Highlights of TURI Alternative Refrigerants report

Dr. Gabriel Salierno
MA Toxics Use Reduction Institute
April 14th, 2025

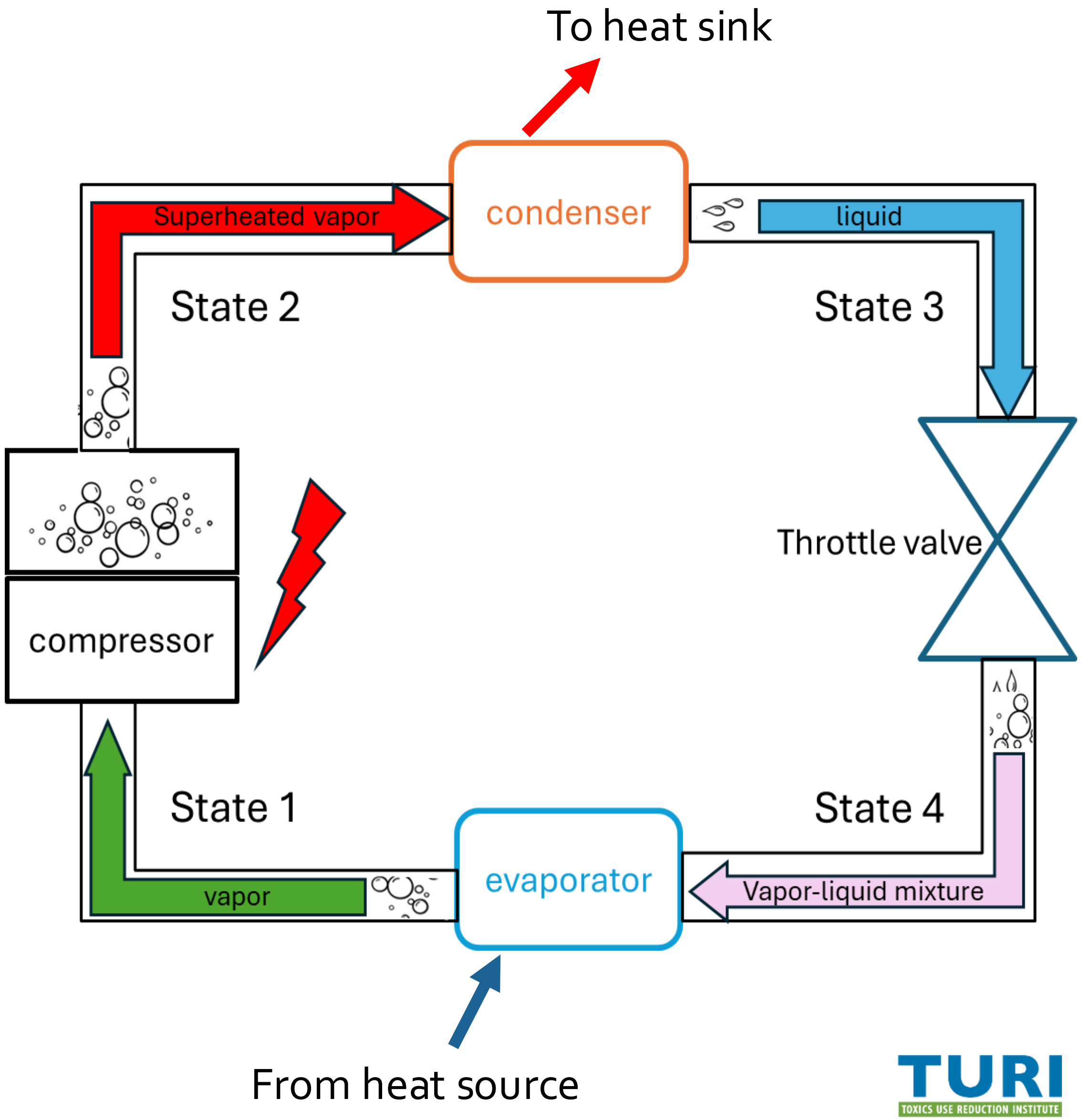
How Refrigerant gases work?

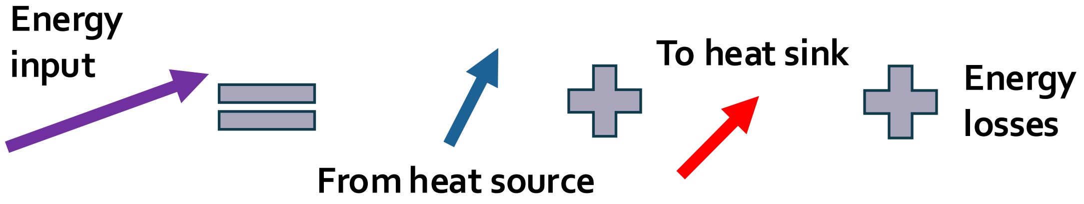
Refrigerant gases undergo an operation called the vapor compression cycle:

- Releasing heat by condensation to a sink* (typically the outside environment)
- And absorbing heat by evaporation from a source* (the space being cooled)

*Heat pumps can exchange their heat source and sink.

For this operation to happen, energy must be invested.





How Refrigerant gases work?

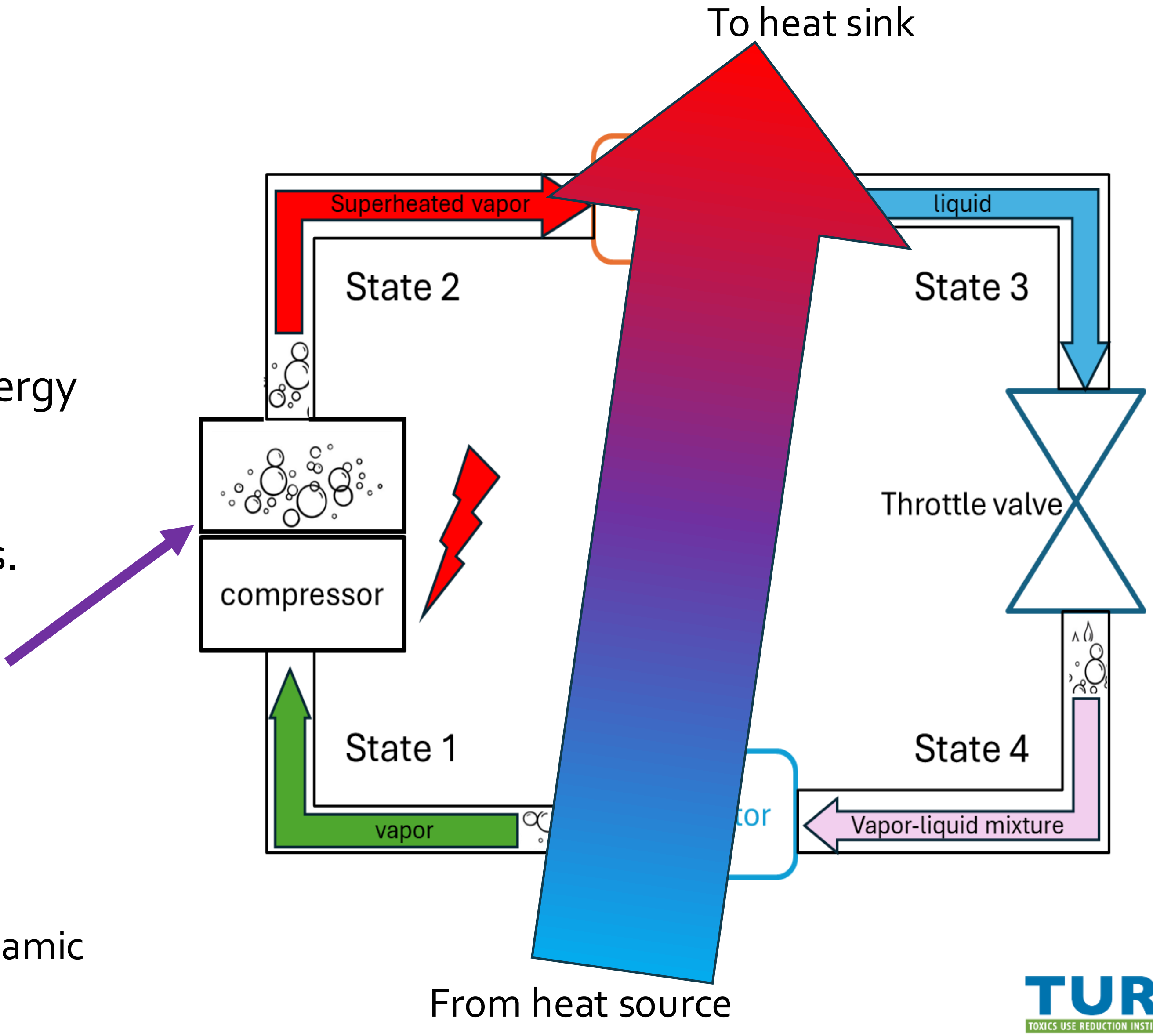
Cooling Capacity (CC): The amount of heat a system can remove per unit of time (e.g., kW or BTUs per hour).
Higher CC means a faster heat transfer rate.

Efficiency: How effectively the system uses energy to cool (e.g., Coefficient of Performance, CoP; Seasonal Energy Efficiency Ratio, SEER).
Higher efficiency leads to lower operating costs.

Key Factors:

- ***Refrigerant properties****.
- Equipment design.
- Temperature differences
- Application.

* Drop-in substitutes require similar thermodynamic properties to the refrigerant being replaced.



Drop-in retrofitting substitutes vs. New equipment purchase

- ***Retrofitted HVACR equipment generally*** exhibits lower efficiency than the newer models, ***contributing to avoidable indirect emissions.***
- HFOs and HFCs/HFOs blends are currently used as a substitute for phasing out HFCs.
- ***Rising F-gas costs and production limitations threaten the availability of drop-in substitutes.***
- Generally lower initial investment.
- Payback period typically 0.7 years.*

- ***Feasibility is translating into wider adoption.***
- More companies manufacturing equipment based on non-fluorinated refrigerants.
- Successful implementation in supermarkets, cold storage, and mobile refrigeration.
- ***Market share growing faster in the EU, given more stringent F-gas policy.***
- Generally higher initial investment.
- Payback period <1 to 3 years.*

* https://www.epa.gov/sites/default/files/2016-03/documents/table_rules_of_thumb.pdf

Financial feasibility of new purchases improves/equalizes when considering energy savings opportunities from modern equipment.

https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

HFC Regulation: Context & Socio-economic Impact

Kigali Amendment to the Montreal Protocol:

- As CFC drop-in replacements, Hydrofluorocarbons (HFCs) dominated the refrigerants market.
- However, HFCs present very high Global Warming Potential (GWP).
- GWP regulatory threshold(s) emerged: 150-300-700 relative to CO_2.

HFC Phase-Down = HFC use reduction

- US-EPA: The net benefits (climate benefits – compliance costs) of the HFC phase-down in 2022–2050, is +$272.7 billion USD. https://www.epa.gov/system/files/documents/2023-07/8838_final-rule_RIA-Addendum_508.pdf

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F-gas refrigerants evolution

- Unsaturated HFCs, known as Hydrofluoroolefins (HFOs), Hydrochlorofluoroolefins (HCFOs), and HFC blends :
  - Introduced to replace HFCs due to their shorter atmospheric lifespan.
  - Intended to be zero-ODP and "climate-friendly" refrigerants.

- Inadvertent consequences:
  - Some high-GWP (>150) HFCs are still used in new refrigerant blends.
  - HFOs are PFAS (according to OECD) and generate TFA in environmental conditions.
  - HFO synthesis involves the use of known Carcinogenic, Mutagenic, and Reprotoxic (CMR) chemicals: Carbon tetrachloride (CTC) and perchloroethylene (PCE).

PFAS remediation costs are estimated in the trillion USD range*, while market forecasts for HFOs and PFAS are valued at around 2-3 billion and 20 billion USD, respectively.

*U.S. Chamber of Commerce: PFOS and PFOA Private Cleanup Costs at Non-Federal Superfund Sites.
Ling (2024) https://doi.org/10.1016/j.scitotenv.2024.170647
https://foreverpollution.eu/lobbying/the-cost-methodology/

The '*average GWP*' blend strategy still uses high GWP HFCs, despite having a weighted average GWP lower than regulatory thresholds.

SNAP approved refrigerant	Composition			GWP	Main applications
	Chemical name	CAS No	% w/w		
HFC-32	Difluoromethane	75-10-5	100	675	Only retrofitting of industrial process chillers
HCFO-1233zd	1-Chloro-3,3,3-trifluoropropene	2730-43-0	100	6	Cold storage, industrial HVACR and ice rinks
HFO-1234ze(E)	1,3,3,3-tetrafluoro-(1E)-propene	29118-24-9	100	6	Commercial; residential; replaces HFC-134a
HFO-1234yf	2,3,3,3-Tetrafluoropropene	754-12-1	100	4	Mobile air conditioning; replaces HFC-134a
R-454A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	65	4	Chillers <90 Kg of charge and cascade systems.
	Difluoromethane (HFC-32)	75-10-5	35	675	
R-454B (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	67	4	Industrial chillers; replaces R-410a blend
	Difluoromethane (HFC-32)	75-10-5	32	675	
R-454C (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	78.5	4	Commercial; residential; heat pumps; replaces R-410a blend
	Difluoromethane (HFC-32)	75-10-5	21.5	675	
R-455A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	75.5	4	Commercial; residential; mobile; replaces HFC-134a
	Difluoromethane (HFC-32)	75-10-5	21.5	675	
	Carbon dioxide (R-744)	124-38-9	3	1	
R-457A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	70	4	Commercial; residential
	Difluoromethane (HFC-32)	75-10-5	18	675	
	1,1-difluoro ethane (HFC-152a)	75-37-6	12	124	
R-516A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	77.5	4	Commercial; residential; replaces HFC-134a
	1,1-difluoro ethane (HFC-152a)	75-37-6	14	124	
	1,1,1,2-tetrafluoroethane (HFC-134a)	811-97-2	8.5	1430	

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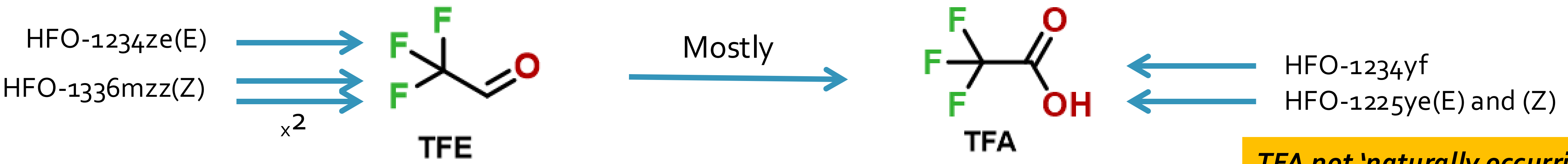
HFOs end of life

- HFOs mostly form TFA, an ultrashort chain PFAS, when released into the environment.

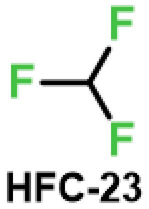


TriFluoro Ethanal
Very reactive and short lived

Trifluoroacetic acid
Chemically resistant and long lasting

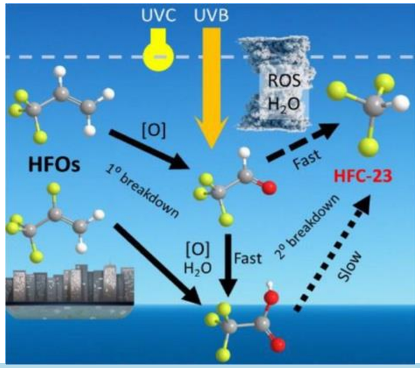
TFA not 'naturally occurring': Joudan et al. (2021): https://doi.org/10.1039/D1EM00306B

- In environmental conditions, TFE and TFA could potentially produce HFC-23.



GWP 14800

- Only would take a 1.2% HFO conversion into HFC-23 for a GWP contribution > 150.



Urgent need for verification of HFC-23 emissions

For more information, check G. Salierno (2024): https://doi.org/10.1002/cssc.202400280 and references therein.

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Fenceline Communities & F-gas Production

Cancer Risk of Communities within 1 mile of HFC Facilities relative to State Averages

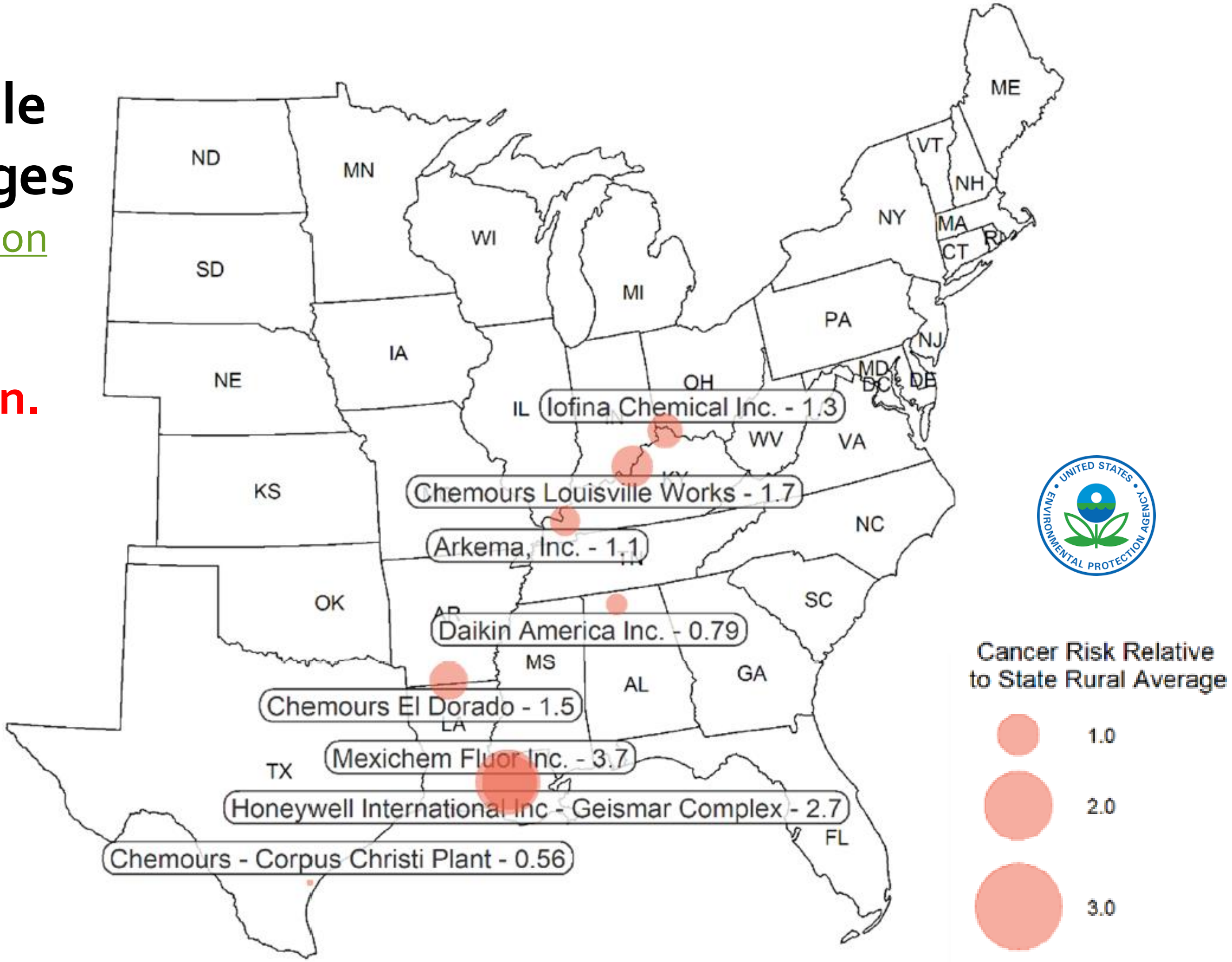
Image source: [US-EPA - RIA for Phasing Down Production and Consumption of Hydrofluorocarbons (HFCs)]

CMR precursors are required for HFO production.

- Proximity to manufacturing sites increases exposure risk to hazardous chemicals (CTC, PCE, HF, toxic HFCs).
- Airborne fluorinated pollutants linked to respiratory issues and other health impacts.

environmental investigation agency

F-Gases at the Fenceline
EIA.org



https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

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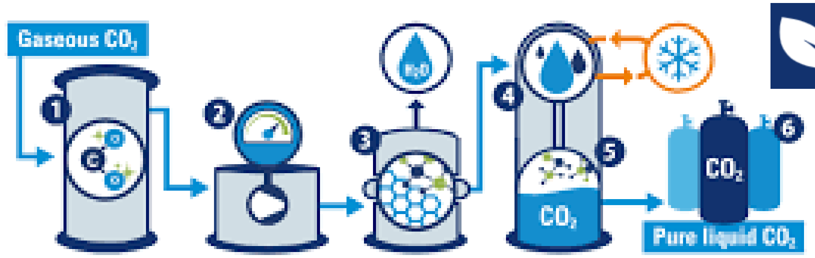
Cleaner production of refrigerant gases

CO_2, NH_3, and HCs have a much lower impact during manufacturing and use.

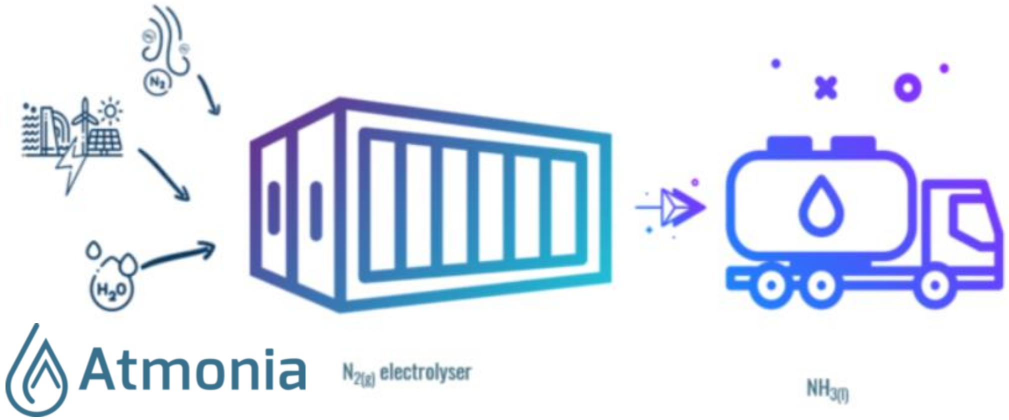
CO_2: Captured and reused, a promising refrigerant due to its low environmental impact.

Ammonia: Novel technology uses water, air, and renewable energy for zero-emission production, as opposed to the traditional carbon-intensive Haber-Bosch process.

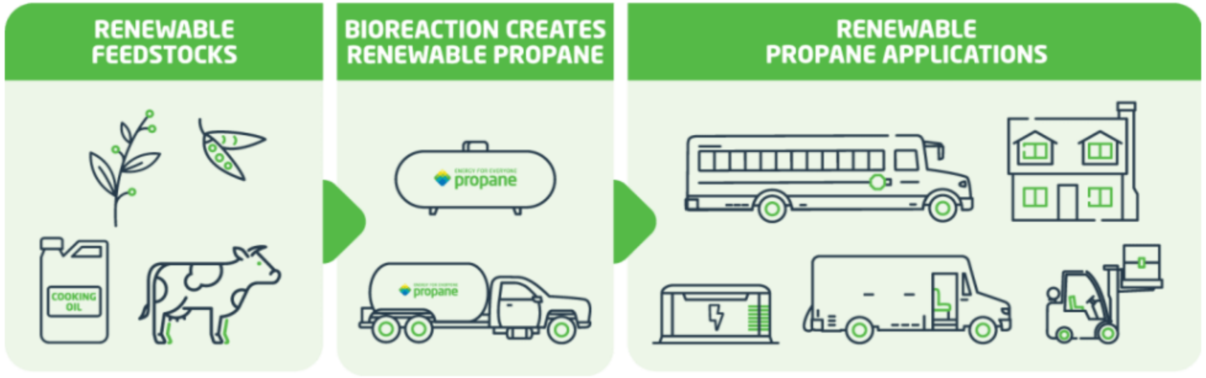
Propane*: 100% renewable propane, made from bio-based waste, could cut fossil reliance.



BRIGHT



* Other hydrocarbons can be produced in the same way.



U.S. DEPARTMENT of ENERGY

https://afdc.energy.gov/fuels/propane-renewable

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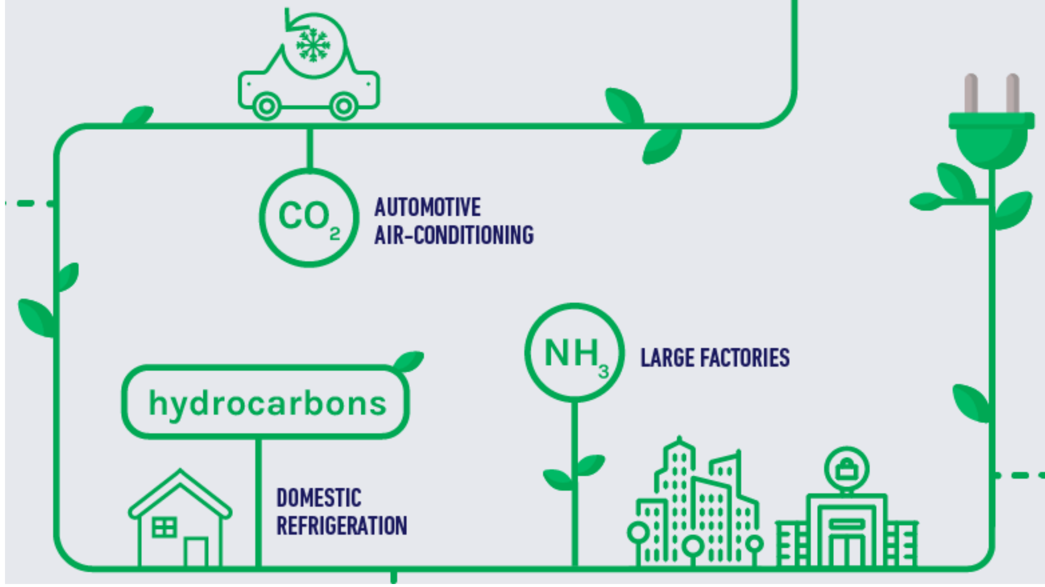
Alternatives to F-gas Refrigerants



HFOs may potentially be regrettable substitutions:
Moderately flammable and LCI is similar to legacy HFCs.

Non F-gases have appropriate market readiness:

- *New CO2 designs offer operational energy savings:* Wide adoption in supermarkets, cold warehouses.
- *Equipment design & safety standards mitigate HC flammability*:
  - 150 g HC charge allowed indoors (US) →
  - 500 g HC charge allowed indoors (Europe; heat pumps)

EPA ENERGY STAR Certified HC-based equipment:

- 600+ household fridges
- 700+ Lab Grade Refrigerators

- Ammonia (NH3) is the preferred industrial refrigerant but not for domestic applications.
- *Ultra Low Charge (ULC)* NH3 *systems* reduce but do not completely eliminate acute toxicity and eutrophication related liabilities.

***Solid-state technologies* (Peltier; magnetocaloric) offer a refrigerant-free cooling solution.**

https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

Market Share Contrast

Strong regulations

+

Clever incentives

↓

Feasible sustainable cooling solutions

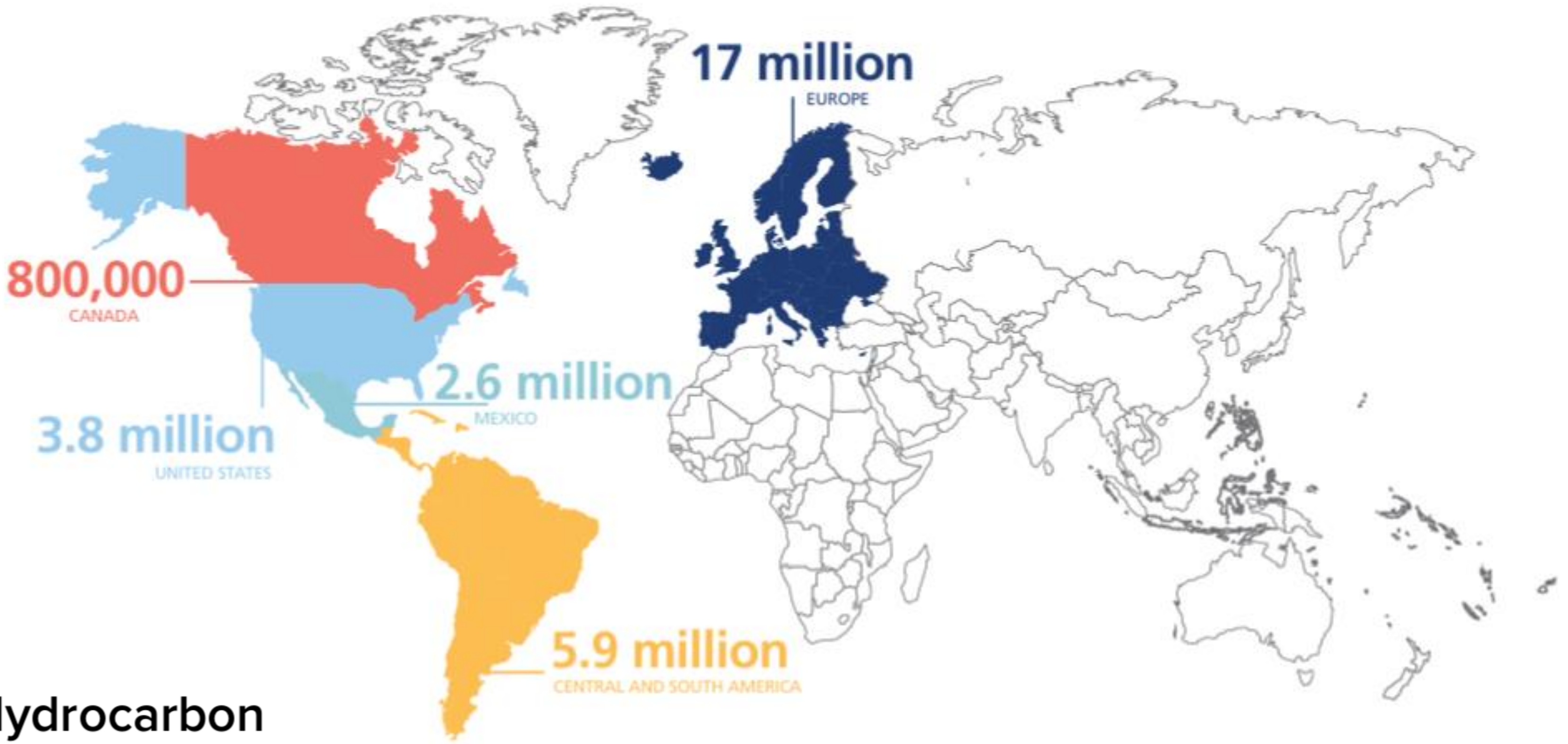


Figure 4: Self-Contained Hydrocarbon Cabinets Installed in Major Regions
(as of December 2024)

ATMOsphere https://atmosphere.cool/atmo-market-report-2024/

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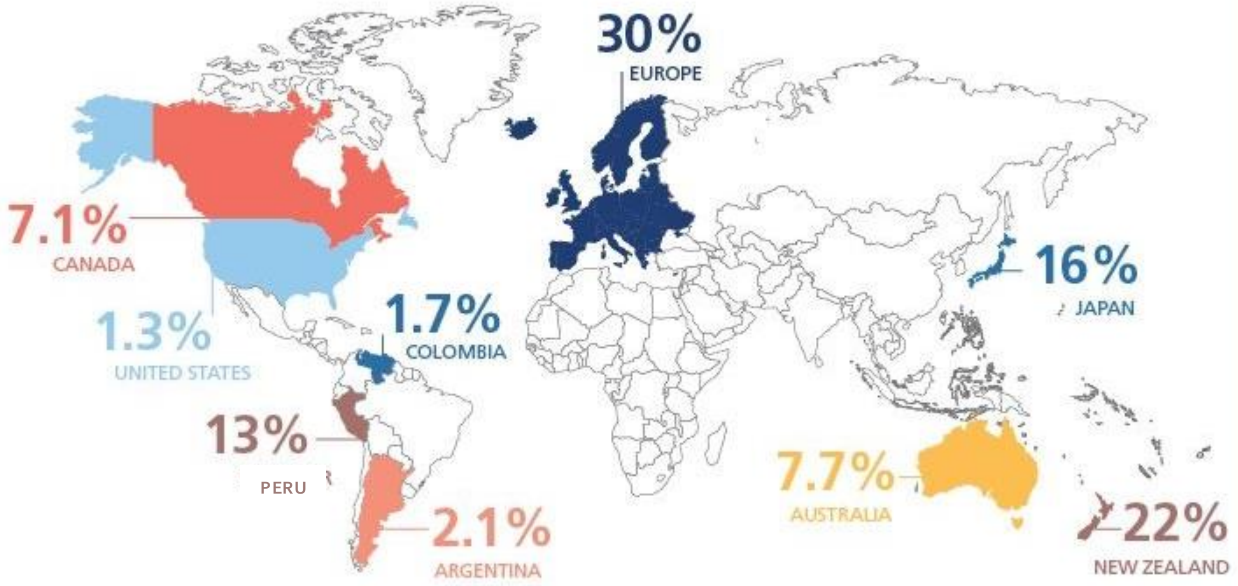
Market Shares of Transcritical CO_2 Refrigeration

2024 - TOP 9

★	1. Europe	30%
★	2. New Zealand	22%
★	3. Japan	16%
	4. Ecuador	13%
	5. Australia	7.7%
	6. Canada	7.1%
	7. Argentina	2.1%
	8. Colombia	1.7%
	9. United States	1.3%

December 2024



https://atmosphere.cool/atmo-market-report-2024/

ASSESSMENT OF AVAILABLE
LOW-GLOBAL WARMING POTENTIAL
ALTERNATIVES TO F-GAS REFRIGERANTS

https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

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Are Modern Fluorinated Refrigerants Safe?

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Safer Refrigerants for Manufacturing, Spring 2025 Toxics Use Reduction Webinar

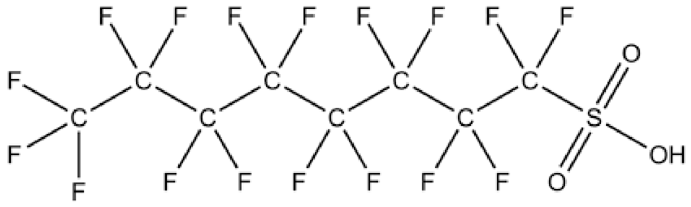
April 14, 2025

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.

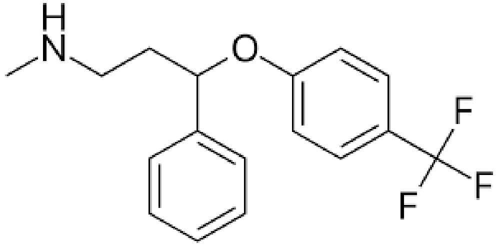
Definitions of Per- and Polyfluoroalkyl Substances (PFAS)

- **OECD** (Organisation for Economic Co-operation and Development) definition
  - "…i.e. substances are PFAS that have **at least one -CF_2- or -CF_3** moiety in their structure"
  - many thousands of **structurally diverse PFAS including trifluoroacetic acid (TFA),** which is a breakdown product of modern fluorinated refrigerants
  - **basis for broad regulation of PFAS in European Union**
- **US EPA** working definition:
  - **at least two adjacent carbon atoms, where one carbon is fully fluorinated and the other is at least partially fluorinated**
  - chemicals with isolated -CF_2- are expected to degrade in the environment
  - most substances with only one terminal carbon (i.e., C-CF_3) "**are expected to degrade to TFA, which is a well-studied non-PFAS**."
  - many modern fluorinated refrigerants excluded from US EPA PFAS definition

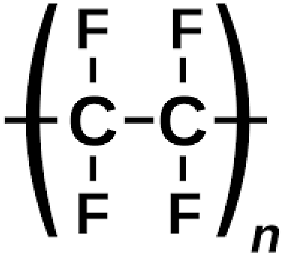
The Diversity of PFAS (OECD definition)



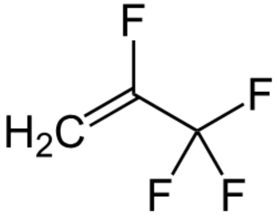
Perfluorooctane sulfonate (PFOS), the most notorious PFAS. Persistent, bioaccumulative and toxic and listed on the Stockholm Convention in 2009.



Fluoxetine (known under tradename Prozac), an antidepressant

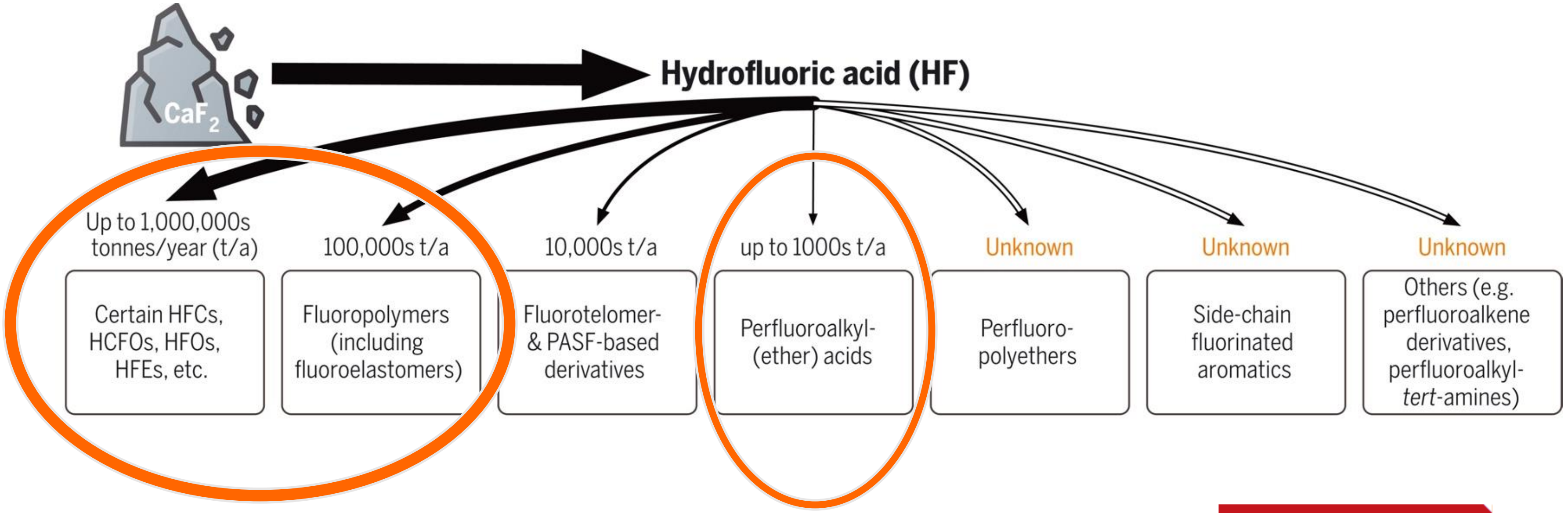


Polytetrafluoroethylene (PTFE, known under its tradename Teflon), used in non-stick cookware, etc.



Hydrofluoroolefin is a gas used as a refrigerant (2,3,3,3-tetrafluoropropene or HFO-1234yf), degrades to TFA

Global Production of PFAS



- Industry wants to protect uses of fluoropolymers and fluorinated gases used as refrigerants, blowing agents, etc.

REVIEW SUMMARY

CHEMICAL POLLUTION

Per- and polyfluoroalkyl substances in the environment

Marina G. Evich†, Mary J. B. Davis†, James P. McCord†, Brad Acrey, Jill A. Awkerman, Detlef R. U. Knappe, Andrew B. Lindstrom, Thomas F. Speth, Caroline Tebes-Stevens, Mark J. Strynar, Zhanyun Wang, Eric J. Weber, W. Matthew Henderson*, John W. Washington*

Madrid Statement

- Published in 2015
- Signed by 250 scientists from 38 countries
- Production and use of PFAS should be limited
- But are all PFAS problematic?
  - they have diverse properties, right?

Perspectives | Brief Communication

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

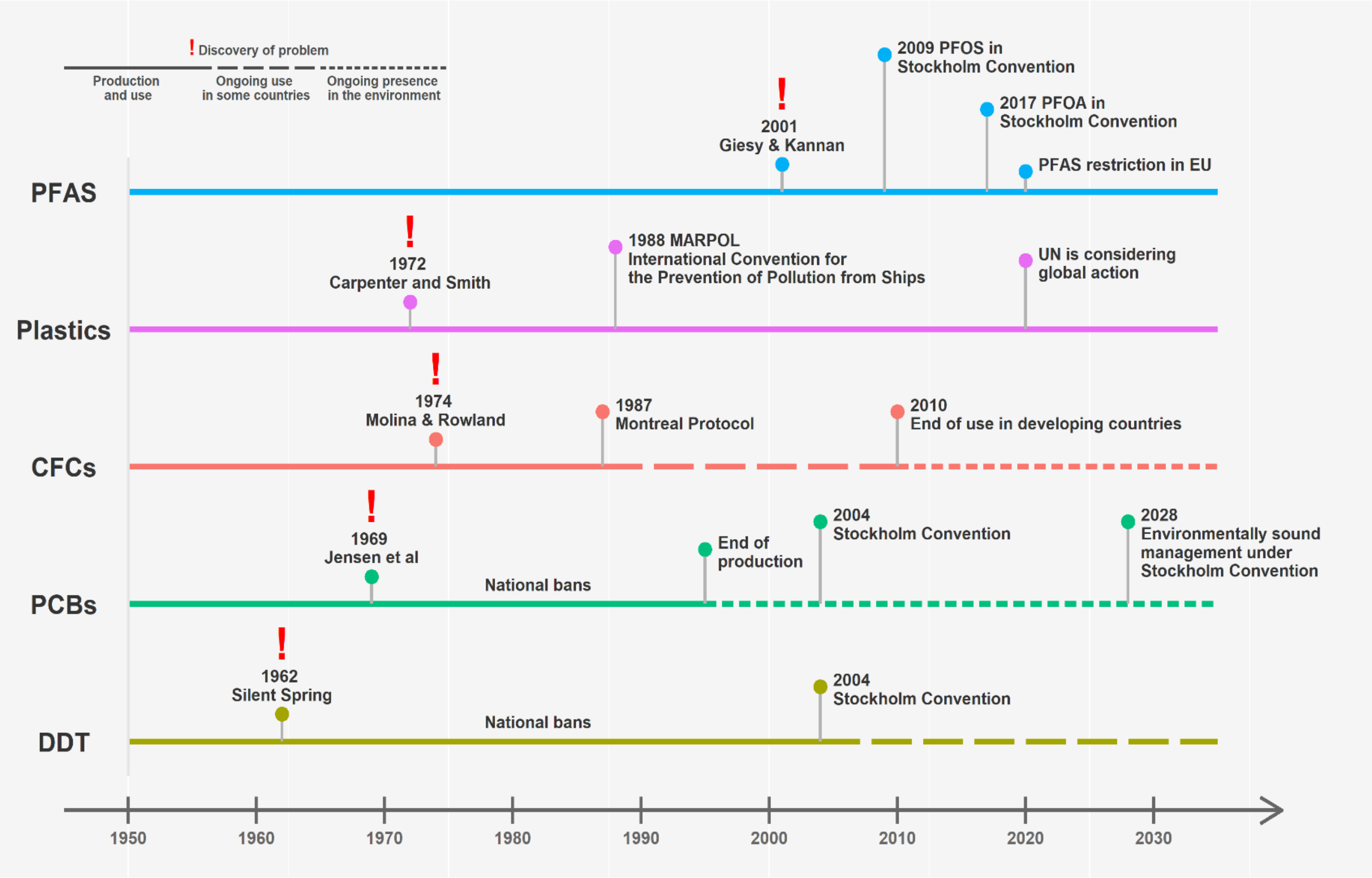
http://dx.doi.org/10.1289/ehp.1509934

Arlene Blum,[1,2] Simona A. Balan,[2] Martin Scheringer,[3,4] Xenia Trier,[5] Gretta Goldenman,[6] Ian T. Cousins,[7] Miriam Diamond,[8] Tony Fletcher,[9] Christopher Higgins,[10] Avery E. Lindeman,[2] Graham Peaslee,[11] Pim de Voogt,[12] Zhanyun Wang,[4] and Roland Weber[13]

Are all PFAS of concern?

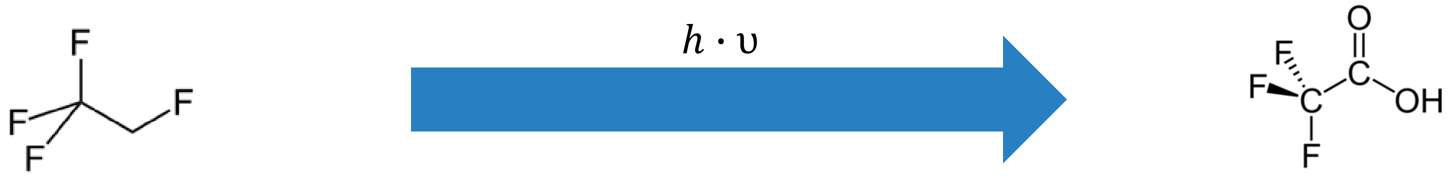
- We know the toxicity of only a few PFAS
- **All PFAS are synthetic and very persistent (vP)** (EU REACH)
    - they are either non-degradable or transform into stable terminal transformation products
    - they are all **vP** with no environmental degradation observed, due to C-F bonds
- Continual release of vP chemicals results in increasing levels and increasing probabilities of known and unknown effects.
- Exposure poorly reversible

Problems with high persistence



The history of the Montreal Protocol is a history of burden shifting via «drop in substitution»

- 1st Gen: Chlorofluorocarbons (**CFCs**) – *Ozone depletion*
- 2nd Gen: Hydrochlorofluorocarbons (**HCFCs**)– less ozone depleting, but powerful *greenhouse gases*
- 3rd Gen: Saturated hydrofluorocarbons (**HFCs**) -> greenhouse gases, *mild formation of TFA*



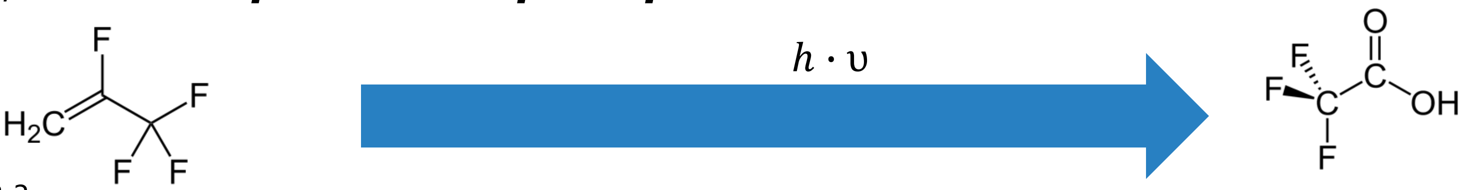
1,1,1,2-Tetrafluoroethane
(HFC-134a, Norflurane)

high global warming potential

Trifluoroacetic acid (TFA) yield between 7- 23%

Extremely persistent and mobile
Accumulates in the environment

- 4th Gen: F-gases after Kigali amendment (2019): Unsaturated hydrofluoroolefins (**HFOs**), less global warming potential, ***increased formation of TFA for certain HFOs***



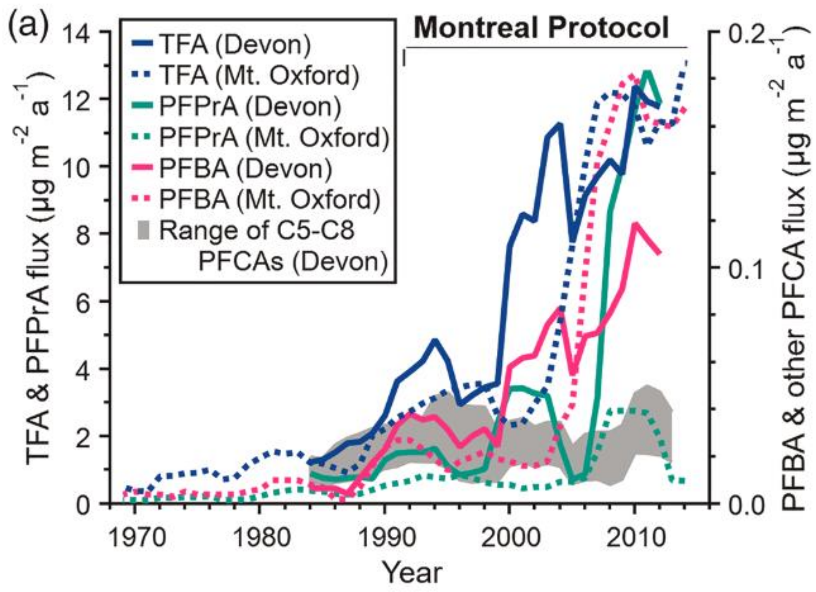
2,3,3,3-
Tetrafluoropropene
(μHFC-1234yf)

low global warming potential

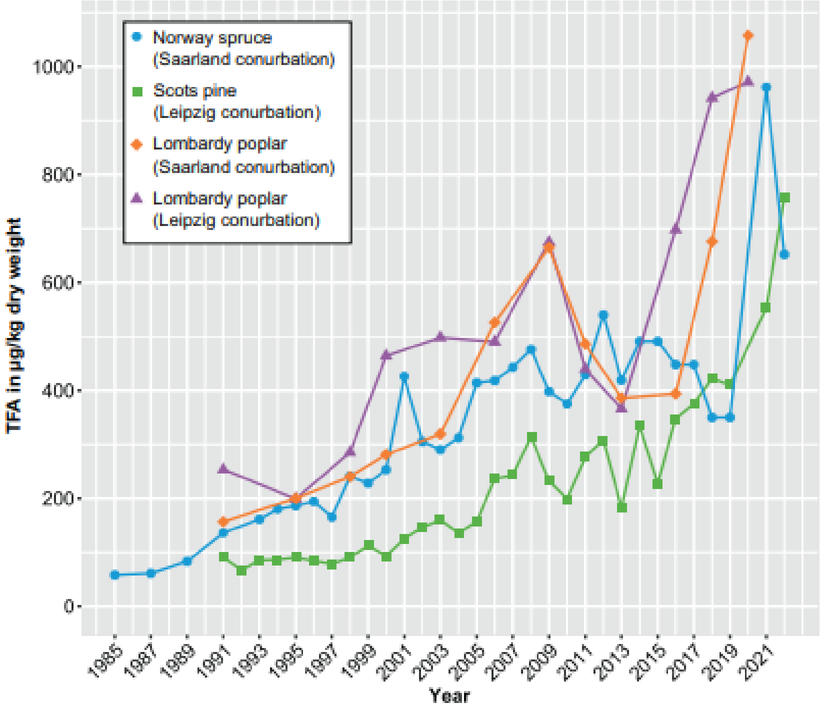
TFA yield = 100% !

TFA is accumulating everywhere, the “poster child” for the problem with high persistence!

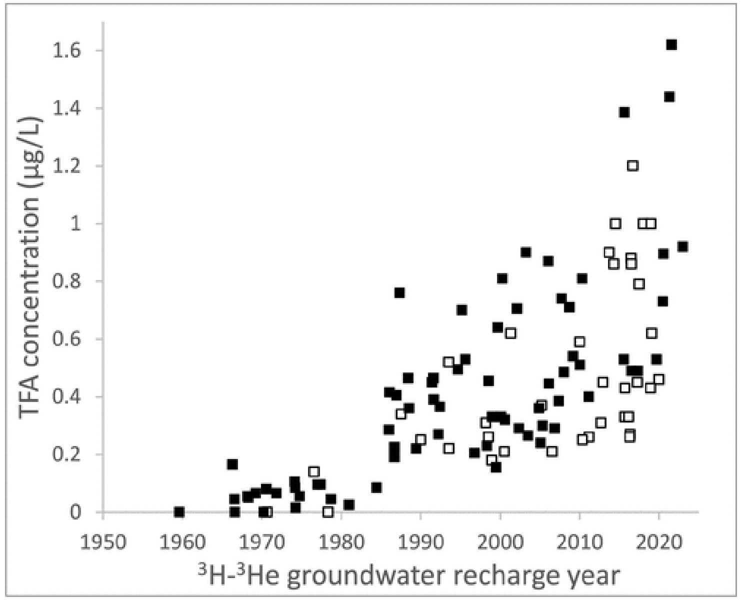
TFA accumulating in arctic ice cores



and in tree leafs



and in groundwater



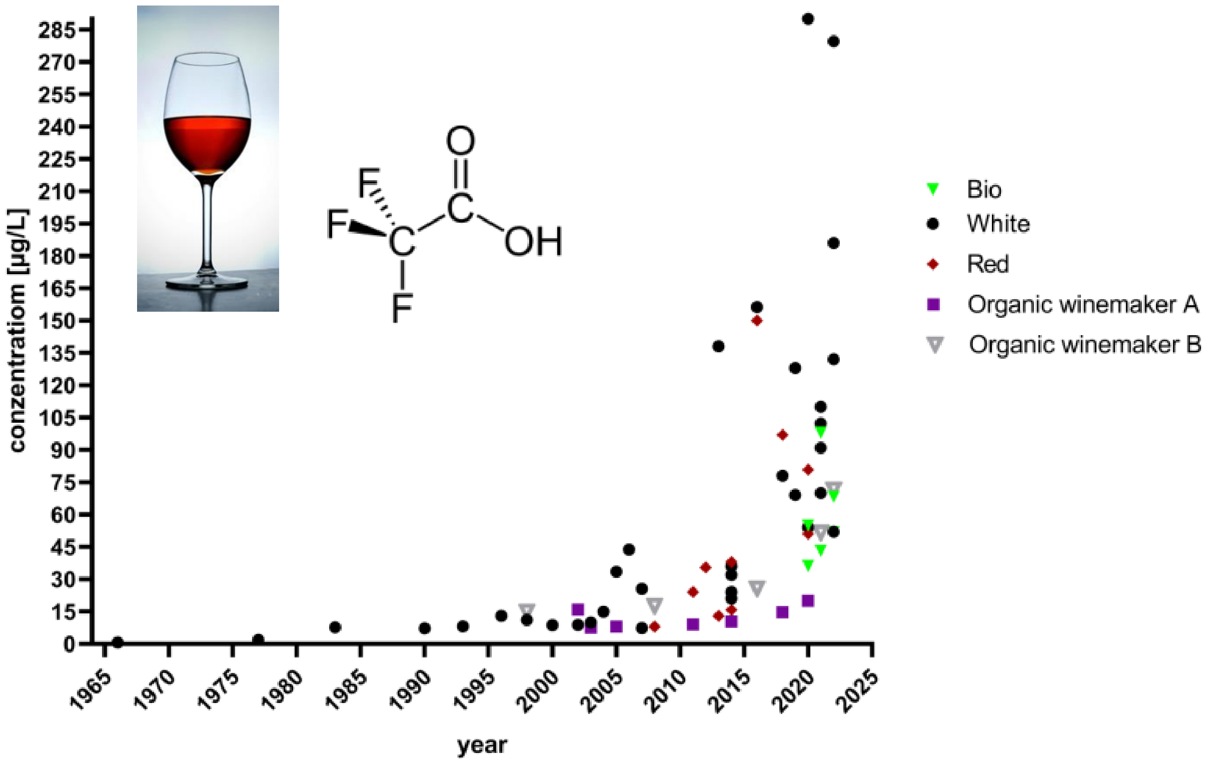
Pickard et al. Geophysical Research Letters (2020),47, e2020GL087535

Freeling and Björnsdotter, Current Opinion in Green and Sustainable Chemistry 2023, 41:100807

Albers and Sültenfuss, Environmental Science & Technology Letters 2024 11 (10), 1090-1095

TFA is increasing in all what we drink

…and in wine



Unpublished data: Michael Müller. Uni. Freiburg
michael.mueller@pharmazie.uni-freiburg.de (used with permission)

Wine image: Sai Balaji Varma Gadhiraju

Drinking water (median)[1,2]

- Germany: 1.5 µg/L
- 19 countries: 0.23 µg/L

Tea (median): 2.4 µg/L[2]

Beer (median) 6.1 µg/L[2]

Orange juice (mean 34 µg/L)[3]

Apple juice (mean 6.2 µg/L)[3]

1. Neuwald et al. *Environmental Science & Technology* **2022** *56* (10), 6380-6390
2. Scheurer & Nödler. *Food Chemistry*, *351*, 129304.
3. Van Hees et al. https://cdnmedia.eurofins.com/european-east/media/uxcnaa2c/eurofins_tfa_tfms_juice_24_final.pdf

Increasing Sources

Agricultural chemicals

Refrigerants and blowing agents

Pharmaceuticals

PFAS production and products

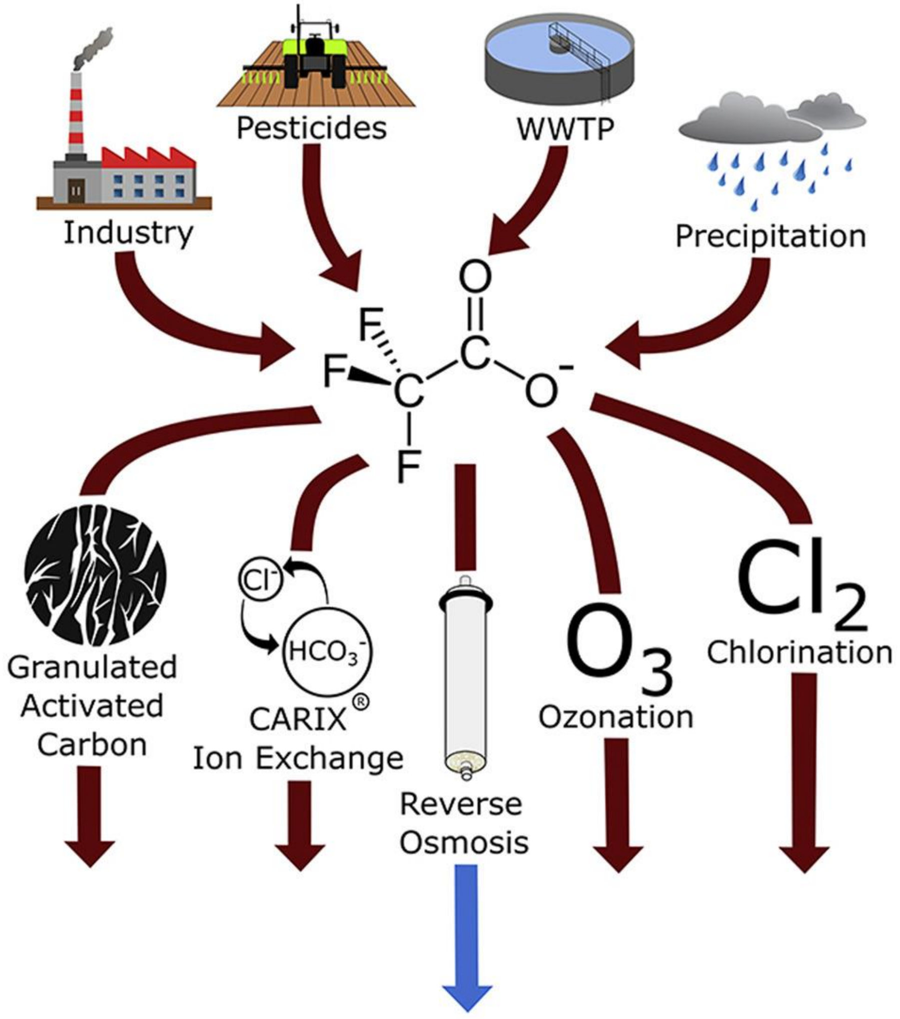
PFAS remediation

No natural sources

PFAS
remediation

Water treatment ineffective at removing TFA, ….or can form TFA

- Sorption techniques (activated carbon, ion exchange resins) -> **do not filter TFA**
- **Enhanced degradation techniques** (ozonation, chlorination, photolysis, electrolysis, incineration, pyrolysos etc.) **can lead to TFA formation from precursors** (along with other PFAS, F-gases)
- **Reverse osmosis** only technique that works for TFA, but requires an expensive destruction step for brines



Scheurer et al. (2017). *Water research*, *126*, 460-471.

Water industry very nervous!

March 2025

EurEau

Position Paper

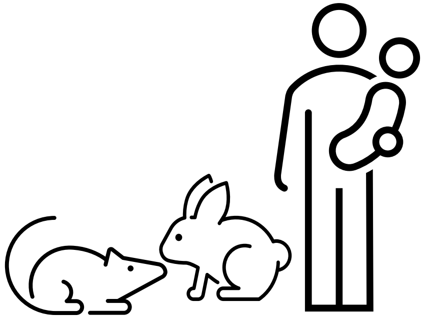
TFA in Drinking Water Resources

TFA is a very persistent, very mobile member of the PFAS group of chemicals. Due to its numerous emissions pathways, TFA is now ubiquitous in the water cycle and hard to remove by conventional water treatments. The EU should recognise the urgent necessity to stop TFA emissions to the environment as a first step towards addressing this pollution.

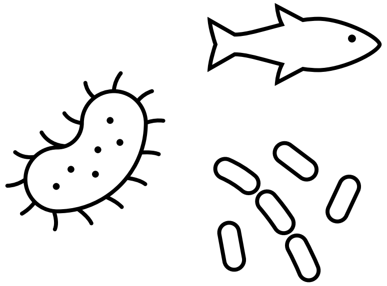
Because TFA is an atypical PFAS, the catch-all "PFAS Total" parameter is inadequate for TFA. A specific TFA limit value in drinking water should be set based on health-derived criteria. Where this value would require additional drinking water treatment, these costs should be borne by the polluters.

EurEau is the European Federation of National Associations of Water Services.

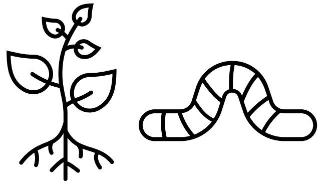
Irreversible effects



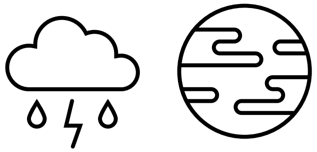
mammals



Aquatic algae / microbes



Soils / terrestrial ecosystems



Planetary boundaries

Toxicity

Mammalian toxicity of TFA

RIVM (2022)
Chronic rat toxicity (feeding)
Dose response: Male liver weight vs dose
Relevant potency factor: TFA is 0.002 x toxic as PFOA

Corresponds to a ***water threshold value of 2.2 µg/L***
Exceeded in an increasing number of areas

ECHA REACH Dossier (2024)
Han Wistar Rabbits
embryo-fetal developmental toxicity <180 mg/kg/day

Category 1B: Presumed human reproductive toxicant

Aquatic toxicity of TFA

- No observable effect concentration (NOEC) of **120 µg/L** for *Raphidocelis subcapitata* (microalga) – (Solvay data reported in Berends et al. 1999, USEEP ECOTOX). Used to derive a PNEC of **0.12 to 12 µg/L**
- Aquatic Concentrations exceeded in TFA hotspots and an increasing number of freshwater environments

Planetary Boundary Threat of TFA

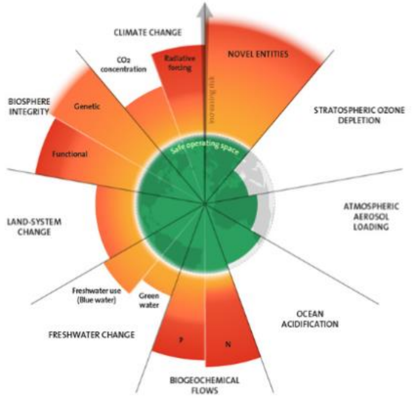
Planetary boundaries

Just Earth System Boundaries ensure a “safe operating space for humanity”

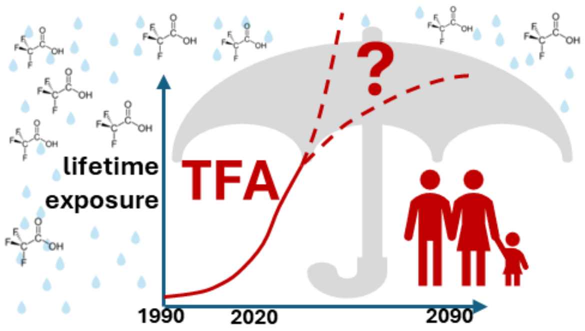
TFA meets the criteria of a planetary boundary threat[1-3] because of:

increasing planetary-scale exposure, where potential irreversible disruptive impacts on vital earth system processes could occur.

Although no global problem yet, it’s not worth the risk to continue on this trajectory!

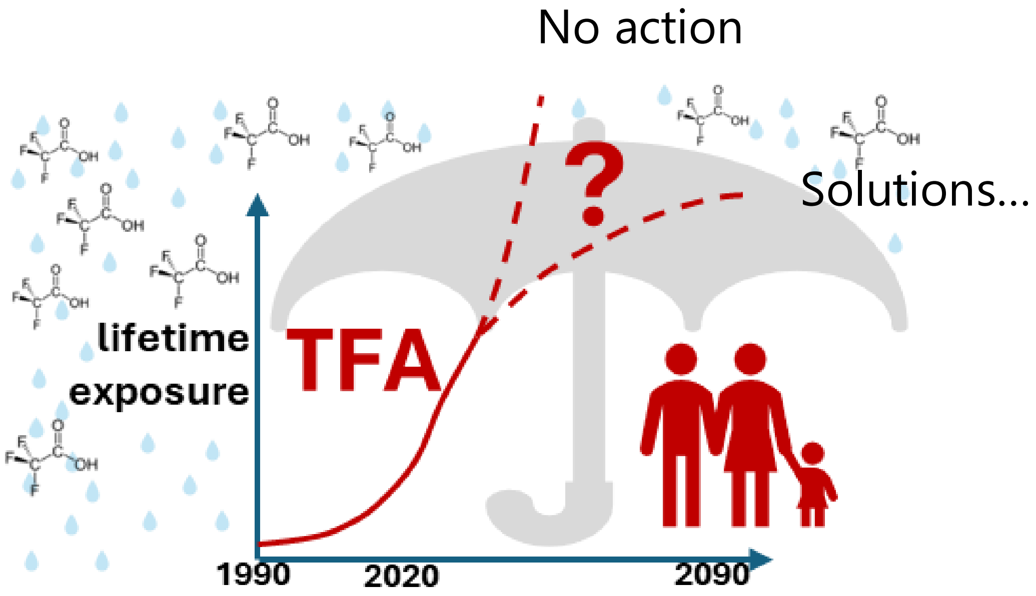


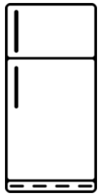
9 boundaries assessed, 6 crossed



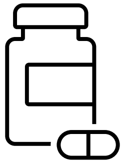
1. Persson et al. *Environ. Sci. Technol.* **2013**, *47* (22), 12619– 12622
2. MacLeod et al. *Science* 373,61-65(2021)
3. Arp et al., *Environ. Sci. Technol.* **2024**, *58* (22), 19925– 19935

Solutions to a Global Threat

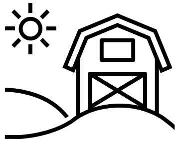




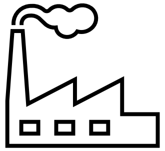
Refrigerants and blowing agents



Pharmaceuticals

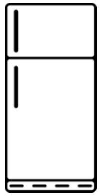


Agricultural chemicals



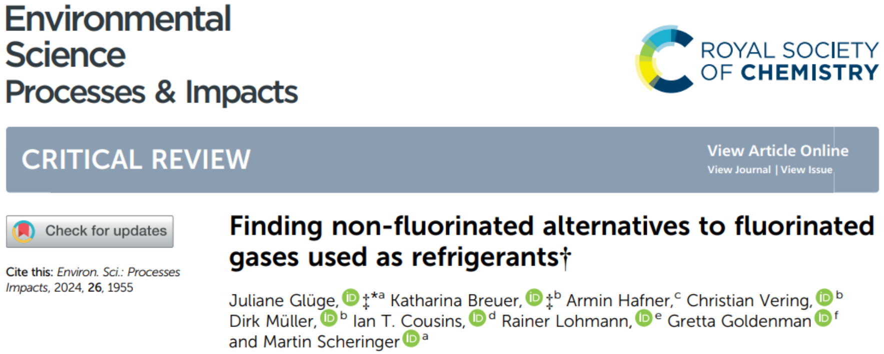
PFAS production and products

Solutions: alternatives to fluorinated refrigerants



Fifth generation of fluorinated refrigerants in the Montreal Protocol can be free of TFA precursors

	CO_2	Ammonia	Propane	Isobutane	Others
Domestic refrigeration				X	
Stand-alone refrigeration systems in commercial stores	x	x	X	x	x
Multipack centralized refrigeration systems in commercial stores	X	x	x		
Industrial refrigeration	x	X			
Transport refrigeration of goods	x		x		x
Ultra-low and low temperature freezers		x	x		x



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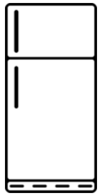
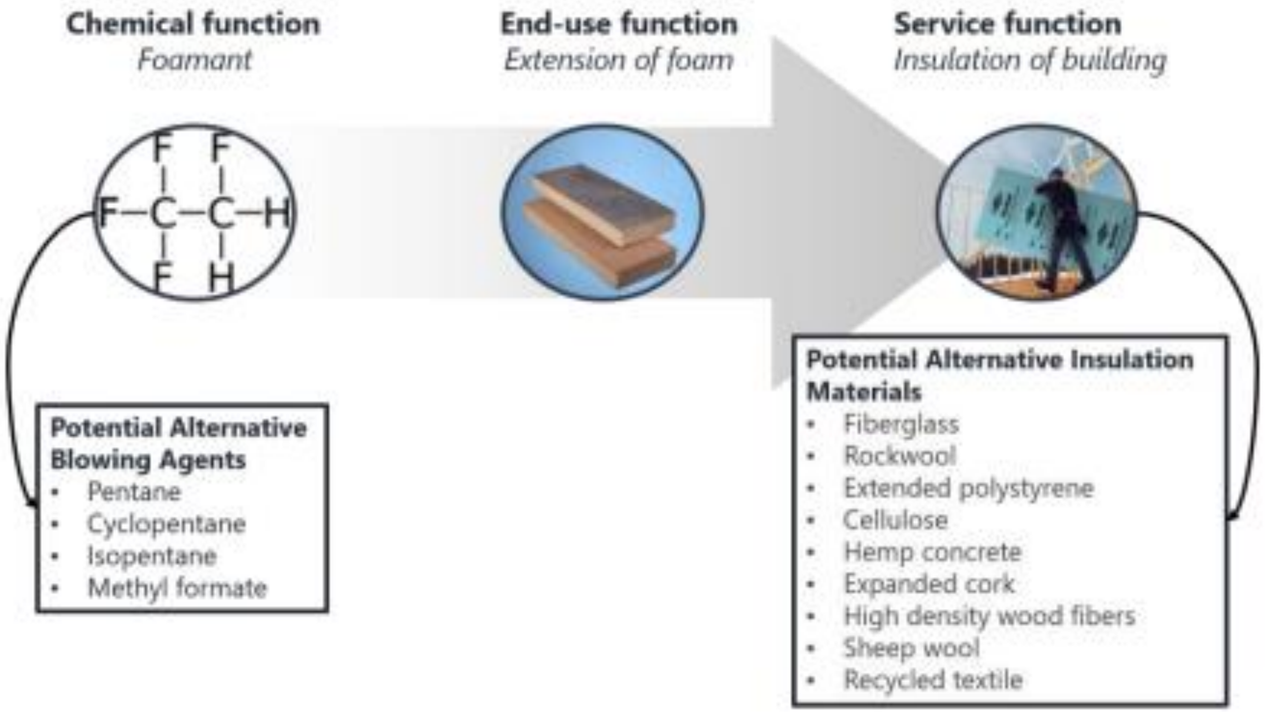
Finding non-fluorinated alternatives to fluorinated gases used as refrigerants†

Juliane Glüge, ‡*[a] Katharina Breuer, ‡[b] Armin Hafner,[c] Christian Vering,[b] Dirk Müller,[b] Ian T. Cousins,[d] Rainer Lohmann,[e] Gretta Goldenman[f] and Martin Scheringer[a]

Solutions: alternatives to fluorinated gases used as blowing agents



Refrigerants and blowing agents



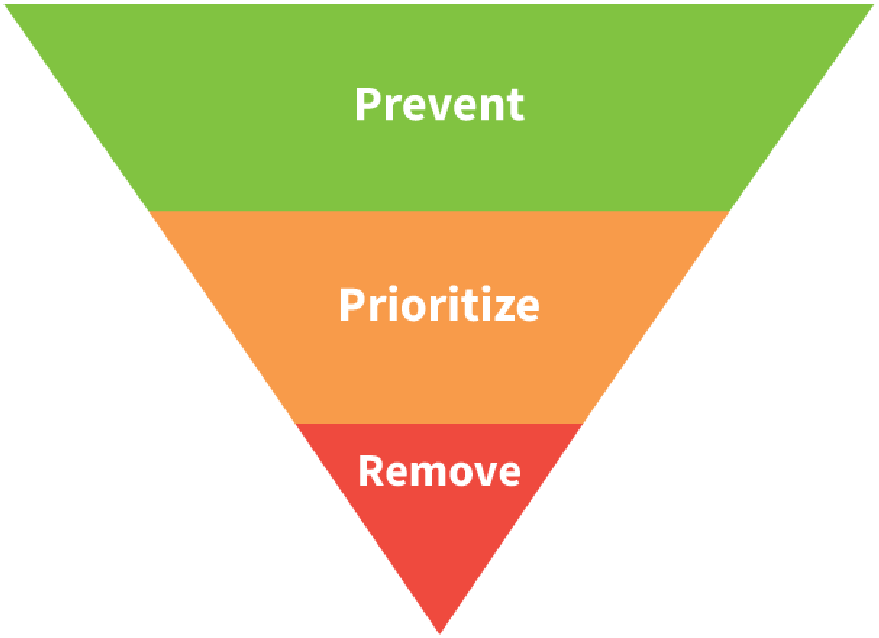
PhD thesis defence - Romain Figuiére

Event by Department of Environmental Science | Stockholm University

Friday 7 March 2025

Paper coming soon!

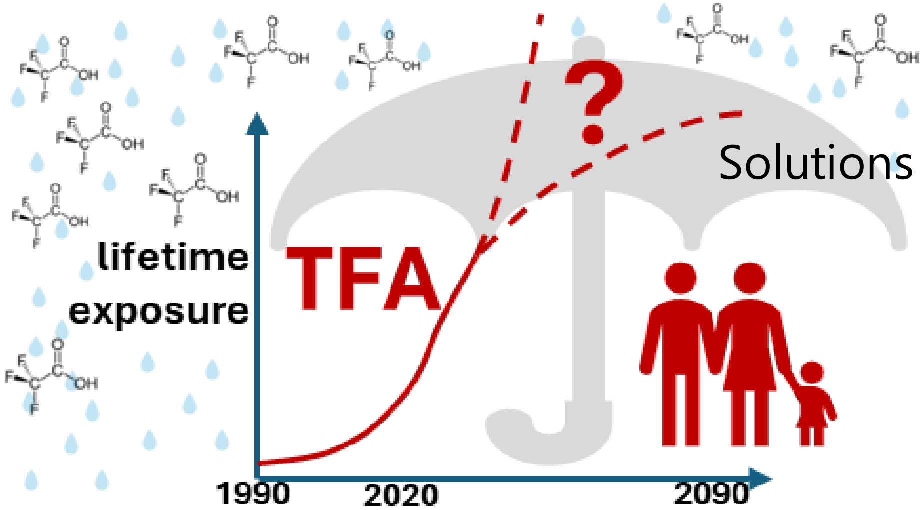
Summary of Solutions



- Transition to alternatives to fluorinated refrigerants:
  - ➢ identify non-essential uses
  - ➢ focus transition on TFA-precursors produced in greatest volume and with highest TFA yields

- Define TFA as a PFAS, and integrate in PFAS reduction strategy

- Minimize gas emissions (better management of fluorinated refrigerants)



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Perspective

The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA)

Hans Peter H. Arp,*,§ Andrea Gredelj,§ Juliane Glüge, Martin Scheringer, and Ian T. Cousins

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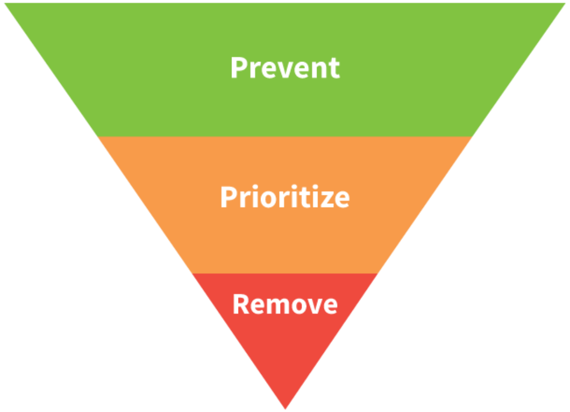

2021-2026

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