Potential Designated Chemicals

PFASs
Perfluoroalkyl and polyfluoroalkyl substances

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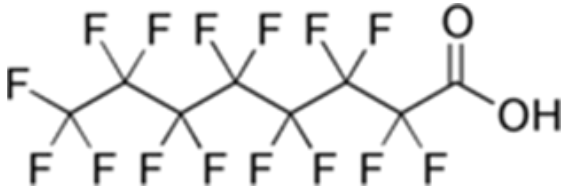
PFASs: Perfluoroalkyl and polyfluoroalkyl substances

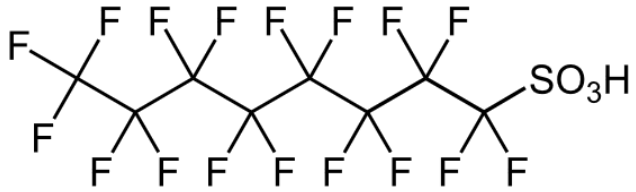
- Perfluoroalkyl substance: all of the hydrogen atoms attached to carbon atoms have been replaced by fluorine atoms
  - A subset of these is on the designated chemicals list
  - Examples include PFOA and PFOS
- Polyfluoroalkyl substance: all of the hydrogen atoms on at least one of the carbon atoms have been replaced by fluorine atoms
  - Examples include fluorotelomer alcohols and polyfluoroalkyl phosphate esters

from Buck et al. (2011)

Example perfluoroalkyl substances

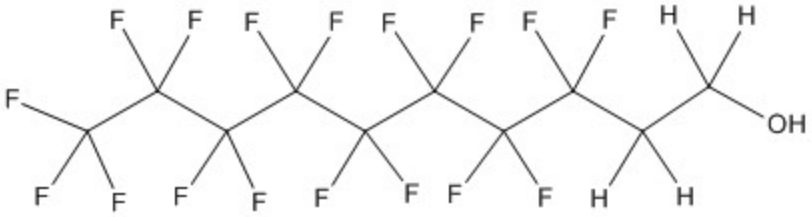


PFOA

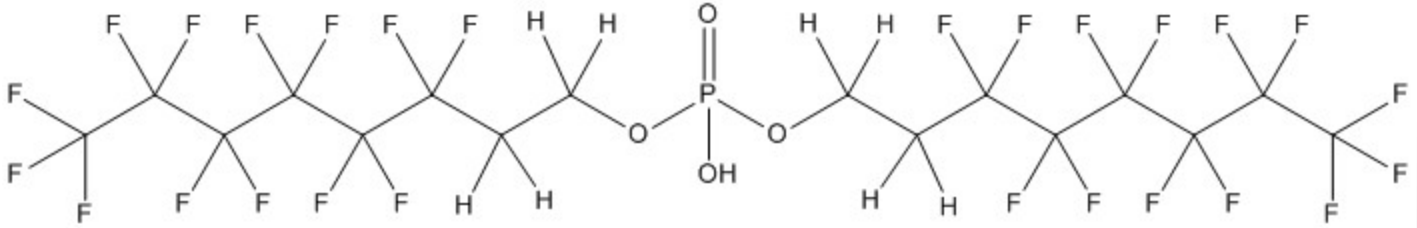


PFOS

Example polyfluoroalkyl substances



8:2 Fluorotelomer alcohol
(8:2 FTOH)



6:2 Polyfluoroalkylphosphate diester
(6:2 diPAP)

Why consider PFASs as a class?

- Large numbers of PFASs are known to be in use as alternatives to PFOS, PFOA and other long-chain PFASs
- Many other PFASs, as well as breakdown products, may also be in the environment
- Extent of human exposure is not well known
- Consider PFASs as a class to:
  - Facilitate broad laboratory screening of these chemicals
  - Allow the Program to look for key emerging chemicals in this large group

Designated Chemicals

- Chemicals that can be considered for biomonitoring by the Program
- Chemicals are designated based on:
  - Inclusion in CDC's National Reports on Human Exposure to Environmental Chemicals program
  - Recommendations by the Scientific Guidance Panel for Biomonitoring California

Criteria for recommending additional designated chemicals

- ***Exposure or potential exposure*** to the public or specific subgroups
- The ***known or suspected health effects*** based on peer-reviewed scientific studies
- The ***need to assess the efficacy of public health actions*** to reduce exposure
- The ***availability of a biomonitoring analytical method*** with adequate accuracy, precision, sensitivity, specificity, and speed
- The ***availability of adequate biospecimen samples***
- The ***incremental analytical cost*** to perform the biomonitoring analysis for the chemical

Major uses of PFASs

- Processing aid in manufacturing fluoropolymers
  - Example: Polytetrafluoroethylene, used to make non-stick coating on pans
- Surface treatments of textiles, leather and carpets
  - Water- and grease-resistance properties
- Surface treatment of food contact materials
  - Grease-resistance of paper plates, fast-food take-out containers, pizza boxes, packaging for microwave food containers
- Chrome plating
  - Wetting agents and mist-suppressing agents
- Firefighting foams

Alternatives to phased-out PFASs

Wang et al. (2013) identified numerous alternative PFASs, such as:

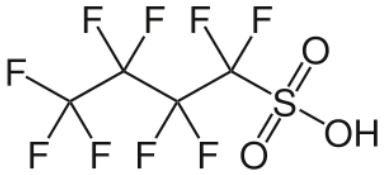
- Ammonium perfluorohexanoate
- Perfluoroether carboxylic acids
- Perfluorobutane sulfonic acid and salts
- Perfluorobutane sulfonyl fluoride-based derivatives
- Perfluorohexane sulfonyl fluoride-based derivatives
- Perfluoropolyether-based derivatives
- 6:2 Fluorotelomer-based derivatives
- 3:1 and 5:1 Fluorotelomer alcohol-based derivatives
- 6:2 Fluorotelomer carboxylic acid
- 6:2 Flurotelomer sulfonic acid salts
- 6:2 Fluorotelomer sulfonamide alkyl betaine
- 6:2 Fluorotelomer sulfonamide aminoxide

New fluorinated alternatives

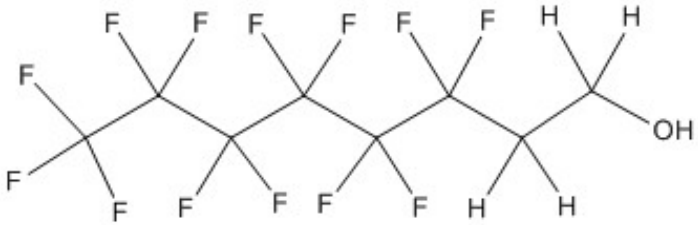
Many have shorter carbon chains -

Toxicity and bioaccumulation typically increase as the length of the carbon chain increases

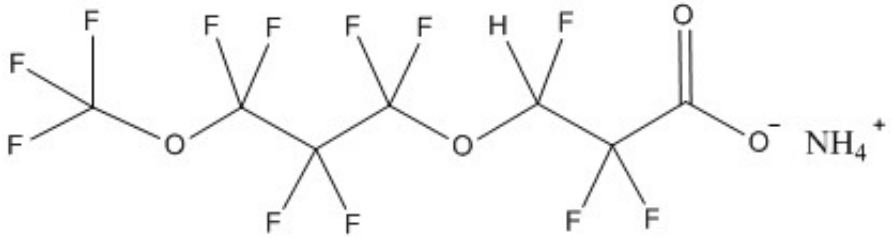
Perfluorobutane sulfonic acid (PFBS)



6:2 Fluorotelomer alcohol



Ammonium 4,8-dioxa-3H-perfluorononanoate



Short chain PFAS alternatives

Example from US EPA website

"Shorter chain-length perfluorinated telomeric substances have been notified as alternatives for a variety of uses including, for example, textile, carpet and paper additive uses and tile surface treatments. ***To date, over 75 premanufacture notices (PMNs) have been received for telomers based on shorter chain alternatives.***" *(emphasis added)*

US EPA on New Chemical Review of Alternatives for PFOA and Related Chemicals
http://www.epa.gov/oppt/pfoa/pubs/altnewchems.html
Last updated September 2014

Exposure or potential exposure

- Food
  - From PFASs in the environment
  - From migration of PFASs in food packaging into oily greasy foods
- Drinking water
- Consumer products
  - Such as carpets and textiles, liquid carpet treatments, floor waxes, sealants
- Indoor air and dust
  - From migration out of consumer products

Exposure or potential exposure (cont.)

Some concerns about shorter chain PFASs

- Removal by water treatment systems is generally more difficult compared to longer chain PFASs
- Released more easily from biosolids (produced during wastewater treatment) compared to longer chain PFASs
- May be more easily taken up by plants

Known or suspected health effects

- Many studies on PFOS and PFOA
- Limited toxicological data available on newer PFASs
- Potential concerns include:
  - Indications of endocrine activity, such as estrogenic activity and effects on steroidogenesis, based on *in vitro* studies
  - Covalent binding to cell proteins
  - Liver toxicity in laboratory animals

Past biomonitoring studies

- PFOA, PFOS, PFNA, PFHxS found in nearly all people tested
- Recent US data indicate levels of some phased-out PFASs, including PFOS and PFOA, are decreasing
- Many PFASs not on Biomonitoring California designated list have been identified in recent biomonitoring studies

Example PFASs found at low levels in recent biomonitoring studies

- Polyfluoroalkyl phosphate diesters (diPAPs)

  (6:2, 6:2/8:2, 8:2)

- Fluorotelomer sulfonic acids (FTSs)

  (8:2, 6:2)

- Perfluoroalkyl phosphinic acids (PFPiAs)

  (C6/C6, C6/C8)

- Perfluoroalkyl carboxylic acids (PFCAs)

  Perfluorobutanoic acid
  Perfluoropentanoic acid
  Perfluorohexanoic acid

From Lee and Mabury (2011); D'eon et al. (2009)

Recent biomonitoring studies (cont.)

Study of ski wax technicians

- Fluorotelomer alcohol (FTOH) metabolites
  - Fluorotelomer unsaturated carboxylic acids (FTUCAs) (6:2, 8:2, 10:2)
  - Fluorotelomer carboxylic acids (FTCAs) (5:3, 7:3)

Study comparing firefighters and controls

- Perfluoroalkyl sulfonic acids
  - Perfluoropentane sulfonic acid
  - Perfluoroheptane sulfonic acid*
  - Perfluorononane sulfonic acid*

**Found exclusively or at significantly greater levels in firefighters compared to controls*

From Nilsson et al. (2012); Rotander et al. (2015)

Bioaccumulation

- Bioaccumulation shown to increase with increasing chain length in rainbow trout
  - Bioconcentration factors in fish may not be the most relevant metric for PFASs
- Short chain PFASs
  - Less bioaccumulative in animals and humans
    - In humans, longer chain PFASs, half-lives measured in years (e.g., PFOS 5.4 years)
    - PFBS half-life estimated at 26 days
  - May accumulate to greater degree in plants

Persistence

- Short chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are similarly persistent as their longer chain homologues
- Many PFASs, such as 6:2 fluorotelomer- and perfluorobutane sulfonyl fluoride-based substances, break down to short chain PFCAs and PFSAs
- Perfluoroether carboxylic acids and perfluoroether sulfonic acids are likely to be highly persistent

From Wang et al. (2015)

Laboratory considerations

- Biomonitoring California has two LC-MS/MS instruments for PFAS analysis
  - Method used to measure 12 PFASs can be expanded to include additional compounds
  - Some PFASs might present difficult analytical challenges
- The incremental cost of the additional PFASs would include purchase of standards, cost of labor and materials during method development and ongoing analysis

Need to assess the efficacy of public health action

- Increasing use of PFASs is expected
- For many PFASs, extent of exposure is unknown and more information is needed
- Including the class on the designated chemical list would allow the State to track levels of important PFASs over time

Options for the Panel

- Recommend adding “perfluoroalkyl and polyfluoroalkyl substances (PFASs)” as a class to the list of designated chemicals
- Defer, pending more information
- Recommend against adding PFASs as designated chemicals