Differentiating PFAS

FSSA Webinar Series

Paul E Rivers PE FSFPE

FSSA Honorary Member

SFPE Past President

15 June 2023

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Agenda

- What is PFAS, why are they important.
- Is FK-5-1-12 singled out?
- Technical/Environmental
- Regulatory Action and the meaning of derogation
- References

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First, a recommendation: Calm down

Halocarbon clean agents aren't going away.

3M's 20 December 2022 statement – honor commitments.

Plenty of sources of FK-5-1-12 supply, irrespective 3M action.

If that doesn't calm you down, consider other technologies.

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Future Supply of FK 5-1-12

- Established and specified in the market.
    - In excess of 100,000 systems installed in 20 years
- 3M™ Novec™ 1230 Fluid patent expired in July of 2020
    - Multiple manufacturers of C6 F-ketone globally, reportedly:
        - 13 with UL Component Recognition
        - 9 with FM Global Approval
    - Irrespective 3M's action, ample supply

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Future Supply of FK 5-1-12

- FK 5-1-12 remains an acceptable fire suppression clean agent per the EPA and NFPA 2001
  - No comments submitted to NFPA GFE Committee affecting FK-5-1-12.
  - Listed as acceptable subject to restrictions, same as other commercial clean agents

Future Supply of FK 5-1-12

- From the 2002 Federal Register:

  "EPA has reviewed the potential environmental impacts of this substitute and has concluded that, by comparison to halon 1301 and other acceptable substitutes, C6-perfluoroketone significantly reduces overall risk to the environment. With no ozone-depletion potential, a global warming potential value of less than 1, and an atmospheric lifetime of less than three days, C6-perfluoroketone provides an improvement over use of halon 1301, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) in fire protection. We find that C6- perfluoro ketone is acceptable because it reduces overall risk to public health and the environment in the end use listed."

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From USEPA Website – SNAP Final Rule [1,2]

C6 F-ketone (FK-5-1-12) Still Acceptable

C_6-perfluoroketone [1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone]	FK-5-1-12, Novec™ 1230, Chemori5112, Luke5112, Waysmos FK5112, MH5112, Noah5112, Dukare1230, Orient5112, Pemall5112, ClimalifeFK-5-1-12	0	<1	December 20, 2002	**Acceptable**	Use of the agent should be in accordance with the safety guidelines in the latest edition of the NFPA 2001 Standard for Clean Agent Fire Extinguishing Systems. For operations that install and maintain total flooding systems using this agent, EPA recommends the following: - install and use adequate ventilation; clean up all spills immediately in accordance with good industrial hygiene practices; and provide training for safe handling procedures to all employees that would be likely to handle containers of the agent or extinguishing units filled with the agent. See additional comments 1, 2, 3, 4, 5.

Additional Comments

1.Must conform with OSHA 29 CFR 1910 Subpart L Sections 1910.160 and 1910.162.
2.Per OSHA requirements, protective gear (SCBA) must be available in the event personnel must reenter the area.
3.Discharge testing should be strictly limited only to that which is essential to meet safety or performance requirements.
4.The agent should be recovered from the fire protection system in conjunction with testing or servicing, and recycled for later use or destroyed.
5.EPA recommends that users consult Section VIII of the OSHA Technical Manual for information on selecting the appropriate types of personal protective equipment for all listed fire suppression agents. EPA has no intention of duplicating or displacing OSHA coverage related to the use of personal protective equipment (e.g., respiratory protection), fire protection, hazard communication, worker training or any other occupational safety and health standard with respect to EPAs regulation of halon substitutes.

1 https://www.epa.gov/snap/substitutes-total-flooding-agents
2 Federal Register https://www.govinfo.gov/content/pkg/FR-2002-12-20/pdf/02-32130.pdf

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What is PFAS?

P – per or poly

F - fluoro

A - alkyl

S - substance

What is PFAS?

- PFAS is a broad category of thousands of materials that are
    - Solids
    - Liquids
    - Gases
- AFFF Foam is a PFAS which contain PFOS and PFOA that
    - Is considered a 'PBT' material – Persistent, Bioaccumulative and Toxic
    - partitions to the groundwater and
    - as a result, their use is being phased out by the EPA and globally
- Halocarbon clean agents meet the definition of a PFAS but unlike PFOS and PFOA, are generally considered Non-PBT
    - Non Persistent
    - Non Bioaccumulate
    - Non Toxic (Low in Toxicity)

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Recent Bloomberg Law© article republished in SFPE Weekly online February 2023, all references to "PFAS", not PFOS/PFOA

Bloomberg Law

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Photo Illustration: Jonathan Hurtarte/Bloomberg Law; Photos: Getty Images

PFAS Foam Replacement Challenges Nation's Fire Departments (1)

DEEP DIVE

Jan. 24, 2023, 2:30 AM; Updated: Jan. 24, 2023, 9:15 AM

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What is PFAS? USEPA National PFAS Testing Strategy:

Identification of Candidate Per- and Poly- fluoroalkyl Substances (PFAS) for Testing

October 2021

USEPA definition

"a structure that contains the unit R-CF2-CF(R')(R''), where R, R', and R'' do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included)."[1]

[1] TSCA Section 8(a)(7) Reporting and Recordkeeping Requirements for Perfluoroalkyl and Polyfluoroalkyl Substances, 86 FR 33926 (web link)

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What is PFAS? European Chemicals Agency (ECHA)

February 2023 Definition from proposed action

- Per- and polyfluoroalkyl substances (PFASs) defined as: Any substance that contains at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom (without any H/Cl/Br/I attached to it).
- A substance that only contains the following structural elements is excluded from the scope of the proposed restriction:

  CF3-X or X-CF2-X',

  where X = -OR or -NRR' and X' = methyl (-CH3), methylene (-CH2-), an aromatic group, a carbonyl group (-C(O)-), -OR'', -SR'' or –NR''R''',

  and where R/R'/R''/R''' is a hydrogen (-H), methyl (-CH3), methylene (-CH2-), an aromatic group or a carbonyl group (-C(O)-).

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What is PFAS? Regulatory

Bottom Line

USEPA

FK-5-1-12 meets the definition. HFCs apparently do not – have an H atom in the molecule.

- The EPA has NOT indicated any intent to restrict production or use of FK-5-1-12 in the USA.

ECHA

All halocarbon clean agents meet the definition. But all are proposed derogated.

derogation noun

der·o·ga·tion ˌder-ə-ˈgā-shən

: a taking away or detraction from something (as the force of a law)

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EUROPEAN CHEMICALS AGENCY

REACH restriction process and the Universal PFAS proposal

EFCTC F-gas webinar

23 May 2023

Bastian Zeiger
Regulatory Officer
European Chemicals Agency

Restriction process

I Phase

Preparation and submission of a restriction proposal

- Starting the restriction process
- Notification of intention to submit a restriction proposal
- Registry of Intentions
- Preparing the restriction dossier
- Submission and conformity check

II-A Phase

Consultations

- Consultation on the restriction report
- Consultation on SEAC's draft opinion

II-B Phase

Opinion development

- Advice from the Forum
- RAC's opinion
- SEAC's opinion

III Phase

Decision and follow-up

- Commission decision on restriction
- Complying with restriction
- Enforcing the restriction

echa.europa.eu/restriction-process

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Status of play and next steps

13 January 2023
Restriction proposal submitted to ECHA

1

2

7 February 2023
Proposal made available on ECHA's website

22 March 2023
Start of a six-month open consultation

3

4

5 April 2023
Online information session

ECHA committees' evaluation

5

6

ECHA's committees adopt their opinions

Opinions of ECHA's committees sent to the European Commission

7

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Annex XV third-party consultation

- → Consultation on proposal open until 25 September 2023
- → Submit any information you consider relevant
- → Information on topics that the Risk Assessment (RAC) and Socio-Economic Analysis (SEAC) committees or the dossier submitter have identified – called 'specific information requests'
- → Comments made without supporting evidence unlikely to have much impact
- → Joint submissions encouraged – e.g. per sector
- → You can claim information confidential

Not all PFAS are created Equal: PBT vs Non-PBT

PBT

Persistent

persists in the environment either in the atmosphere, soil, or water

Bioaccumulative

partitions and accumulates in live organisms such as plants, animals, and humans

Toxic

has ability to cause harmful effects

NON-PBT

NON-Persistent

breaks down and does NOT remain in the environment

NON-Bioaccumulative

does NOT accumulate

NON-Toxic

does not have the ability to cause harmful effects with proper use

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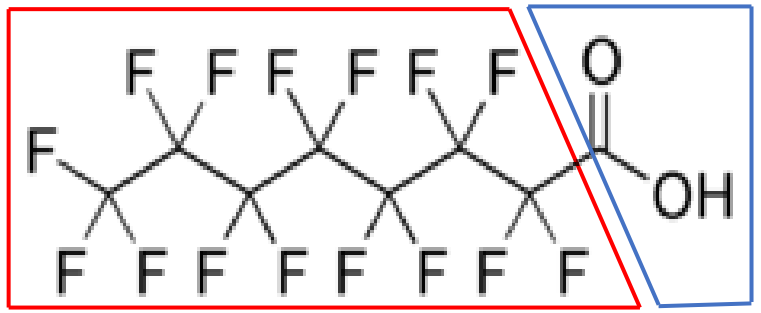
PFAS's with different properties

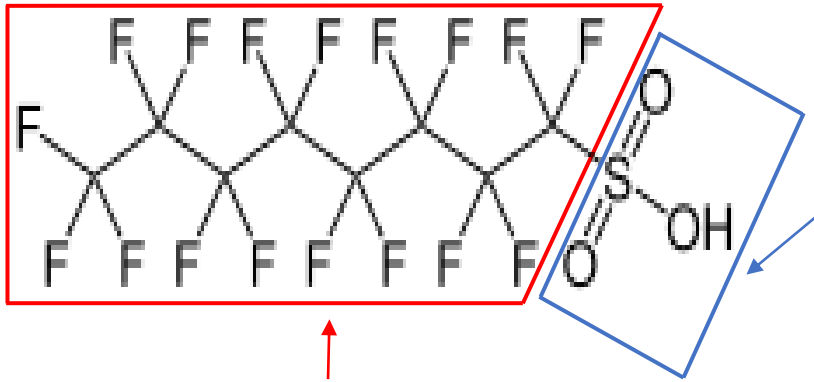
PBT PFOA and PFOS found in AFFF

PFOA
Perfluoro-octanoic Acid

Hydrophobic tails



PFOS
Perfluor-octane-sulfonic Acid

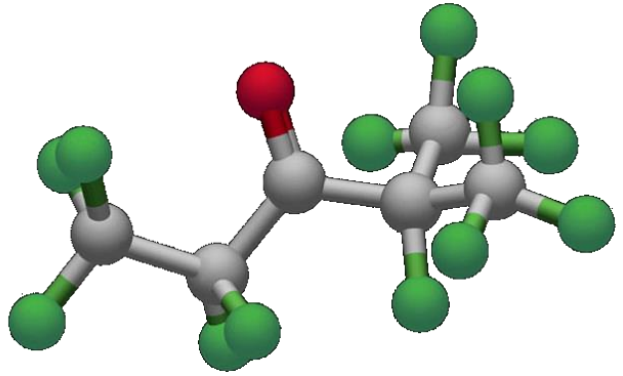


Hydrophilic heads want to mix with water

Hydrophobic tails do not want to mix with water which gives compound water resistant properties

Non-PBT Clean Agent

FK-5-1-12



Hydrophobic – does not mix with water

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Water vs C6 F-ketone (FK-5-1-12)

Property	Unit	Water	FK-5-1-12	
Boiling Point	°C	100	49.0	
Freezing Point	°C	0	-108	
Solubility FK-5-1-12 into water and water into FK-5-1-12	ppm	~1	20 ppm max	
Specific Heat, vapor, Cp @ 25°C	kJ/kg·°C	1.87	0.891	
Vapor Pressure @ 25°C	kPa	3.17	40.36	> 12X
Heat of Vaporization @ 25°C	kJ/kg	2442	94.9	< 25X

✓ Evaporates 50x faster than water

3M 2002 NFPA Conference

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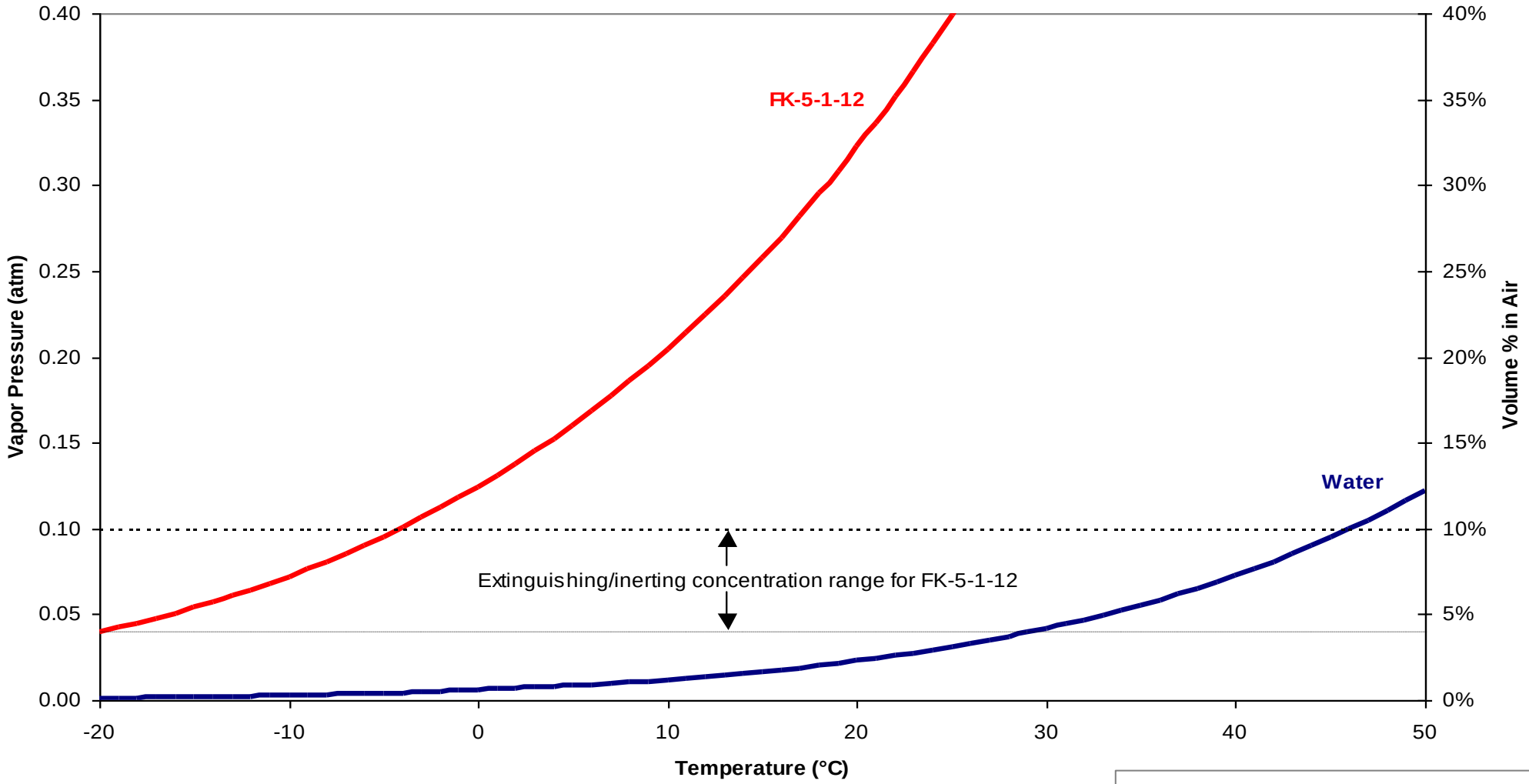
Comparison of FK 5-1-12 and Water – Saturation curves in air



Justin Shmeer
WPI/3M

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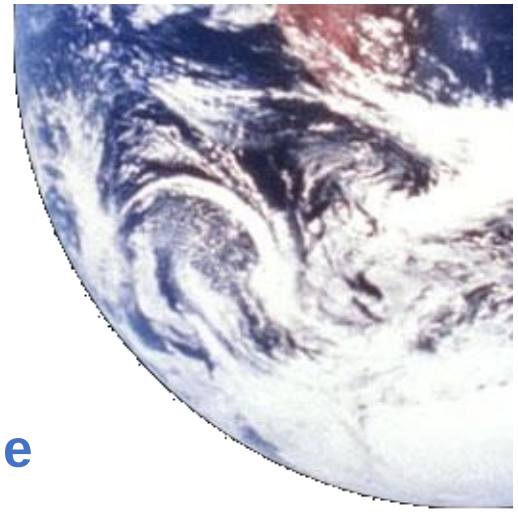
2003 Halon Options Technical Working Conference

Atmospheric Lifetime

Controlling Factors for FK-5-1-12



Oxidation → ✗ Reactivity with •OH

Requires high reaction rate to produce very short lifetime

Rain Out → ✗ Dissolution and Deposition

Requires high water solubility and low volatility

Photolysis → UV Absorbance and Dissociation

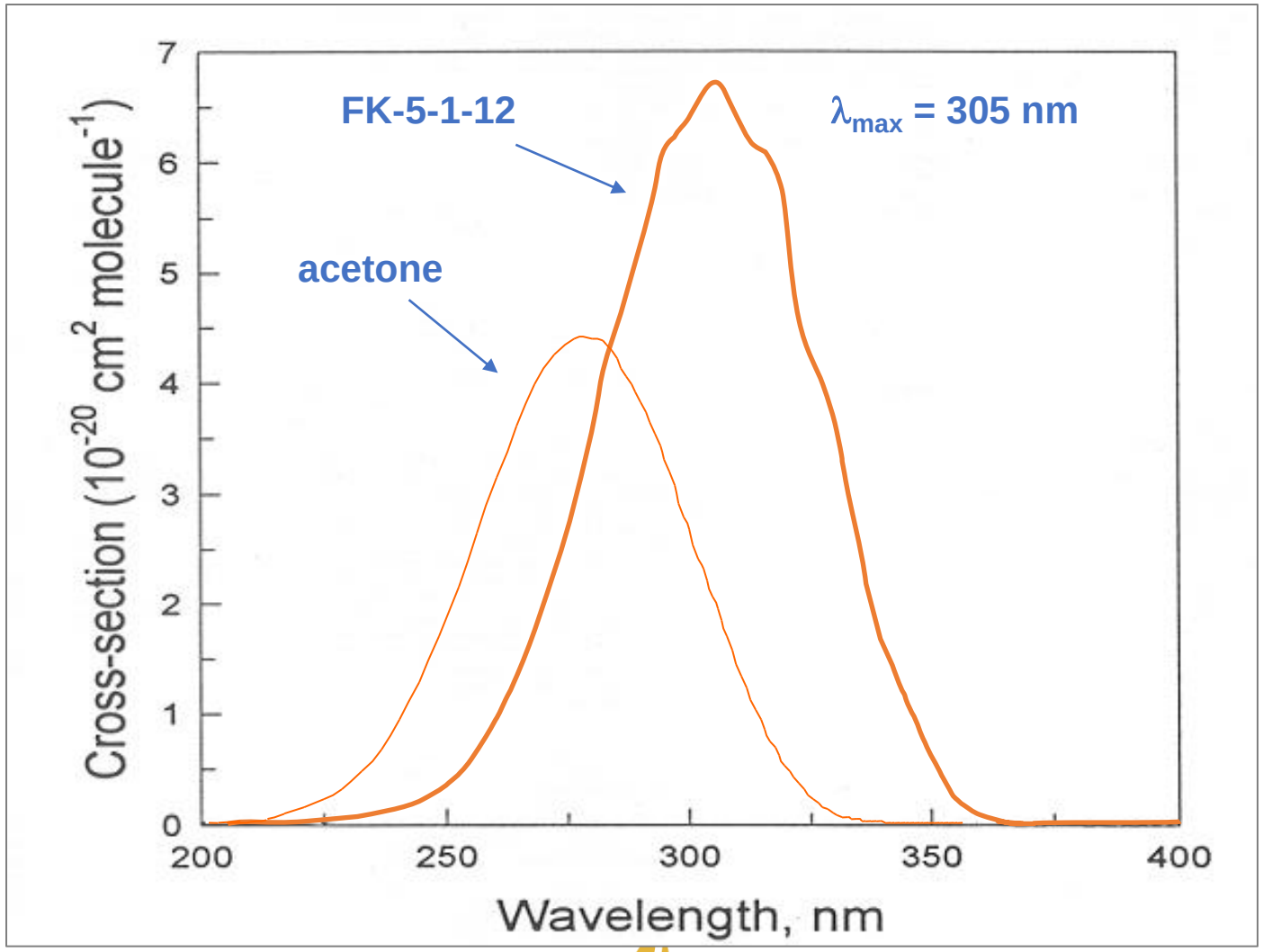
Requires strong absorbance in the near UV to produce short lifetime

John Owens, 3M

Photolysis of FK-5-1-12

Altitude	Solar λ	
75 km	**<200 nm**	100's of years into mesosphere
30 km	**<290 nm**	1 to 3 years into stratosphere
10 km	**300 nm**	days to weeks to reach tropopause
1 km	**>300 nm**	hours to reach planetary boundary layer

UV Absorption of Ketones



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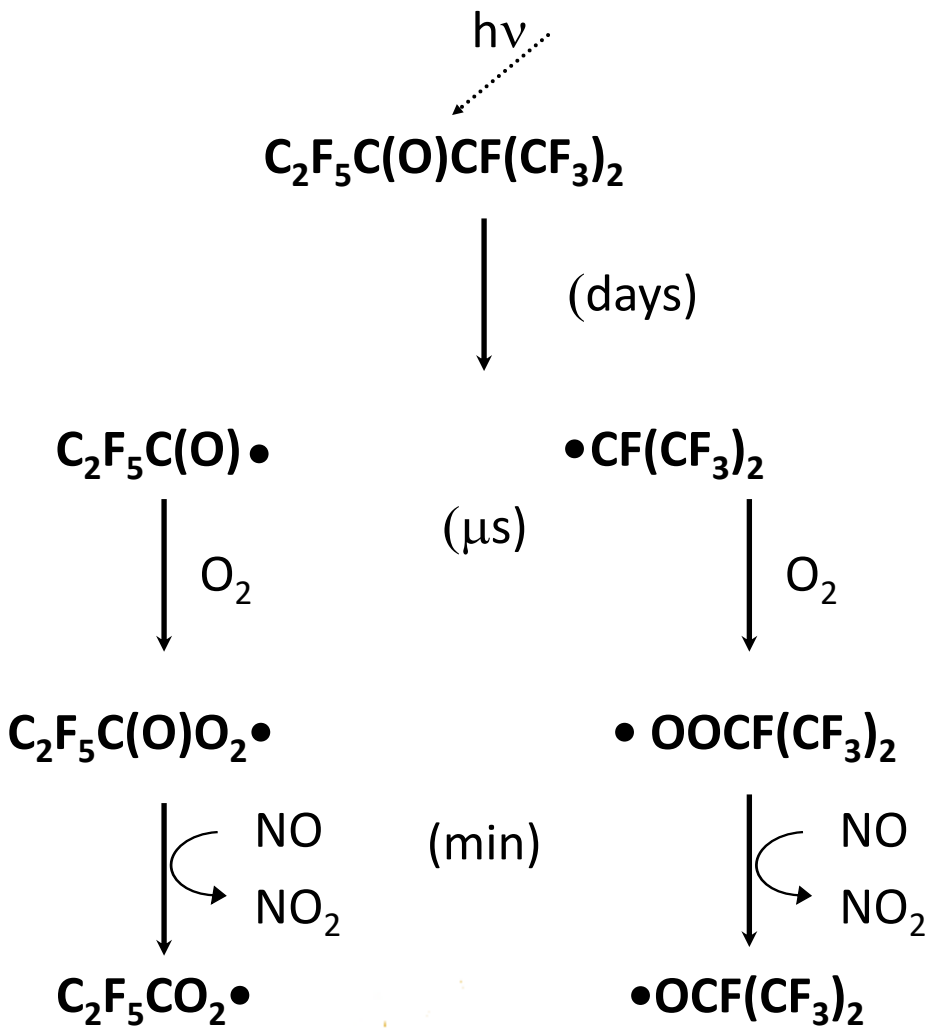
Photolysis of FK-5-1-12

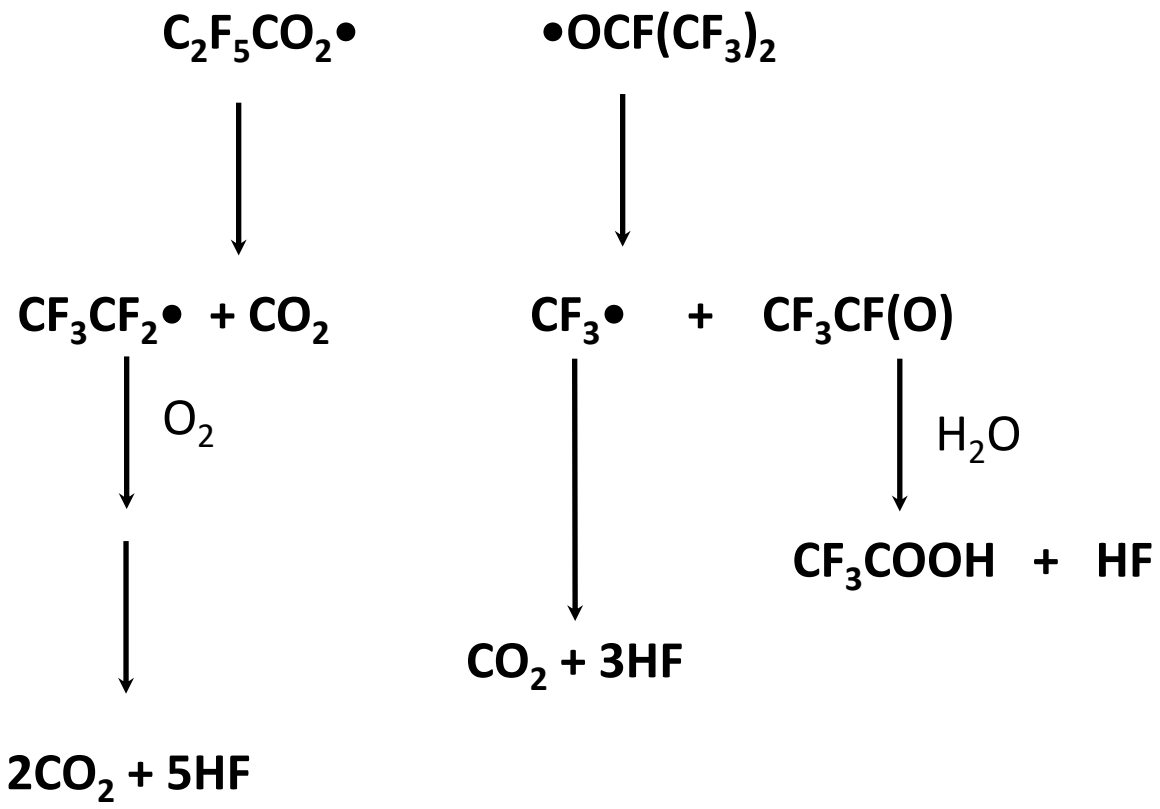
Guschin, *et al*	3-5 day atmospheric lifetime
3M Study 1	3 day atmospheric lifetime
3M Study 2	5 day atmospheric lifetime
Taniguchi, *et al*	1-2 week atmospheric lifetime

→ Photolysis leads to lifetime of ~ 5 days or 1 week

Atmospheric Degradation Mechanism



Atmospheric Degradation Mechanism



Atmospheric Degradation Mechanism of FK-5-1-12

$$C_2F_5C(O)CF(CF_3)_2 \longrightarrow 4CO_2 + CF_3COOH + 9HF$$

KETONE	MW	COMPOSITION	TOTAL	% PRODUCT	MASS GMS
C6F14O	316	1	316	--	316
PRODUCT					
CF3COOH	114	1	114	24.3%	114
HF	20	9	180	38.3%	180
CO2	44	4	176	37.4%	176
			470		470

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Atmospheric Degradation Mechanism of FK-5-1-12

$$C_2F_5C(O)CF(CF_3)_2 \longrightarrow 4CO_2 + CF_3COOH + 9HF$$

"Photolysis of $C_2F_5C(O)CF(CF_3)_2$ in air gives $CF_3C(O)F$ and COF_2. $CF_3C(O)F$ will be incorporated into air/cloud/seawater where it will undergo hydrolysis to give trifluoroacetic acid. Similarly, COF_2 will undergo hydrolysis to give CO_2 and HF. At the concentrations expected in the environment, none of these degradation products is considered harmful….As a result of its short atmospheric lifetime, the global warming potential of $C_2F_5C(O)CF(CF_3)_2$ is negligible."

Taniguchi, et al., J. Phys. Chem. A, 2003, *107*, 2674-2679

FK-5-1-12

- ✓ Evaporates 50x faster than water
- ✓ Has little to no affinity to water
- ✓ Will not partition to ground water in end use
- ✓ Will partition to the atmosphere and be broken down via UV ray absorbance in about a week

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Bottom Line

- Understand Fire Protection PFAS differences
  - PFOS/PFOA in foams, partition to water
  - Know that ALL clean extinguishing agents partition to atmosphere
  - Know PBT vs Non-PBT differentiation
- Inform your companies, customers, specifiers and AHJs noting PFAS differences
- Stay Calm

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References

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- USEPA – https://www.epa.gov/snap/substitutes-total-flooding-agents (web link), and https://www.epa.gov/system/files/documents/2021-10/pfas-natl-test-strategy.pdf (web link)
- European REACH/ECHA – https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal (web link)
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- Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis and Hydration, American Chemical Society Publications, 25 March 2011. Derek A. Jackson,† Cora J. Young,† Michael D. Hurley,‡ Timothy J. Wallington,‡ and Scott A. Mabury*,†
  †Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON, Canada M5S 3H6
  ‡Ford Motor Company, Mail Drop SRL-3083, Dearborn, Michigan, 48121 United States
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- Schmeer, J.S. et al., WPI/3M, "Consideration of Liquid to Gas Phenomena for a Sustainable, High Boiling, Tropodegradeable Halocarbon", HOTWC 2003, May 2003

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Questions?

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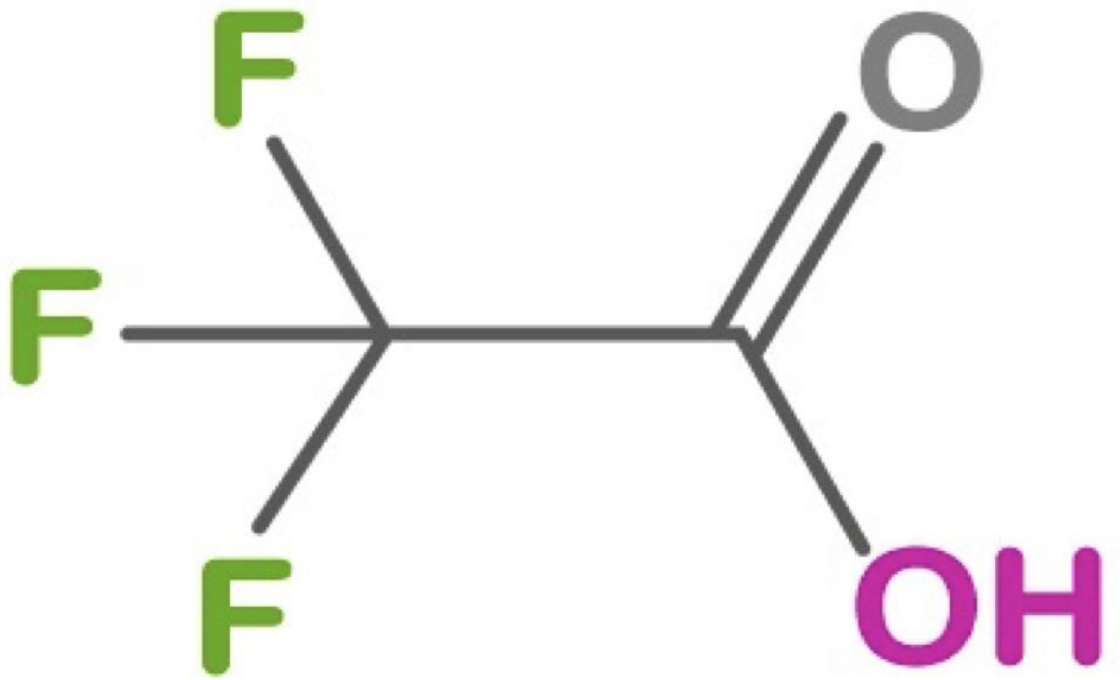
TFA – trifluoroacetic acid

TFA FORMULA



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Columbia Climate School Center for International Earth Science Information Network, *"Atmospheric Production and Fate of Trifluoroacetic Acid"*, Sept, 2001

"The source of the currently observed levels is unknown and puzzling. The observed TFA concentrations are orders of magnitude larger than those predicted to result from the atmospheric degradation of the replacement HCFCs and HFCs."

https://sedac.ciesin.columbia.edu/ozone/docs/UNEP98/UNEP98p56.html

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"Trifluoroacetate in Ocean Waters", ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 36, NO. 1, 2002

Purpose: " Determination of TFA in ocean waters has been undertaken in order to estimate the global abundance of this strongly hydrophilic, persistent environmental chemical and to assess whether today's levels are mainly of anthropogenic origin or whether biological and/or geological sources must be considered."

Conclusion: "TFA is present in the global environment in two major compartments: (a) In ocean water (b) In the atmosphere, in precipitation, in freshwaters, and in needles of conifers), it is likely to stem mostly from anthropogenic sources of which HFC release is perhaps a minor fraction. In any case, the total amount of TFA present in the global environment greatly exceeds what may be expected to be contributed from various industrial sources.

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"Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols." Journal of Toxicology and Environmental Health, Part B, 19(7), 289–304 (2016).

Conclusion: "Based on current projections of future use of HCFCs and HFCs, the amount of TFA formed in the troposphere from substances regulated under the MP is too small to be a risk to the health of humans and environment."

https://doi.org/10.1080/10937404.2016.1175981

2023 ECHA, Trifluoroacetic Acid PBT Assessment

PBT Status: "the substance is not PBT / vPvB"

"Though trifluoroacetic acid fulfils the criteria for persistency, the available data indicate that it is neither fulfilling the criteria for toxic and bioaccumulative (PBT-substances), nor the criteria for very bioaccumulative substances (vPvB-substances) according to REACH directive, Annex XIII and as laid down in the TGD R.11 of the European Chemicals Agency (ECHA)."

https://echa.europa.eu/de/registration-dossier/-/registered-dossier/5203/2/3
June, 2023

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