PFAS: Forever Chemicals DO have Safer Solutions

Dr. Greg Morose – Research manager Dr. Gabriel Salierno – Green chemist Heather Tenney – Director of Science Policy Baskut Tuncak – Director

March 26, 2025





Toxics Use Reduction Act (TURA), Mass. 1989







- Applies to listed chemicals and classes of chemicals
 - Does not ban or restrict any substance

Businesses that use certain amounts of toxic chemicals listed under TURA are required to:

- Report annually on their chemical use,
- Conduct Toxics Use Reduction (TUR) Planning every two years, and
- Pay a fee.

The fees support the work of the TURA implementing agencies, including:

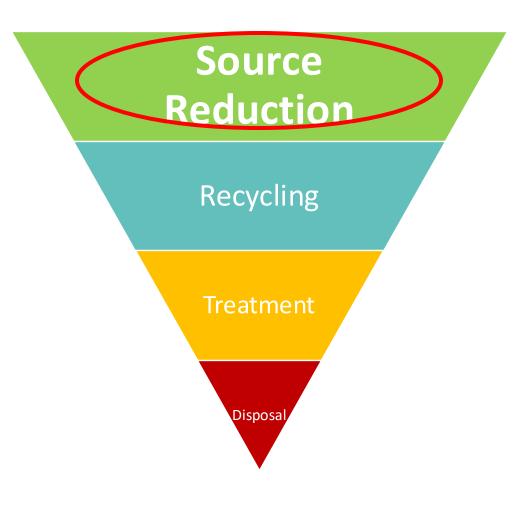
- Training, education, data, compliance, and enforcement,
- Updating the TURA list, including supporting SAB
- Providing grants to support safer solutions, and
- Providing technical assistance, including RD&D.

The experiences are shared

- TURA offers free services to all MA businesses
- TURI services are available to all businesses, not just MA-based
- Case studies provide input into national and international efforts to reduce pollution and protect workers



Our Approach: Toxics Use Reduction



Reduce toxics at the source (use-based analysis)

Focus on inherent hazard of chemicals used

Identify suite of opportunities to eliminate or reduce hazard

Implement affordable and effective opportunities





How TURI Supports Development of Safer Alternatives

Academic research leads to new solutions



Industry research develops reliable options



Grants support implementation that demonstrates viability



Training professionals ("Planners") builds capacity for change



Alternatives assessment reports spread knowledge



Tools facilitate discovery and evaluation of options



TURA PFAS TIMELINE

TURA SAB Reviewed PFAS from 2016-2020

Recommended listing a large category of PFAS

Identified sectors of expected use in Massachusetts

Guidance and education of companies

TURA brings preventative approach to other efforts

First reporting July 2023

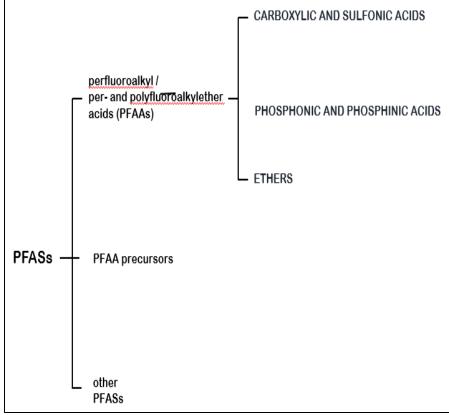


TURA SAB PFAS Evaluation

To understand the characteristics of a range of PFAAs, the SAB examined eight substances of varying chain lengths: PFNA (C9); PFOS and PFOA (C8); PFHpA (C7); PFHxA and PFHxS (C6); and PFBA and PFBS (C4).

The SAB then reviewed two ethers (GenX and ADONA), and phosphonic and phosphinic acids (PFPA and PFPiAs) of varying chain lengths.

The SAB reviewed various health impacts as well as a number of degradation/transformation pathways, through which a PFAS precursor breaks down into one of the end degradation products.





Chronic Health Effects

	PFNA	PFOA	PFOS	PFHpA	PFHxA	PFHxS	PFBA	PFBS	GenX	ADONA	PFPA/ PFPiA
Cancer		Kidney, Testicular							Х		
Immunotoxicity	Х	Ulcerative colitis	Х					Х	Х		
Thyroid		Х			Х	Х	Х	Х		Х	Х
Endocrine (other than thyroid)					Х	Х	Х	Х			
Hematological		cholesterol				Х	Х	Х			
Liver/metabolic	Х			Х	Х	Х	Х	Х	Х	Х	Х
Reproductive	Х	PIH							Х	Х	Х
Developmental	Х			Х	Х		Х	Х	Х		
Neurodevelopmental						Х					
Neurotoxicity	Х				Х	Х		Х			
Asthma						Х		Х			
Other	Mutagenicity				Kidney			Kidney	Kidney		Acute toxicity
Note: The SAB did r	not conduct					OA due	to the vol	ume of	inform	ation ava	· · · · ·

through authoritative bodies and large scale epidemiological studies.

Persistence, Presence in the Environment, and Bioaccumulation

	PFNA	PFOA	PFOS	РҒНрА	PFHxA	PFHxS	PFBA	PFBS	GenX	ADONA	PFPA/ PFPiA
Persistence	Х	Х	Х	х	Х	Х	Х	Х	Х	Х	Х
Bioaccumulation	Х	Х	Х	х	Х	Х	Х	х	Х		Х
Presence in the environment	х	х	х	х	х	х	х	х	х		
Presence in biota, ncluding humans	х	х	Х	х	х	х	х	Х	х		х



Health and Environmental Effects

• Highly persistent and mobile in the environment

• Do not break down under normal environmental conditions

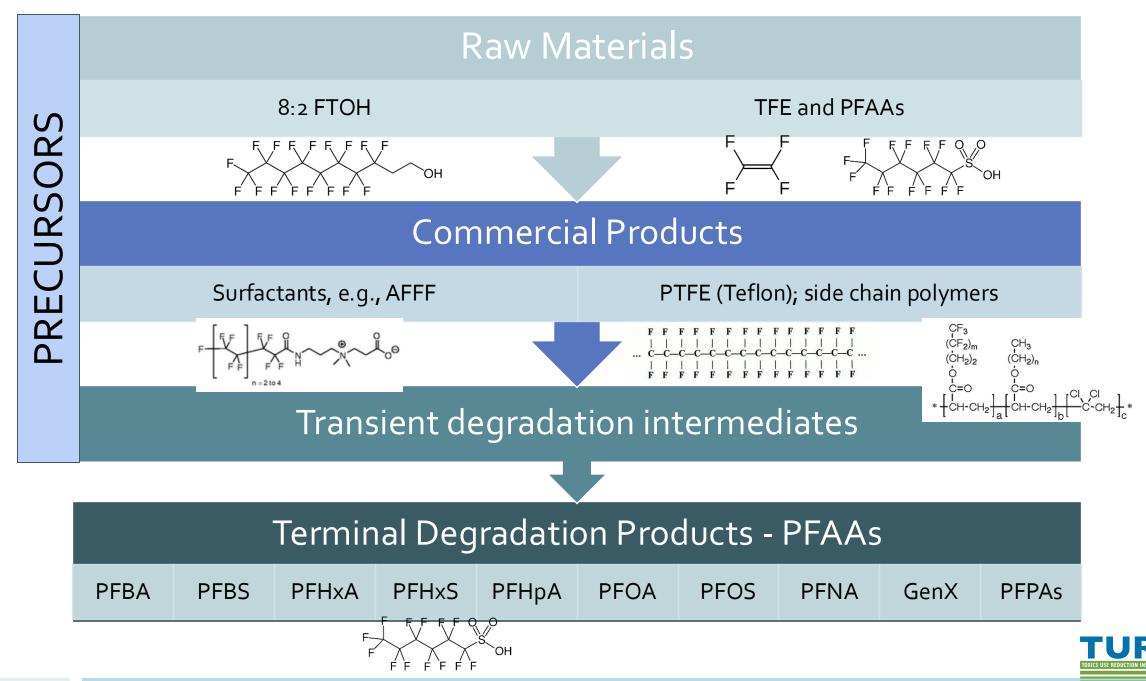
Bioaccumulative

• In animals or plants

Health effects include:

- Effects on endocrine system, including liver and thyroid
- Immunotoxicity (with implications for vaccines)
- Metabolic effects
- Developmental effects
- Neurotoxicity





TURA Certain PFAS NOL Listing

Those PFAS that contain:

a perfluoroalkyl moiety with three or more carbons

a perfluoroalkylether moiety with two or more carbons

and that are not otherwise listed.



PFAS (on?) SDSs

PFAS may not be listed in Section 3 or may be listed as 'proprietary'

Sometimes the product or ingredient name gives clues that PFAS are present

Sometimes fluorinated breakdown products in Section 15 give clues

Reaching out to the supplier is always a good idea

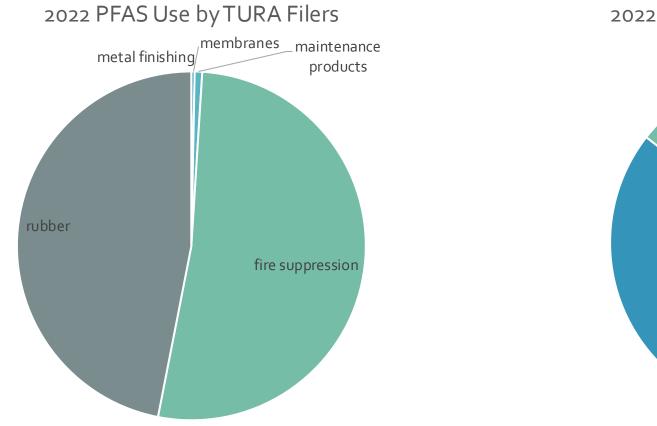


Expected Sectors in Massachusetts

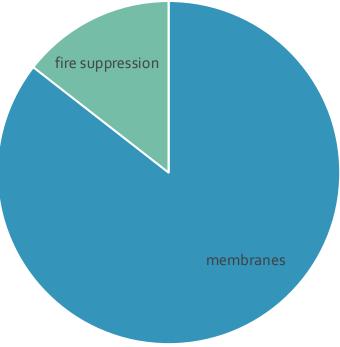




Use and Release of PFAS by TURA Filers



2022 PFAS Releases by TURA Filers



membranes maintenance products fire suppression rubber metal finishing

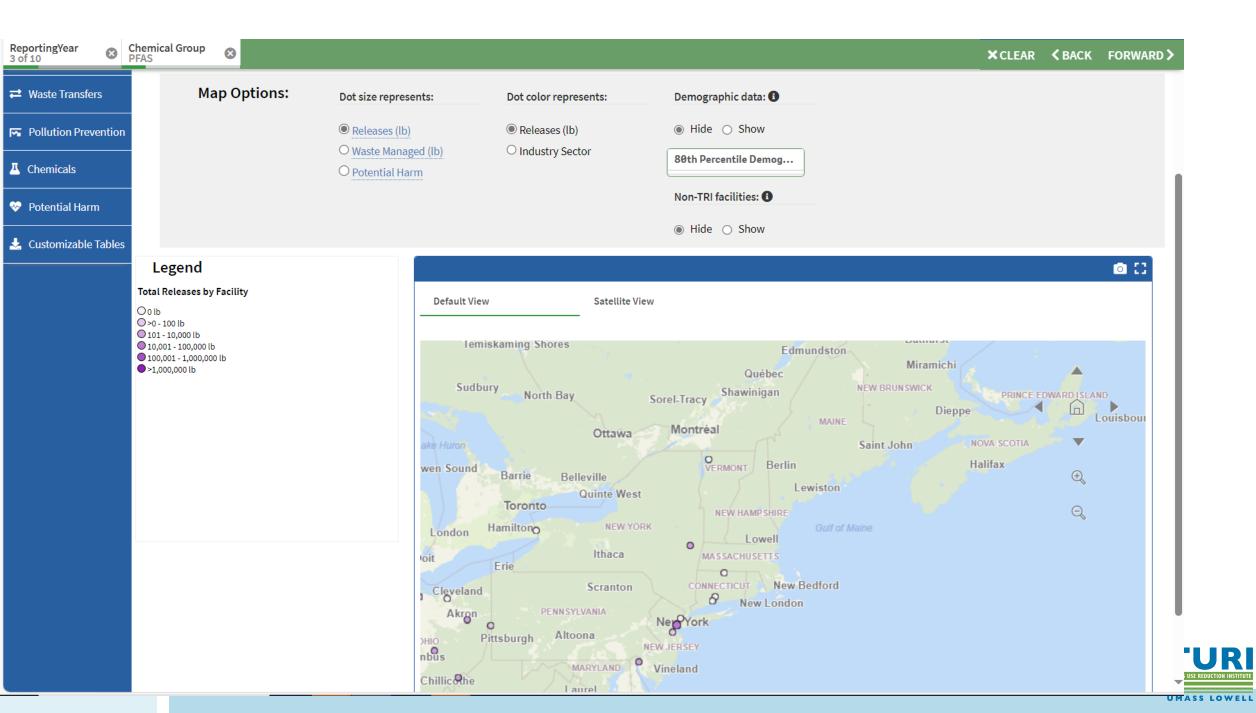


membranes maintenance products fire suppression rubber metal finishing

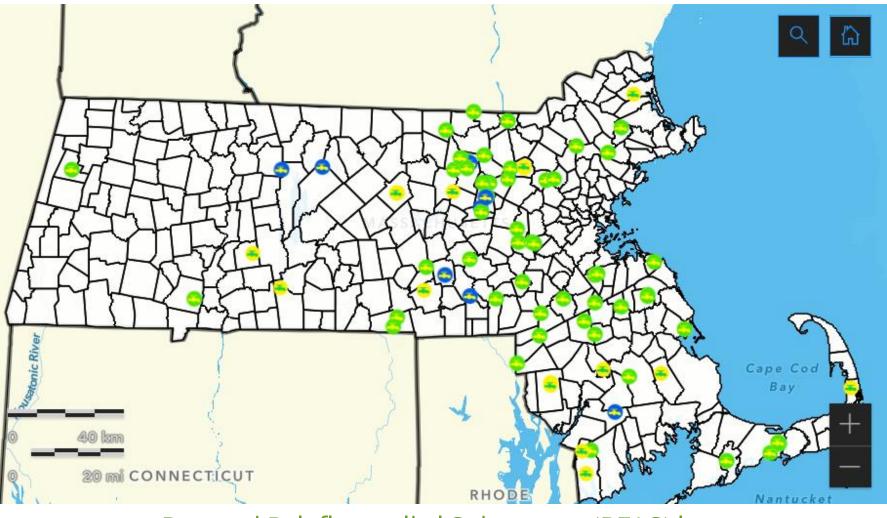
2022 TURA Certain PFAS NOL Use and Releases

Company	Use	Release
Entegris	11,647	7,596
AW Chesterton	26,700	Ο
Kidde Fenwal	1,998,080	1,285
Cri-Tech	1,060,863	Ο
Titeflex	769,750	Ο
	3,837,042	8,881





Why a preventative approach?



Per- and Polyfluoroalkyl Substances (PFAS)



<u>Mass.gov</u>

Firefighter Gear

TURI Community Grant funded pilot study on PFAS exposure from turnout gear and low-PFAS gear alternatives

18 Firefighters provided skin wipes before and after training, a sample or wipe of their turnout gear, a blood sample, and a questionnaire

Firefighter PFAS blood levels were twofold higher than the general population



Firefighter Gear con't

PFAS were found in the majority of the gear samples and skin wipes

PFOA was found in legacy and next generation gear but not PFZero gear

Next-generation gear contained primarily 6:2 FTMAC at levels much higher than PFAS in legacy gear

PFZero gear contained 6:2 FTMAC in moisture barrier wipes as well as in after-training skin wipes

PFAS concentrations were higher in skin wipes collected after training event compared to those collected immediately prior



5 min break 5 min 3 min 1 min 4 min 2 min We're back!

https://www.turi.org/Our Work/Resources

Visit our website <u>www.turi.org</u> for **Resources**

- Databases and tools
 - <u>www.Cleanersolutions.org</u>
 - <u>https://P2OASys.turi.org</u>
 - <u>www.TURAdata.org</u>

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Alternatives Assessment

A process for identifying and comparing potential chemical, material, product or other alternatives that can be used as substitutes to replace chemicals of high concern (e.g. PFAS chemicals).



Are the Alternatives Safer?

TURI's Pollution Prevention Options Analysis System (P2OASys):

Compares potential Environmental Health and Safety (EHS) hazard categories:

Sourcertand by the constraint of the cons		ethylene	vdueous	neous		nod.	Alcohol
Acute Human Effects848688Chronic Human Effects942562Ecological Hazards842484Environmental Fate & Transport944465Atmospheric Hazard622222Physical Properties1046598Process Factors745444Life Cycle Factors1034464		chloro	utral A	idic Aq	based	rdocar	odified
Chronic Human Effects942562Ecological Hazards842484Environmental Fate & Transport944465Atmospheric Hazard622222Physical Properties1046598Process Factors745444Life Cycle Factors1034464	Categories	Tri	Ne	Aci	Bic	Hγ	Ĕ
Ecological Hazards842484Environmental Fate & Transport944465Atmospheric Hazard622222Physical Properties1046598Process Factors745444Life Cycle Factors1034464	Acute Human Effects	8	4	8	6	8	8
Environmental Fate & Transport944465Atmospheric Hazard6222222Physical Properties1046598Process Factors745444Life Cycle Factors1034464	Chronic Human Effects	9	4	2	5	6	2
Atmospheric Hazard62222Physical Properties1046598Process Factors745444Life Cycle Factors1034464	Ecological Hazards	8	4	2	4	8	4
Physical Properties1046598Process Factors745444Life Cycle Factors1034464	Environmental Fate & Transport	9	4	4	4	6	5
Process Factors745444Life Cycle Factors1034464	Atmospheric Hazard	6	2	2	2	2	2
Life Cycle Factors 10 3 4 4 6 4	Physical Properties	10	4	6	5	9	8
	Process Factors	7	4	5	4	4	4
Product Score 8.4 3.6 4.1 4.3 6.1 4.6	Life Cycle Factors	10	3	4	4	6	4
	Product Score	8.4	3.6	4.1	4.3	6.1	4.6

- Both quantitative data and qualitative input.
- Each category is rated using values, key phrases, GHS classifications, or other hazard designations.

https://p2oasys.turi.org

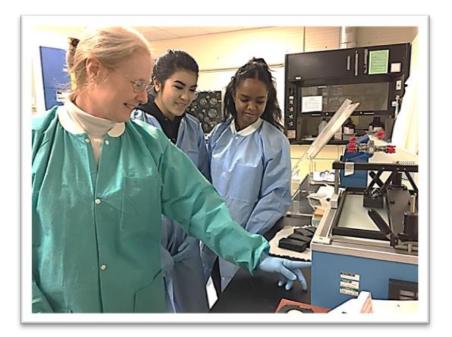


P2OASys Scores

Color	Level of Hazard	Score Range
	Low (L)	2 < 4
	Medium (M)	4 < 6
	High (H)	6 < 8
	Very High (VH)	8 - 10



Academic Research Grant Process



www.turi.org/research

On an annual basis, TURI provides Academic Research Grants to provide seed funding to discover new solutions to reduce the use of toxic chemicals by industry.

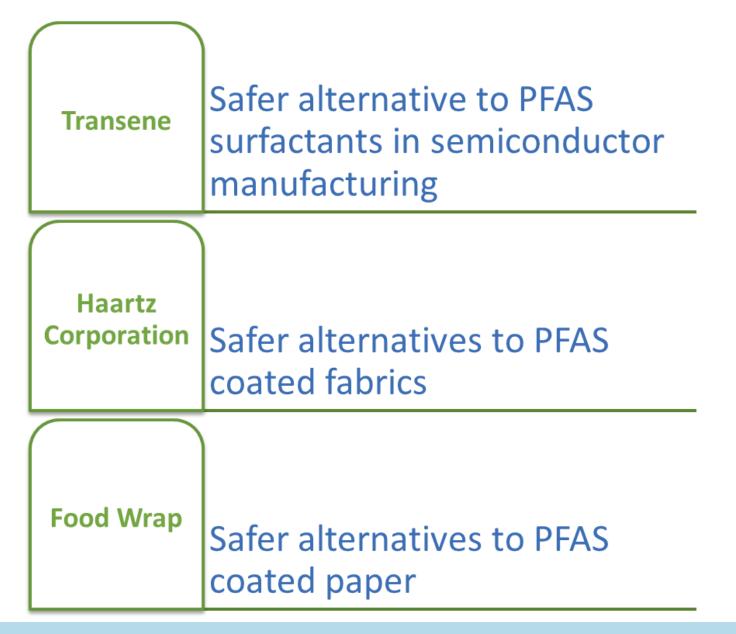
Focuses on companies' specific toxics use reduction challenges

Funding of up to \$35,000 provided to the academic research team to cover graduate/undergraduate student work and research materials.

Builds deeper understanding of technical and economic feasibility of solutions.



Academic Research Grant Projects



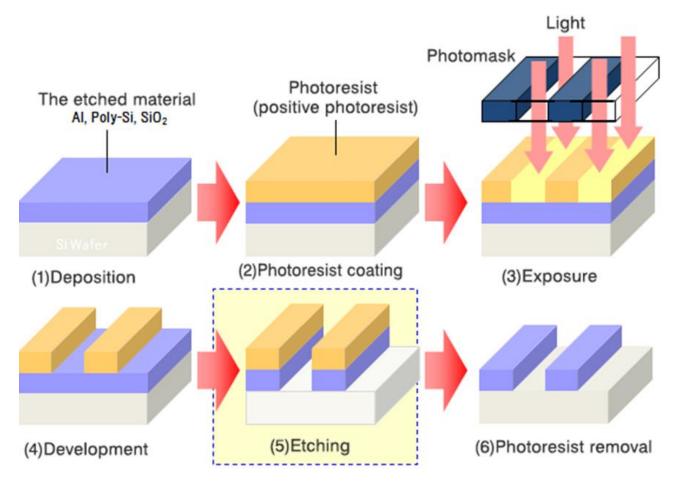


Problem Statement

- Transene Inc. a Massachusetts-based supplier of chemical etchants, photoresists, dielectrics, etc. for the electronics and aerospace industry
- > PFAS is used as a surfactant to improve the wettability of the chemical etchants
- The alternative surfactants must:
 - Be compatible with: Strong acidic/oxidizing solutions nitric acid, phosphoric acid, etc.
 - Reduce the etchant's surface tension: Etching solutions' surface tension reduction should be comparable to PFAS surfactants for better wettability of the substrate (less than 0.1 wt.% consumption)
 - > Be less hazardous and toxic (No sodium Ions)
 - Stability: > 1-year shelf life



PFAS surfactants in the semiconductor industry



PFAS surfactants:

- Increase the wettability of the etching solution
- Effective at low concentrations
- Used for wetting complex geometries of the substrates



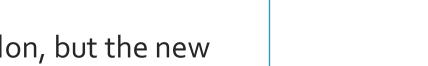
Semiconductor Manufacturing Applications

Parameter	Buffered Oxide Etchants (BOE)	Chrome Etchant	PAN	ТМАН
Composition	NH4HF2: HF mixture 6:1	Ceric ammonium nitrate + acid (perchloric/nitric/ acetic)	Phosphoric, Acetic & Nitric Acids	Tetramethyl ammonium hydroxide (2.38%)
рН	pH = 3-5	pH <1	pH < 2	pH=13-14
Color	Colorless	Orange	Colorless	Colorless
PFAS-based surfactant	Novec 4200	FC95	Novec 4300	Novec 4200
Substrate	Glass	Chromium	Aluminum	Photoresist
Compatible Alternative Surfactant	CG-50	Brij 35 Brij S100	BG-10	BG-10



Project Results

- Replaced Novec-4200 and other PFAS based surfactacts with PFAS-free surfactants
 - Engaged with TURI's academic research team to develop and test options
 - Overcame challenging performance requirements
 - New products are less expensive
- Successfully converted over 90% of its customers to the new products.
- PFAS-based surfactants cost \$2,400 per gallon, but the new safer surfactants cost only \$80 per gallon.



Journal of Cleaner Production 415, 20 (2023) 137879 https://doi.org/10.1016/j.jclepro.2023.137879



TRANSENE

COMPANY, INC.

Safer Alternatives to PFAS Coatings

Project Team:

- TURI
- UMass Lowell Plastics Engineering Department
- Haartz Corporation

Phase 1

• PFAS free coatings for cotton fabric

Phase 2

• PFAS free coatings for acrylic fabric for automobile applications



PFAS free stain-resistant cotton textiles

A Comparative Study of PFAS-free Liquid-Repellent Coatings on Cotton Fabric. Progress in Organic Coatings, 195 (2024) 108670 <u>https://doi.org/10.1016/j.porgcoat.2024.108670</u>

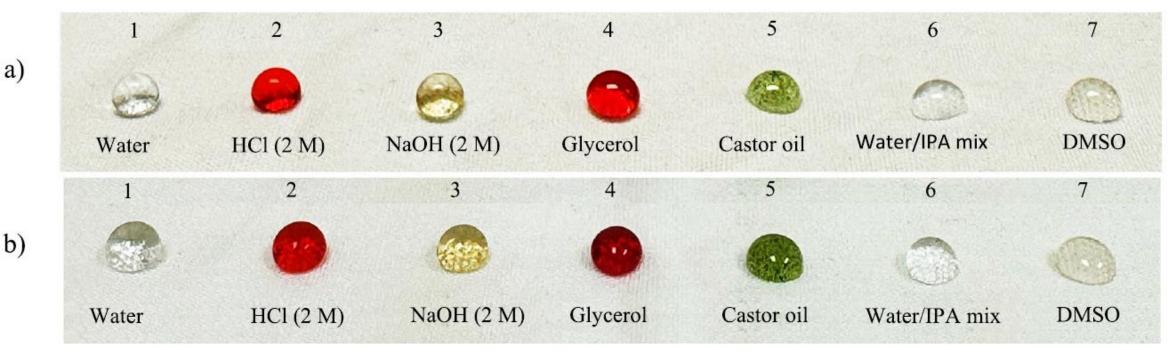


Fig. 9. Liquid-repellent cotton fabrics, a) F-C12 b) F-3600 (The droplets are dyed to enhance visibility).

F-C12: n-dodecyl triethoxy silane

F-3600: polydimethylsiloxane (PDMS)

HCI: hydrochloric acid

NaOH: sodium hydroxide



PFAS Free Acrylic Coatings: Project Timeline

January 2025 Crosslinking optimizations Oil repellency improvement **March 2025** Alcohol repellency ٠

June 2025

Final report ٠

Publication ٠

October 2024

Starting first approach with bio • based molecules

November 2024

spectroscopy

Characterization, with Fourier

Sample preparation for Haartz

Transform Infrared (FTIR)

- Optimizing synthesis process
- Meetings with Haartz

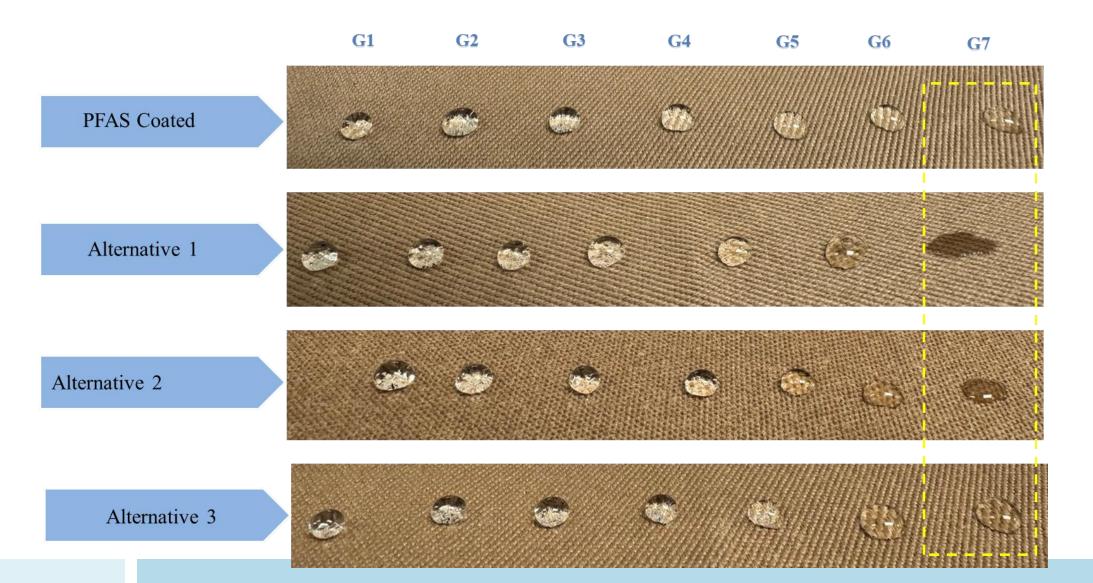
December 2024

- Crosslinking bio based molecules •
- Scanning electron microscope (SEM) analysis ٠
- Durability testing and comparison

- FTIR ٠



PFAS Free Textile Coatings – Isopropyl Alcohol/Water Repellency for Acrylic Coatings





PFAS-free options for food packaging

• Alternatives are readily available, EU and FDA full ban feasible.

Restriction of PFAS under REACH: Sufficiently strong evidence that technically and economically feasible alternatives to PFAS use are available for packaging. https://echa.europa.eu/de/-/restriction-of-per-and-polyfluoroalkyl-substances-pfass-under-reach

Two approaches to achieve combined water and oil/fat repellency of paper

Dual layer: Hydrophobic material / oleophobic material

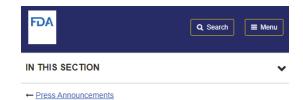
The paper is coated twice:

- First, with an oleophobic polymer such as alginate and chitosan.
- Then, with a hydrophobic layer (waxes, some proteins, silanes, lignin)

Modified polymer single layer coatings

The surface is coated once with a modified polymer.

- Hydrophilic biopolymers, such as cellulose, enhance hydrophobicity.
- Hydrophobic polymers, such as silanes, enhance hydrophilicity.



FDA NEWS RELEASE

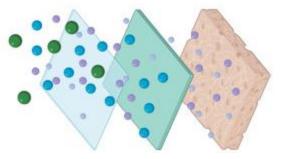
FDA, Industry Actions End Sales of PFAS Used in US Food Packaging

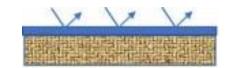
The following is attributed to Jim Jones, Deputy Commissioner for Human Foods

For Immediate Release:

February 28, 2024

https://www.fda.gov/news-events/press-announcements/fdaindustry-actions-end-sales-pfas-used-us-food-packaging

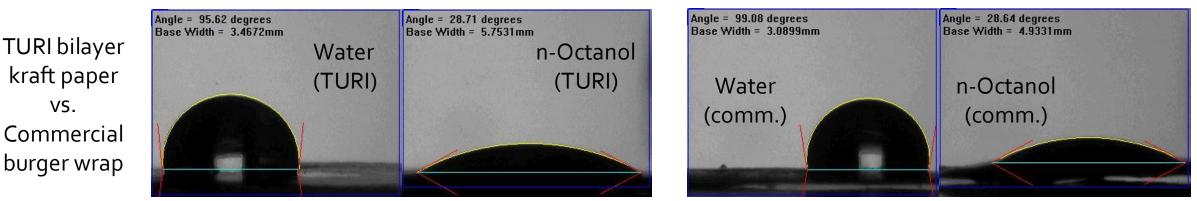






Dual layer coating – results at TURI

- Bilayer optimization of a biowax and hydrophilic biopolymer was performed.
- Weight gain, visual appearance, and drop test contact angle were utilized to characterize the films.
- Higher contact angle values correlate with improved liquid repellency.



The optimal combination for hydrophobicity showed fair oleophobicity but was comparable or superior to most commercially available food wrap paper. UML researchers are conducting further optimization and testing for mechanical properties and stability under a TURI Research Grant FY2025.

				Contac	tan	gle (°)		
Sample		Wat	er	n-Oo	ctan	ol	Sun	flow	er oil
Optimized bilayer 1	80	±	17	25	±	3	39	±	6
Optimized bilayer 2	87	±	29	23	±	4	43	±	3
Commercial wraps	83	±	11	29	±	6	36	±	20



Everyone is Kindly Invited to Our Next Webinar!

Spring 2025 Toxics Use Reduction Webinar Safer Refrigerants for Manufacturing

Learn about the environmental concerns of fluorinated refrigerants and discover practical, safer alternatives for household, commercial, mobile, and industrial refrigeration and air conditioning applications.

April 14, 2025 10:00 AM Eastern | Virtual <u>Registration via zoom here</u>



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





Refrigerant gases overview

Fluorinated gases (F-gases) are currently used in 80% of refrigeration and air conditioning

Kigali Amendment to the Montreal Protocol:

Hydrofluorocarbons (HFCs) have very high Global Warming Potential (GWP).
A GWP regulatory threshold emerged: 150 relative to CO₂.

•Policies solely targeting ozone depletion and GWP reduction could have the unforeseen effect of exacerbating halocarbon and PFAS pollution.

HFC Phase-Down :

- American Innovation and Manufacturing (AIM) Act: Phase *down* 85% of high GWP HFCs stepwise by 2036.
- 10% cut since 2019, a steep cut by 2024 (40%), and a 30% cut planned by 2029.
- 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





F-gas refrigerants evolution

- HFCs, Hydrofluoroolefins (HFOs), Hydrochlorofluoroolefins (HCFOs), and 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.
 - HFC-23 super greenhouse gas production when released into the environment.
 - *PFAS pollution*: HFOs are also PFAS according to the OECD definition.

While PFAS remediation costs amount to at least hundreds of billion USD*, market value forecasts for HFOs and PFAS are 2-3 billion and about 30 billion USD, respectively.

* <u>U.S. Chamber of Commerce: PFOS and PFOA Private Cleanup Costs at Non-Federal Superfund Sites.</u> Ling (2024) <u>https://doi.org/10.1016/j.scitotenv.2024.170647</u>



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

SNAP approved	Composition				Main annliestions	
refrigerant	Chemical name	CAS No	% w/w	GWP	Main applications	
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	
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	65	4	Chillers to a Kar of charge and can and a sustained	
R-454A (blend)	Difluoromethane (HFC-32)	75-10-5	35	675	Chillers <90 Kg of charge and cascade systems.	
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	67	4	Industrial chillers;	
R-454B (blend)	Difluoromethane (HFC-32)	75-10-5	32	675	replaces R-410a blend	
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	78.5	4	Commercial; residential; heat pumps;	
R-454C (blend)	Difluoromethane (HFC-32)	75-10-5	21.5	675	replaces R-410a blend	
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	75.5	4		
R-455A (blend)	Difluoromethane (HFC-32)	75-10-5	21.5	675	Commercial; residential; mobile;	
	Carbon dioxide (R-744)	124-38-9	3	1	replaces HFC-134a	
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	70	4		
R-457A (blend)	Difluoromethane (HFC-32)	75-10-5	18	675	Commercial; residential	
	1,1-difluoro ethane (HFC-152a)	75-37-6	12	124		
	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	77.5	4	Commercial, residential,	
R-516A (blend)	1,1-difluoro ethane (HFC-152a)	75-37-6	14	124	Commercial; residential;	
	1,1,1,2-tetrafluoroethane (HFC-134a)	811-97-2	8.5	1430	replaces HFC-134a	

F-gas Refrigerants and PFAS

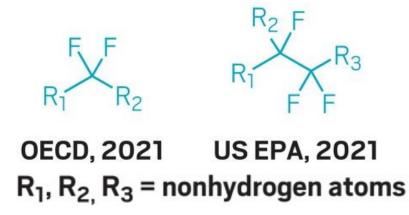
• HFCs, HCFCs, and HFOs are also used as feedstock for PFAS production.

• Are HFCs and HFOs considered PFAS?

✓ Yes, by the internationally adopted OECD definition.

×No by the EPA definition utilized by the Office of Chemical Safety and Pollution Prevention (OCSPP) in the Toxic Substances Control Act (TSCA) listing or the Office of Water (OW) Definition for the draft Contaminant Candidate List (CCL5) rule (2021).

OECD definition: At least one CF_3 group or at least one CF_2 group



EPA working definition:

A CF₂ attached to a CF both carbons are saturated with no bond to hydrogen.

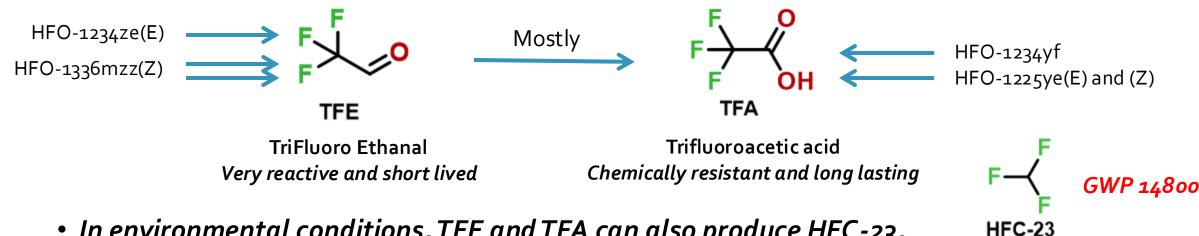
Image source: Hogue (ACS C&EN, 2022): How to define PFAS. https://cen.acs.org/policy/chemical-regulation/define-PFAS/100/i24



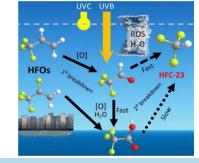
HFOs life cycle

• HFO production involves the use of carbon tetrachloride (CTC) and PCE as precursors.

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



- In environmental conditions, TFE and TFA can also produce HFC-23.
- Only takes a 1.1% HFO conversion into HFC-23 for a contribution of GWP > 150.



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



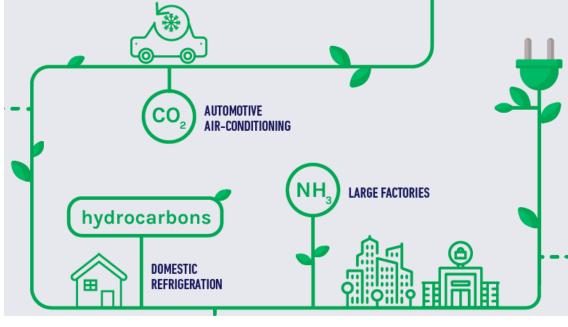
Alternatives to F-gas Refrigerants

HFOs are potentially regrettable substitutions.

Non F-gases have appropriate market readiness:

- *New CO2 designs offer operational cost 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)
- Ammonia (NH₃) is the preferred industrial refrigerant and is not used for domestic applications. *Ultra Low Charge (ULC)* NH₃ *systems* reduce but not completely eliminate acute toxicity and eutrophication related liabilities.

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



EPA ENERGY STAR Certified HC-based equipment:

- 600+ household fridges
- 700+ Lab Grade Refrigerators

Drop-in retrofitting substitutes vs. New equipment purchase

- 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.
- Retrofitted HVACR equipment generally exhibits lower efficiency than the newer models, contributing to avoidable indirect emissions.
- Payback period typically 0.7 years.*

- Growth of equipment manufacturers based on non-fluorinated refrigerants.
- Successful implementation in supermarkets, cold storage, and mobile refrigeration.
- Growing market share faster in the EU, given a more stringent F-gas policy.
- Feasibility is translating into wider adoption.
- Payback period <1 to 3 years.*
- Incentives can implemented to expedite transition.

Electrification of heat building management by heat pumps has a payback period of 5 years*, but that affects equipment based on any refrigerant.

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



Near future PFAS alternatives assessments at TURI

• PFAS detection:

- Total fluorine detection using Particle-induced gamma emission (PIGE): Sorting cosmetics, plastics, and water samples for further PFAS detection with more expensive (but precise) analysis.
- Laser Induced Breakdown Spectroscopy for PFAS semi-quantification.
- Integrate Artificial Intelligence (AI) for:
 - Data gap filling: Quantitative Structure-Activity Relationship (QSAR) to predict toxicity and environmental fate.
 - Tracking PFAS along the supply chain, in partnership with SmarterX[®].
 - Automatic database retrieval.



Too many unknown PFAS

sources and exposure due to

supply chain information loss

and trade secrets.

https://qsartoolbox.org/



https://smarterx.com/



PubChemPy/



Contact Us

Visit our website <u>www.turi.org</u> for **Resources**

- Databases and tools
 - <u>www.Cleanersolutions.org</u>
 - <u>https://P2OASys.turi.org</u>
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- Featured Videos
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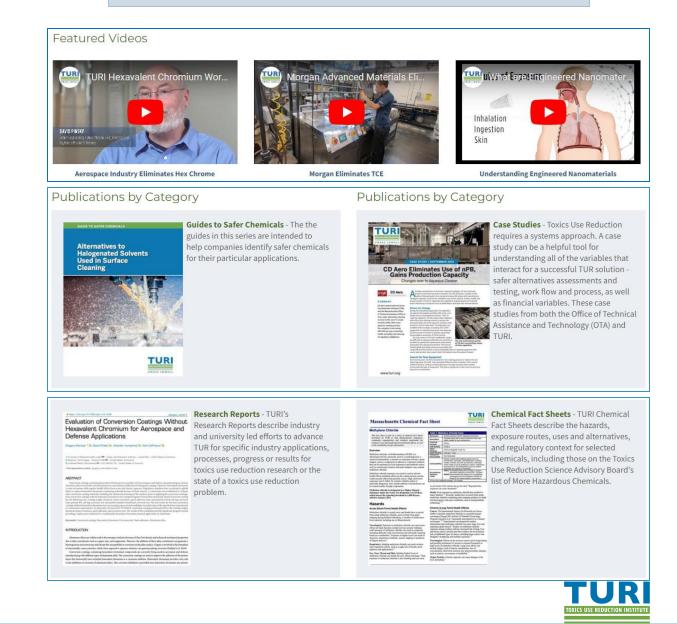
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