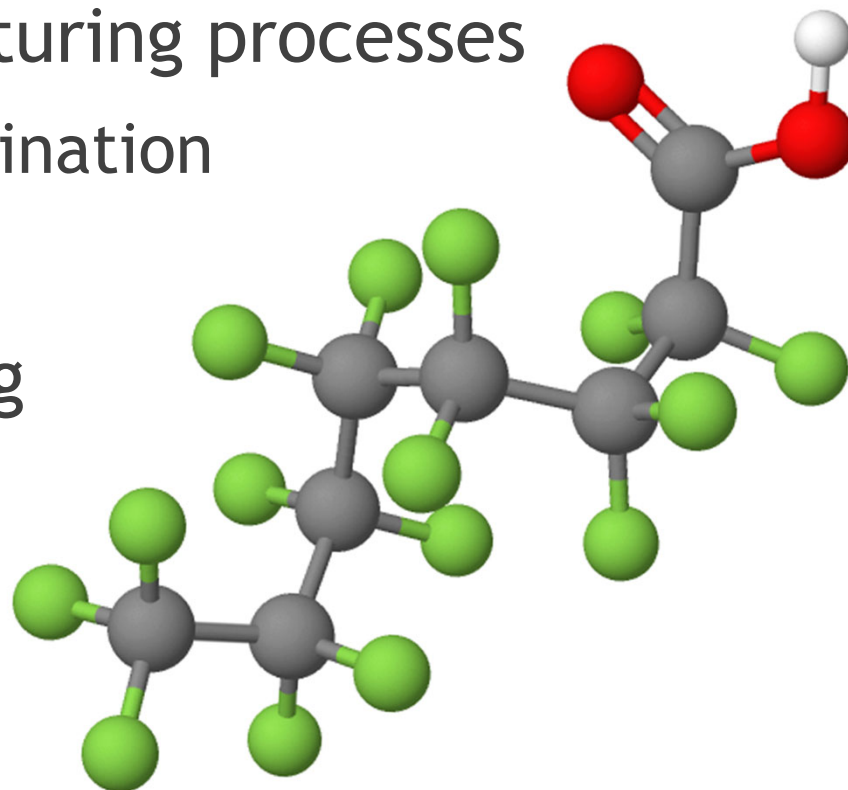
Identifying Linear and Branched Isomers from Standard PFAS Analysis for Source Delineation

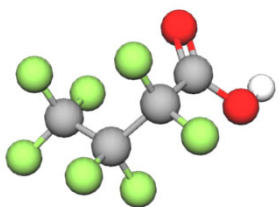
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February 14, 2019

Overview

- Primary PFAS manufacturing processes
 - Electrochemical fluorination
 - Telomerization
- Differences in resulting chemistry
 - Homologs
 - Isomers
- Consumer products
- Utility of isomer data for source differentiation

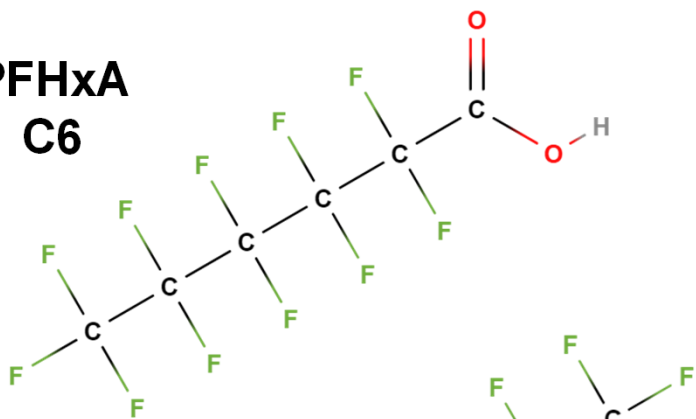




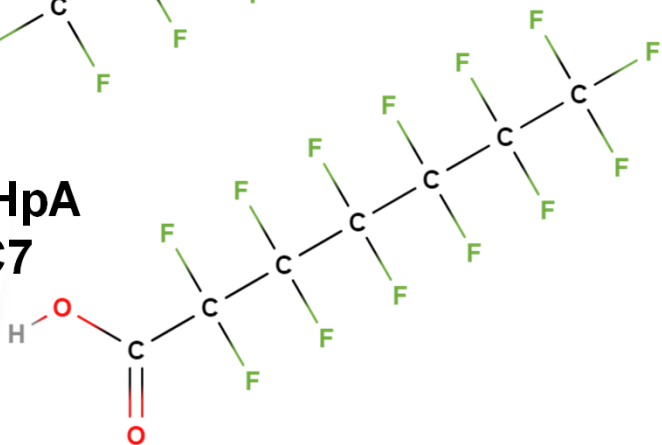
Homologs

Same functional group,
different carbon chain lengths

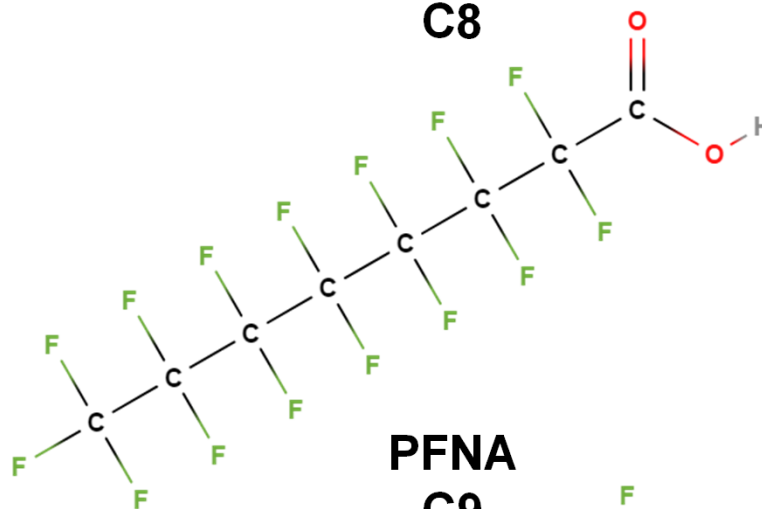
PFHxA
C6



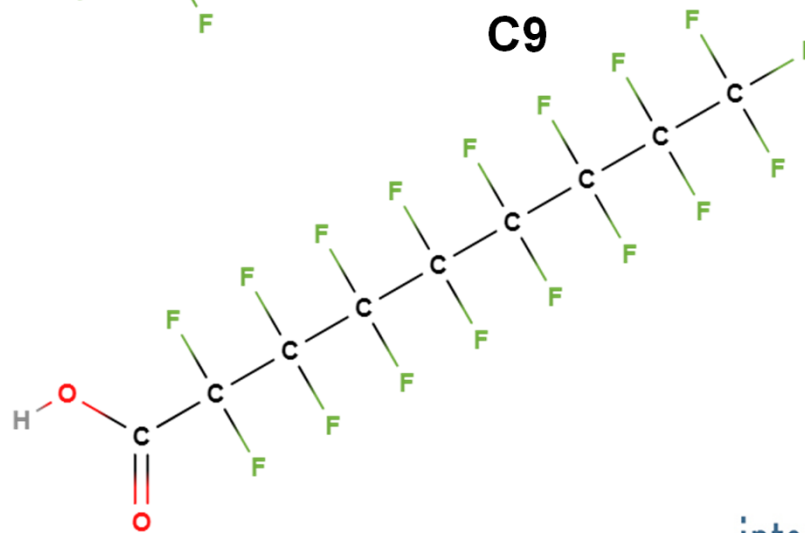
PFHpA
C7



PFOA
C8



PFNA
C9



Images from molview.org

Manufacturing Processes

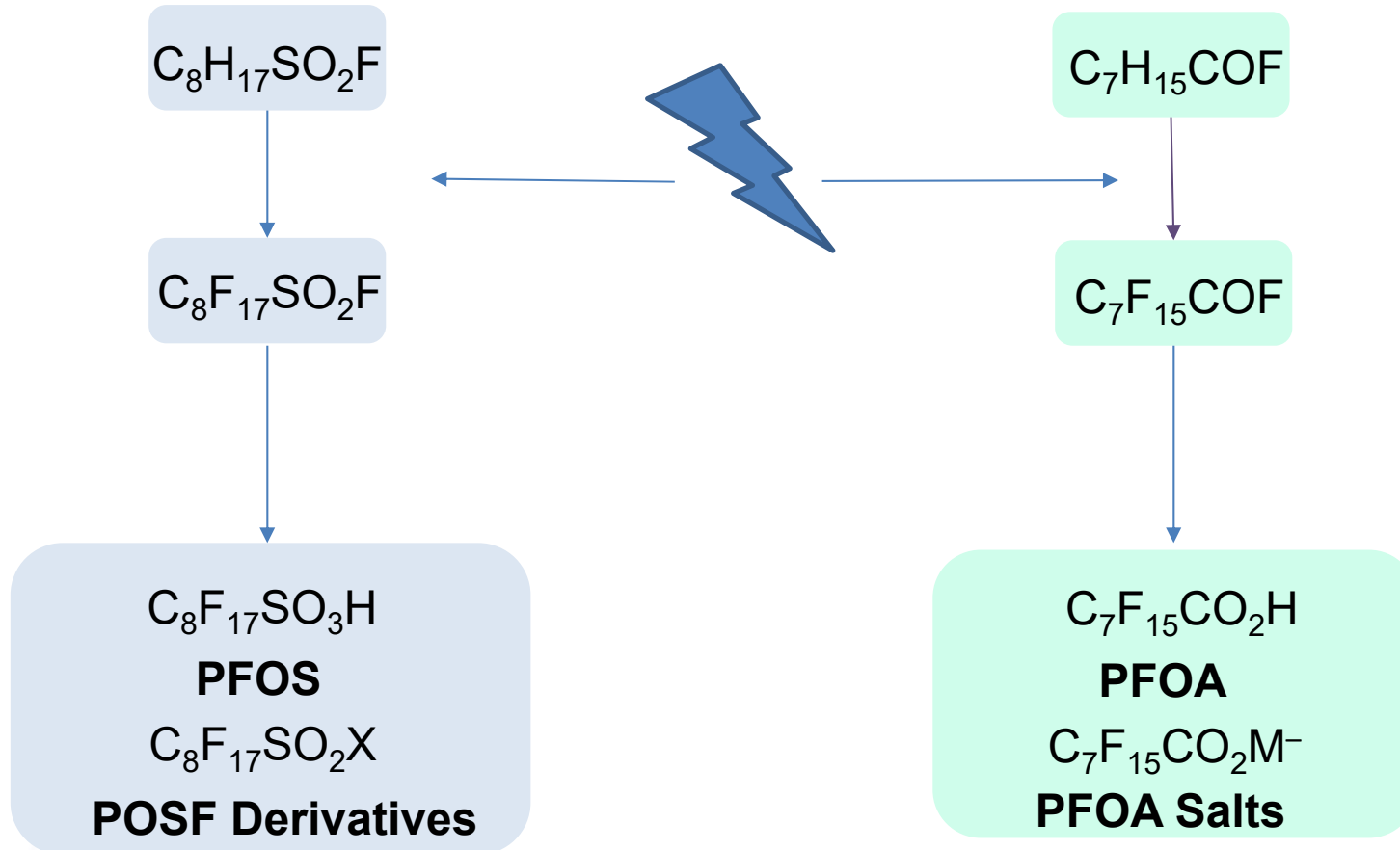
Process	Date Range	Primary Homolog	
		Odd / Even	Carbon Length
ECF	1960s to 2002	Even	8
Telomerization	1970s to Present		
Telomer Iodide		Even	8
Telomer Olefin		Odd	9

After Prevedouros et al. (2006)

Electrochemical Fluorination

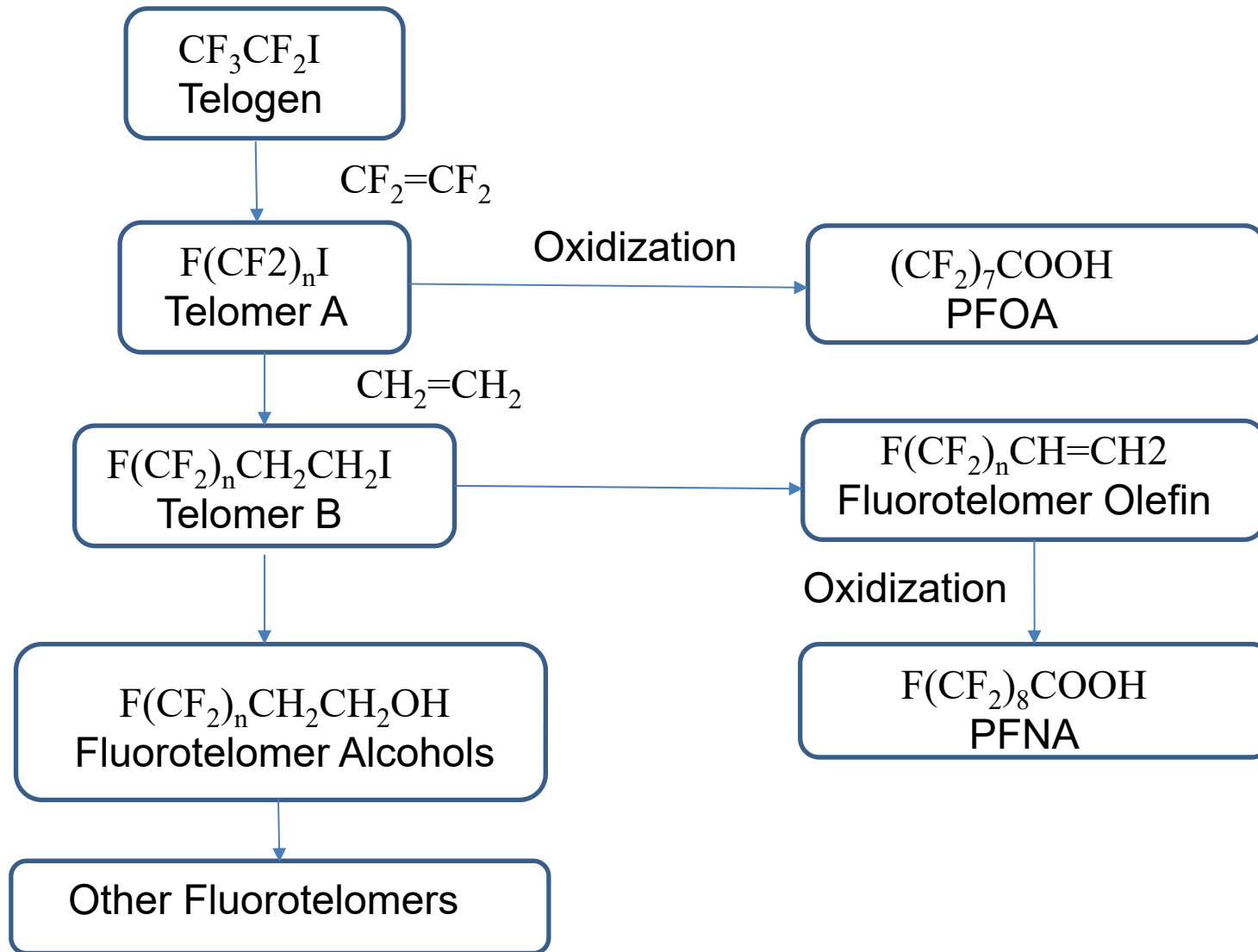
Perfluorooctane sulfonyl derivatives

Perfluorooctanoyl derivatives



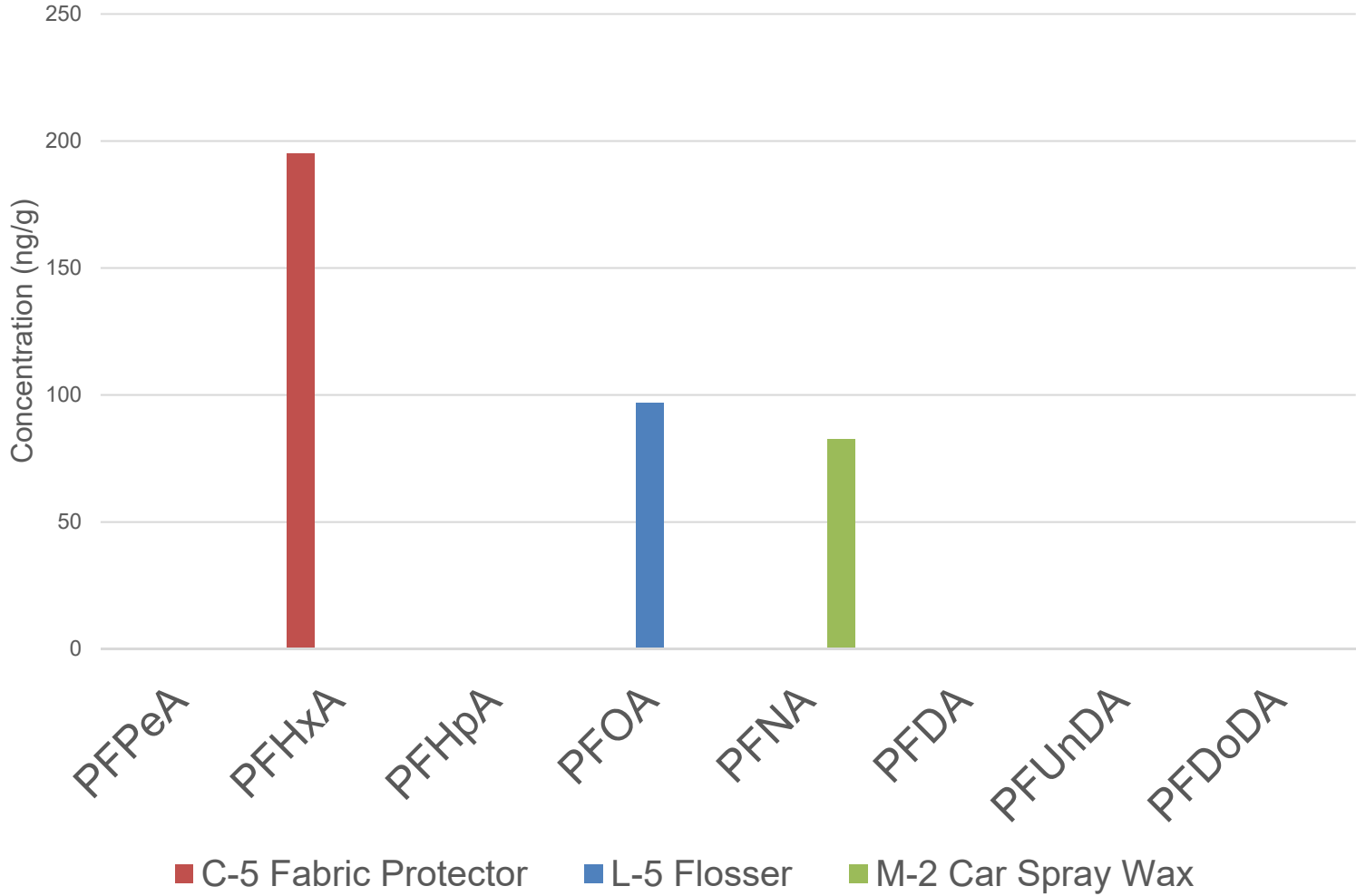
Adapted from Buck et al. (2011)

Telomerization



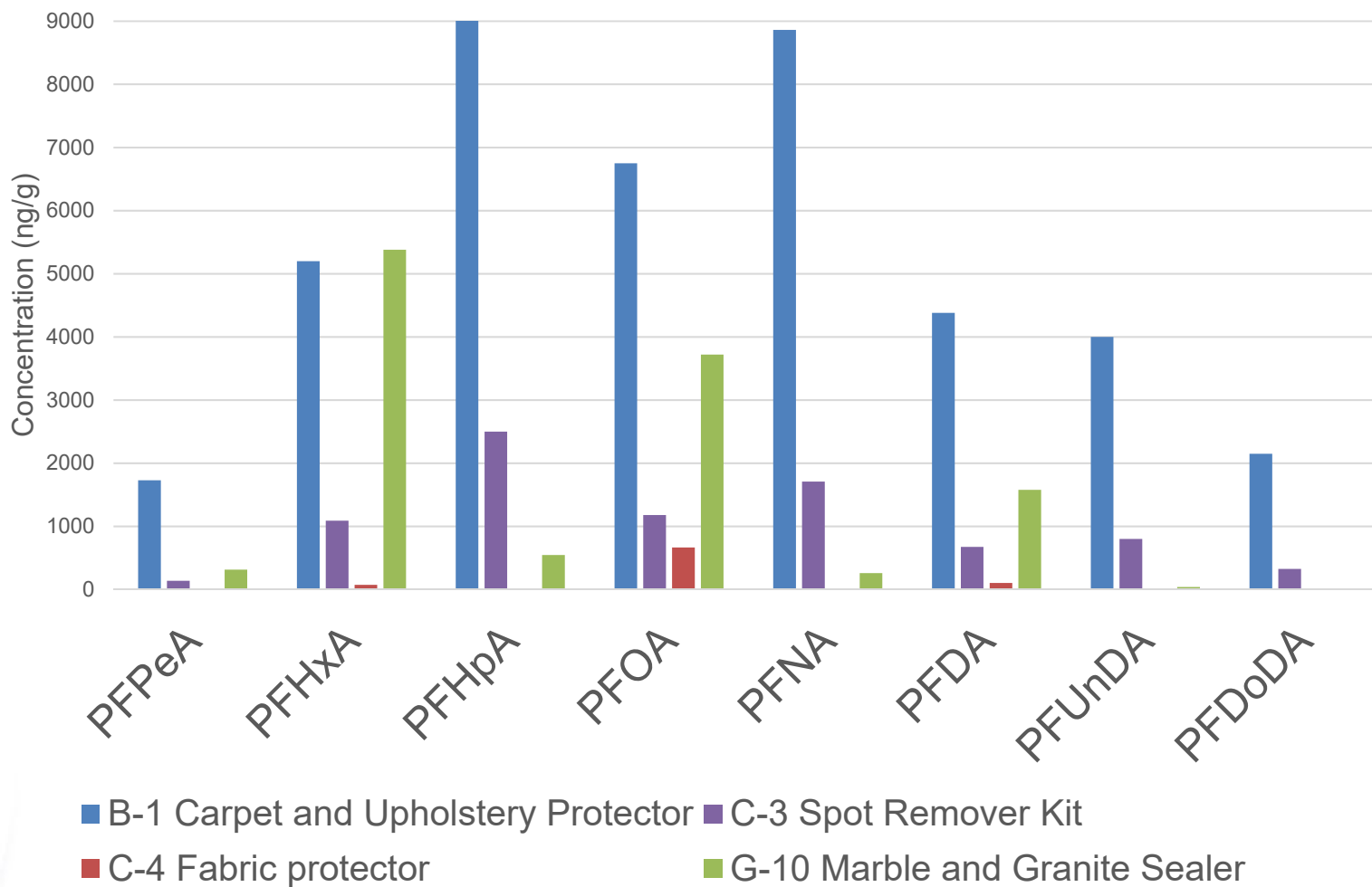
Consumer Products

Consumer Products



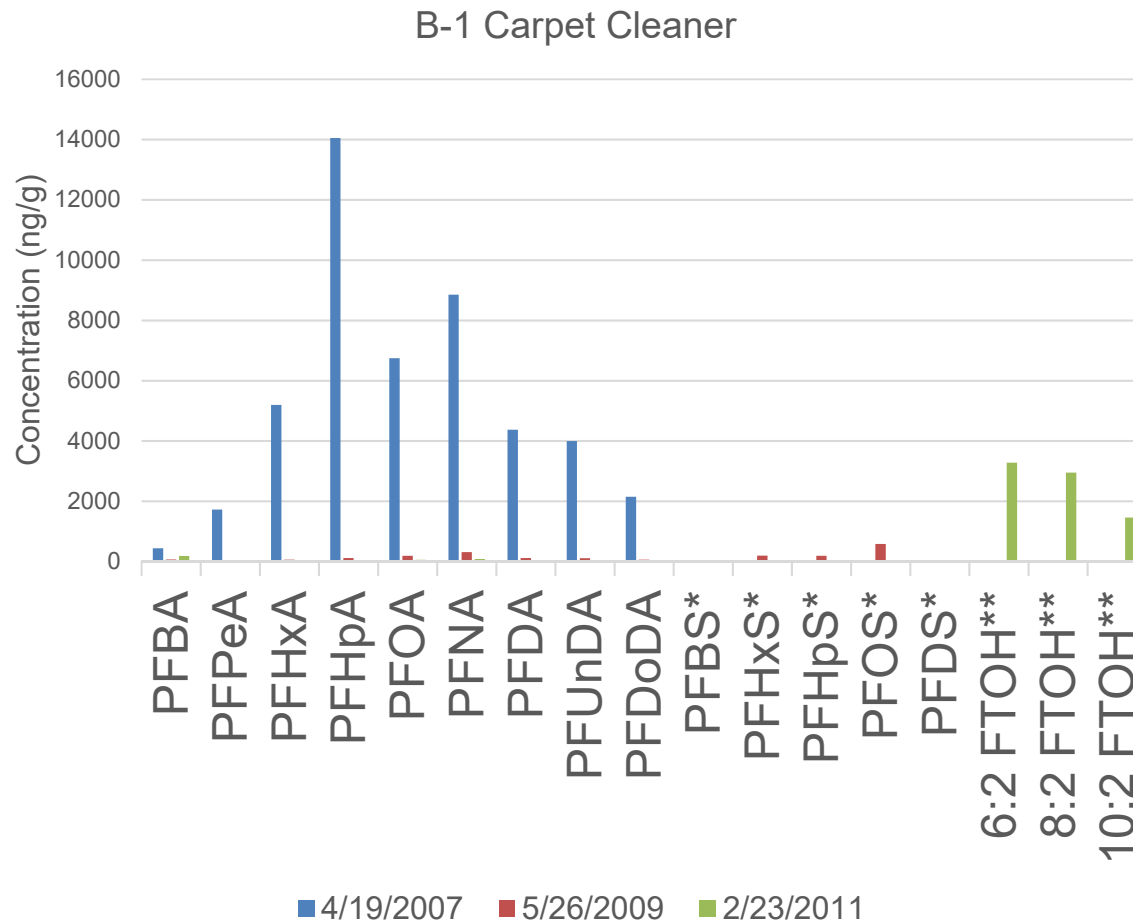
Guo et al. (2009).

Consumer Products



Guo et al. (2009).

Formulations Change Over Time



* PFASs analyzed in 2009 sample only. ** FTOHs analyzed in 2011 sample only.

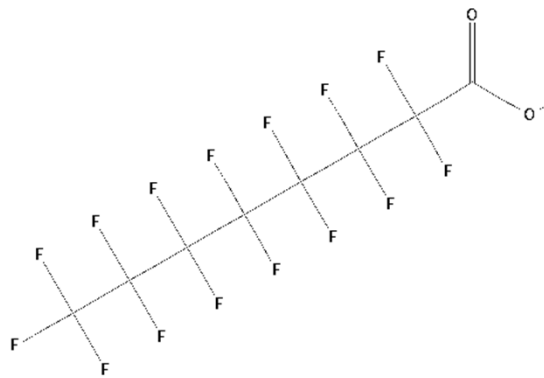
Liu et al. (2012)

What We See in the Environment

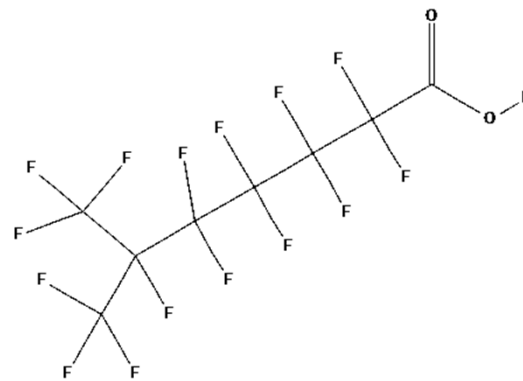
- Some industrial point sources may match a process or product
- More often a mix of processes or products
 - Landfills, AFFF sites
- Homolog profiles have been used to differentiate sources
 - Unmixing
 - Hierarchical clustering

Isomers

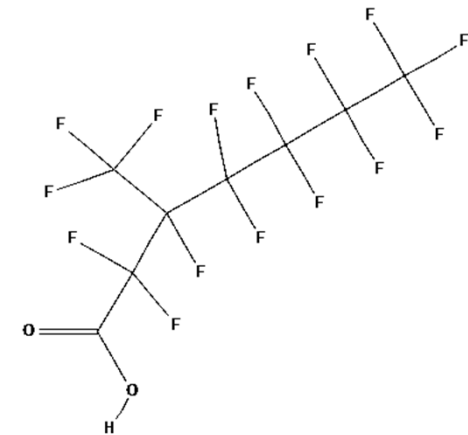
- Same functional group and carbon chain length, different structure



Linear PFOA



Isopropyl-PFOA



3 methyl-PFOA

Images from PubChem

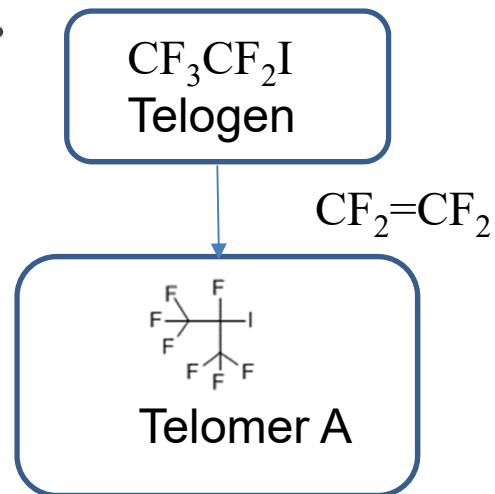
Manufacturing Processes

Process	Date Ranges	Primary Homolog		Primary Isomers
		Odd / Even	Carbon Length	
ECF	1960s to 2002	Even	8	Linear / Branched
Telomerization	1970s to Present			
Telomer Iodide		Even	8	Linear
Telomer Olefin		Odd	9	Linear

After Prevedours et al. (2006)

Side Note

- Starting with a branched telogen it is possible to use telomerization to produce branched isomers.
- However, commercial production of branched isomers by telomerization has not been confirmed.



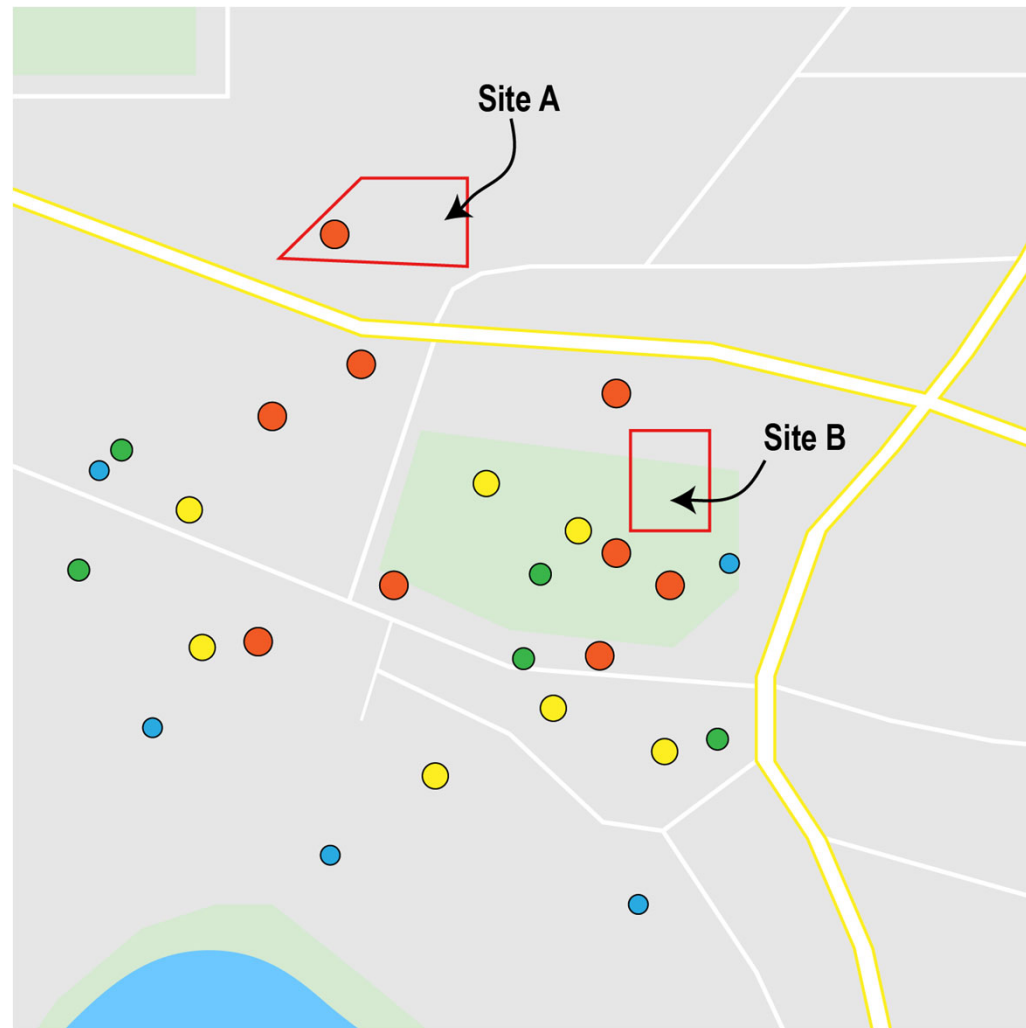
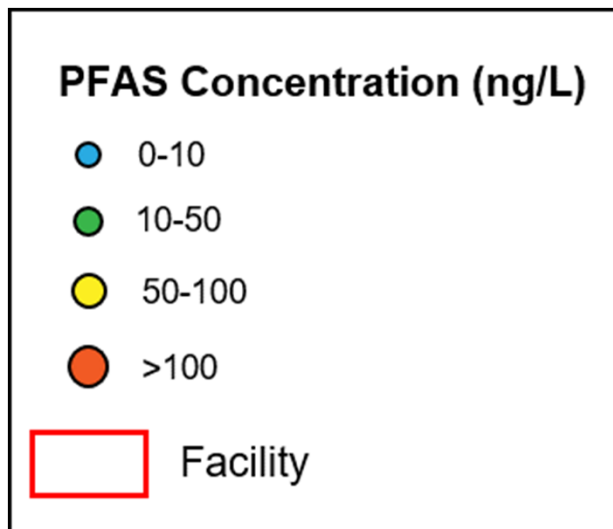
Using Isomer Data

- Isomer profiles have been used for source evaluation
 - Benskin (2011) sediments
 - Absence of branched isomers suggests telomerization source
 - Brick Township / Metedeconk River Watershed
 - Branched PFOA isomers suggest ECF source

Isomer Data Evaluation

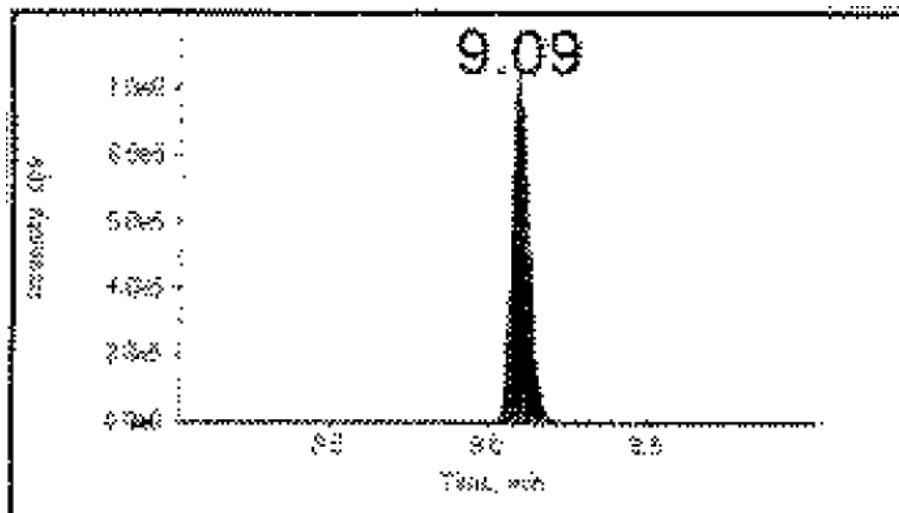
Example Sites

- Two industrial sites
- Similar concentrations

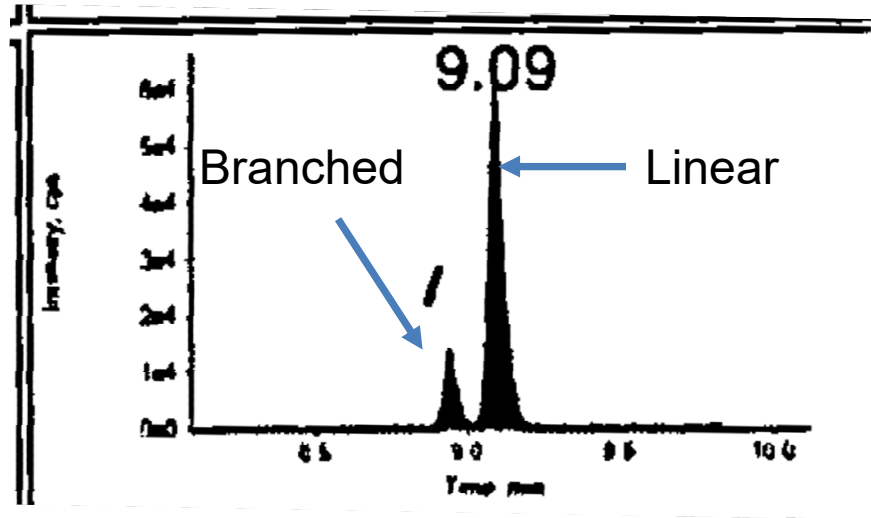


Linear and Branched Isomers Determined by Chromatography

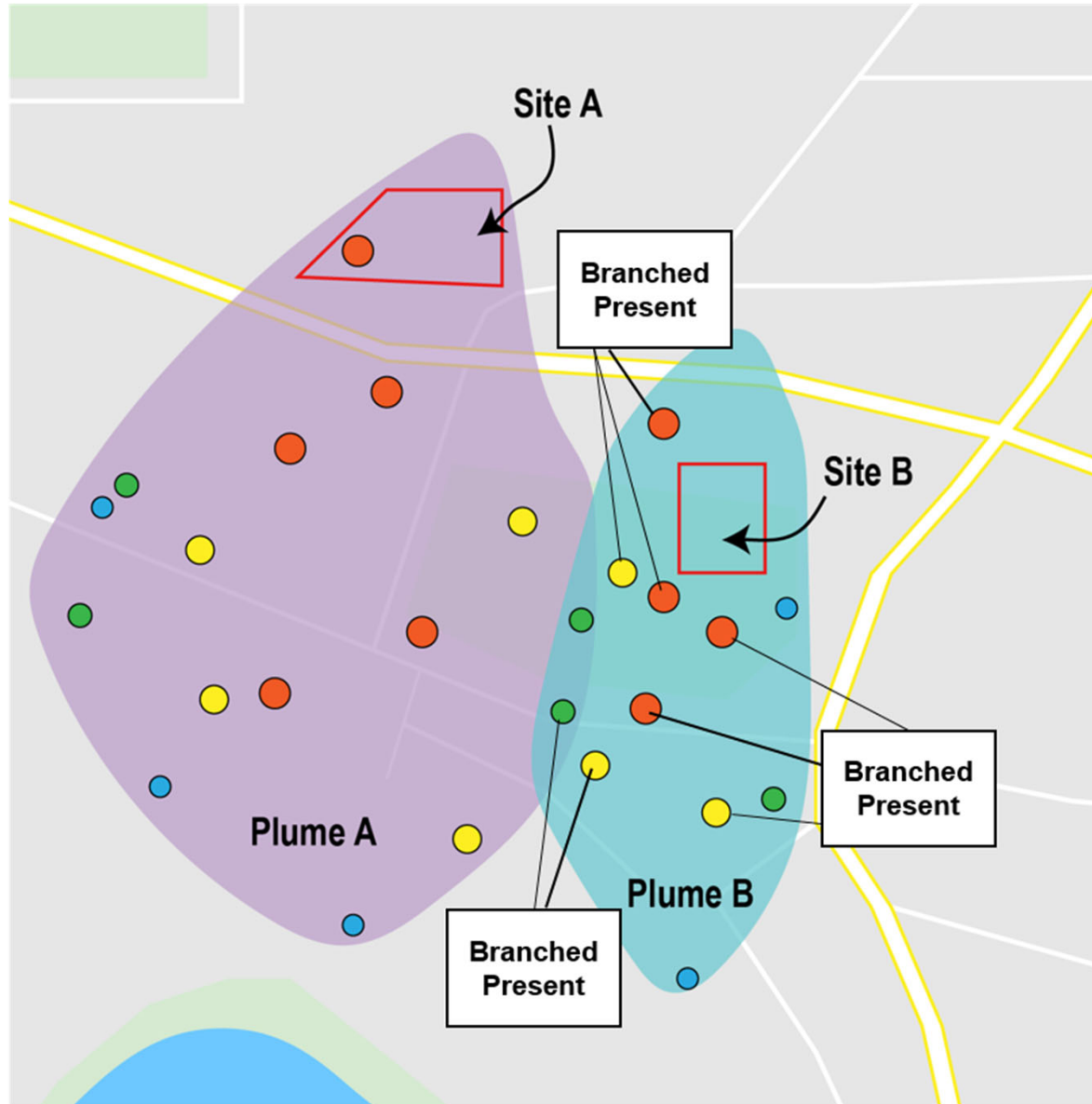
Only Linear PFAS



Linear and Branched PFAS



Isomer Data



Take Aways

- ECF generally produced even carbon chains with branched isomers
- Telomerization can produce even or odd carbon chains
 - Primarily linear isomers
 - Branched isomers only possible if branched telogen used - no confirmed commercial use
- Isomer data can be useful in differentiating sources



Questions?



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References

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- Brick Township Municipal Utilities Authority. 2015. Identification of Perfluoroalkyl Compounds (PFCs) in the Metedeconk River Watershed, Final Report. NJDEP Grant Contract No. SR11-016. April.
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- Prevedouros, K., I.T. Cousins, R.C. Buck, and S.H. Korzeniowski. 2006. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* 40(1):32-44.