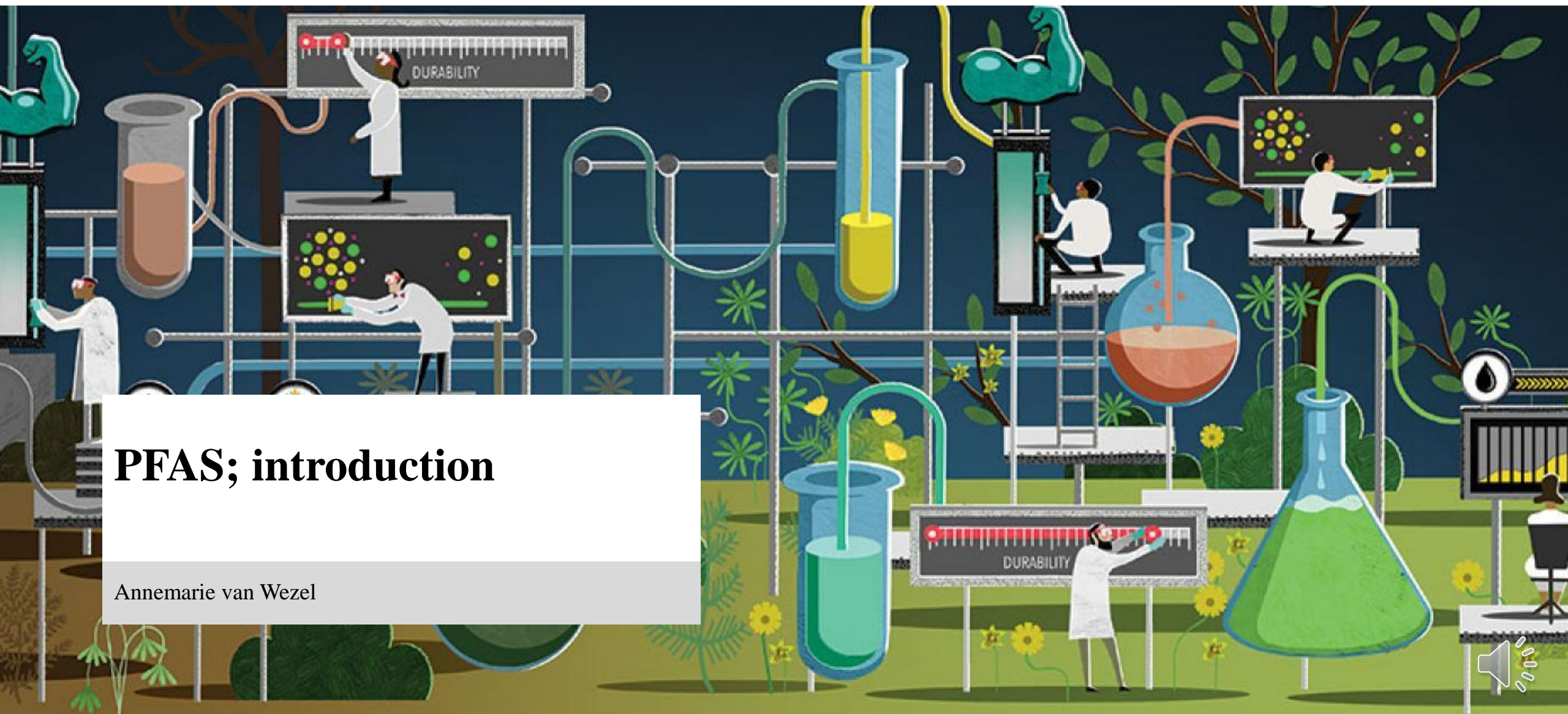


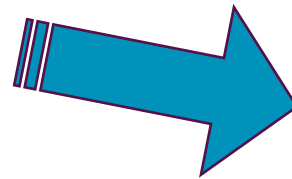


PFAS; introduction

Annemarie van Wezel



PFAS are used a lot for their nice properties



PFAS are used in almost all industry branches and in many consumer products

Industry branches

Aerospace (7)	Mining (3)
Biotechnology (2)	Nuclear industry
Building and construction (5)	Oil & gas industry (7)
Chemical industry (8)	Pharmaceutical industry
Electroless plating	Photographic industry (2)
Electroplating (2)	Production of plastic and rubber (7)
Electronic industry (5)	Semiconductor industry (12)
Energy sector (10)	Textile production (2)
Food production industry	Watchmaking industry
Machinery and equipment	Wood industry (3)
Manufacture of metal products (6)	

Other use categories

Aerosol propellants	Metallic and ceramic surfaces
Air conditioning	Music instruments (3)
Antifoaming agent	Optical devices (3)
Ammunition	Paper and packaging (2)
Apparel	Particle physics
Automotive (12)	Personal care products
Cleaning compositions (6)	Pesticides (2)
Coatings, paints and varnishes (3)	Pharmaceuticals (2)
Conservation of books and manuscripts	Pipes, pumps, fittings and liners
Cook- and bakingware	Plastic, rubber and resins (4)
Dispersions	Printing (4)
Electronic devices (7)	Refrigerant systems
Fingerprint development	Sealants and adhesives (2)
Fire-fighting foam (5)	Soldering (2)
Flame retardants	Soil remediation
Floor covering including carpets and floor polish (4)	Sport article (7)
Glass (3)	Stone, concrete and tile
Household applications	Textile and upholstery (2)
Laboratory supplies, equipment and instrumentation (4)	Tracing and tagging (5)
Leather (4)	Water and effluent treatment
Lubricants and greases (2)	Wire and cable insulation, gaskets and hoses
Medical utensils (14)	

OECD list; 4730 PFAS

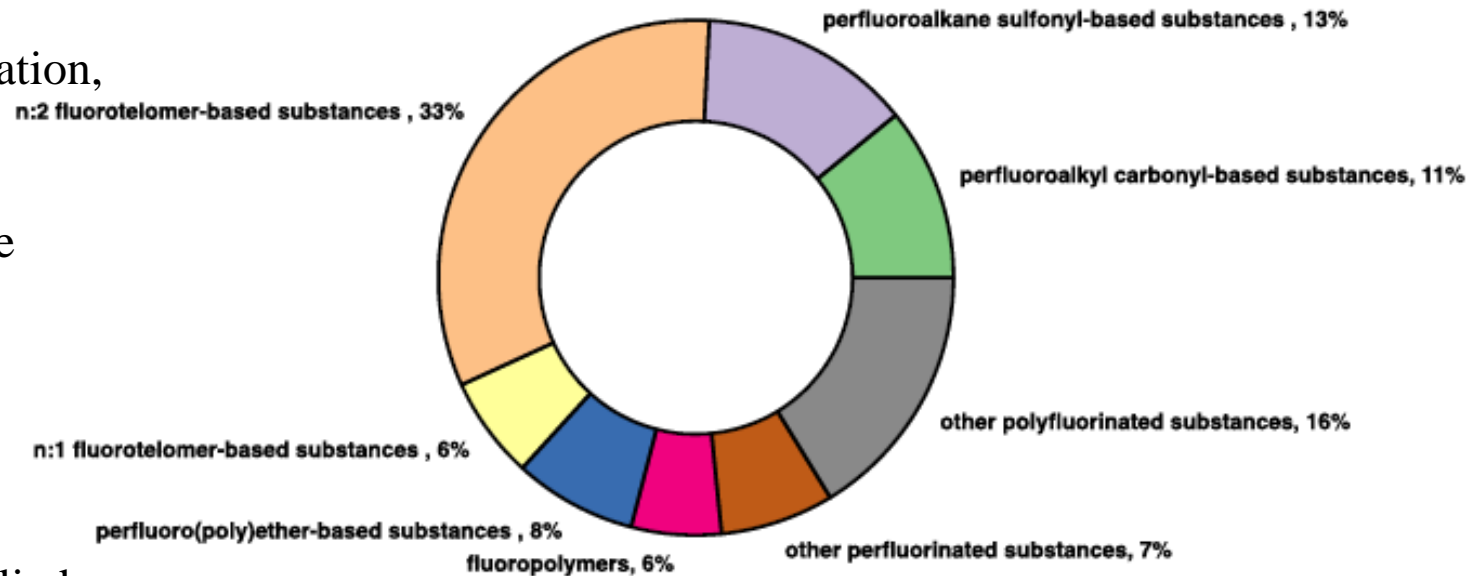
Never more in focus than now (AFFF contamination, EU phase-out, Hollywood movies, etc.)

New PFAS often shorter C-chains and thus more mobile

Ca. 1000 preregistered and 107 registered in REACH, 2 as pesticides

All other PFAS should not be made, traded, applied or used

Severe scarcity on emission data!



The Grand Challenge of PFAS

In 2018, OECD published an updated PFAS List

- Over 4,000 CAS numbers identified
- Commonality is that they are, or break down to form, highly persistent substances

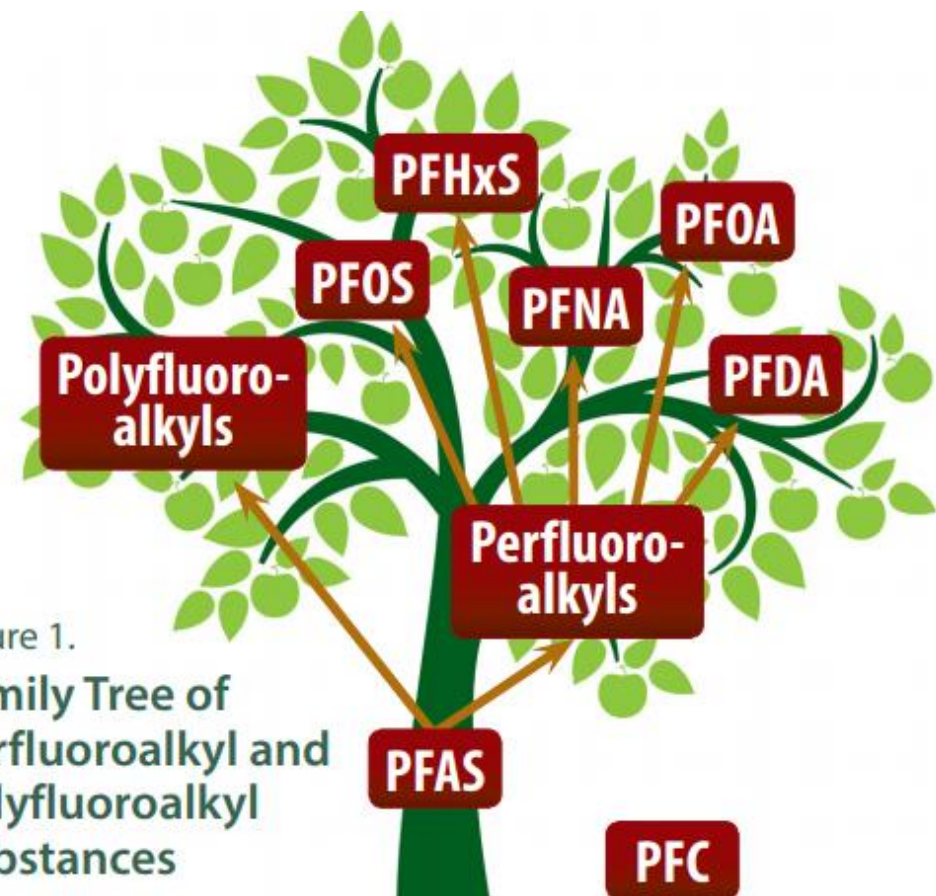
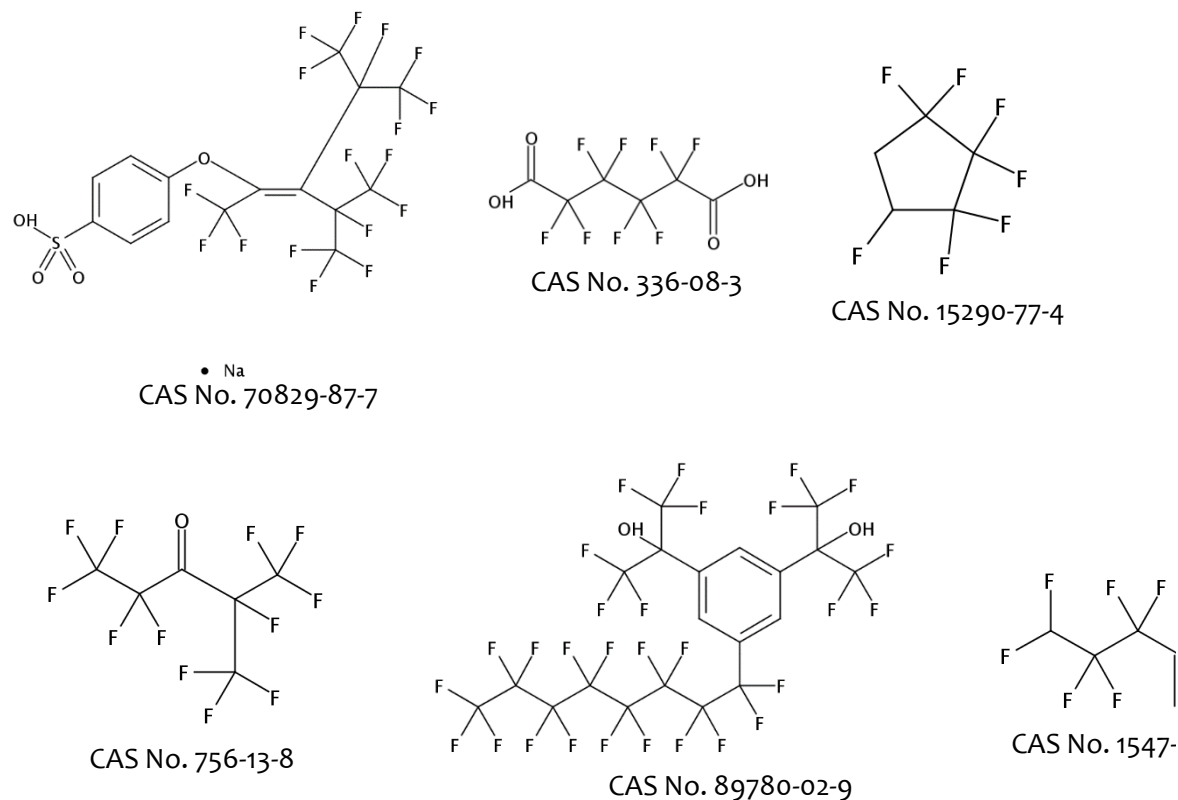
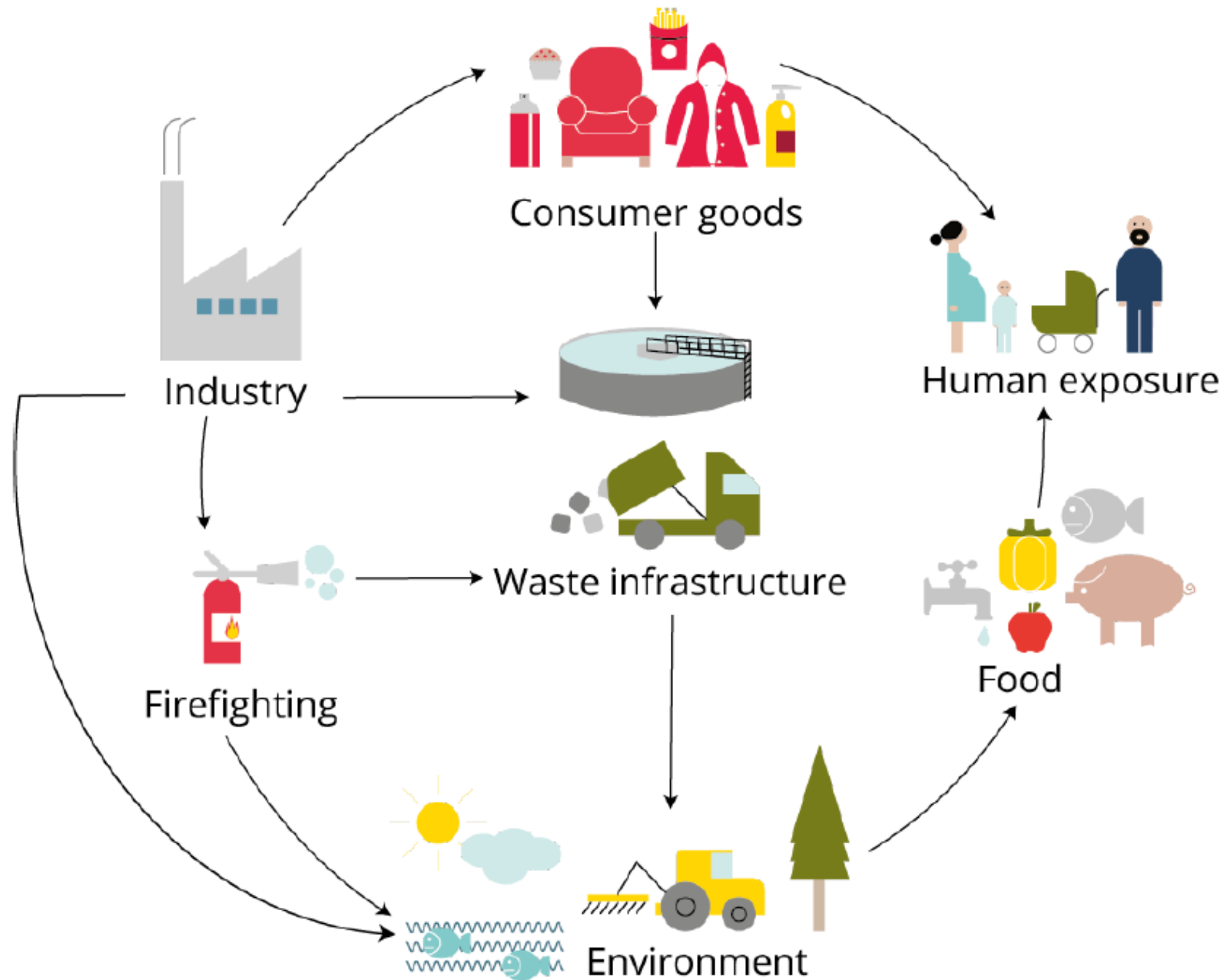


Figure 1.
Family Tree of
perfluoroalkyl and
polyfluoroalkyl
Substances

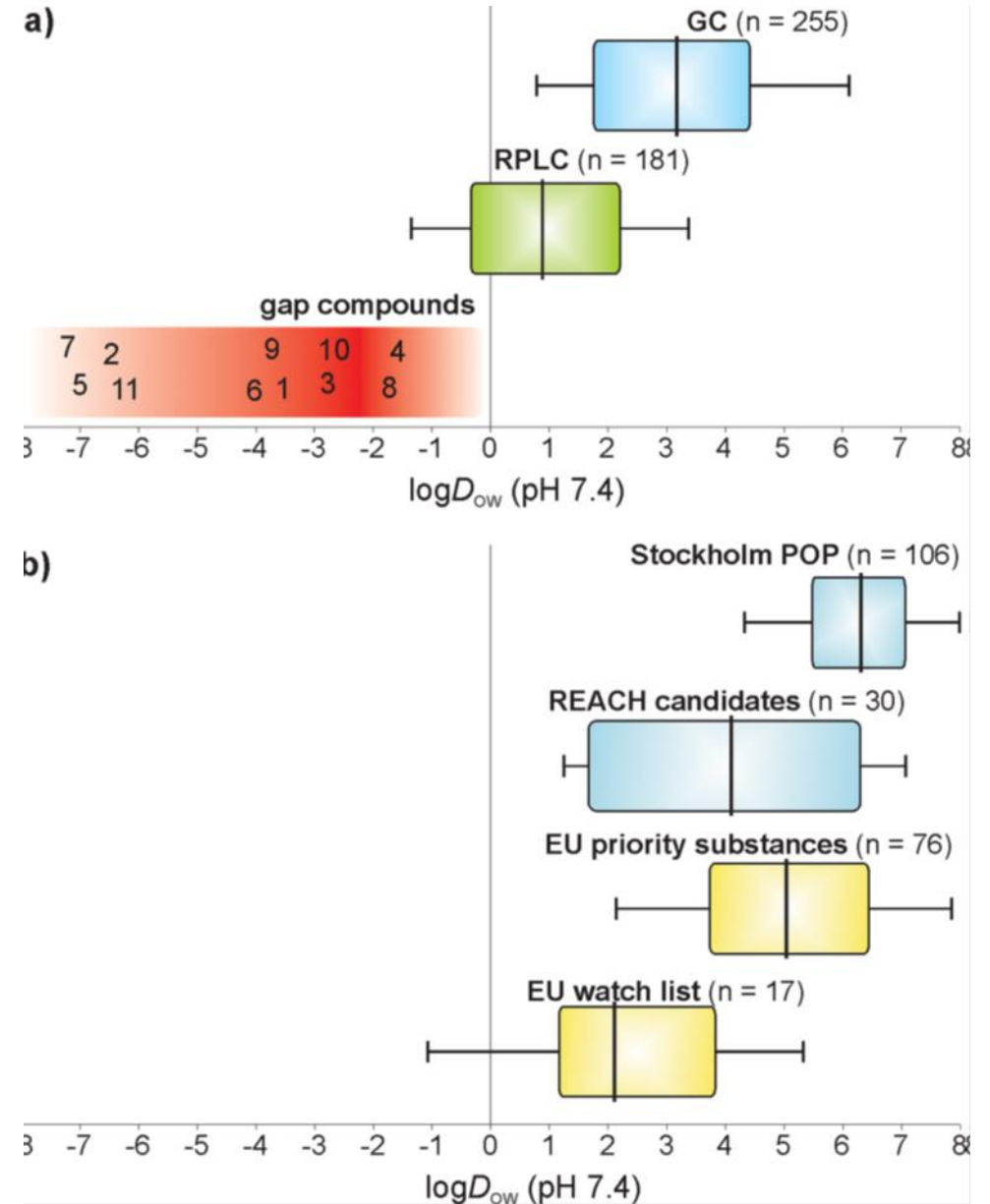


PFAS are PMT compounds

Mind the gap!

More polar chemicals are;

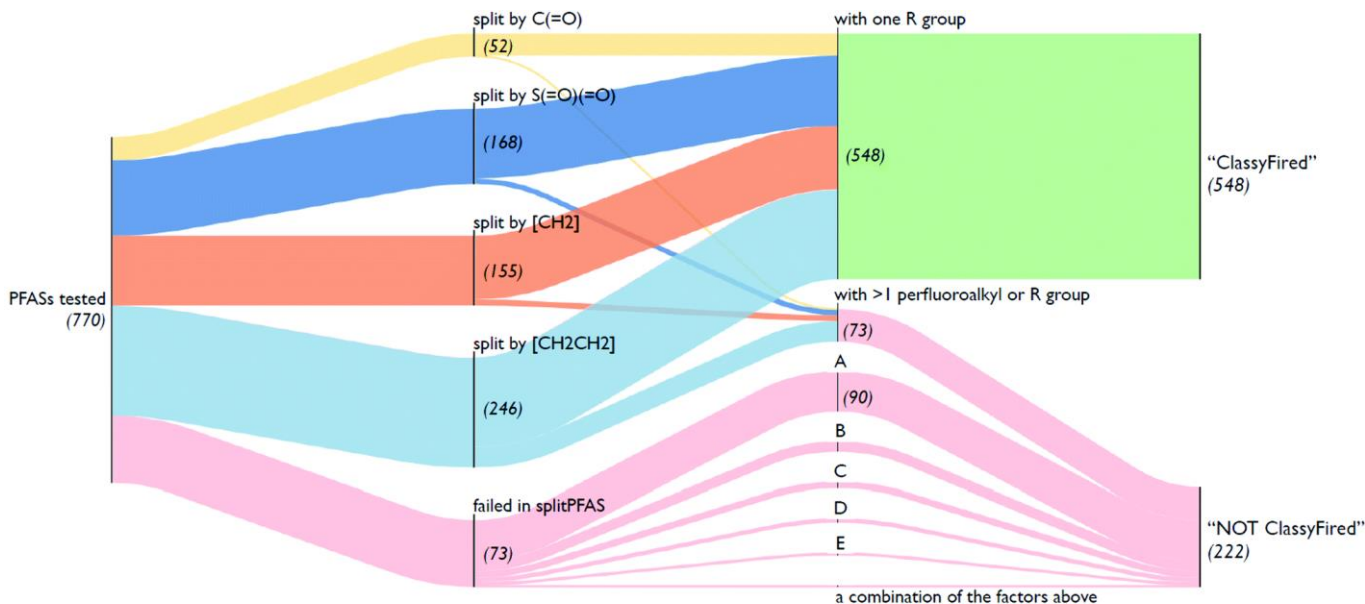
- Less regulated
- Less easy to measure analytically
- Less easy to remove in water treatment



Analytical methods

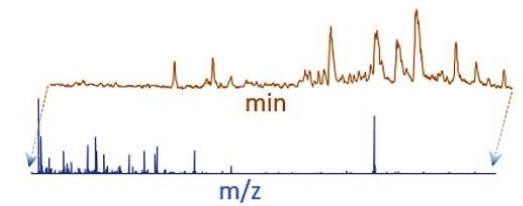
High resolution MS, combined with suspect lists (eg NORMAN PFAS list)

→ more than 750 PFASs, belonging to more than 130 diverse classes, found in strategically selected environmental samples, biofluids or commercial products



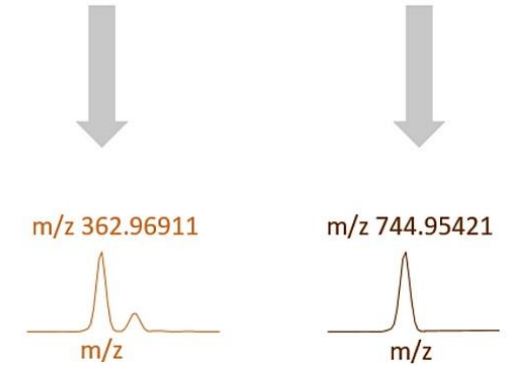
Cases failed in splitPFAS:
A: X not in pre-defined SMARTS; B: POLY-, NOT PER-fluoroalkyl; C: R = fluorine; D: branched/cyclic perfluoroalkyl chain; E: unsaturated perfluoroalkyl chain

(1) HRMS full-scan data



(2) prospective PFAS feature identification

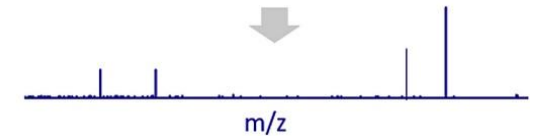
- feature reduction
- mass defect filtering
- homologous series searching
e.g. CF₂-normalized mass defect plots
- study design
e.g. case-control
- diagnostic fragments or neutral losses
e.g. data-dependent acquisition
data-independent acquisition
all-ion-fragmentation
in-source fragmentation
- parallel HRMS & F-detection instruments



(3) molecular formula assignment

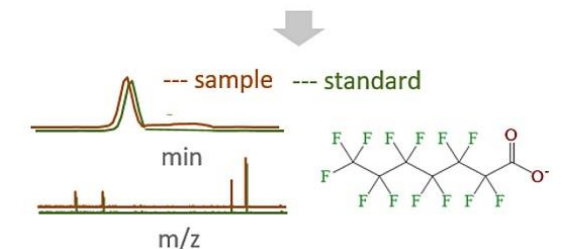
C₇F₁₃O₂⁻ 0.8 ppm
C₁₀F₁₁H₂S⁻ -2.4 ppm
...

(4) structural characterization by MSⁿ (n≥2)



(5) Structural proposal & confirmation

- based on MSⁿ profiles
- matching to database suspects
- standard comparison



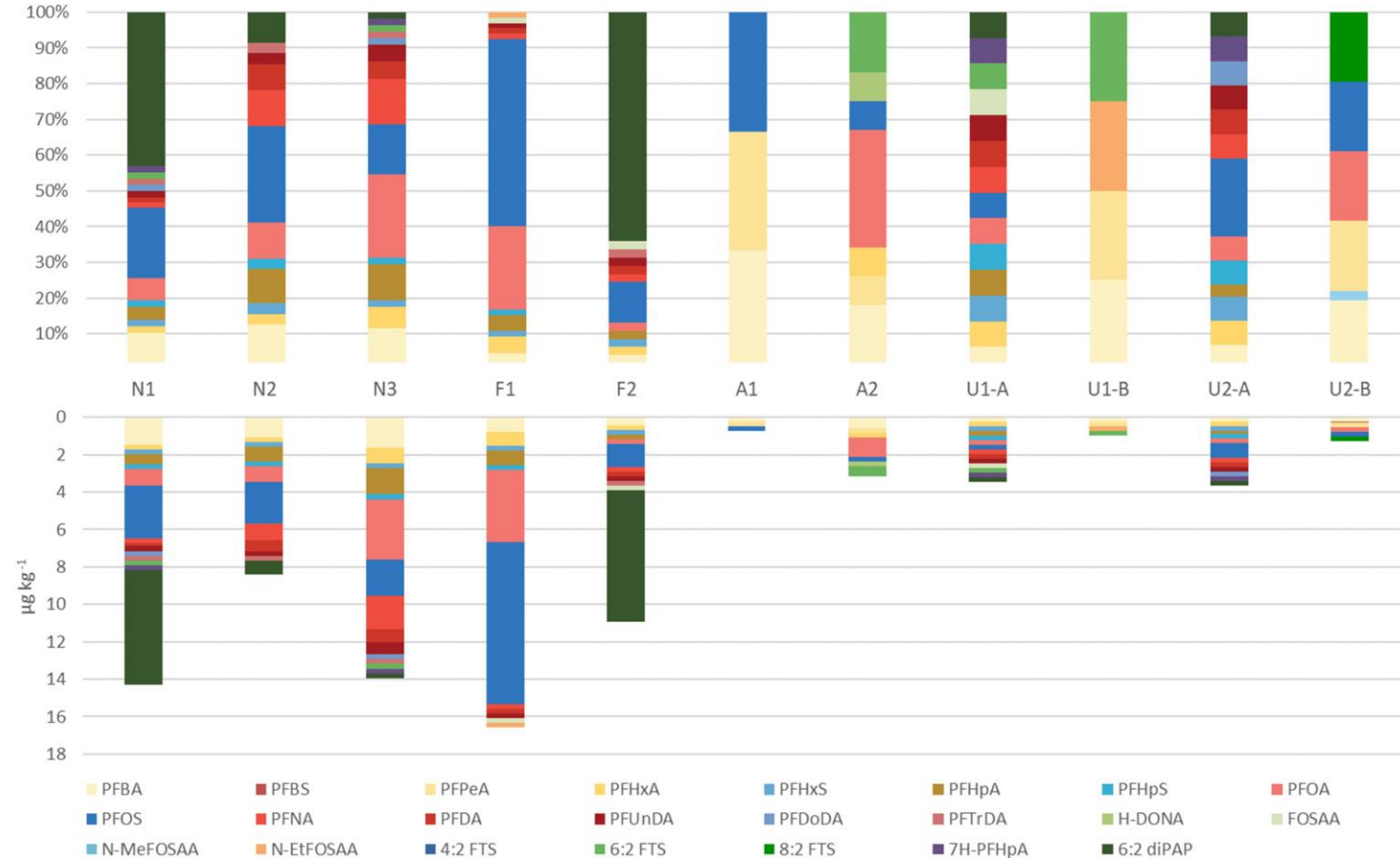
Heterogeneity in occurrence

Germany 41 PFAS including perfluoroalkyl acid (PFAA) precursors, ESB

Of 100 environmental samples only one sample was PFAS free

Due heterogeneity... no means to derive general environmental background levels

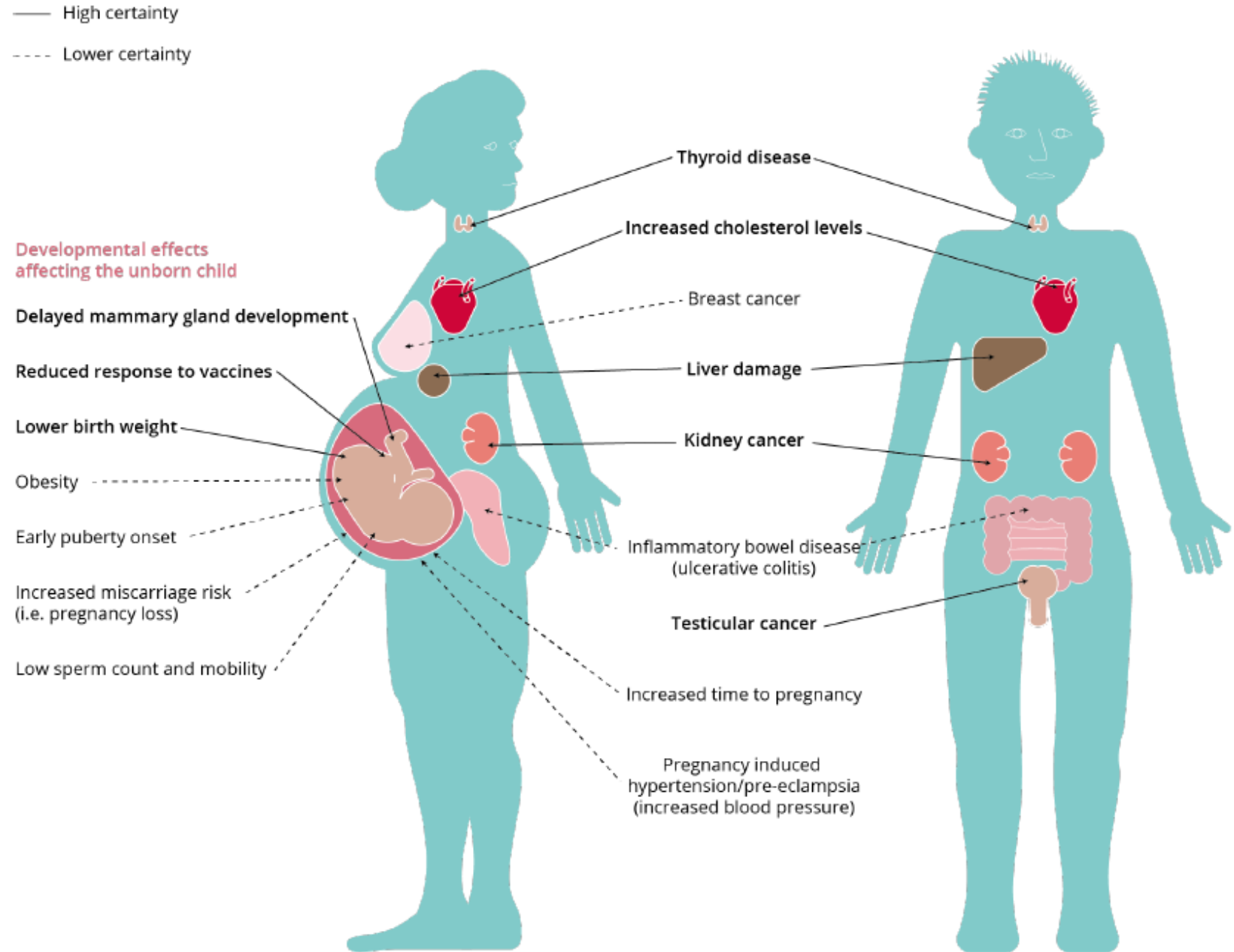
PFAS present in soils across the globe



Health effects

Associations between PFAS exposure and human health effects; eg obesitas after prenatal exposure, lipid metabolism, immune system, liver failure, renal function, thyroid hormone – important for cognitive development.

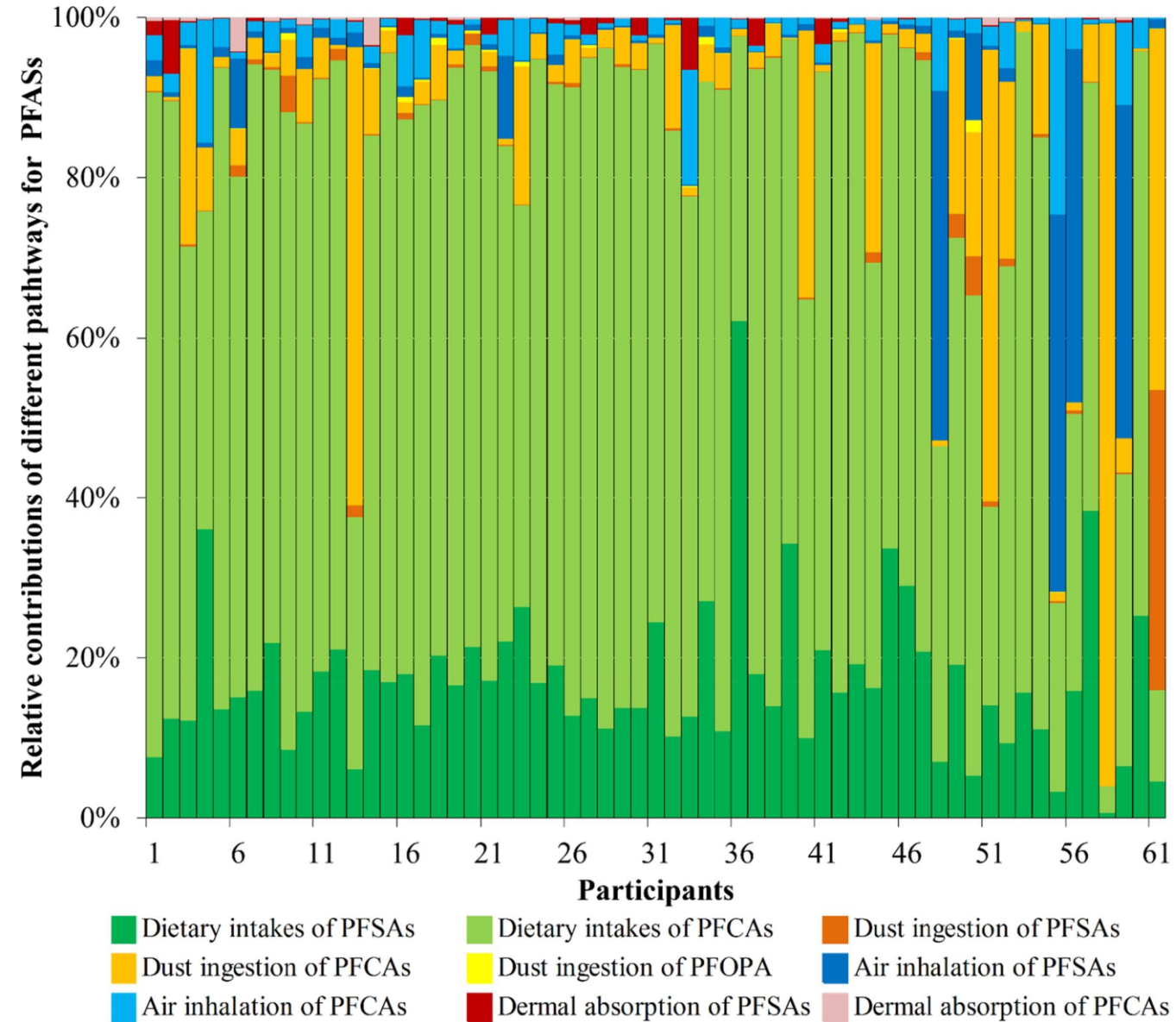
For most PFAS no well established risk assessment and ADI derived.



Human exposure

Dietary exposure from food and drinks
predominant exposure pathway

House dust, indoor air, hand wipes of less
importance



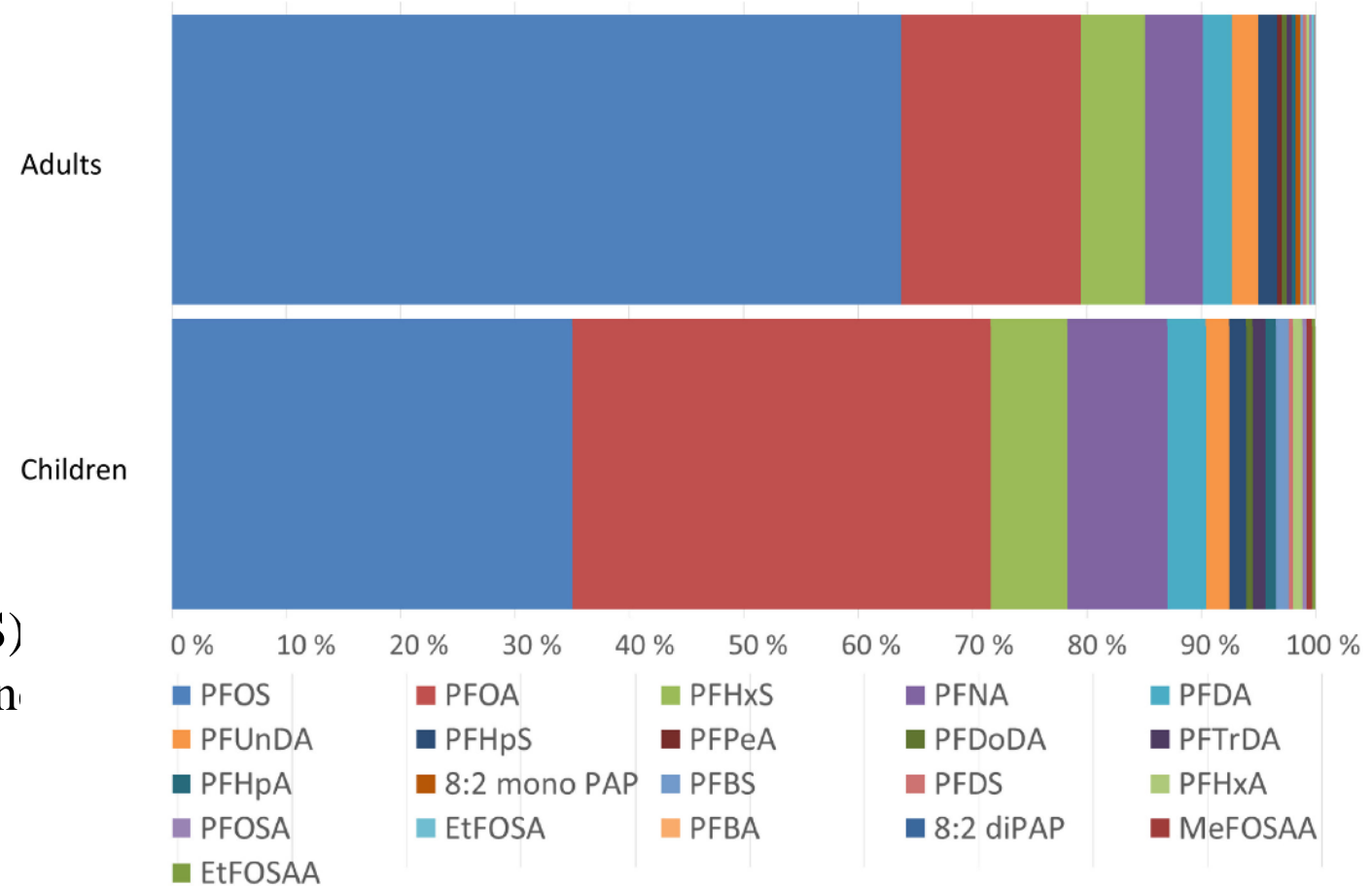
EFSA opinion (sep '20)

EFSA '20 propose single group TWI of 4.4 ng/kg bw per week for sum PFOA, PFNA, PFHxS and PFOS

Europeans partly exceed this TWI, which is of concern

Seven most prominent PFASs (PFOS, PFOA, PFHxS, PFNA, PFDA, PFUnDA, 2626 PFHpS) contributed with 96.6% and 93.4% for adults and children, respectively

Decreasing concentrations have been observed for PFOS, PFOA and in some studies PFHxS after 2000, while concentrations of PFNA, PFDA and PFUnDA increased.



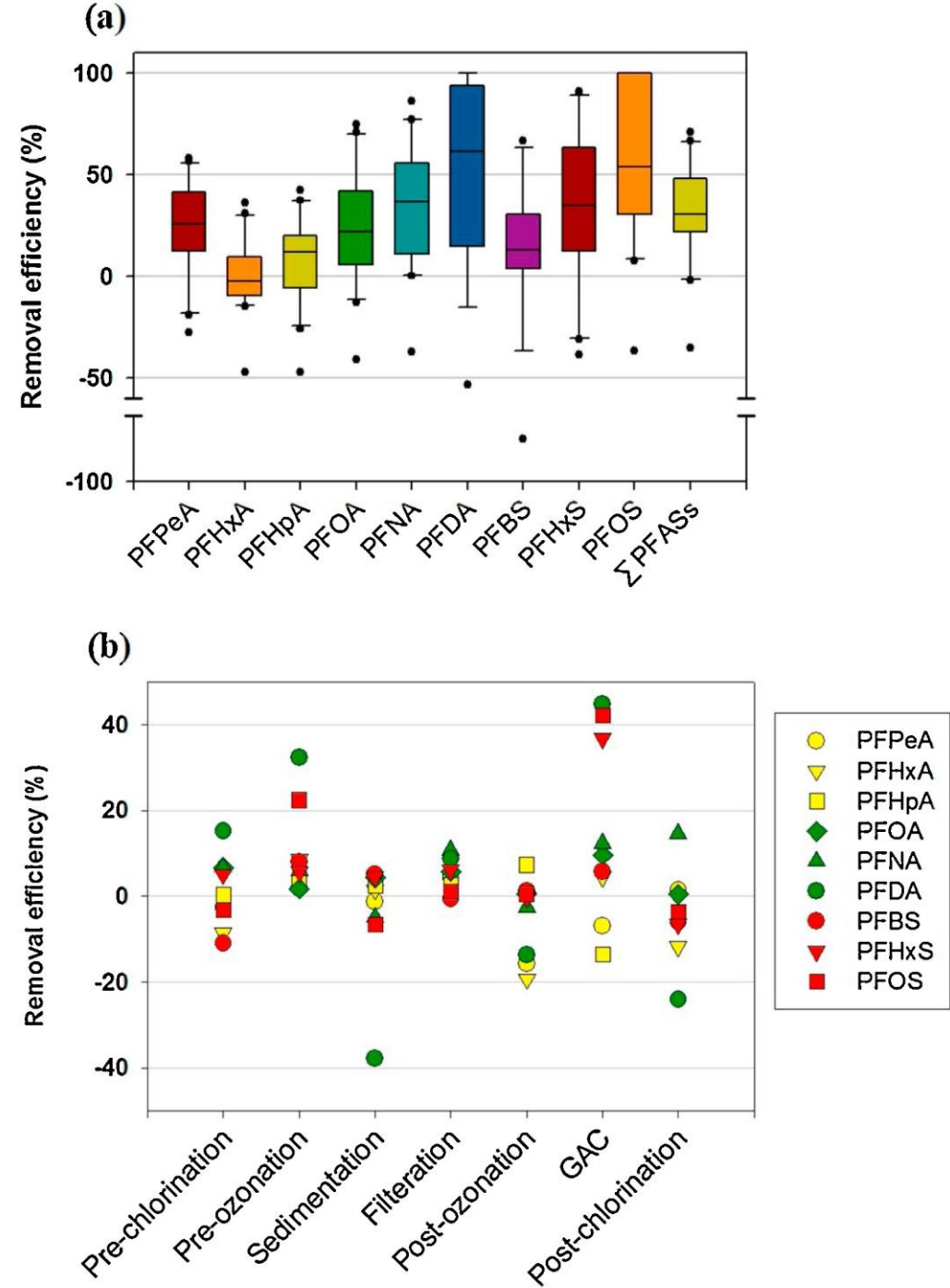
Environmental health

Worldwide PFAS found in environmental organisms. Most PFAS detected in the environment reported concentrations are below predicted no effect concentration. However, lack of information on new PFAS, precursors and degradation products, mixture toxicity → our understanding is incomplete



Removal efficiencies

Removal efficiency increase as the perfluorocarbon chain length increase



Policy responses

Continued use → increased environmental concentrations

Two PFAS groups are identified as SVHCs based on PMT, i.e. GenX and perfluorobutane sulfonic acid (PFBS), replacers of PFOA and PFOS respectively

PFOS and derivatives are priority hazardous substance under EU WFD, with EQS limit value of 0.65 ng/L in surface waters. Report on compliance with the PFOS EQS by 2021. Samples taken in 2013 in Northern Europe exceed EQS in 27% of river sites and 94% of Baltic Sea and Kattegat seawater (Nguyen et al., 2017).

Current call for evidence on broad PFAS restriction, with a possible date of entry in 2025.



Essential elements for a Chemicals strategy for sustainability

Legislation (OS-OA), chemical design & essentiality, technology



Essential use?

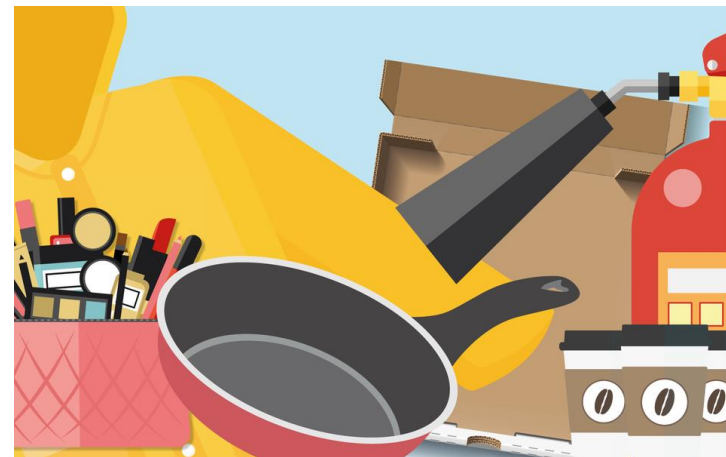


Table 1 Three essentiality categories to aid the phase out of non-essential uses of chemicals of concern, exemplified with PFAS uses

Category	Definition	PFAS examples
(1) “Non-essential”	Uses that are not essential for health and safety, and the functioning of society. The use of substances is driven primarily by market opportunity	Dental floss, water-repellent surfer shorts, ski waxes
(2) “Substitutable”	Uses that have come to be regarded as essential because they perform important functions, but where alternatives to the substances have now been developed that have equivalent functionality and adequate performance, which makes those uses of the substances no longer essential	Most uses of AFFFs, certain water-resistant textiles
(3) “Essential”	Uses considered essential because they are necessary for health or safety or other highly important purposes and for which alternatives are not yet established ^a	Certain medical devices, occupational protective clothing

^a This essentiality should not be considered permanent; rather, a constant pressure is needed to search for alternatives in order to move these uses into category 2 above.



Essentiality & benign-by-design

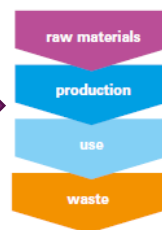
Necessary for
health, safety or
critical for societal
functioning



No available technically
and economically
feasible non-chemical
alternatives



LINEAR ECONOMY



PRODUCT CHAINS WITH RECYCLING

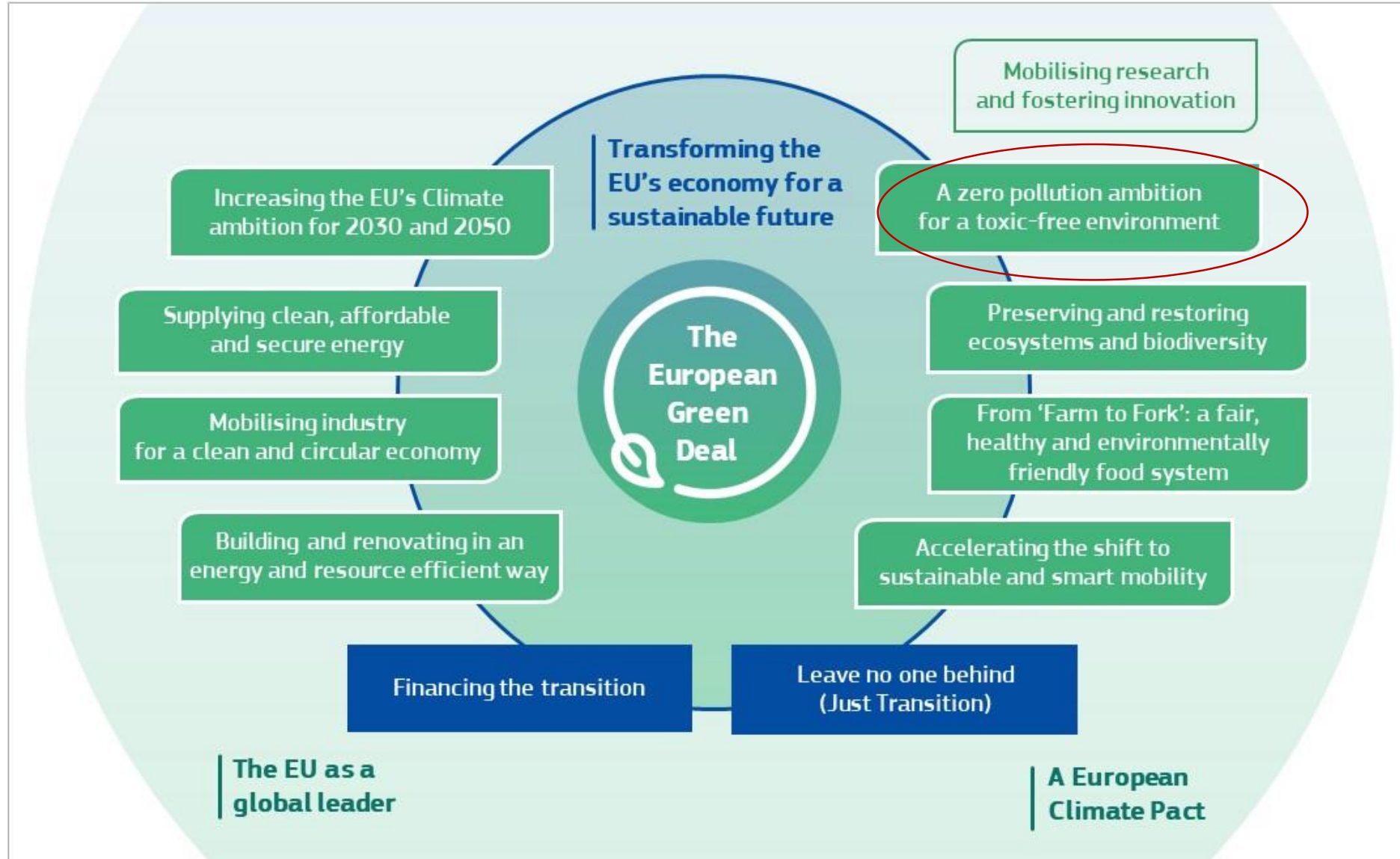


CIRCULAR ECONOMY



Equal/better functionality
Less hazardous
Less persistent/More durable
Lower emissions

Dec 2019: EU Green Deal





Innovative Training Network (ITN) to train a new generation of creative, entrepreneurial and innovative ESRs, able to face current and future challenges and to convert knowledge and ideas into products and services for economic and social benefit

Started: 1st Jan 2020, Ends: 31st Dec 2023

15 'Early Stage Researchers' (ESRs)

Based at 13 'Beneficiaries' from 6 countries (Sweden, Germany, Netherlands, Norway, Switzerland, UK) – VU & UvA in NL

11 'Partner' organizations – KWR in NL



PERFORCE³

AIMS

Develop analytical tools to better characterize total PFAS exposure

Improve understanding of **PFAS exposure pathways and health effects** in humans

Find **solutions to PFAS contamination** problems

Improve communication with policy makers, stakeholders, general public

Train the **next generation of scientists** to face future challenges, fostering creativity, innovation and entrepreneurship

Equip young researchers with **research and transferable skills and competences**

Enhance career perspectives through international, interdisciplinary and intersectoral **mobility** opportunities

STRUCTURE

Multidisciplinary, multisectoral network

WP1: Analytical tools and exposure science (ESRs 1, 2, 3, 4, 5,)

WP2: Toxicology and epidemiology (ESRs 6, 7, 8, 9, 10)

WP3: Solutions (ESRs 11, 12, 13, 14, 15)

WP4: Translation of research results for regulatory and/or stakeholder uses (All ESRs)

WP5: Training (All ESRs)

WP6: Network management (Project management team)

WP7: Dissemination and outreach (All ESRs)

OUTCOME

Advanced **understanding** of PFASs

Improved risk assessment **framework and policies**

Alternative **green chemistries**

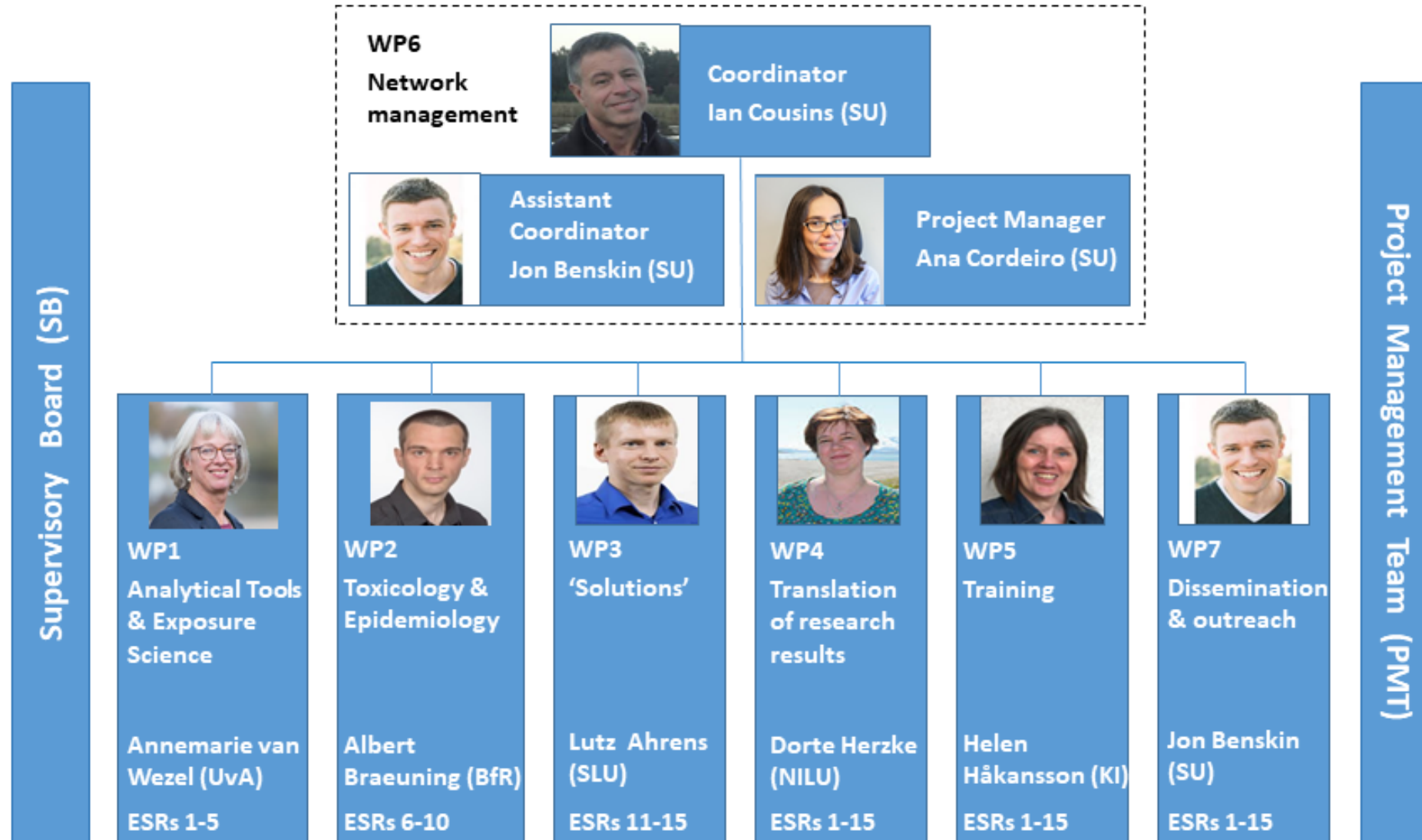
New tools for **remediation** and environmental **monitoring**

New thinking for improved **health protection** and promoting **societal sustainability**

Improved EU doctoral training addressing needs of academic and non-academic employers

Next generation of (15) **internationally competitive creative scientists and innovators** with **broad career perspectives** across multiple sectors

PERFORCE³



Network Assembly (NA)