Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS?

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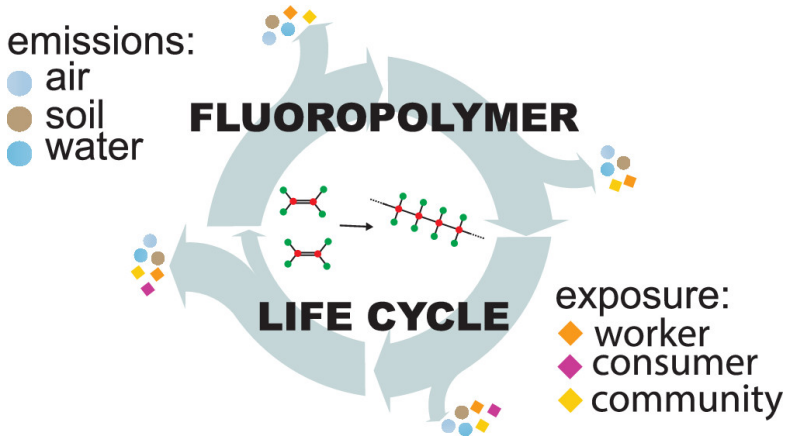
By way of introduction



- What are fluoropolymers?
- Should they be of low concern to regulators?
- Past and current processing aids for fluoropolymers
- Production and use - losses of monomers, oligomers, small PFAS
- (unknown) toxicity and capability of uptake by organisms
- Persistence and disposal
- Are fluoropolymers distinct from other PFAS?
- Finally.. Should fluoropolymers be produced without restrictions?

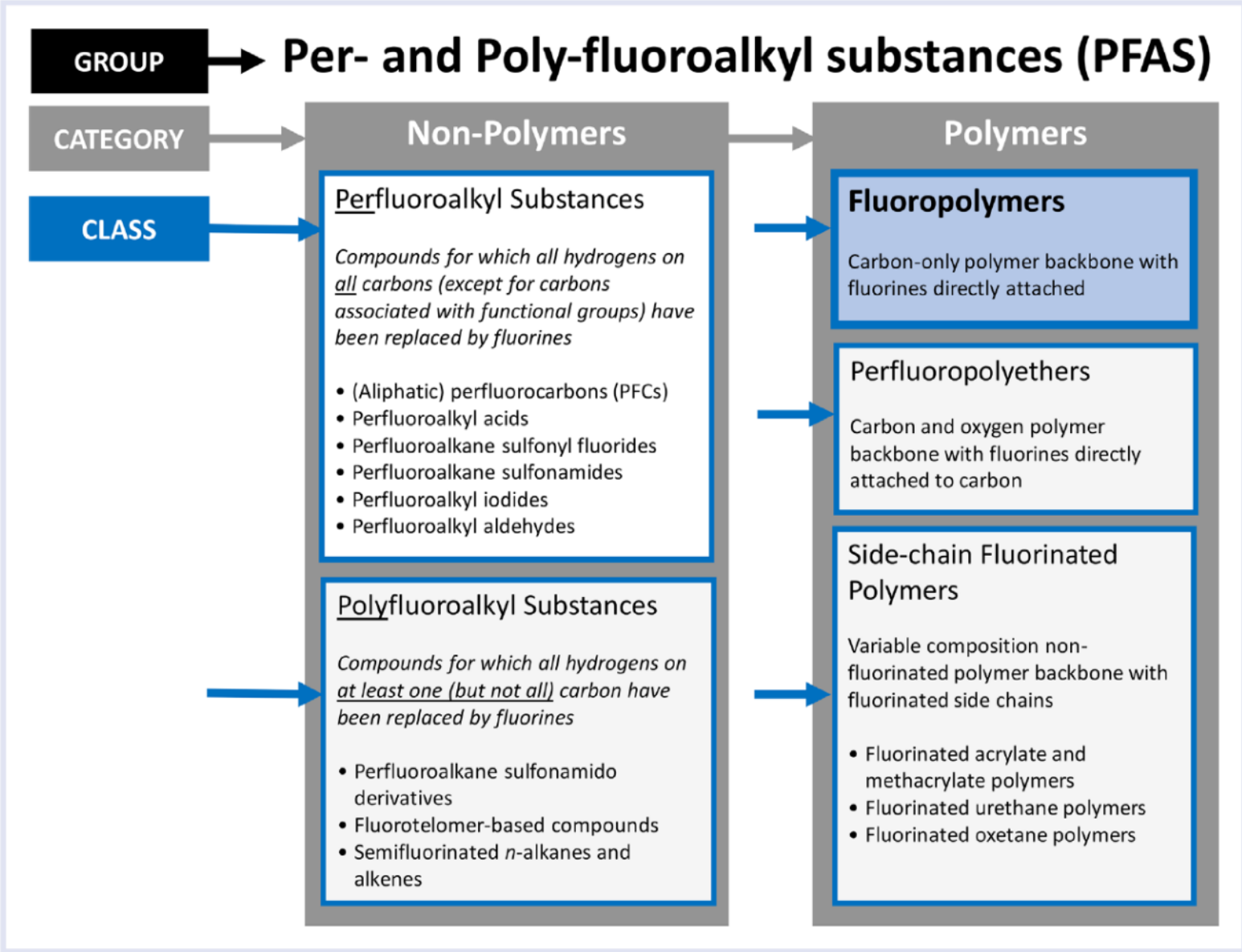


Figure 1. Per- and polyfluoroalkyl substances (PFAS).

(Henry et al., 2018)

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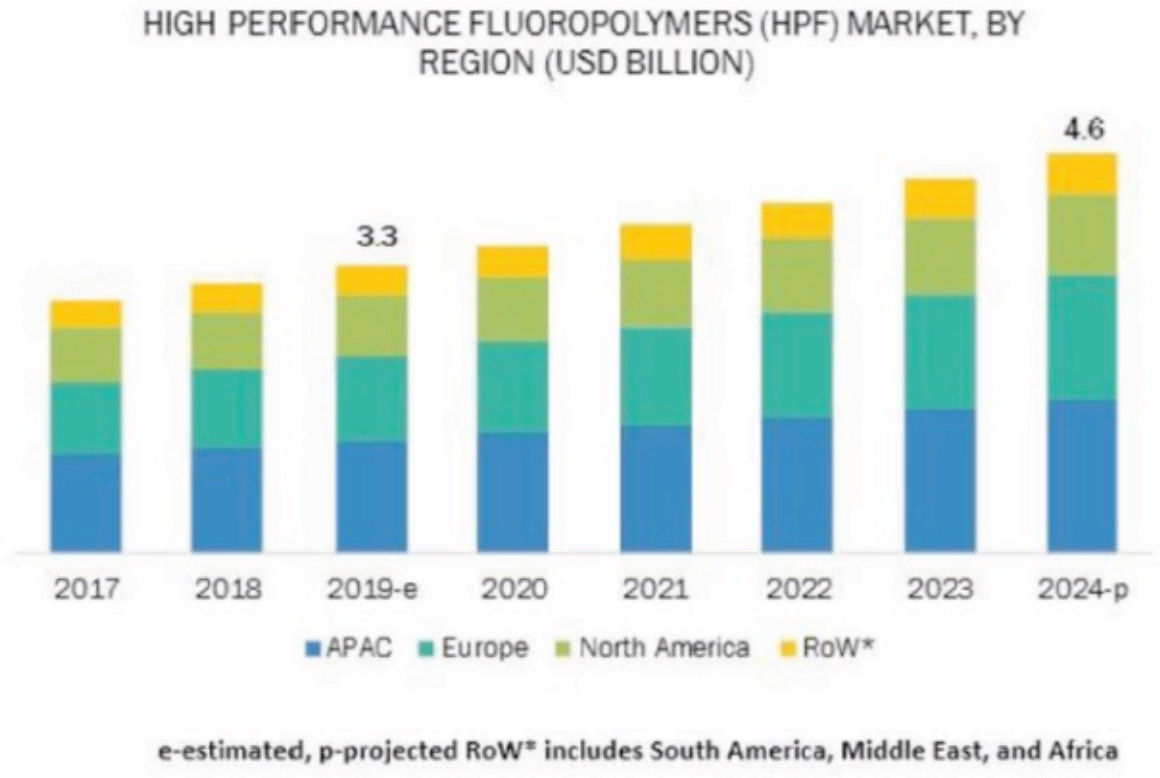
The Promising Future of Fluoropolymers

Bruno Améduri



(Macromol. Chem. Phys. **2020**, *221*, 1900573)

Are fluoropolymers polymers of low concern?

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Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

Barbara J Henry,† Joseph P Carlin,† Jon A Hammerschmidt,† Robert C Buck,‡ L William Buxton,‡ Heidelore Fiedler,§ Jennifer Seed,‖ and Oscar Hernandez#*

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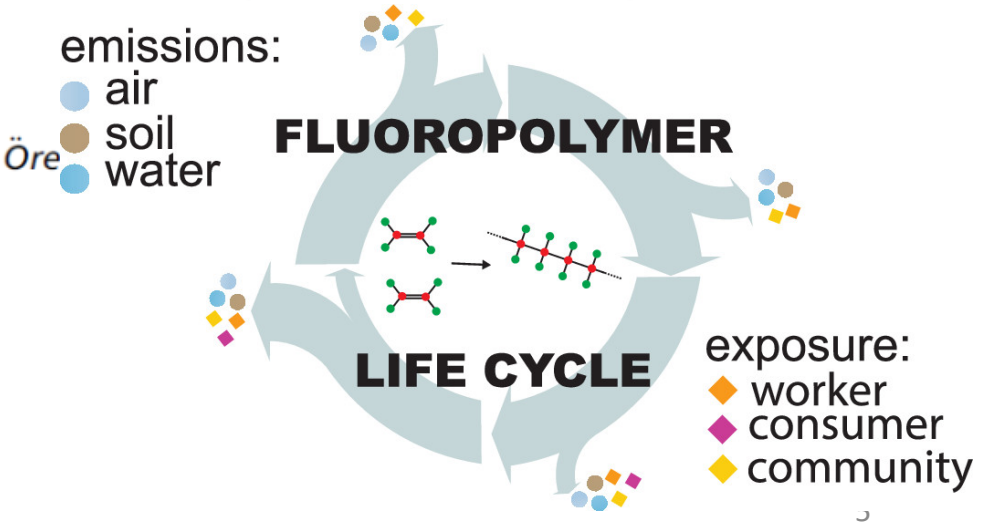

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Policy Analysis

Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?

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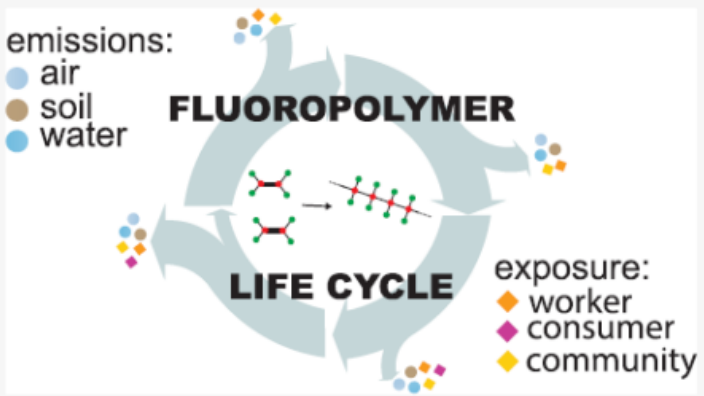
ABSTRACT: Fluoropolymers are a group of polymers within the class of per- and polyfluoroalkyl substances (PFAS). The objective of this analysis is to evaluate the evidence regarding the environmental and human health impacts of fluoropolymers throughout their life cycle(s). Production of some fluoropolymers is intimately linked to the use and emissions of legacy and novel PFAS as polymer processing aids. There are serious concerns regarding the toxicity and adverse effects of fluorinated processing aids on humans and the environment. A variety of other PFAS, including monomers and oligomers, are emitted during the production, processing, use, and end-of-life treatment of fluoropolymers. There are further concerns regarding the safe disposal of fluoropolymers and their associated products and articles at the end of their life cycle. While recycling and reuse of fluoropolymers is performed on some industrial waste, there are only limited options for their recycling from consumer articles. The evidence reviewed in this analysis does not find a scientific rationale for concluding that fluoropolymers are of low concern for environmental and human health. Given fluoropolymers' extreme persistence; emissions associated with their production, use, and disposal; and a high likelihood for human exposure to PFAS, their production and uses should be curtailed except in cases of essential uses.



https://dx.doi.org/10.1021/acs.est.0c03244
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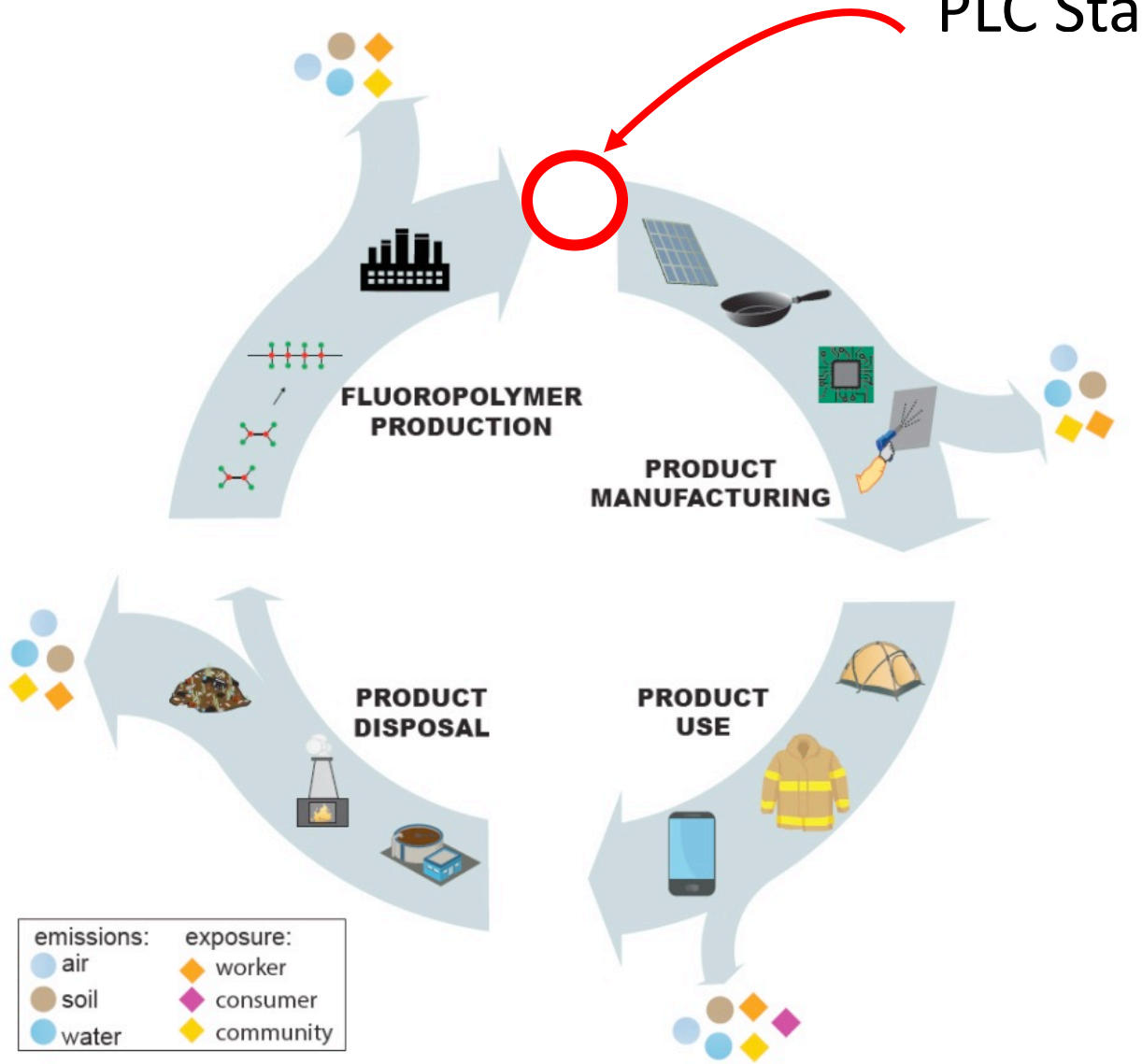
What it boils down to..



What are Fluoropolymers?

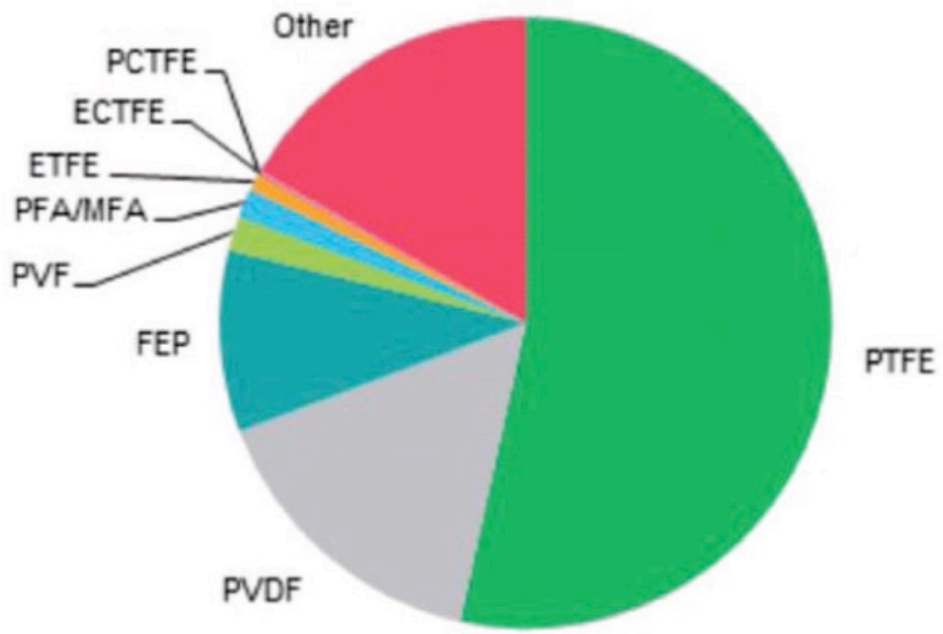


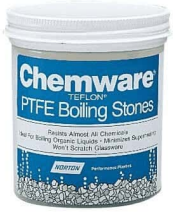
Figure 1. Global situation of the production of various FPs (2019).[16]

Dominated by

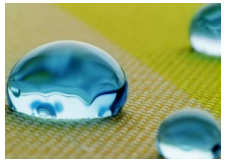
- PTFE;
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- tetrafluoroethylene-copolymers
- polyvinylidene fluoride (PVDF)
- polyvinyl fluoride (PVF) and fluoroelastomers.

- Also Nafion® (produced by Chemours), PTFE-based fluoropolymer-copolymer incorporating perfluorovinyl ether groups terminated with sulfonate groups.
- ~ 320 300 t of fluorinated plastic materials in 2018[4], and production is steadily increasing.

Some definitions



- fluoropolymer substances (PTFE, FEP, PVDF) - material of known chemical structure
- fluoropolymer product
  - actual material produced/ sold by manufacturer (e.g. Chemours, Solvay, Daikin, Asahi Glass, etc.),
  - in different grades (e.g. Teflon-granulate, Teflon-fine powder, etc.)
  - may contain impurities from the production process
- fluoropolymers in finished articles
  - PTFE tape
  - GoreTex jacket
  - Teflon-cookware



- Many different processes of making fluoropolymer products.
  - some fluoropolymers do not require PFAS-based processing aids (suspension polymerization (e.g. granular PTFE),
  - other fluoropolymers (e.g. fine powder PTFE and PVDF) are manufactured using PFAS-based processing aids during emulsion polymerization.
- Diverse production of Fluoropolymers
  - as granulates, fine powders or aqueous dispersions
  - through emulsion or suspension polymerization
  - different grades), shipped, and used

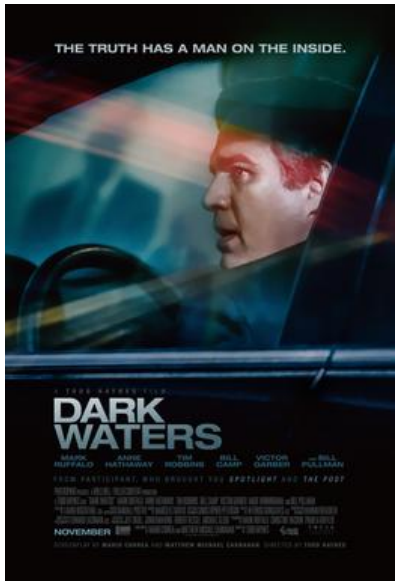
1. History of pollution from fluoropolymer production is closely tied to use of PFAS as polymer processin

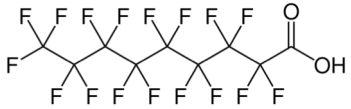
ENVIRONMENT

NJ proposes strict new drinking water standards for cancer-linked chemicals

James M. O'Neill NorthJersey

Published 4:39 p.m. ET Apr. 1, 2019 | **Updated 6:57 p.m. ET Apr. 1, 2019**

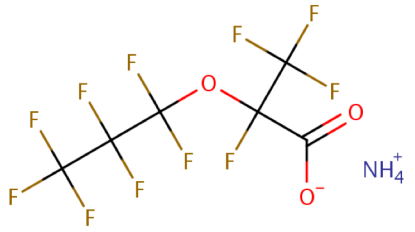


- PFOA – e.g., W Virginia
- PFNA – e.g., New Jersey  (NJ suing Solvay)
- Mostly phased out under US EPA 2010/15 Stewardship Program

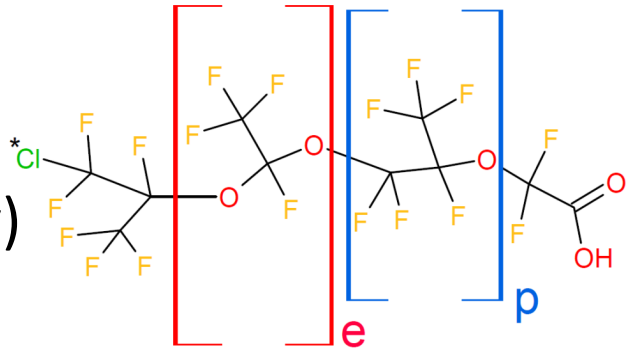
Other manufacturers, though, still utilize PFOA as a processing aid; high PFOA emissions in China/Asia

2. Substitute fluoropolymer processing aids raise similar concerns

a) Ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or GenX) detected in the environments of North Carolina and the Netherlands.



b) Functionalized PFPE reported in Wang et al. 2013 (CAS 329238-24-6) now observed in Bormida River (Italy) and New Jersey (Washington et al., 2020).



PERSISTENT POLLUTANTS

Seeking PFAS cleanup, New Jersey sues Solvay and Arkema

State seeks information about chloroperfluoropolyether carboxylates

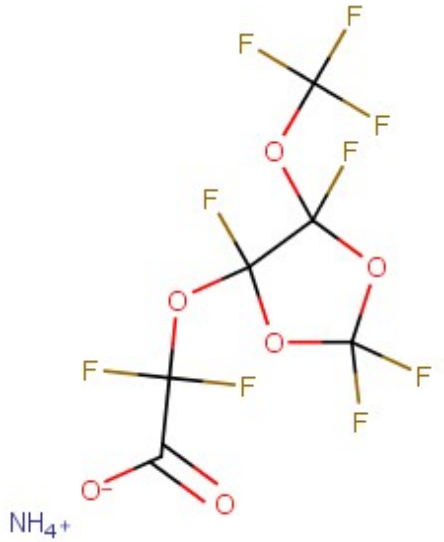
by Cheryl Hogue

NOVEMBER 13, 2020

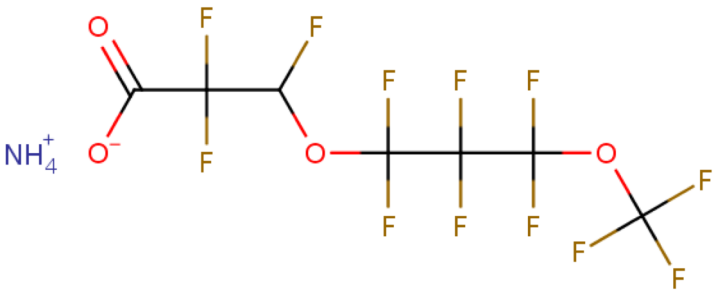
Note: the e = ethyl group can range from 0 - 2 units and p = propyl group can range from 1 – 4 units with the ethyl group most likely being closest to the chlorine. Additionally, the chlorine can be on the terminal carbon as shown or on the C2 position as $CF_3CF(Cl)CF_2$-O.

More substitute FP processing aids

c) Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1) (cC604) now observed in ground- and surface water in the Veneto region (Italy). https://echa.europa.eu/substance-information/-/substanceinfo/100.207.411



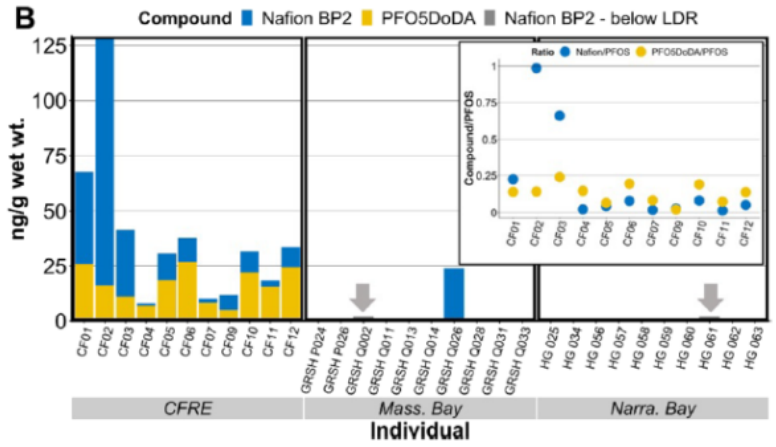
d) Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8) (ADONA) detected in the Rhine River and serum samples.



- *All these replacement PFAS already detected in environment*

3. Monomer, oligomer and synthesis by-product emissions during the production of fluoropolymers

- Many ultrashort-chain fluorinated by-products are highly volatile, difficult to capture, and might have large GHG potential.
- Detection of oligomers in stack emission samples (McCord et al, 2019)
- PVDF production (Decatur, AL): series of polyfluoroalkyl CAs with + CF_2CH_2 (Newton, 2017)
- Chemours (NC) confirmed > 250 unknown, potentially unique, PFAS in WW
- *Nafion* byproducts present in the environment, fish, birds, & humans downstream of producer*



(Robuck et al., 2020)

4. Leaching of low-molecular-weight PFAS from fluoropolymers during processing

- Low molecular weight PFAS can remain in fluoropolymers
- residual levels of PFAAs (0.3-24 ppm) in personal care artic
- Levels of leachables (e.g. processing aids, synthesis by-pro products/finished articles are largely unknown
- Fluoropolymer-coated food contact materials (e.g. metal c
  - Known to occur in chromatographic instrumentation, at the pp
- Low residuals finished PTFE products – sign of safety?
  - reflect “aggressive” steps taken to wash out residuals and drive

With High PFOA Contamination In North Bennington, State To Expand Testing Area

By HOWARD WEISS-TISMAN • MAR 21, 2016

Share Tweet Email

Gov. Peter Shumlin points to a map showing the new areas the state will test for the contaminant PFOA. Shumlin spoke at a community meeting in North Bennington Wednesday night.

- *Drying step (sintering) of fluoropolymers has caused wide-spread (atmospheric) PFAS dispersion around PTFE*
  - *production sites (West Virginia (US)[29] and Netherlands)*
  - *use sites in the US (North Bennington, VT; Merrimack, NH, Hoosick Falls, NY)*

5. Toxicity of fluoropolymer processing aids, monomers and oligomers

- Legacy processing aids (i.e., PFOA, PFNA) with known health effects
  - certain types of cancer, immunotoxicity, reproductive and developmental toxicity, liver toxicity, and thyroid disease.
- A replacement processing aid, HFPO-DA, shows a similar toxic potency in rodents as PFOA [41]
- Little known for PFECAs, such as ADONA or the PFECA CAS 329238-24-6

replacement chemicals (need to) have similar properties to legacy processing aids, and are as persistent

6. “Polymers are too large to penetrate cell membranes” ?

- PS nanoparticles of ~ 100 nm diameter enter stem cells (Jiang et al., 2011)
- PS nanoparticles of ~ 42 nm present in tissue and organs of maternally and co-parentally exposed F1 embryos/larvae (Pitt et al., 2018)
- Inhaled spherical PTFE microparticles migrated into the surface lining layer of hamster alveoli (Geiser et al., 2003)

Blanket statement that polymers cannot enter cells is factually inaccurate.

- Fluoropolymers (0.3 t) only small part of all polymer (300 Mio t), but
- PTFE microparticles detected in Mediterranean fish and remote Arctic Ocean sediment samples

Occurrence, exposure to, and toxicity of nano-plastics with many unknowns

7. Persistence and disposal of fluoropolymers

- Fluoropolymers are extremely persistent under environmental condition.. (microplastics..)
- Industrial recycling of clean PTFE waste or scraps is already happening,
  - conversion into PTFE micropowder (so-called fluoroadditives) and then using them to reduce wear rate and friction.
  - pilot-scale industrial high-temperature recycling process (vacuum pyrolysis) to regenerate gas-phase monomers
- Little to no recycling of fluoropolymers in consumer articles (other substances and fillers).
- Commercial bakeries remove fluoropolymer coatings after 1-2 yrs via burning or blasting
  - In Sweden, 20 000 baking pans are 'recoated' - 'burning off' at 450 °C for 4-5 h grit or water blasting .. Emissions???
- Landfilling of fluoropolymers = PFAS in leachates; releases of plastics and microplastics.
- Does incineration destroy PFAS? forms fluorinated or mixed halogenated organic by-products..
  - CF4 and C2F6 as combustion by-products; also TFA between 250 °C and 600 °C (relevant for uncontrolled burning)
  - polychlorotrifluoroethylene (PCTFE) releases many byproducts (Myers et al., 2014), including Cl/F-benzenes,naph.
  - Is incineration in MSWI safe? Unclear evidence; problem with highly corrosive HF.

Hence, production of persistent polymers, such as the highly persistent fluoropolymers, should occur only in time-limited essential use categories, i.e., critical for the safety, health and functioning of society.

8. Can fluoropolymers be considered separately from the use of PFAS as processing aids?

- Can emulsion polymerized fluoropolymers (in contrast to suspension polymerization) be produced without the use and emissions of PFAS as processing aids?
- Cape Fear: It took regulatory action after “Gen X” contaminated Cape Fear watershed
  - Zero” emission policy to water was mandated in North Carolina.
  - PFAS-containing liquid processing waste - deep well injection out of state
- In Dordrecht (Netherlands), regulations exist for
  - air emissions (which are now restricted to 450 kg/y)
  - direct (surface water) emissions (recently restricted to 5 kg/yr) and
  - indirect emission to a local WWTP (recently restricted to 140 kg/yr, was 6 tonnes/yr in 2017)
- Emulsion polymerization with less or without PFAS use possible.. Realistic?

A phase-out of all PFAS as fluoropolymer processing aids would be a vast improvement, but would not address the current problems associated with impurities, as well as a lack of recycling and disposal.

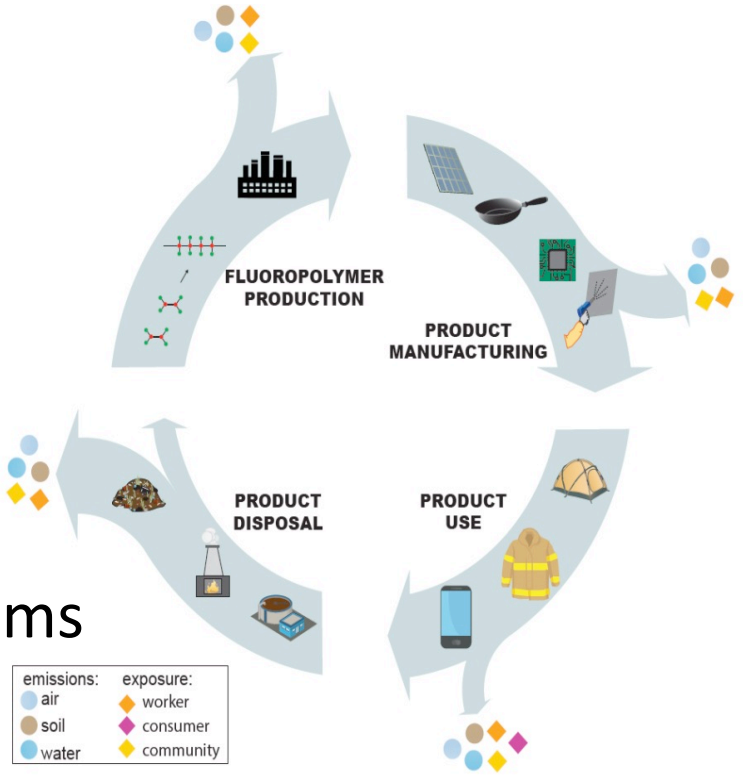
9. Are fluoropolymers polymers of low or high concern?

- Not sufficient evidence to consider fluoropolymers as PLCs for environmental and human health.
- The group of fluoropolymers is too diverse to warrant a blanket exemption
- Their extreme persistence and the emissions associated with their production, use, and disposal result in a high likelihood for human exposure as long as uses are not restricted.
- Need to consider life-cycle of fluoropolymer products
- No scientific basis to separate fluoropolymers from discussions of other PFAS
- limited information on the compositions, grades, etc. of the available fluoropolymer products
- PLC assessment should be performed on a product-by-product basis

Our recommendation is to move toward the use of fluoropolymers in closed-loop mass flows in the technosphere and in limited essential-use categories, unless manufacturers and users can eliminate PFAS emissions from all parts of the life cycle of fluoropolymers.

In conclusion

- Fluoropolymers should be of concern to regulators!
- Problems with past and current processing aids for fluoropolymers
- Losses of monomers, oligomers, small PFAS during production and use
- (unknown) toxicity and capability of uptake by organisms
- Persistence and disposal
- Fluoropolymers are “conjoined twins” with low MW PFAS



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Questions?

Thanks to

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You for listening!