

INTRODUCTION TO PFAS AND FLUOROPOLYMERS

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Bio-Process Systems Alliance
Advancing Single-Use Worldwide



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PFAS are Related – But Different!



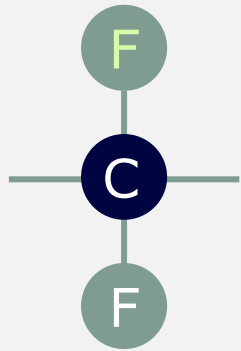
Overview

Per- and Polyfluoroalkyl Substances (PFAS)

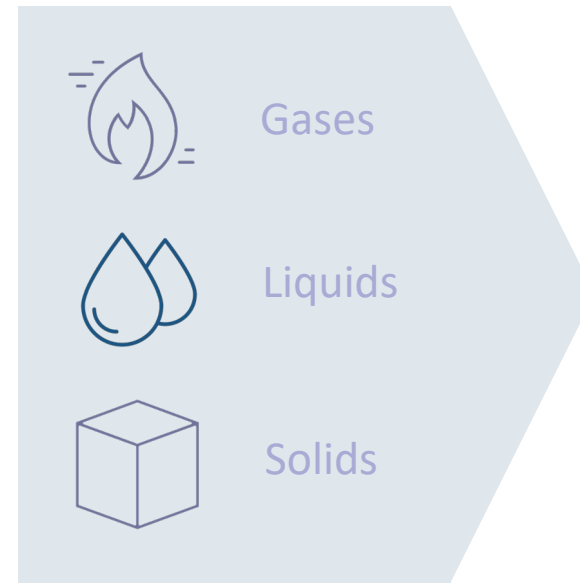
Thousands of PFAS

with a wide variety of properties

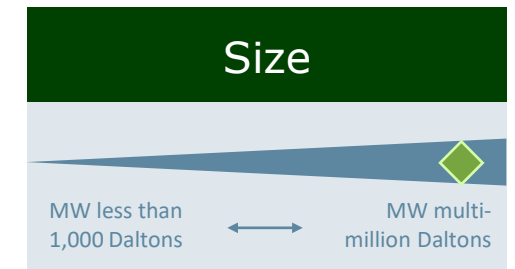
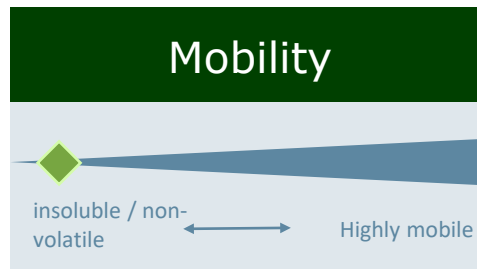
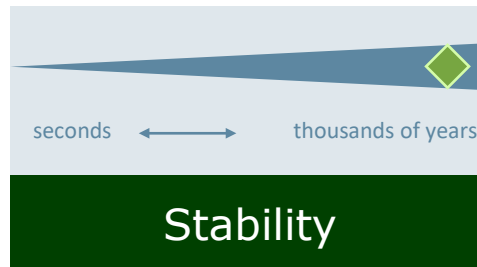
Similarities



Differences

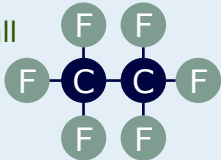
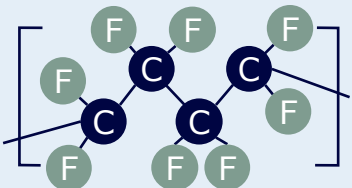
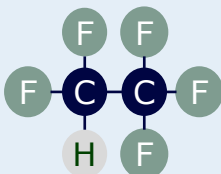
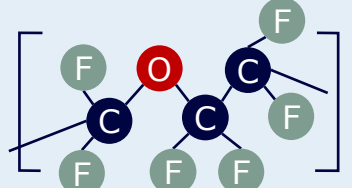
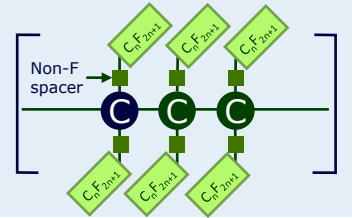


PTFE on the spectrum



Overview

Per- and Polyfluoroalkyl Substances (PFAS)

1 Group	PFAS Per- and Polyfluoroalkyl substances	
2 Categories	Non-Polymers	Polymers
5 Classes <div data-bbox="147 654 509 829">Perfluoroalkyl Acids (PFAAs) such as PFOA, PFOS, PFHxS, etc.</div>	Perfluoroalkyl Substances Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines 	Fluoropolymers Carbon-only polymer backbone with fluorines directly attached 
	Polyfluoroalkyl Substances Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines 	Polymeric Perfluoropolyethers Carbon and oxygen polymer backbone with fluorines directly attached to carbon  Side-chain Fluorinated Polymers Variable composition non-fluorinated polymer backbone with fluorinated side chains 

Per- and Polyfluoroalkyl Substances (PFAS)



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How many (commercialized) PFAS are there?

- OECD (2018): 4,730 PFAS
- US EPA (2019) 7,000 PFAS using CompTox Chemicals Dashboard
- PFAS # depends on the PFAS definition
 - Buck et al., 2011: highly fluorinated aliphatic (organic) substances with ≥ 1 C with all H replaced by F, so $C_nF_{2n+1}-$, when $n=1$, $F=3$
 - OECD 2018: highly fluorinated substances with ≥ 1 C with all H replaced by F, so they have ≥ 1 aliphatic PFC moiety, such as: $-C_nF_{2n}-$.
 - CA Environmental Contaminant Biomonitoring Program: chemicals containing ≥ 1 fully fluorinated C atom (CF_2 or CF_3)
- # of PFAS notified to EPA (TSCA PMN) \neq # of PFAS in commerce
 - 256 PFAS are "commercially relevant" globally (Buck et al., Integr Environ Assess Manag 2021;17:1045-1055.)
- TSCA Inventory lists >1,000 PFAS, of which ~ half are known to be commercially active within the last decade. (PFAS Action Plan)

Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

Barbara J Henry,† Joseph P Carlin,† Jon A Hammerschmidt,† Robert C Buck,‡ L William Buxton,‡ Heidelore Fiedler,§ Jennifer Seed,|| and Oscar Hernandez#*

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that are in the focus of researchers and regulators due to widespread presence in the environment and biota, including humans, of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Fluoropolymers, high molecular weight polymers, have unique properties that constitute a distinct class within the PFAS group...This paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that **fluoropolymers satisfy widely accepted assessment criteria to be considered as “polymers of low concern” (PLC)**. This review concludes that **fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS** and should be separated from them for hazard assessment or regulatory purposes. Grouping fluoropolymers with all classes of PFAS for “read across” or structure–activity relationship assessment is not scientifically appropriate.

OECD Polymer of Low Concern Criteria

13 Criteria



Polymer composition



MW, M_n ,
MWD



wt% oligomer



Electrical charge



Reactive Functional
Groups (RFG)



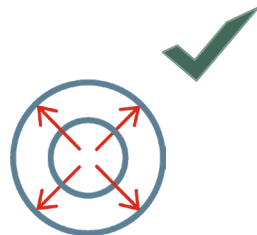
Functional Group
Equivalent Weight
(FGEW)



Low MW leachables



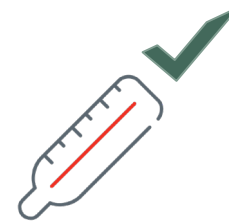
Water/lipid
solubility, octanol
water partition



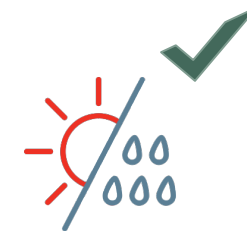
Particle size



Polymer stability



Thermal stability



Abiotic stability



Biotic stability

Fluoropolymers, generally, have low Health and Environmental Hazards

- These OECD PLC properties *are predictive* of low health and environmental hazard
- Not bioavailable - *Very high molecular weight* (and “rule of 5”) prevents crossing cell membrane
- Not toxic (Supplement to Henry et al., 2018)
- Not bioaccumulative (not bioavailable)
- Stable at environmentally relevant conditions
 - PTFE, for ex. is thermally stable for years at 260°C
 - Doesn't oxidize, hydrolyze, photolyze, not degraded by microorganisms
- Inert; not chemically reactive; *doesn't transform to PFAAs*
- Not mobile; not water soluble, doesn't adsorb to soil; not volatile

Fluoropolymers Toxicity and Clinical Data

PTFE, FEP, and a TFE/PAVE copolymer passed these GLP tests		
Cytotoxicity (MEM)	(ISO 10993-5)	Not Cytotoxic
Skin Sensitization	(ISO 10993-10; OECD 406)	Non-Sensitizing
Irritation	(ISO 10993-10; OECD 406)	Not Irritating
Acute Systemic Toxicity	(ISO 10993-11; OECD 408)	Not Toxic
90-Day Subchronic Systemic Toxicity	(ISO 10993-11; OECD 408)	Not Toxic
Two <i>In Vitro</i> + One <i>In Vivo</i> Genotoxicity	(ISO 10993-3; OECD 471, OECD 474, OECD 476)	Not Mutagenic
2- or 4-Week Implantation	(ISO 10993-6)	No Significant Response
Hemocompatibility	(ISO 10993-4; ASTM F756. ASTM F2382)	Hemocompatible

Note: 90-Day Subchronic Toxicity Studies included hematology, urinalysis, clinical chemistry, gross pathology, microscopic histopathology, organ weights, clinical observations. Histopathology performed on: ovaries, testes, brain, heart, liver, kidneys, spleen, thymus, adrenal glands, lymph nodes

45 years of patients receiving permanently implanted PTFE, FEP or TFE/PAVE copolymer cardiovascular medical devices demonstrate no chronic toxicity, carcinogenicity, reproductive, developmental or endocrine toxicity.

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Don't Group All PFAS Together

- PFAS: No structural similarities beyond -CF₃
- Presence of -CF₃ alone is not predictive of health or environmental hazard
- 5 Classes of PFAS do not share a mode of action. (Those with very high MW, like PLC fluoropolymers, are not even bioavailable to have a mode of action.)
- 5 classes do not share chemical or physical properties (e.g., MW, solubility, vapor pressure, mobility, stability, etc.)
- 5 Classes do not share toxicity endpoints
- Fluoropolymers, especially PLCs, should be separated from other PFAS

All PFAS are Hazardous ~ All Birds are Hazardous



Thank You

Questions?

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July 11, 2023

U.S. and EU PFAS Update

Owen P. Jappen

10th BPSA International Single-Use Summit

Agenda



01

STATES

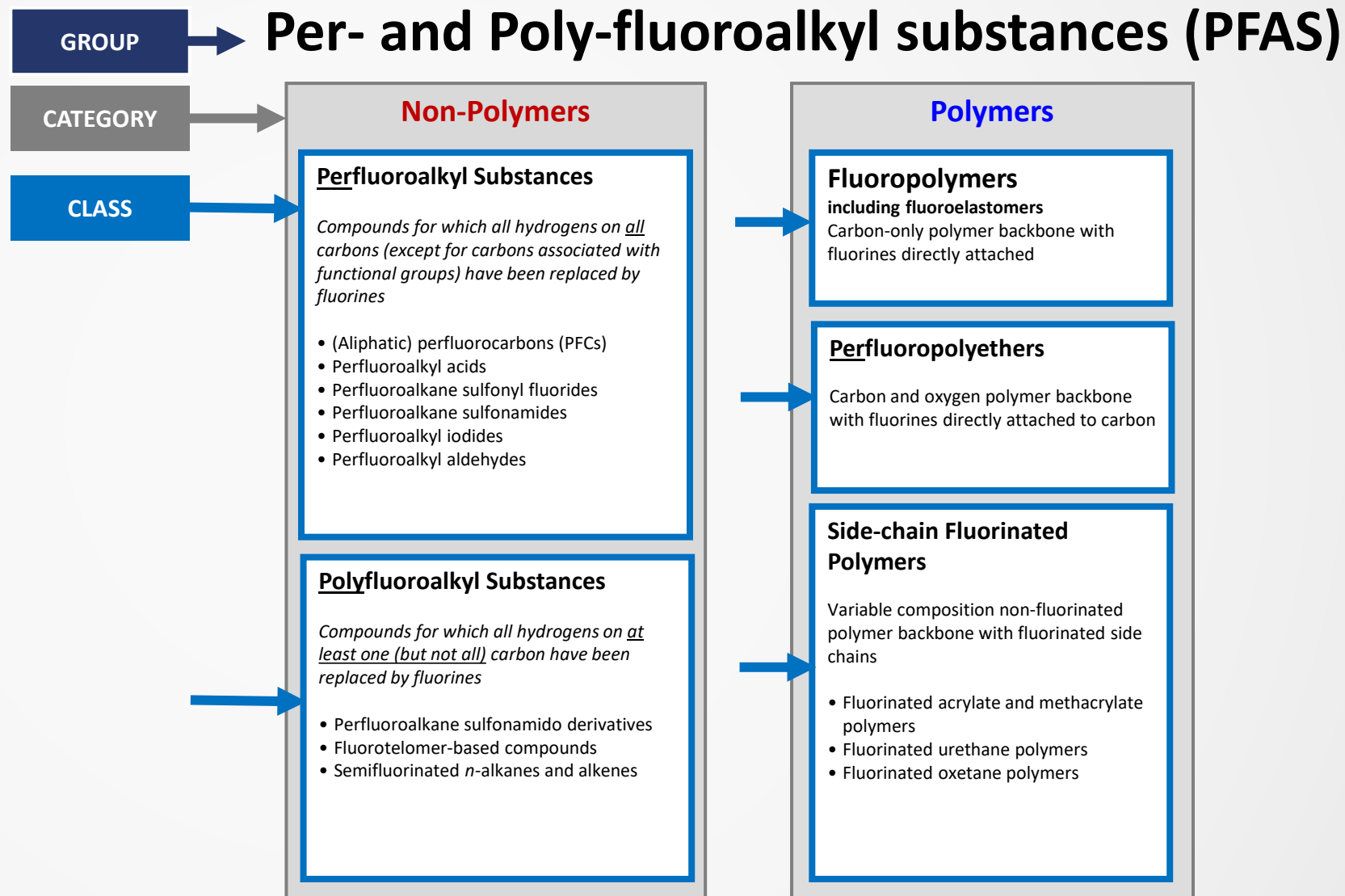
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FEDERAL

03

EUROPE

Not All PFAS Are The Same





2023 State Activity at a Glance

- 235+ PFAS-related bills introduced in 2023
- Issue areas
 - Bills restricting uses, some specific and some constructed broadly
 - Bills requiring notification of PFAS intentionally used in products
 - Maximum contaminant levels and clean up standards
 - Biosolids and relief for land (incl. groundwater) contaminated by PFAS
- Consistent use of a broad definition of PFAS
 - Fluorinated organic chemicals containing one fully fluorinated carbon atom (if it has but one CF_3 - or - CF_2 - group, it's in)

Maine

- Public Law 447 enacted July 15, 2021
- Beginning January 1, 2023:
 - Manufacturers of a product for sale in ME that contains intentionally added PFAS to submit written notification of product description, PFAS purpose, amount, etc. to Dept. of Env. Protection (DEP);
 - Prohibits sale of carpet/rug or fabric treatment that contains intentionally added PFAS.
- Over 2,000 companies were been granted notification deadline extensions to July 1, 2023.
- Multiple bills introduced to amend P.L. 477.
 - Proposed changes in those bills include modifying the definition of “PFAS”, extending the reporting deadline to 2025, eliminating the 2030 ban, adequately protecting confidential business information, small business exemption for reporting, and others.

Maine

- As of January 1, 2030, sale or distribution permitted only if DEP determines by rule that the use is “currently unavoidable”.
- [Proposed rule](#) defines “currently unavoidable use” as “essential for health, safety, or the functioning of society”
 - Includes, but is not limited to, technologies to address climate mitigation, critical infrastructure, delivery of medicine, lifesaving equipment, public transport, and construction.
 - Required by federal or state laws and regulations
 - [And](#) for which alternatives are not reasonably available.

Minnesota

Multi-Use Ban Bill

- Carpets and rugs
- Cleaning products
- Cookware
- Cosmetics
- Fabric treatments
- Juvenile products
- Ski wax
- Textile furnishings
- Upholstered furniture

Notification

- By January 1, 2025
- Fees to be established by rule
- Certificate of compliance

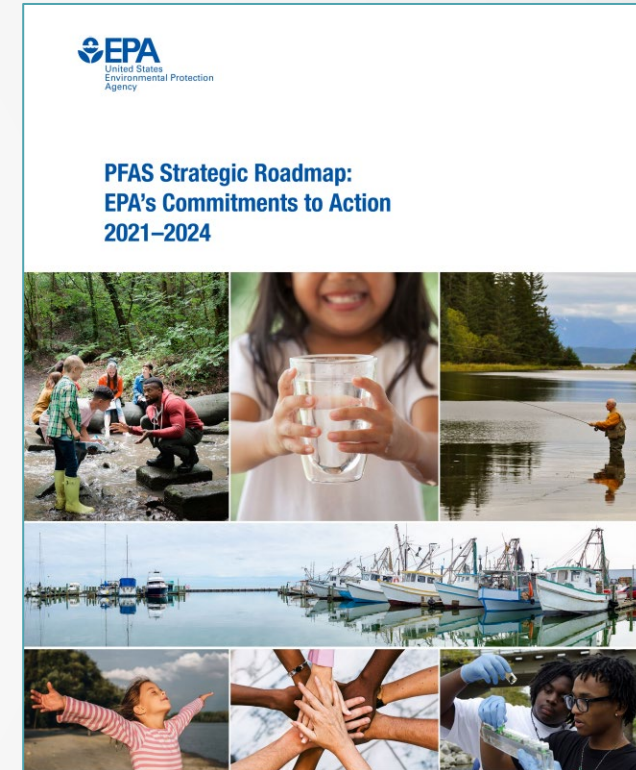
Currently Unavoidable Use

- January 1, 2030
- Determination by rule
- Can be specific products or categories of products

Federal

U.S EPA's PFAS Strategic Roadmap

- Three pillars: Research, Restrict, Remediate
- ~600 PFAS substances in commerce
- Strong focus on contaminated drinking water
- EPA working to identify groups (not one class)
- Risk-based approach
- Environmental justice considerations throughout
- Permanent disposal and/or destruction
- Validated methods
- Several future rulemakings (TSCA, air, water, etc.)



Proposed National Primary Drinking Water Regulation

- Proposed March 14, 2023 ([link to EPA website](#))
- Proposal includes PFOA, PFOS, PFNA, HPFO-DA, PFHxS, PFBS
- Would require public water systems to monitor, notify the public of levels, reduce levels if in exceedance of the proposed standard
- Proposed levels:
 - 4.0 ppt (ng/L) PFOA and PFOS
 - 1.0 (unitless) Hazard Index for others, assuming additive effects
- EPA hopes to finalize by the end of 2023

Proposed CERCLA Designation

- Designation of PFOA and PFOS as hazardous substances – proposed Sept 2022
- First time EPA has proposed to use CERCLA §102(a) listing authority
- Issues raised by the proposal
 - Potential for significant unintended consequences for local governments and others
 - Uncertainty about appropriate disposal/destruction approaches
 - Cleanup target levels defined by MCL, once established

Proposed TSCA 8(a)(7) Reporting Rule

- Mandated by National Defense Authorization Act (NDAA) of fiscal year 2020
- Requires electronic reporting of information regarding PFAS uses, production volumes, disposal, exposures, and hazards
- Manufacturers that manufacture or have manufactured covered chemical substances in any year since January 1, 2011.
- Articles containing PFAS, including imported articles, are in scope.
- Structural definition of PFAS:
 - Per and polyfluorinated substances that structurally contain the unit $R-(CF_2)-C(F)(R')R''$. Both the CF_2 and CF moieties are saturated carbons and none of the R groups (R , R' or R'') can be hydrogen

Proposed Significant New Use Rule (SNUR)

- Would apply to ~330 PFAS that are “Inactive” on the Toxics Substances Control Act Inventory and are not already subject to a SNUR.
- “Inactive” means that a substance has not been manufactured, imported, or processed in the United States since June 21, 2006.

Europe

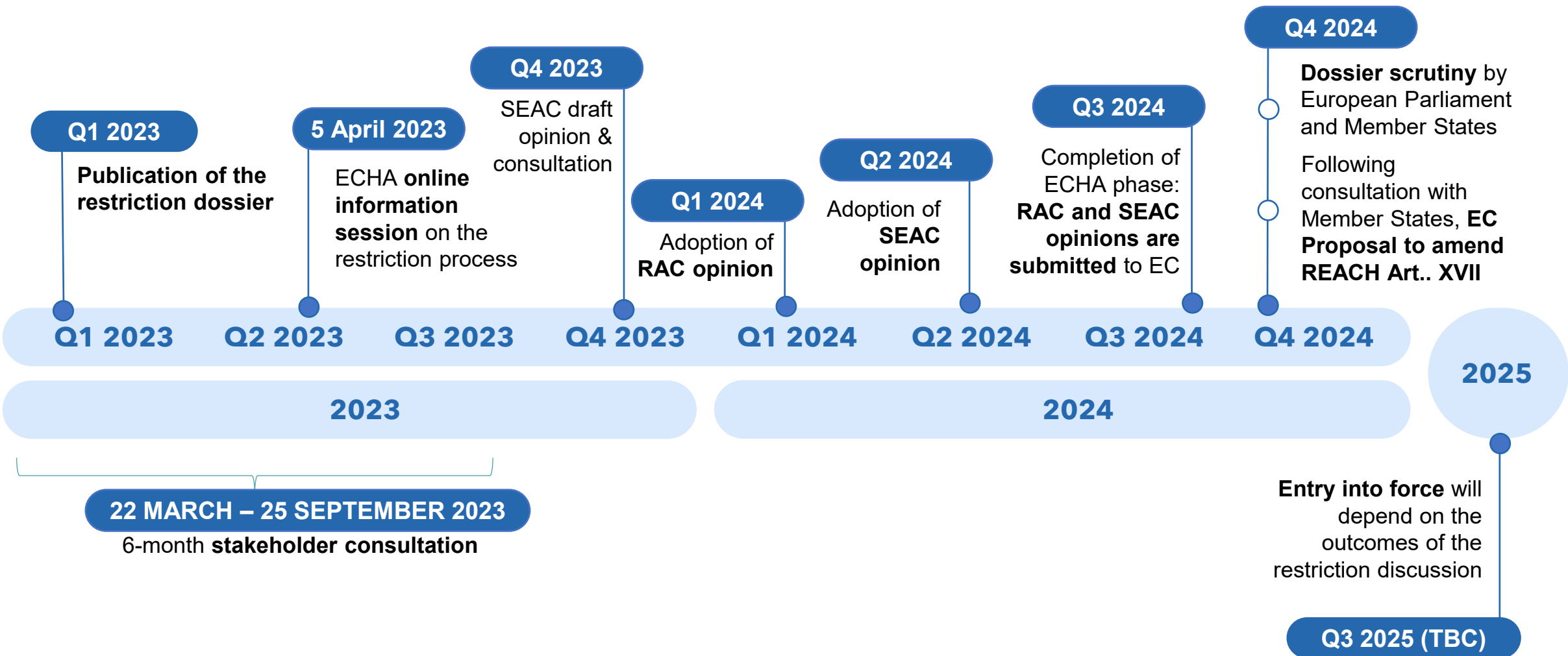
REACH Restriction Proposal

- Denmark, Germany, The Netherlands, Norway, and Sweden
- Envisions restricting the manufacture, placing on the market, or use of PFAS
 - Inclusive of PFAS-containing mixtures and articles
 - “[A]ny substance that contains at least one fully fluorinated methyl (CF₃-) or methylene (-CF₂-) carbon atom (without any H/Cl/Br/I attached to it)”
 - Some exemptions for plant protection and biocidal products, others
 - Covers PFAS broadly, including future “theoretical” PFAS, to avoid one PFAS being replaced with another
 - Proposes ban on the manufacture and use of all fluoropolymers in all applications

REACH Restriction Proposal

- PFAS manufacturing
- Fluorinated gasses
- Medical devices
- Transport
- Electronics and semiconductors
- Energy sector
- Consumer mixtures
- Cosmetics
- Ski wax
- Construction products
- Lubricants
- Petroleum and mining
- Textile, upholstery, leather, apparel and carpets
- Food contact materials and packaging
- Metal plating and manufacture of medical products

Tentative timeline of EU PFAS REACH Restriction: 2023-2025



REACH Restriction Proposal

- 18-month transition period after finalization (“entry into force”)
- Time-limited derogations (or lack thereof) are based on specific uses and the proposers’ understanding of the availability of suitable alternatives
- 1.5 years (transition period) for uses with no derogations
 - Chemical industry, pharmaceutical manufacturing, aerospace, military and defense, semiconductor manufacturing, water and wastewater treatment
 - Any use that does not have a proposed derogation mentioned in the text

**Thank
You!**

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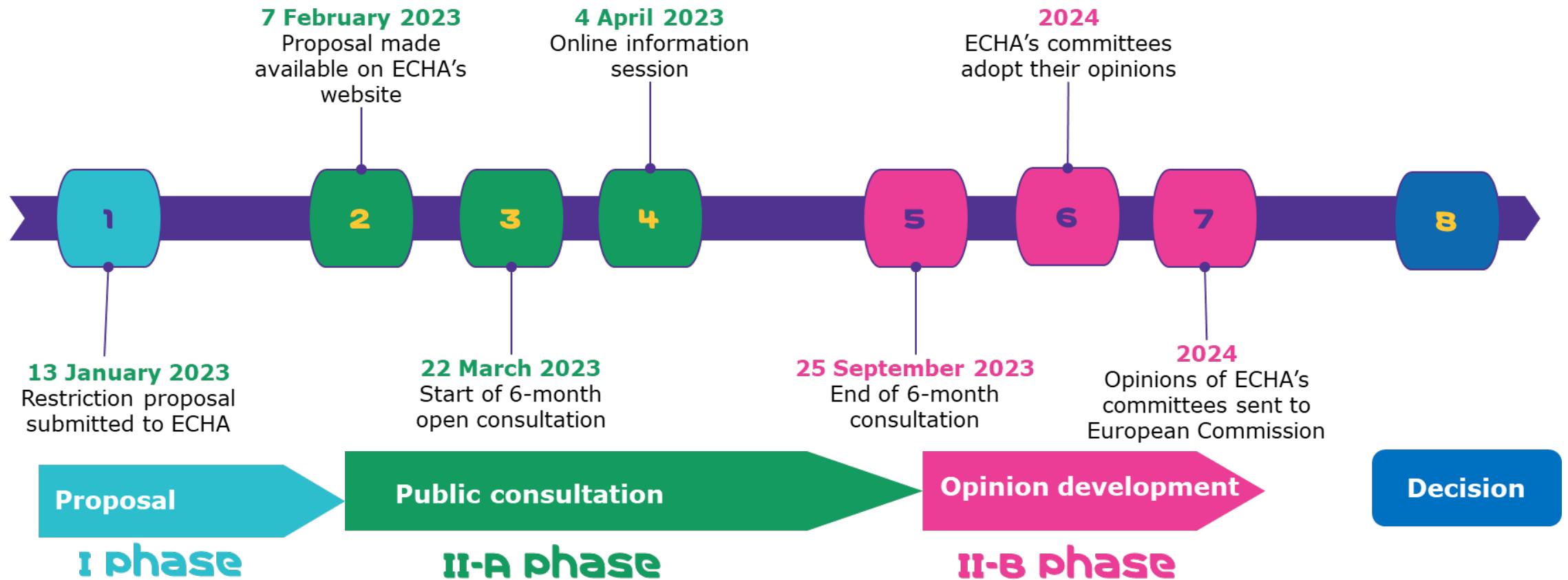
PFAS Customer Inquiries

COLLABORATION, TECHNOLOGY & INNOVATION: SHAPING THE FUTURE OF SINGLE-USE

Monica Cardona –Senior Program Manager, Single Use & Integrated Systems

JULY 10-JULY 12, FOUR SEASON HOTEL, WASHINGTON, DC

General Time-Line



Customer Inquiries - General

Have you performed an impact assessment?

Which Filtration & Single Use products are impacted?

**Have you identified replacements?
If so, provide alternate SKU's**

If not yet identified, What is your timeline for replacement, qualification & availability



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Customer Inquiries – Specific

- Which PFAS is contained in products supplied to us, CAS #, function and quantity used ?
- Do you use PFAS chemicals in the production process for any of the products you supply to us, or even for products not supplied to us?
 - This is primarily to aide us in cross contamination probability assessment.
- Do you suspect that the products we use could unintentionally contain PFAS?
 - If yes, could you let us know the rationale?

Customer Inquiries



Challenges

- For liquid (hydrophilic) applications, there are functional replacement options.
- For air/vent (hydrophobic) applications, functional replacement options currently limited/ challenging.