Fluorinated Products of Incomplete Combustion in EPA's New Chemicals Program

Summary

Fluorinated products of incomplete combustion (PICs) may be formed and released during thermal treatment of wastes containing organofluorine chemicals. However, there are significant uncertainties around the identities and amounts of PICs that may be formed, as well as any long-term effects they may have on human and ecological receptors. Based on these concerns, EPA's New Chemicals Division (NCD) will include language in its fate assessment reports describing our concerns about fluorinated PICs for relevant new chemical substances.

Background

Environmental concentrations of short-chain PFAS and small fluorinated acids are increasing over time. These compounds occur both from intentional use and from transformation of other fluorinated compounds by natural and anthropogenic processes.[1,2] Thermal treatment of organofluorines has been identified as one source of small, fluorinated compounds, owing to the substantial stability of the C-F bond and its ability to withstand high temperatures capable of mineralizing other types of organic compounds.[3]

Many of these PICs are highly mobile in the environment due to characteristics such as low molecular weight and high water solubility. They may not be readily broken down by natural transformation processes such as biodegradation and therefore exhibit a high degree of persistence.[2] When released to the atmosphere, these compounds can undergo wet deposition and move freely throughout the water cycle, resisting removal in wastewater treatment and accumulating in drinking water and plant resources.[4,5,6,7] As a result, they are now broadly dispersed in the environment, potentially causing increasing exposure for human and ecological receptors. While many fluorinated PICs have relatively short clearance half-lives in humans,

[1] Jordan, A *et al*. 1999. Trifluoroacetate in the environment: Evidence for sources other than HFC/HCFCs. Envir Sci Technol 33(4):522–527.
[2] Brendel, S *et al*. 2018. Short-chain perfluoroalkyl acids: Environmental concerns and a regulatory strategy under REACH. Environ Sci Eur 30:1–11.
[3] Ellis, DA *et al*. 2001. Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. Nature 412(6844):321–324.
[4] Cahill, TM *et al*. 2001. Accumulation of trifluoroacetate in seasonal wetlands in California. Environ Sci Technol 35(5):820–825.
[5] Scheurer, M *et al*. 2017. Small, mobile, persistent: Trifluoroacetate in the water cycle–Overlooked sources, pathways, and consequences for drinking water supply. Water Res 126:460–471.
[6] Neumann, M and Schliebner, I. 2019. Protecting the sources of our drinking water: The criteria for identifying persistent, mobile and toxic (PMT) substances and very persistent and very mobile (vPvM) substances under EU Regulation REACH (EC) No 1907/2006. UBA TEXTE, 127, p.2019.
[7] Scheurer, M and Nödler, K. 2021. Ultrashort-chain perfluoroalkyl substance trifluoroacetate (TFA) in beer and tea–An unintended aqueous extraction. Food Chem 351:129304.

they are nonetheless consistently detected in human serum, in some cases at concentrations positively correlated with age, indicating that body burdens may increase over time.[8,9]

These factors suggest the potential for continuous exposure that is mechanistically distinct from the lipid partitioning-based bioaccumulation historically associated with NCD's persistent, bioaccumulative, and toxic (PBT) framework.[10] These compounds thus present challenges with the historical analytical and regulatory approaches.[11] In response to this novel problem, European regulators have developed the classifications persistent, mobile, and toxic (PMT) and very persistent and very mobile (vPvM) to complement the PBT classification.[12] Trifluoroacetic acid, a widely studied fluorinated PIC, has been placed in the vPvM category.[13]

Sources of Uncertainty

Under the Toxic Substances Control Act, fate assessments are conducted for new chemical substances and any degradation products of concern that are reasonably anticipated to form from them, including products of incomplete combustion. While the problem of highly persistent and mobile chemicals has been recognized, quantitative fate assessments of fluorinated PICs that may form from new organofluorine chemicals remains challenging due to several major sources of uncertainty:

- The operating conditions of municipal waste combustors (MWC) are not standardized. Good combustion practices recommended by EPA include the use of a process temperature of at least 980 °C, but these practices are not legally enforceable. EPA data from 1988 found MWC operating temperatures in the range of 760–927 °C. Currently, NCD is not aware of any additional data on operating temperatures that are readily available.
- The formation rates of fluorinated PICs under various conditions are poorly defined. It has been established that a range of PICs can form from combustion of PFAS at

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[8] Boutonnet, JC *et al*. 1999. Environmental risk assessment of trifluoroacetic acid. Hum Ecol Risk Assess 5(1):59–124.

[9] Duan, Y *et al*. 2020. Distribution of novel and legacy per-/polyfluoroalkyl substances in serum and its associations with two glycemic biomarkers among Chinese adult men and women with normal blood glucose levels. Environ Int 134:105295.

[10] 64 FR 213 pp.60194–60204. https://www.govinfo.gov/content/pkg/FR-1999-11-04/pdf/99-28888.pdf; accessed 27 Sep 2024.

[11] Reemtsma, T *et al*. 2016. Mind the gap: persistent and mobile organic compounds—water contaminants that slip through. Environ Sci Technol 50:10308–10315.

[12] European Chemicals Agency. 2023. New hazard classes 2023. Available at: https://echa.europa.eu/new-hazard-classes-2023. Accessed: 27 Sep 2024.

[13] Arp HPH, Hale SE. 2019 REACH: Improvement of guidance and methods for the identification and assessment of PM/PMT substances. UBA Texte 126/2019. Project number: FKZ 3716 67 416 0. ISSN: 1862-4804. German Environmental Agency (UBA), Dessau-Rosslau, Germany. 129 p. https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2019-11-29_texte_126-2019_reach-pmt.pdf. Accessed 27 Sep 2024.

temperatures below 1,100 °C, but the science does not currently support predictions of their identities and concentrations in the combustion exhaust under a given set of conditions.[14,15] Monitoring data from real-world combustion units are very limited or nonexistent because MWCs are not required to monitor for PFAS.[16]

- As noted above, there are other known sources of fluorinated PICs aside from combustion of organofluorines. For example, trifluoroacetic acid is a known product of the atmospheric breakdown of chlorofluorocarbon replacement chemicals.[17] As such, the increase in fluorinated PICs from a given new chemical substance must be considered in light of the already-sizeable background levels in the environment.
- The primary exposure pathway of concern for these compounds—atmospheric release followed by wet deposition to surface water or groundwater (via soil infiltration) and subsequent entry into drinking water resources—is highly complex. This pathway is challenging to model quantitatively in the TSCA New Chemicals Program given the available screening-level tools and the statutory timeline associated with new chemical review.
- Human and ecological hazard data are very limited or nonexistent for many fluorinated PICs. Even in cases where traditional acute or chronic endpoints are available, these may not accurately represent the hazards associated with continuous, lifelong exposures via the pathway mentioned previously in this document.

Conclusion

Thus, in lieu of a quantitative fate assessment of a specific PIC compound, NCD now includes the following qualitative statement in its fate assessments of new organofluorine chemicals[6,18]:

> Combustion of the new chemical substance may potentially lead to the formation and release of very persistent and very mobile fluorinated products of incomplete combustion (USEPA 2024). However, there are significant uncertainties around the identities and amounts of PICs that may be formed, as well as any long-term effects they may have on human and ecological receptors (Neumann and Schliebner 2019).

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[14] Shields, EP *et al*. 2023. Pilot-scale thermal destruction of per-and polyfluoroalkyl substances in a legacy aqueous film forming foam. ACS ES&T Eng 3(9):1308–1317.

[15] Mattila, JM *et al*. 2024. Characterizing volatile emissions and combustion byproducts from aqueous film-forming foams using online chemical ionization mass spectrometry. Environ Sci Technol 58(8):3942–3952.

[16] https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-60/subpart-CCCC; accessed 8 Nov 2024.

[17] Wujcik, CE *et al*. 1998. Trifluoroacetic acid levels in 1994–1996 fog, rain, snow and surface waters from California and Nevada. Chemosphere 36(6):1233–1245.

[18] US EPA. 2024. Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances—Version 2. Available at https://www.epa.gov/pfas/interim-guidance-destroying-and-disposing-certain-pfas-and-pfas-containing-materials-are-not; accessed 25 June 2024.

Ongoing research by the scientific community, including EPA's Office of Research and Development, will, in time, help us better understand the uncertainties listed earlier in this document, potentially facilitating quantitative fate assessments of PICs in the future.