IC2/TURA PFAS Webinar, presented by ACC/FluoroCouncil – Jan 30, 2019

FluoroCouncil follow up re: questions that were not addressed during the webinar

Substance universe, classification and uses

1. Refrigerants and fluorinated aromatics are not considered PFAS, however some refrigerants such as R-134A are also used as propellants. Why are refrigerants carved out of the PFAS classification? Would the use of R-134A as a propellant be considered a PFAS?
    - *Ans: The per- and polyfluoroalkyl substances (PFAS) classification was created for a specific intent and purpose. It was not created for nor intended to be used to describe all fluorinated substances. It is important to be clear, specific, and descriptive when discussing PFAS chemistries. Refrigerants and fluorinated aromatics do not meet the definition of PFAS because of their chemical structure, not because their use, such as refrigerants or blowing agents.*
2. Where do all the chemicals with other functional groups or co-polymers fit in your 5 boxes? e.g., fluorinated siloxanes, aromatics or cyclic compounds with fluoroalkyl chains. Do they result in other terminal degradation products besides the familiar PFCAs, PFSAs?
    - *Ans: Fluorinated siloxanes may be non-polymeric PFAS depending upon their specific structure. If a perfluoroalkyl moiety can be severed from the siloxane, then it is likely to follow the same degradation pathway as the simpler substances we are familiar with such as the fluorotelomer-based substances. All aromatic substances are not considered PFAS, even if they have a fluoroalkyl chain attached to them. This is currently a point of discussion (e.g., at OECD).*

    a) Follow-up: what are the terminal breakdown products of the aromatics with side alkyl chains?
        - *Ans: This question is more appropriate for the makers of the aromatic substances.*

    b) Does it depend on whether there are fluorines on the aromatic ring?
        - *Ans: The biodegradation pathways of aromatic substances can be very different from aliphatic substances and are dependent upon what the substituents on the aromatic are and where. See 2a above.*
3. What is the function for the PFAS in biocides and pesticides? Are they used as surfactants or are they part of the pesticidal action?
    - *Ans: Fluorosurfactants (FS) have been used as dispersing agents and the bulk of that use is no longer practiced to our knowledge. One well-documented ongoing use is sulfuramid, which continues to be used as an active agent for fire ants in Brazil. To our understanding, the perfluoroalkyl phosphinic, and phosphonic acids were used as dispersing agents in pesticides. We have no information suggesting these uses are still ongoing.*

    a) Follow-up: Is the sulfuramid part of the pesticidal action?
        - *Ans*: The common sulfuramid is N-ethyl perfluorooctane sulfonamide.

    b) What is the mechanism of action as a pesticide?
        - *Ans: From the literature, the mode of action (MOA) appears to be "Uncouplers of oxidative phosphorylation via disruption of the proton gradient." The MOA classification appears to be a "Respiration Target." See IRAC-online.org, Dec 2018:*

https://www.irac-online.org/latest-version-of-the-moa-classification-incorporating-bio-insecticides-now-available/

4. Can you please address the purity of the polymers -- are there non-polymeric PFAS in the final commercial polymer products?
    - *Ans: The presence of non-polymeric PFAS impurities depends upon the manufacturing and use processes for a given polymer. Typically, residual impurities are driven out during fluoropolymer processing. (see* Henry et al 2018 *review paper on fluoropolymers). E.g., medical devices are tested for residuals. Supplemental information in that paper shows no residual.*

    a) Follow-up questions: what is the detection limit of the extraction and what solvent is used? maybe just a reference of the test method would be helpful?
        - *Ans: Please refer to the Henry et al 2018 paper as well as the recently published (Jan 2019) Guide to the Safe Handling of Fluoropolymer Resins, prepared by The Plastics Industry Association. A copy of the new handbook is attached for your review and reference.*

    b) What about unreacted monomers?
        - *Ans: See Answer to 4a. above.*
5. Please provide approximate volumes of the different chemicals in each use in the table in your slide
    - *Ans: As a follow up to the Answer that was given in the webinar, companies do not share volume information as it relates to either production or products.*
6. Is HFPO DA a Raw material, Commercial Product or both?
    - *Ans: HFPO-DA is manufactured for use as a polymer processing aid; it is a site-limited intermediate, it is not a raw material. Generally, HFPO-DA may be present as an impurity in the manufacture of products made from HFPO – hexafluoropropylene oxide.*
7. Is the definition of "short chain" as C6 and below vs C8 and below dependent on the process used to produce?
    - *Ans: It is important to anchor the short- and long-chain designation to the specific perfluoroalkyl acid (PFAA) group: perfluorocarboxylate (PFCA) or perfluoroalkane sulfonate (PFSA) and their potential precursors. This terminology acknowledges the substantial difference in the biological properties between short- and long-chain PFAAs in these two groups, PFCAs and PFSAs. The definition is here:* http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/
        - *For example, fluorotelomer-based C6 substances are short chain because they link to perfluorohexanoic acid, a short-chain perfluorocarboxylic acid (PFCA).*
        - *Today's electrochemical fluorination (ECF) processes utilized in the US result in C4 PFSAs, which are short chains. Perfluorohexane sulfonate (PFHxS), the C6 sulfonate made by the ECF process, is designated as a long-chain substance because it exhibits similar biological properties to PFOS, not because of the number of carbons. Note that perfluorobutane sulfonate (PFBS) is a short-chain PFSA.*
8. How would one determine what PFAAs or precursors are being used in MA manufacturing facilities?
    - *Ans: Today's PFAAs or their precursors are essential to many important products, including some utilized in the following industries: aerospace, semiconductor, textile, paper packaging, wire & cable, and chemical/pharma .*
9. What common medical implanted devices contain PFAS? Specifically, PTFE

- *Ans: Fluoropolymers serve as high dielectric insulators that are critical to the proper function of electronics that rely on high frequency signals such as pacemakers. See* Henry et al 2018 *for general information on this subject.*

10. PFAS have also been found in cosmetics/ personal care products. Do you know what type of PFAS are used and what the purpose is?
    - *Ans: Some perfluoropolyether-based substances are registered as cosmetics ingredients. There have been a few recent reviews on the use of certain PFAS compounds in cosmetics. Please see Danish Environmental Protection Agency (DEPA). 2018. Risk assessment of fluorinated substances in cosmetic products. https://www2.mst.dk/Udgiv/publications/2018/10/978-8793710-94-8.pdf And also:* Safety Assessment of Polyfluorinated Polymers as Used in Cosmetics https://www.cir-safety.org/sites/default/files/fluoro092018FR.pdf
11. What are the specific substances used in AFFF (with CAS #'s)?
    - *Ans: See* Perfluoroalkyl Substances in the Environment*, D.M. Kempisty, Y Xing and L. Racz editors, CRC Press, 2019; specifically, Chapter 1 and references therein: Fluorosurfactants in Firefighting Foams: Past and Present.*
12. Substances such as PFBS (CAS 375-73-5) and Potassium Perfluorobutane Sulfonate (CAS 29420-49-3) do not appear on the 2016 TSCA CDR – why?
    - *Ans: The US Environmental Protection Agency (EPA) manages the TSCA CDR; therefore, this question is more appropriately directed to the agency*
13. We pulled the list of substances from the OECD master list that were tagged as TSCA CDR 2016 – is that all the TSCA listed substances in use in the US, or are there a lot that are trade secret? Are polymers that are exempt not listed? If so, are those just the solid resins, or are all polymers excluded?
    - *Ans: FluoroCouncil cannot respond to inquiries about specific chemicals.*
14. Are the non-alkyl fluorinated substances similarly persistent? E.g., aromatics, refrigerants.
    - *Ans: In general, persistence depends on the chemical structures and the conditions (environment) available for transformation (biotic, abiotic).* Please refer to the published data regarding the *environmental fate of refrigerants, pharmaceuticals, and pesticides.*

    a) If we look for total organic fluorine, or total oxidizable fluorine will we be finding them as well?
        - *Ans: Yes, however, these are general, non-specific methods to identify the presence of organofluorine-containing substances. Neither of these methods identifies what specific organofluorine-containing substances are present. These methods should be augmented by analytical methods that can speciate the chemical structure.*
15. Are there specific things you disagree with on the current (2018) OECD chart of PFAS? (note from after presentation, we assume the aromatics listed in the "b) other highly fluorinated substances that match the definition of PFASs but have not yet been commonly regarded as PFASs" is one such disagreement).
    - *Ans: We strongly believe that clear, specific, and descriptive terms and classification are needed and are most useful in distinguishing substances that are vastly different from one another. The term PFAS alone does not accomplish this. This is currently the subject of significant debate in the scientific community. Further comments on the OECD as well as on the Buck/Franklin et al schematics are expected to be forthcoming in 2019.*

16. What fluorinated chemicals are used in ion exchange and PEM fuel cell membranes?

- *Ans: There are a number of commercially available fluoropolymer membranes that are used for this purpose. Some of them incorporate sulfonated polytetrafluorethylene as well as perfluorovinyl ether groups, among others.*

a) If they are side chain fluorinated polymers, what chain length are they typically?

- *Ans: They are not side-chain fluorinated polymers.*

17. How small are the PTFE particles in a dispersion, e.g., a PTFE coating product? (in Da and nm) Are they sometimes small enough to be considered oligomers?

- *Ans: See the new Handbook noted earlier (attached) and the Henry et al 2018 publication.*

18. What types of coatings contain PFAS, and how widespread are those product uses? What is the purpose of PFAS in those coatings products, and what types of PFAS are used? Are there chemicals, trade names or key words that would identify the substances on an SDS or tech sheet?

- *Ans: "Coatings" describes a very large space of uses. Uses are broadly described on the FluoroCouncil website. Fluoropolymers, like PTFE, are used in lots of industrial applications. Additional information is available in Henry et al. 2018. Fluorosurfactants also have many uses in "coatings." Useful references include the following: Chemistry, Properties and Uses of Commercial Fluorinated Surfactants. In Handbook of Environmental Chemistry, Volume 17, Polyfluorinated Chemicals and Transformation Products, Knepper, T. P.; Lange, F. T., Eds. Springer: 2011 and Fluorinated surfactants and repellents. Surfactant Science Series, Marcel Dekker, New York, NY* ***2001,*** *97, (2nd Edition).*

Hazard, toxicity, PBT

1. You say some are not bioaccumulative but are they all persistent?
   - *Ans: Whether a particular substance is persistent and/or bioaccumulative depends on its specific structure and properties; gross generalizations are inappropriate.*
2. Did the companies give human hazard data to EPA equal to the Green Screen endpoints?
   - *Ans: Submission of hazard data is a filing requirement of EPA's Premanufacturing Notice (PMN) process. The data varies by PMN. The types of data supplied may include animal, fish, bird, and related data. The EPA may model relevant endpoints for which no specific test data is provided. Human data comes from biomonitoring as well as epidemiology studies.*
3. What is their opinion on the proposed Mobile and Very Mobile rules in Europe-saying that bioaccumulation is not required for a short chain PFAS to be hazardous due to extreme persistence and mobility?
   - *Ans: This is currently the subject of much debate. These proposed rules would still require a chemical to be toxic, in addition to persistent and mobile, to qualify as hazardous. FluoroCouncil's view is that this equation is more complicated than it appears – a compound may be mobile and persistent but other factors need to be accounted for, such as toxicity and exposure and at what level and frequency.*
4. Have exposure limits been set for fluoropolymers? Or any PFAS?
   - *Ans: Yes. There are exposure limits that have been set for a large number of PFAS compounds. See the Fluoropolymer Handbook cited in question 4 above. For fluoropolymers which are regarded as inert, not bioavailable, not water soluble, etc. (as discussed at length in*

Henry et al 2018), setting these exposure limits under normal use conditions is likely not necessary. However, one must consider each polymer and each end use before making any final determination of exposure limits.

For PFHxA specifically: *Three new recently published peer-reviewed studies supported by the FluoroCouncil provide valuable information for perfluorohexanoic acid (PFHxA). These articles look at exposure, health effects, and hormone (endocrine) activity. The studies conclude that PFHxA is not carcinogenic, is not a selective reproductive or developmental toxicant, and does not disrupt hormone (endocrine) activity.*

i. *Perfluorohexanoic acid toxicity, part I: Development of a chronic human health toxicity value for use in risk assessment. Regulatory Toxicology and Pharmacology* ***2019,*** *103, 41-55. https://doi.org/10.1016/j.yrtph.2019.01.019 (The study presents a chronic human health-based reference dose (RfD) for PFHxA of 0.25 mg/kg-day that informs public health decisions.)*

ii. *Perfluorohexanoic acid toxicity, part II: Application of human health toxicity value for risk characterization. Regulatory Toxicology and Pharmacology* ***2019,*** *103, 10-20. https://doi.org/10.1016/j.yrtph.2019.01.020 (The study findings indicate that PFHxA currently poses minimal risk to the health of the general U.S. population. The findings also show that human exposure is low and infrequent. In addition, daily intake rates for infants exposed to PFHxA through breast milk, formula and baby food clearly demonstrate very high margins of safety for PFHxA. The RfD in the first study was applied in this partner study to derive a drinking water lifetime health advisory value of 1400 ppb and residential ground water screening level for children of 4000 ppb.)*

iii. *A hypothesis-driven weight-of-evidence analysis to evaluate potential endocrine activity of perfluorohexanoic acid. Regulatory Toxicology and Pharmacology* ***2018,*** *99, 168-181. https://doi.org/10.1016/j.yrtph.2018.09.001 (A critical review that concluded that PFHxA would not be characterized as an endocrine (hormone) disruptor as defined by the World Health Organization. The weight of the evidence analysis evaluated the potential endocrine disruptor activity of PFHxA as defined by the World Health Organization, and found that it did not induce adverse hormone (endocrine)-related effects.)*

5. Where is the matrix of EPA test data referenced on slide 50 located? Similar: Where is the matrix of EPA test data available?
   - *Ans: EPA is the most appropriate source to provide the matrix of data needs that the agency uses in the PMN/TSCA approval process. Please see the attached website that explains how EPA makes their assessments: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca*
6. Have there been any biomonitoring studies that looked for whether medical devices are a sources of exposure to any PFAS (parent or breakdown)?
   - *Ans: Medical devices use high molecular weight fluoropolymers. The data presented in Henry et al. 2018 shows no quantifiable amount of extractable PFAS were found in the results presented. The article further lays out the data requirements for this use.*

Breakdown pathways - general

1. Do the oligomers, e.g., polyPFPE oligomers, break down into PFECAs?

- *Ans: "Break down" occurs by many potential mechanisms and is always in the context of use. There is no general Answer; whether "break down" occurs depends on the specific chemical substance. This reinforces the need for clear, specific, and descriptive terms and substance classes so that similar substances are appropriately grouped together.*

2. Can you provide a list of all terminal degradation products?
    - *Ans: In the webinar, we listed the primary terminal degradation products – normally the PFAAs – perfluorocarboxylic acids and perfluoroalkane sulfonates (see chart 61, for example).*
3. What is the breakdown product of a cyclic PFAS like perfluoro-4-ethylcyclohexanesulfonate (PFECHS, CAS 335-24-0)?
    - *Ans: This is a substance made by the ECF process. FluoroCouncil member companies do not utilize this technology; therefore, we cannot respond.*

    a. Do you consider it a PFAS (you said you didn't consider aromatics as PFAS)?
        - *Ans: Yes, it is considered a PFAS. It is an aliphatic substance, not an aromatic substance.*

    b. Is it similarly persistent and potentially bioaccumulative and/or toxic as the PFAS we have been looking at?
        - *Ans: This is a substance made by the ECF process. FluoroCouncil member companies do not utilize this technology; therefore, we cannot respond.*
4. I understood that breakdown of C6 FTOH would result in C6 or shorter PFCAs, you show PFHpA also? Is that from product impurity? (slide 59)
    - *Ans: The literature has shown that 6:2 FTOH, when in the presence of soil, sludge, and/or mixed bacteria, does not produce quantifiable PFHpA. Metabolism and biodegradation studies on 6:2 fluorotelomer iodide (see Chart 24 – 6:2 FTI) and fluorotelomer-based phosphates do show that trace levels of PFHpA can be formed.*
5. We asked for experimental degradation data for chemicals in use and intermediates. You provided 2 example breakdown pathways for generic products, one for C6 fluorotelomer and one for short chain ECF (?assume PFBS, although the terminal degradation products go all the way to PFOS, so not necessarily short chain?). Can you provide, or provide references, showing degradation pathways of specific currently used substances?
    - *Ans: Here are two review articles on this topic: Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. Environment International **2013,** 61:98-114. http://dx.doi.org/10.1016/j.envint.2013.08.022 and Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review. Environmental Toxicology and Chemistry **2014,** 33(2):243-267. http://dx.doi.org/10.1002/etc.2407*

Breakdown pathways – heat and incineration

1. What happens with AFFF in incinerators? Since it is used to put out fires, how does it behave in an incinerator? Are there any data on stack testing for burning this material in a regulated incinerator?
    - *Ans: In the early 2000's under an EPA enforceable consent agreement, industry companies did a controlled set of incineration studies. If the incineration is done properly at ≥1000 Centigrade, the fluorinated materials get mineralized.*
2. Have there been any studies of municipal incineration under typical rather than "optimal" conditions?

- *Ans: None that we are aware of on fluorinated materials.*

a) Please provide references for all the incineration studies you are aware of.

- *Ans: Here are some studies we are aware of:*

PFOS

i. *Final Report – Laboratory Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Precursors; University of Dayton Research Institute (UDRI): 2003;* https://cswab.org/wp-content/uploads/2019/02/Taylor-PFAS-3M-Study-Incineration-PFAS-Degradation2000-Degrees-Fahrenheit-40-seconds-2003.pdf.

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ii. *Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment. Chemosphere* ***2014****, 110:17-22. http://dx.doi.org/10.1016/j.chemosphere.2014.02.037*

iii. *Thermal degradation of fluorotelomer treated articles and related materials. Chemosphere* ***2005****, 61(7):974-984. http://dx.doi.org/10.1016/j.chemosphere.2005.03.025*

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iv. *W.L. Gore, PTFE Incineration Study,* ***2018****. https://www.gore-tex.com/sites/default/files/docs/2019_PFCEC_Goal%20and%20Roadmap%20Update.pdf*

v. *Taylor, P. H. ECA INCINERATION TESTING PROGRAM: LABORATORY-SCALE INCINERATION TESTING OF FLUOROPOLYMERS; Dayton, OH, 2009. USEPA Enforceable Consent Agreement Study Results.*

vi. *Emissions from incineration of fluoropolymer materials. A literature survey; Norwegian Air Research Institute (NILU): Trömso, Norway, 14 December 2009.*

3. "What are the breakdown products during fires? (house fires w/ fluorinated materials? Hydrocarbon/fuel fires?) Is that a reasonably foreseeable use, especially for firefighter exposure?

- *Ans: AFFF is intended for use in liquid fuel-based (Class B) fires. In a firefighting situation with AFFF where you generate firewater, one would have fuel, combustion products, etc.; there are technologies (coagulation, etc) that will separate the fluorinated fragments from the other substances in firewater, so you can then destroy the fragments by incineration.*

a) Followup: How about for residential and commercial fires (not using AFFF), what are firefighters exposed to by fluorinated products burning? And are these all reasonably foreseeable uses/exposures for firefighters?

- *Ans: There is no documented data on this question. Given the number of articles expected to be treated with PFAS products and the expected and documented low treatment levels (ppms in many cases), total exposure from a home fire would be expected to be very low, especially in comparison to normal combustion products. Please note that there is no documented data to our knowledge.*

4. Can you be more specific about what you mean by "fragments" as incomplete combustion of PFAS chemicals in fires?

- *Ans: As incomplete combustion has not been robustly studied with data published; therefore, we do not have sufficient data to respond.*

5. What are the fumes created in polymer fume fever? Is it reasonable to think that consumers will not heat consumer products above temperatures? Similar: Has the specific chemical(s) responsible or toxicity of "polymer fume fever" been identified?
    - *Ans: The available literature notes "pyrolysis products of PTFE" as the cause of the polymer fume fever. We are not aware of whether the actual byproducts that cause the "fever" have been formally identified. The Polymer Handbook cited in Question 4 provides decomposition points for many fluoropolymers in common use. In addition, consumer products that use fluoropolymers provide specific use temperatures and conditions that need to be observed.*
6. If a manufacturer processes a fluorinated resin a) at, or b) above the recommended temperature, what substances will they be exposed to? E.g., for PTFE? Or FEP? Or other resins?
    - *Ans: Please see the Fluoropolymer Handbook cited above.* Plastics Europe 2012 Guide for the Safe Handling of Fluoropolymer Resins. *(Plastics Industry Association 2018 Guide to the Safe Handling of Fluoropolymer Resins, Fifth Edition.)*
7. What is the thermal decomposition temperature for the various polymers? similar question: What are the typical decomposition temperatures? For example, for PTFE and cookware *(Answer was given, but would be good to give reference for this?)*
    - *Ans: Please see the Fluoropolymer Handbook cited above.*
8. Can you incinerate PFPEs? It says they are thermally stable.
    - *Ans: All fluoropolymers can and will decompose if heated beyond their decomposition points. Please see the Fluoropolymer Handbook cited above. Yes, fluoropolymers are thermally stable – within the operating range given for each polymer and each end use.*
9. What is the ballpark thermal decomposition temperature for PTFE used on outdoor wear? Could it be degraded in a home dryer and/or a firefighting situation?
    - *Ans: Handling of PTFE is described in the Fluoropolymer Handbook cited above. The home dryer, under normal home use, does not reach temperatures that will decompose the products used to treat textiles. The firefighting situation was described above in an earlier question.*

Breakdown pathways, disposal and cleanup

1. Since the final degradation PFASs are persistent and are highly mobile in the environment, proper disposal is important. But what is proper disposal? Haz waste landfill? Haz waste incineration? Both have environmental justice implications. Are the Fluorocouncil members willing to be responsible for developing proper and local/on-site disposal options like was done for chemical weapons?
    - *Ans: These are individual company decisions, so we cannot Answer as FluoroCouncil.*
2. They mention nothing about the cost of clean-up. It would be nice for the companies to be clear, specific, and descriptive on what is used, so we could figure out what is being used where. As a toxicologist, I don't have enough information to assess safety.
    - *Ans: In general, the specific class of chemicals for the various end uses has been documented in various publications such as the "OECD Synthesis" paper and others. The AFFF chemicals in use previously and in current use have been called out in the Kempisty et al publication (cited above) and its cited references in Chapter 1.*
3. *What is the cost of cleaning up all of the contaminated drinking water in the US?*

- *Ans: Appropriate clean up levels developed by EPA to be protective of human health and the environment are currently pending review in the Office of Management and Budget. Costs cannot be calculated without understanding the clean-up levels for specific chemistries.*

4. What are the degradation products in an anaerobic landfill of the various fluorinated products (e.g., DWRs, stain and grease resistant coatings, abraded fluoropolymer coatings, fluorosurfactants)? Same question for aerobic composting operation (e.g., for grease resistant substances in food service ware, pesticide residuals)?
    - *Ans: The charts presented in the webinar give a sense of the terminal degradation products. We have attached some relevant literature studies to provide more granular details. Fluoropolymers are inert and do not undergo transformation as noted in the webinar. For the ECF-based and fluorotelomer-based substances, these recent review articles are a good starting point. Also, subsequent papers that have cited these include the following: Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. Environment International* ***2013,*** *61:98-114. http://dx.doi.org/10.1016/j.envint.2013.08.022 and Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review. Environmental Toxicology and Chemistry* ***2014,*** *33(2):243-267. http://dx.doi.org/10.1002/etc.2407*