TURA Science Advisory Board

Potential PFAS Category Definition Based on OECD 2018 Methodology and Database

Definition using subset of OECD definition, built around the database organization:

- **PFASs that contain a perfluoroalkyl moiety with three or more carbons (i.e. $–C_nF_{2n}–$, n ≥ 3; or CF_3-C_nF_{2n}-, n≥2) or a perfluoroalkylether moiety with two or more carbons (i.e. $–C_nF_{2n}OC_mF_{2m}–$, n and m ≥ 1).**
    - Includes all but 2 substances on OECD database spreadsheet (359-70-6 and 375-51-9)
    - No max limit on C, therefore includes polymers
    - Includes perfluorocarbons (PFCs)
    - Does **not** include:
        - C1 or C2 alkyl chain lengths unless ether moiety is present.
            - Note that PFBA, the shortest fluorinated carbon chain evaluated by the SAB has 3 fully fluorinated carbons + 1 non-fluorinated carbon so while it is commonly referred to as a 'C4' chemical, it has a C3 perfluoroalkyl chain.
        - other halogen substituents in minimum perfluoroalkyl moieties.

- Of 4728 substances listed in above definition and using OECD indication of precursor:
    - 88% precursors; 7% PFAAs and terminal degradation products; 5% other non-precursors (neither precursors or PFAAs)

- **88% Precursors**: Indication as precursor is based on the chemical structure having a non-perfluorinated carbon or iodine atom linked to the perfluorinated carbon moiety (personal communication Zhanyun Wang). Other evidence of degradation from the literature was not considered by OECD.
    - Note: within subcategories, there may be an individual substance that is not listed as a precursor, but has similar structure as others noted as precursor. These individual outliers were not pulled out as "other non-precursors" unless indicated as listed under TSCA
    - Note that some fluoropolymers are listed as precursors
        - those with poly-fluorinated backbones , e.g., ETFE ethylene tetrafluoroethylene - $[CH_2CH_2]_n$-$[CF_2CF_2]_m$- may be susceptible to attach and fragmentation
        - non-perfluorinated side or end functional groups (includes some functionalized PTFE) where side or end groups may be susceptible to attack

- **7% PFAAs and terminal degradation products**:
    - Includes PFCAs, PFSAs, PFPAs, Di-acid PFAAs, PFECAs (e.g., GenX), PFESAs

- **5% other OECD non-precursors -** Substances included in the OECD database that are not presumed to be PFAA precursors or PFAAs/terminal degradation products. (see table below)
    - Fully fluorinated PFCs (604) and fully fluorinated Perfluoroalkyl ethers (501) (all fluorinated except ether linkages)
    - Fluoropolymers – (Note that some are listed as precursors, see above)
        - Fluoropolymers that are assumed to be highly persistent under ordinary environmental conditions are not listed as precursors; they would only be subject to thermal degradation (includes PTFE)

Other OECD Non-precursors

Subcategories with chemicals that are not either PFAA's/terminal degradation products or identified as precursors

OECD subcategory	#	Description	Precursor Evidence from literature
Perfluoroalkyl ethers	501	Fully fluorinated alkyl chains connected by one or more ether linkages	Lee 2004 ref. w/ UV irradiation breaking Freon E2 (CAS 3330-14-1) down to carboxylic acid and acid fluoride https://academiccommons.columbia.edu/doi/10.7916/D8HX1JWN/download
Perfluoroalkanes and aromatics	604	Fully fluorinated alkanes, cyclics and aromatics	from Buck 2011: "Those PFCs that contain a CnF2n+1– moiety are, by definition, members of the PFAS family, but PFCs are chemically very stable substances, and it is uncertain whether any of them can actually degrade in the environment (e.g., in the upper atmosphere) to give functionalized PFASs such as PFCAs that might ultimately be deposited to the Earth's surface." Perfluorohexane (355-42-0) >3000 yr atmospheric lifetime, 100 yr GWP=6800; vBvP, OSPAR chemicals of concern, ME and WA lists. Three subst. incl. in TURA C1-C4 Halogenated HC NOL category. Thermolysis: O'Mahony 1993 and Tsai 2009: pyrolysis products include PFIB, TFE; thermal breakdown mirrors fluoropolymers; possibility of PFAAs
Fluoropolymers	800 series	Fluoropolymers (perfluorinated backbone) with no obvious susceptibility to attack	Thermolosis and Pyrolysis (see refs in thermal breakdown summary) Also potential for mechanical degradation

Supplemental Information

OECD 2018 Database Precursor Assumption

- Precursors based on: The general assumption was made based on studies as reviewed in Young and Mabury (2007), Liu and Avendaño (2013), Butt et al. (2014), Wang et al. (2014) and others; Please note that the time scale of such degradation is not taken into consideration, i.e., it may take still years to decades or longer for a substance to degrade into stable PFAAs. In particular, side-chain fluorinated polymers, some fluoropolymers, and fluoroelastomers may first need a substantial amount of time to break down to much smaller fragments that would then be bioavailable and subject to further degradation.
- E-mail communication with Zhanyun Wang: The author generally considered anything with a nonperfluorinated carbon or iodine atom linked to the perfluorinated carbon moiety, to be a PFAA precursor
- Additional communication from Zhanyun Wang re: fluoropolymer precursor designation on why some fluoropolymers (800 sub categories) are potential precursors and others not:
    - Fluoropolymers include polymers that are either with PERfluorinated or POLYfluorinated backbones.
    - The Perfluorinated backbones are highly persistent, but as you said, some non-perfluorinated functional groups on the side or at the end may be cut-off and degrade to PFAAs (e.g. if

perfluoroalkyl moiety-containing functional groups are connected to the polymer backbone via ester bonds).

- In contrast, the non-fluorinated parts in the POLYfluorinated backbones may be susceptible to attack (e.g. ehtylene tetrafluoroethylene, ETFE, -$[CH_2CH_2]_n$-$[CF_2CF_2]_m$-). So it could be the non-fluorinated parts break down, and ETFE slowly fragmented into small pieces. The issue here is generally we don't know what's the average chain length of fluorinated parts in the polymer backbone, so they may still be huge, or could be like C10 or C20.