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WtERT Biennal Conference 2024

Sustainable Waste Management: pushing the forefront of innovation

New York, 2-4 october 2024

PFAS characterization and behavior in Waste-to-Energy technologies

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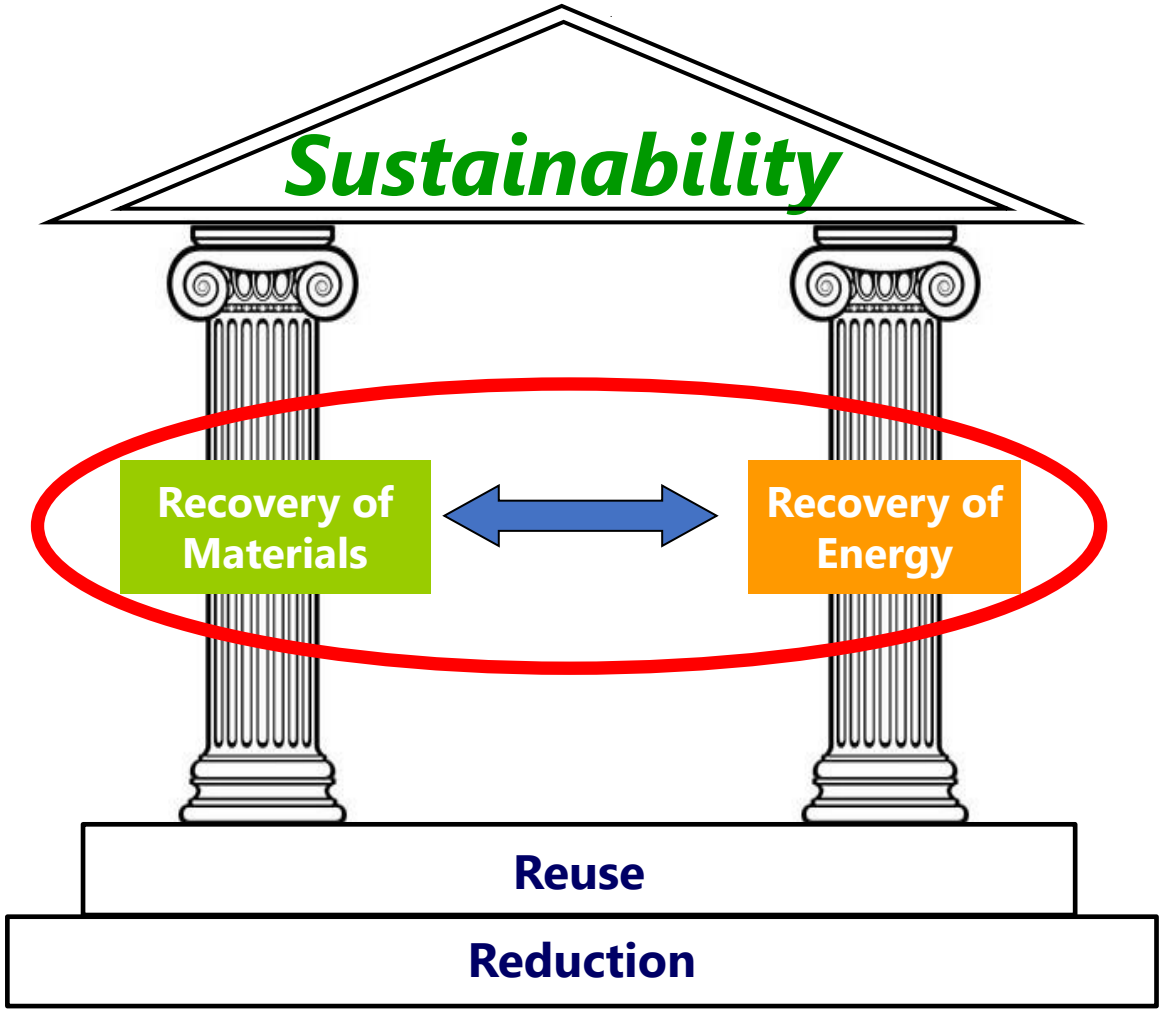


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MatER (Materials & Energy from Residues) Study Center approach

Our Mission



Recovery of Materials and Energy are both necessary for Sustainability

Strict interconnection between material / energy recovery:

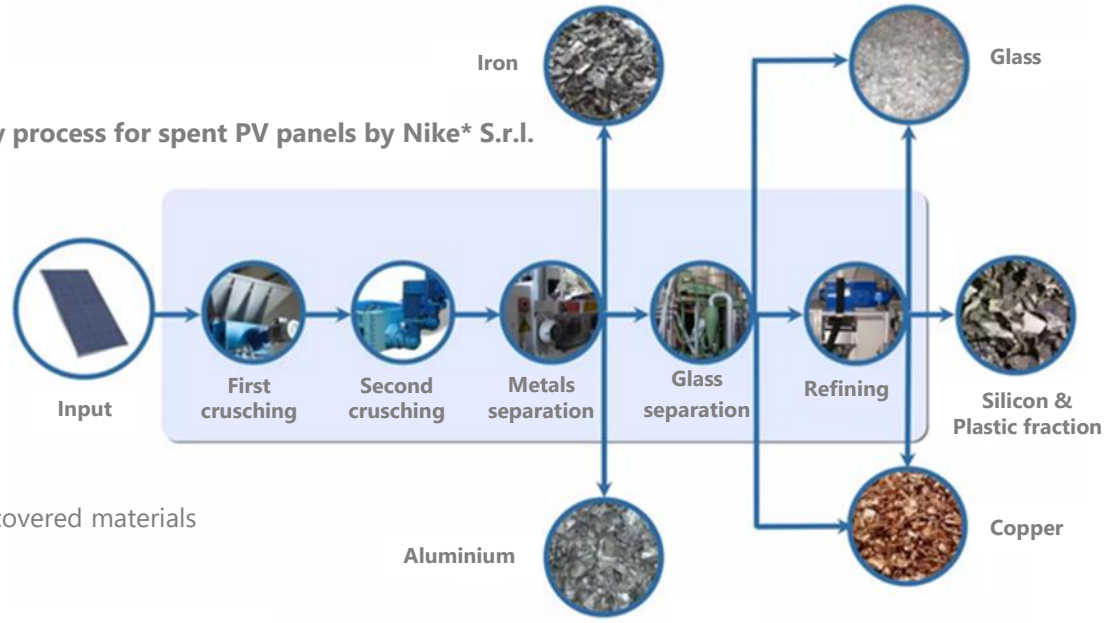
- **recovery of materials generates inputs for energy recovery (materials that cannot be recycled)**
- **recovery of energy generates materials that can be recovered (metals, ashes)**

MatER Spotlight Projects

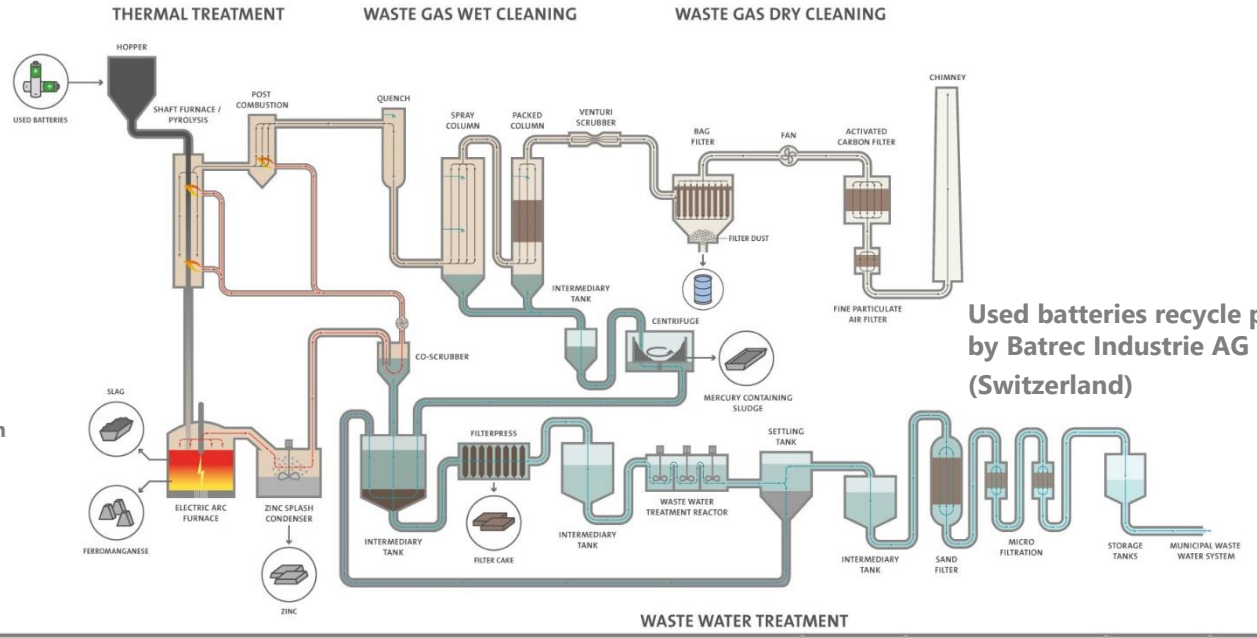
Project 1 - Recovery of materials for energy transition

- **State of the art of recovery technologies available globally with a focus on the Italian context in terms of regulatory framework and plant assets**
- Quantitative estimation of expected flows for each type of waste in accordance with the objectives of the national strategic plans (PNIEC, PNRR)
- Assessment of the capacity of the analysed framework to handle expected flows and recommendations on promising technologies and the evolving regulatory context

Recovery process for spent PV panels by Nike* S.r.l. (Italy)



~88% recovered materials



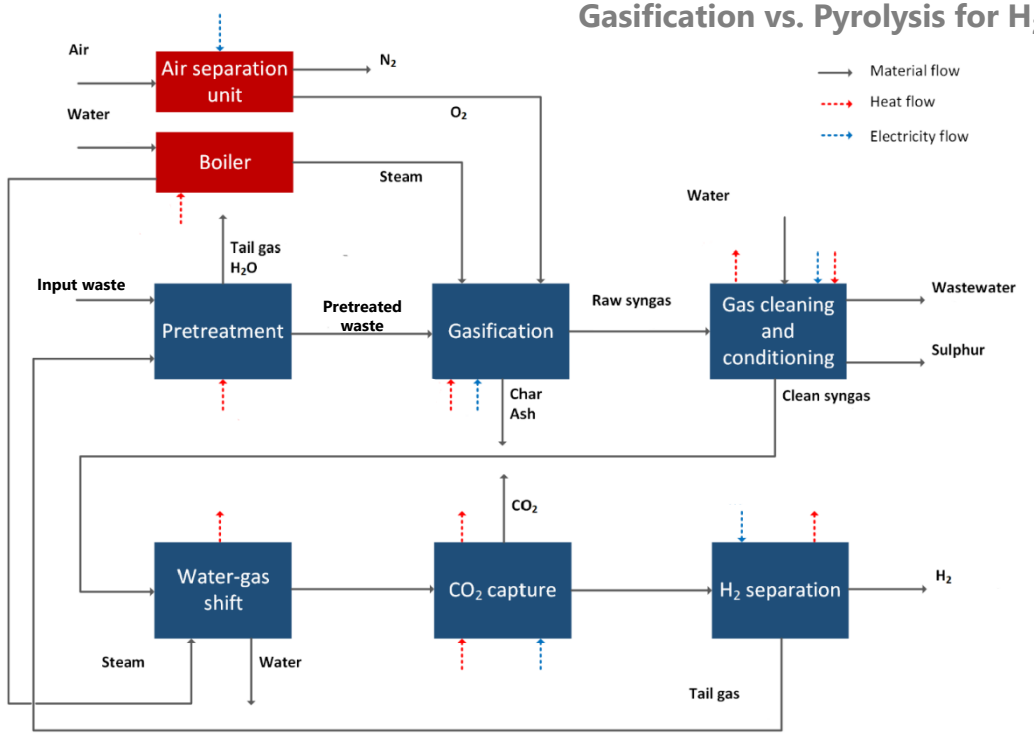
Used batteries recycle plant by Batrec Industrie AG (Switzerland)

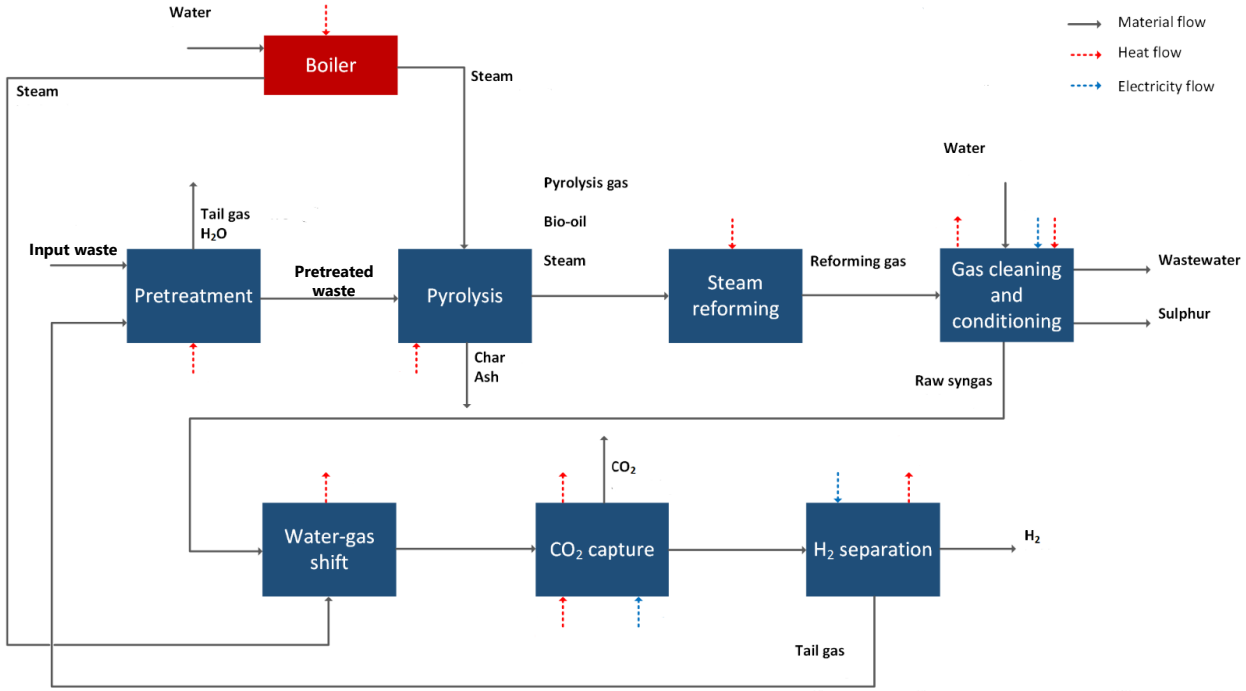
Project 2 - Waste-to-Chemicals

- **Waste-to-Chemicals technologies and processes**
- **Requirements and potential of some Waste-to-Chemicals technologies**
- Italian chain of waste types identified, current and future destinations
- Assessment of expected energy and environmental performance



Gasification vs. Pyrolysis for H_2 production from residual waste/pmixed plastic waste

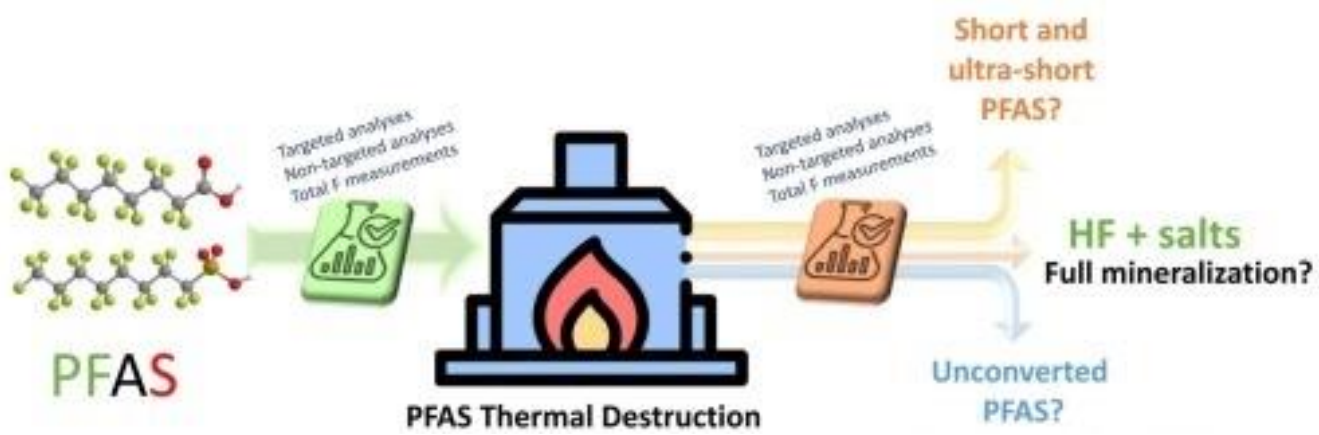




MatER Spotlight Projects

Project 3 - Per and Poly-Fluorinated Alkyl Substances (PFAS) and thermal treatment of waste

- Background on PFAS in the environment
- Regulatory provisions concerning PFAS in waste
- PFAS-containing waste entering waste-to-energy plants
- PFAS behaviour in combustion processes
- PFAS emissions from thermal waste treatment plants
- Measurement methods





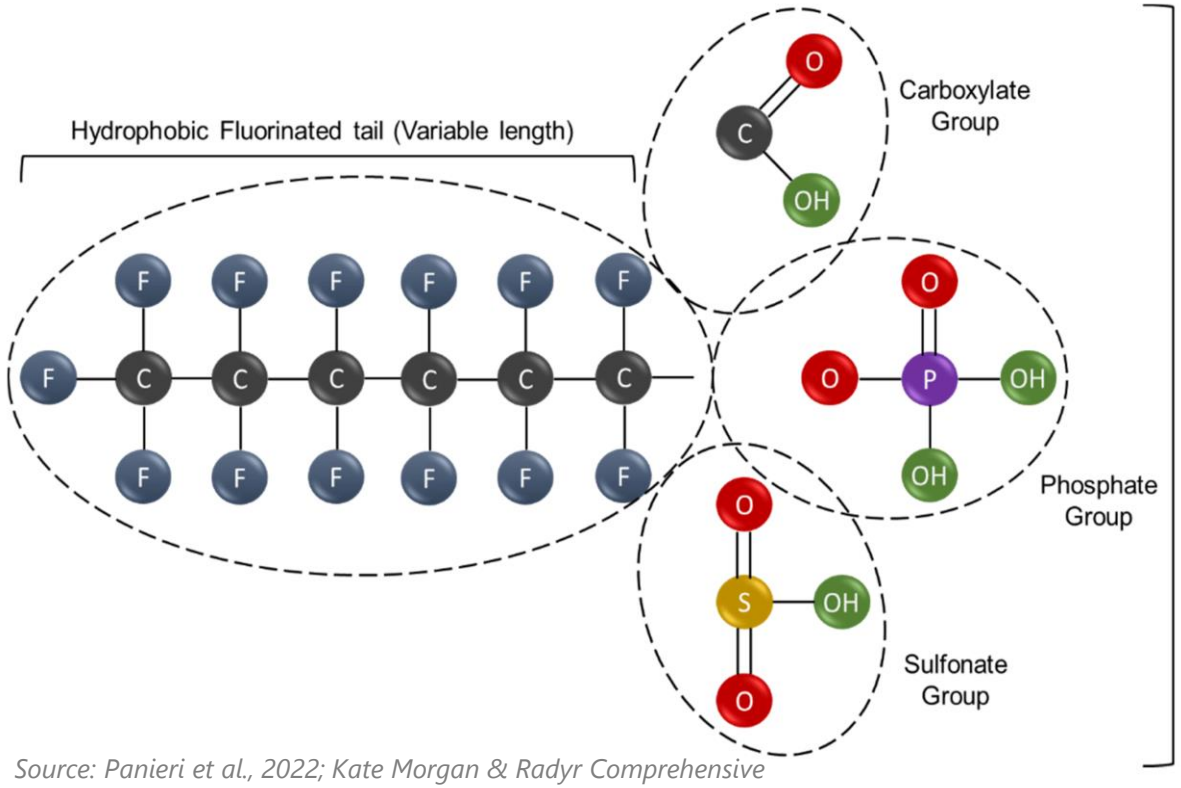
Source: Truckee Meadows Water Authority, Vargette et al., 2023

Introduction

PFAS classification

Per and Poly-Fluorinated Alkyl Substances

- hydrophobic alkyl chain with at least one perfluoroalkyl group and one hydrophilic functional group
- consistency: ~ 200 in 2011 (Buck), over 4,700 in 2018 (OECD, 2018)
  - 2013 proposal (SE,DK,DE,NL,NO) to European Chemical Agency for total ban on production and use

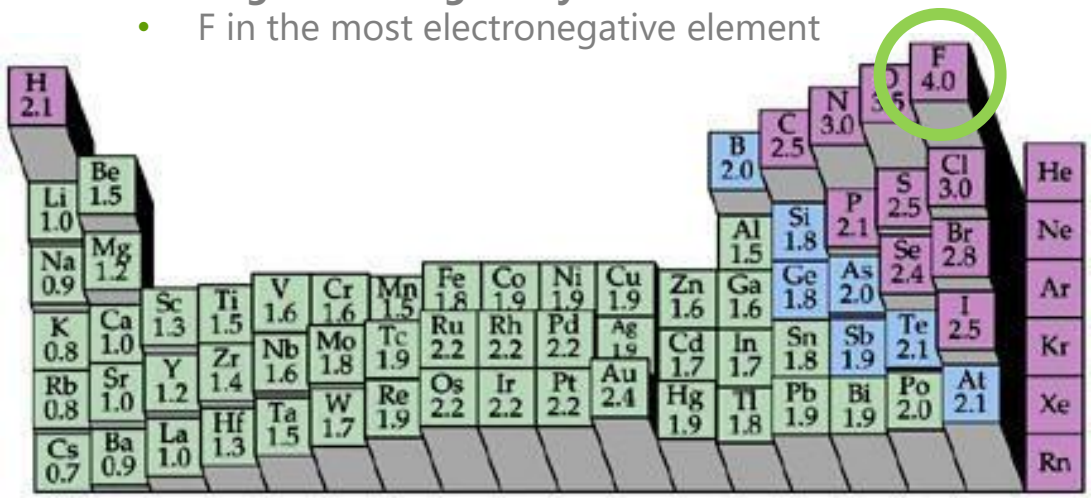


Source: Panieri et al., 2022; Kate Morgan & Radyr Comprehensive

General structure of non-polymeric, perfluorinated PFAS substances

Pauling electronegativity scale

- F in the most electronegative element

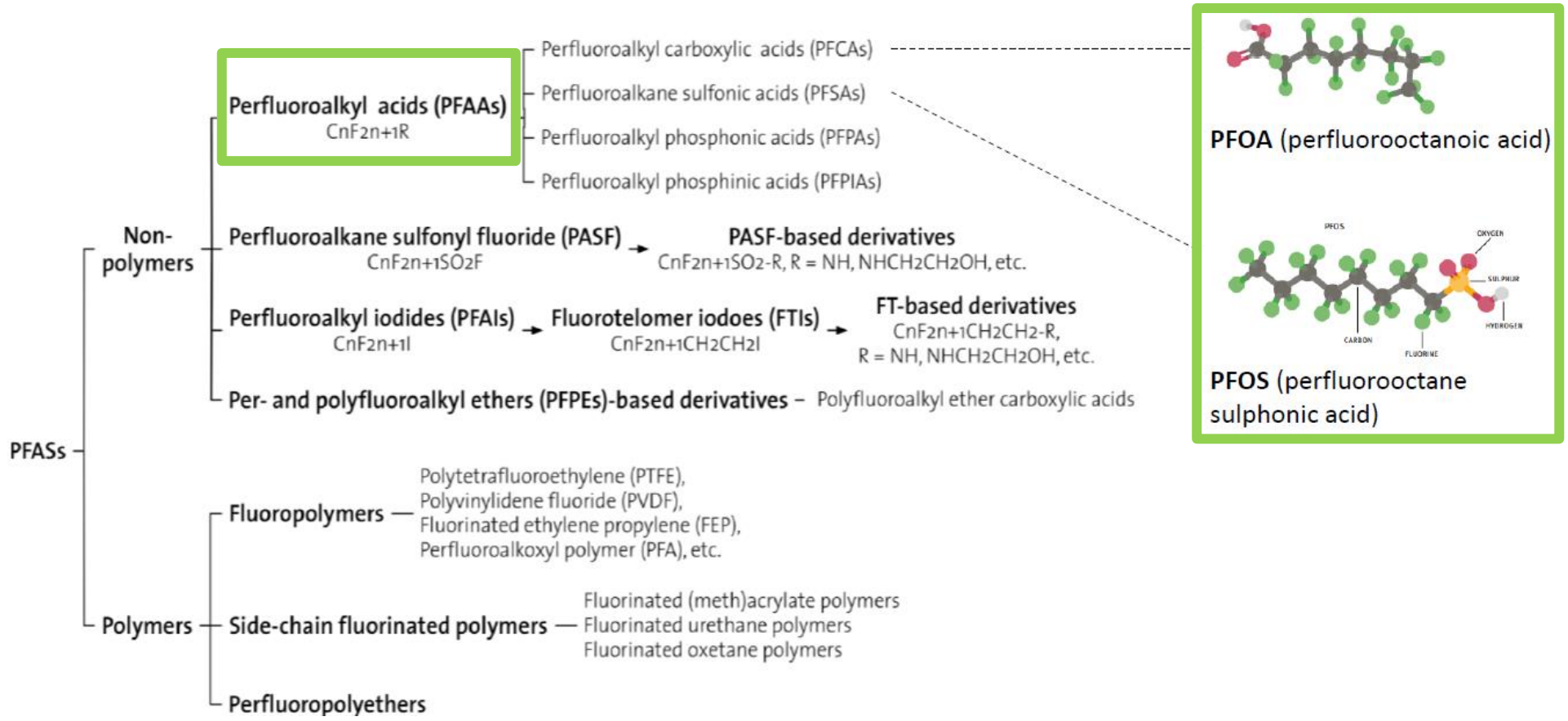


Introduction

PFAS classification

Perfluoroalkyl acids (PFAAs)

- perfluorocarboxylic (PFCA) and perfluorosulphonic (PFSA) acids, including perfluorooctane sulphonic acid (PFOS) and perfluorooctanoic acid (PFOA) most widely used and investigated for persistence and adverse environmental effects



Source: OECD, 2013

Introduction

PFAS: from production to waste

Advantages

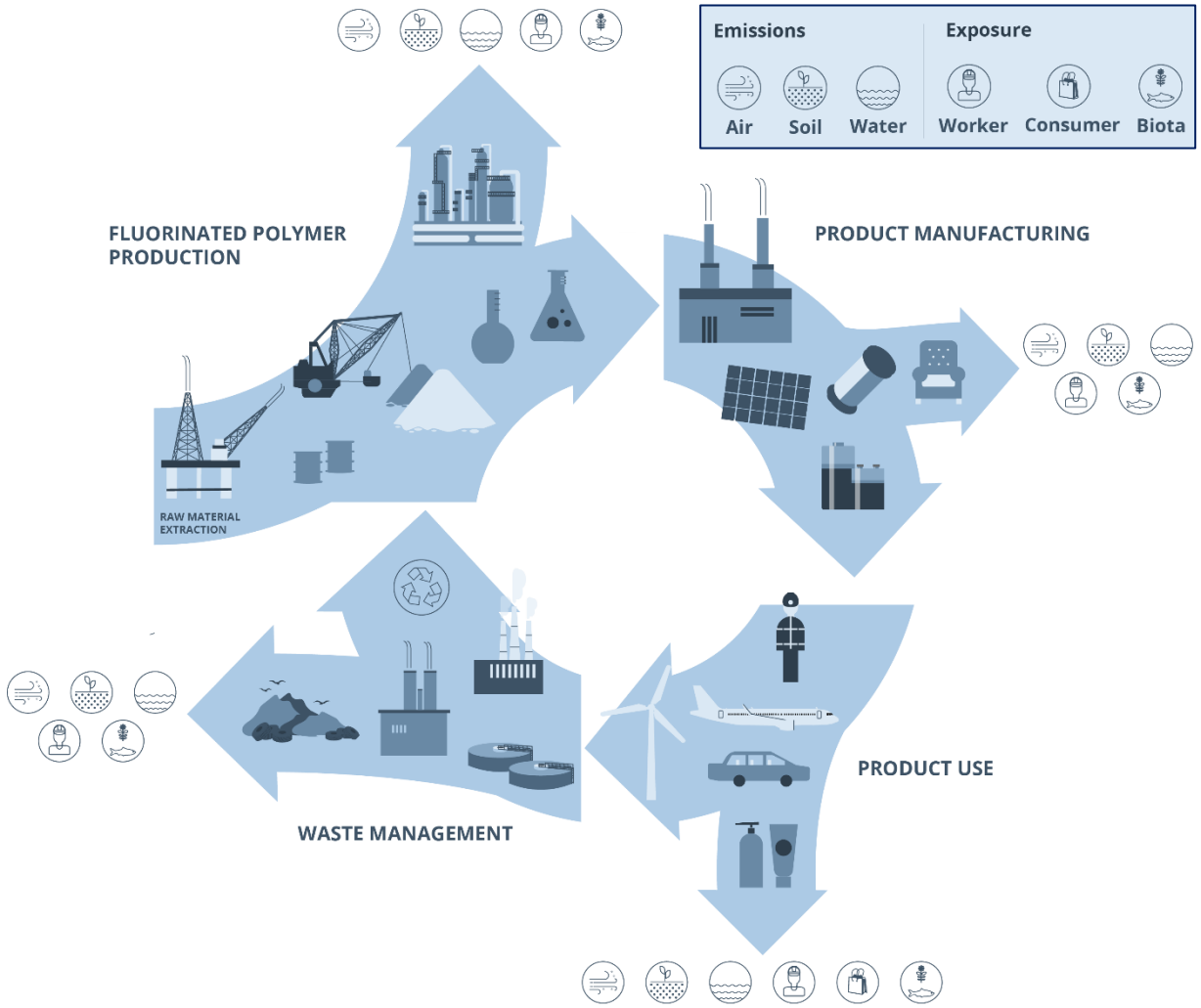
- appealing technical properties (i.e. heat, oil, grease and water resistance)
- widely used in building and consumer products, pesticides, vehicles, energy production, …

Disadvantages

- emissions throughout the life cycles of these products, including production, manufacturing, product use and waste management
- ubiquitous in the environment (i.e., air, soil, water - most in water and residues of product manufacturing))
- hazardous because persistent and bioaccumulating (chemical and thermal stability due to C-F bonds)
- difficulty in achieving complete mineralization with production of persistent oxidation intermediates not present in reactant mixtures
- adverse health impacts of PFAS: endocrine, immune, reproductive and developmental effects

Source: European Environmental Agency

Life cycle of PFAS emissions



Regulatory framework

US framework overview

EPA's recent initiatives

- Perfluorooctanoic acid(PFOA) and perfluorooctane sulphonic acid (PFOS) designated as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (April 2024)
- National Primary Drinking Water Regulation (NPDWR) for six PFAS (April 2024)
- Rule that prevents companies from starting or resuming the manufacture or processing of 329 PFAS (January 2024)
- New three methods to better measure PFAS in the environment (January 2024)
    a. Final EPA Method 1633 - test for 40 PFAS in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue
    b. Final EPA Method 1621 - screen for the presence of chemical substances that contain carbon-fluorine bonds, including PFAS, in wastewater
    c. Other Test Method (OTM)-50 - measure of 30 volatile fluorinated compounds in air
- Addition of seven PFAS to the list of chemicals covered by the Toxics Release Inventory (TRI), consistent with the Fiscal Year 2020 National Defense Authorization Act

PFAS in waste

- EPA Updated Interim Guidance on Destroying and Disposing of PFAS (April 2024)
- EPA Technical Brief. Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams (August 2019)

Regulatory framework

EU framework overview

No comprehensive EU regulation on PFAS release and presence in environmental matrices

- PFAS are listed as priority contaminants in:
  a. International conventions and regulations on production and market products.
  b. European Directives on concentration limits and environmental quality standards.

Key EU legislation

- Directive 2013/39/EU on priority substances
- Proposed Directive (under review) amending:
  a. Water Framework Directive (2000/60/EC)
  b. Groundwater Directive (2006/118/EC)
  c. Environmental Quality Standards (2008/105/EC)
- Directive (EU) 2020/2184 on water quality for human consumption.
- Regulation (EU) 2019/1021 on persistent organic pollutants.
- Commission Regulation (EU) 2024/2462 on Perfluorohexanoic acid (PFHxA)

Summary of key Conventions/Regulations

Conventions/Regulations	Included PFAS	Limits (if any)
Stockholm Convention on Persistent Organic Pollutants - 2001	PFOA (Annex A) PFOS (Annex B)	Annex A: substances to be eliminated, then avoid their production and use. Annex B: substances with restrictions in both production and use
Commission Regulation 552/2009 - REACH (Registration, Evaluation, Authorization and restriction on CHemicals)	PFOS	Not be placed on the market in semi-finished or manufactured articles or parts of them if the concentration of PFOS is equal to or higher than 0.1 % by weight or, for coated fabrics or other coated materials, if the amount of PFOS is equal to or higher than 1 µg/m2 of the coated material
ZDHC (Zero Discharge Hazardous Chemicals programme)	PFOS, PFOA, PFBS, PFHxA, 8:2 FTOH, 6:2 FTOH.	Voluntary programme within the textile industry that aims to eliminate - hazardous substances, which can remain in textiles and cause skin irritation, allergic reactions; - substances that are used in production processes and may be released into the environment in liquid effluents. Limits for industrial effluents 0.01 µg/L for PFOS, PFOA, PFBS, PFHxA 1 µg/L for 8:2 FTOH, 6:2 FTOH

Regulatory framework

Most relevant EU regulations concerning the presence of PFAS in solid wastes



Classification of waste

- EU Commission Decision 955 /2014
- EU Commission regulation 1357/2014
- 2017/997/EU



Recovery and disposal

- Annex IV and V of Regulation (EU) 2019/1021
- Directive 1999/31/CE (Landfill)



End of waste

- Article 6 (1) and (2) of the Waste Framework Directive
- Reach Regulation
- Annex IV and V of Regulation (EU) 2019/1021
- POPs under the Stockholm Convention – Annex A and B

The concentration for the target chemical decreses



No direct provisions are set for PFASs

Specific provisions are set only for PFOA, PFOS and PFHxS.

Restriction and elimination measures for production and use are currently set only for PFOA, PFOS, PFHxS and C9-C14 PFCAs .

Proposed measures are in discussion for PFHxA and PFASs (according to the definition of OECD, 2021)

Limits on PFAS

No limits

1-2,000 mg/kg (or 1E3-2E6 ppb)

→ Limits with implications on:

- The disposal or recovery operations that may lead to recovery, recycling, reclamation, or re-use of wastes
- Potentially on the classification of wastes

0.025-20 mg/kg (or 25-20,000 ppb)

→ Limits with implications on the end-of-waste procedure

Source: Pivato et al., 2024

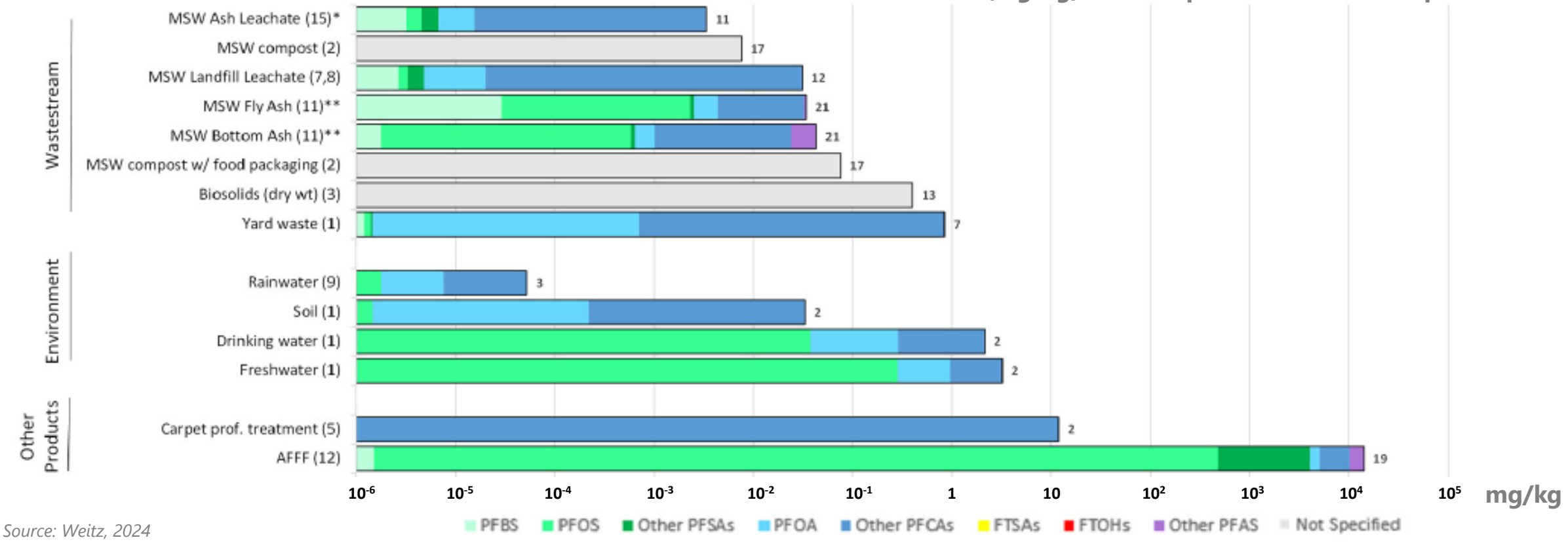
Presence of PFAS in waste - US

US framework

Few, fragmentary references with widely varying ranges for unsorted/mixed waste

- range: < detection limit - ≥1 mg/kg (or 1,000 ppb)
- conservative lower bound = 0,01-0,05 mg/kg total PFAS (or 10-50 ppb)

PFAS concentration (mg/kg) and composition in different products and waste



Source: Weitz, 2024

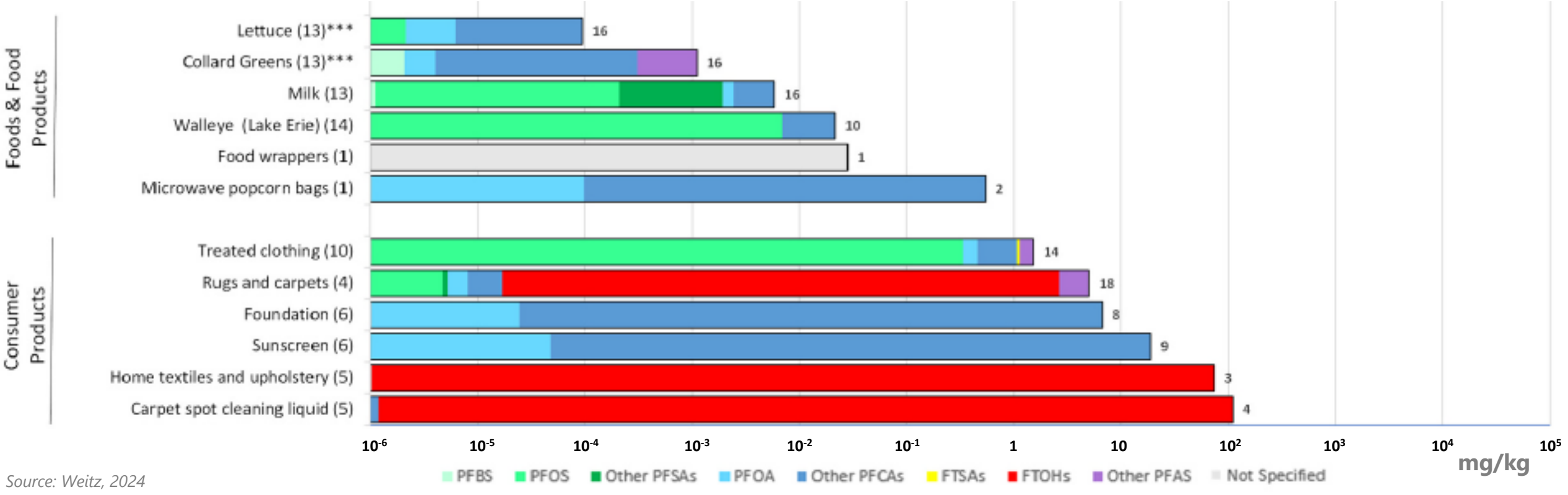
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PFAS concentration (mg/kg) and composition in different products



Source: Weitz, 2024

Presence of PFAS in waste - EU

EU framework

Bibliographic review of the most relevant product classes: paper, plastics, leather and textiles, metals

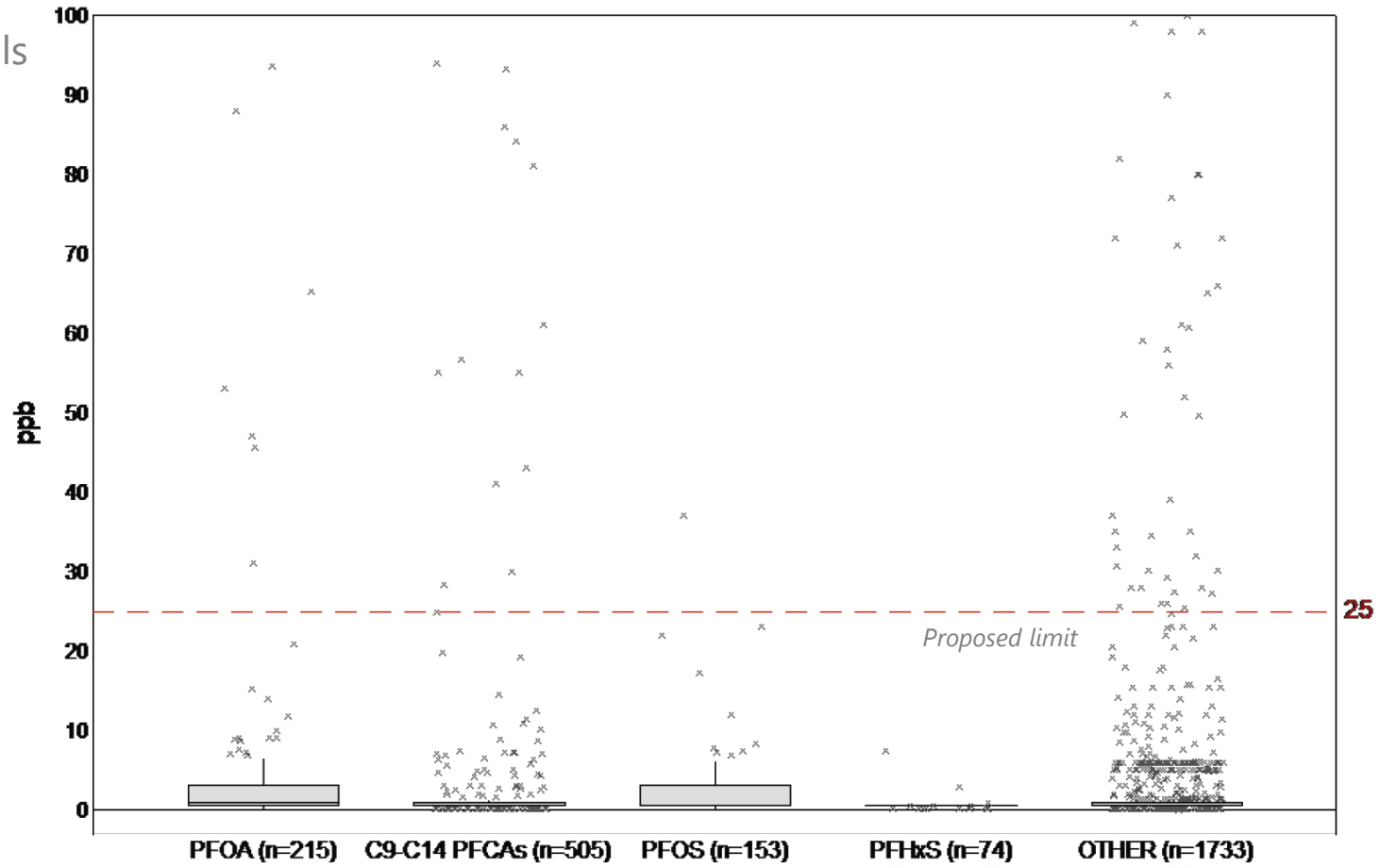
- limited data, pronounced variability caused by uneven sampling, extraction and analysis protocols
- significant acquisitions < detection limit
- range: < detection limit - >2,000 mg/kg

Max values (ppb)

- PFOA: 2,356
- C_9-C_{14} PFCA: 2,111
- PFOS: 36,992
- PFHxS: 7.45
- Other: 12,700

Total PFAS
(sum of median values): 3.36 ppb

PFAS concentration (ppb) and composition
Paper and cardboard waste



Source: Pivato et al., 2024

Presence of PFAS in waste - EU

EU framework

Bibliographic review of the most relevant product classes: paper, plastics, leather and textiles, metals

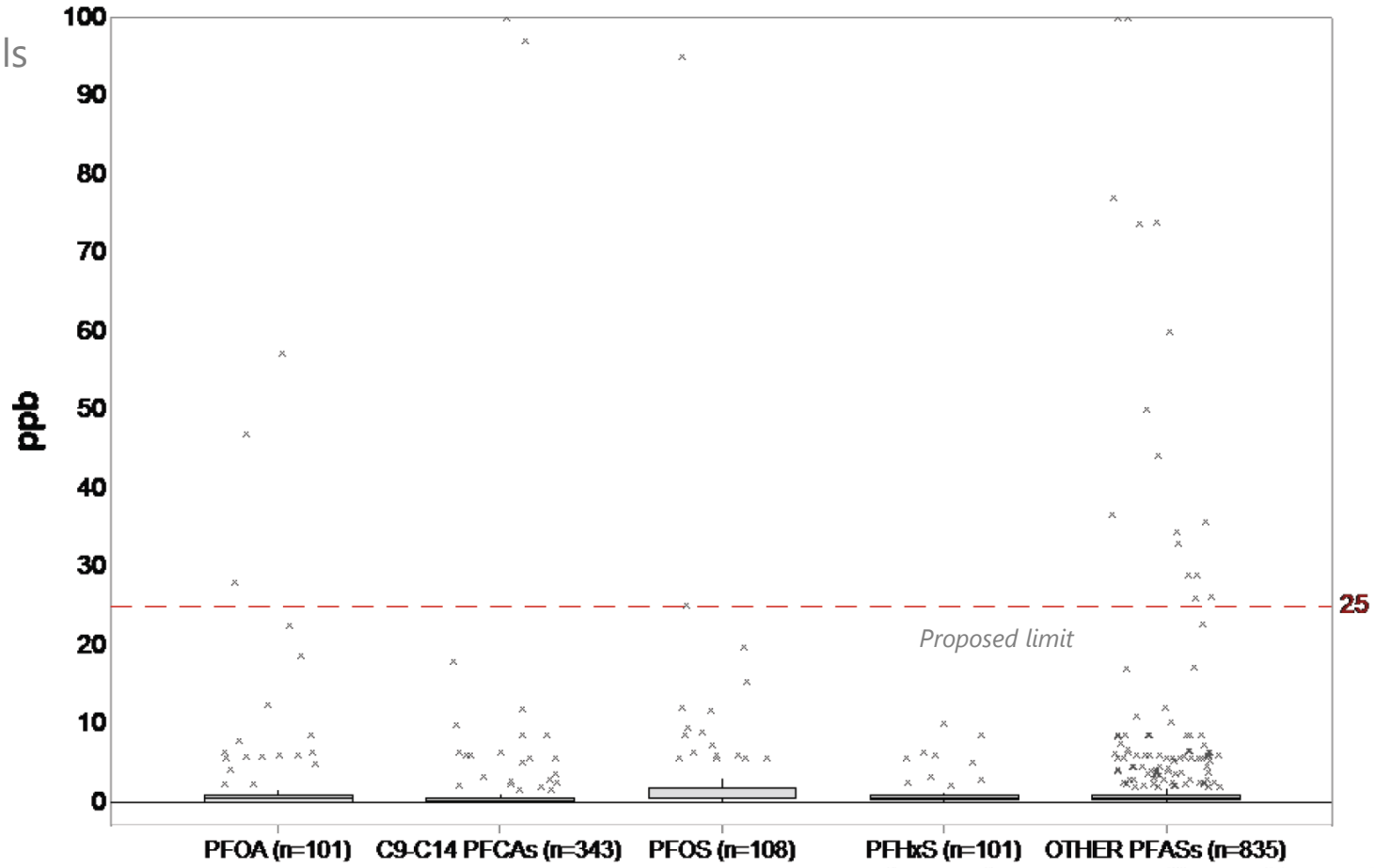
- limited data, pronounced variability caused by uneven sampling, extraction and analysis protocols
- significant acquisitions < detection limit
- range: < detection limit - >2,000 mg/kg

Max values (ppb)

- PFOA: 57.2
- C_9-C_{14} PFCA: 530
- PFOS: 8,849
- PFHxS: 1,085
- Other: 40,900

Total PFAS
(sum of median values): 2.59 ppb

PFAS concentration (ppb) and composition
Textile and leather waste



Source: Pivato et al., 2024

Presence of PFAS in waste - EU

EU framework

Bibliographic review of the most relevant product classes: paper, plastics, leather and textiles, metals

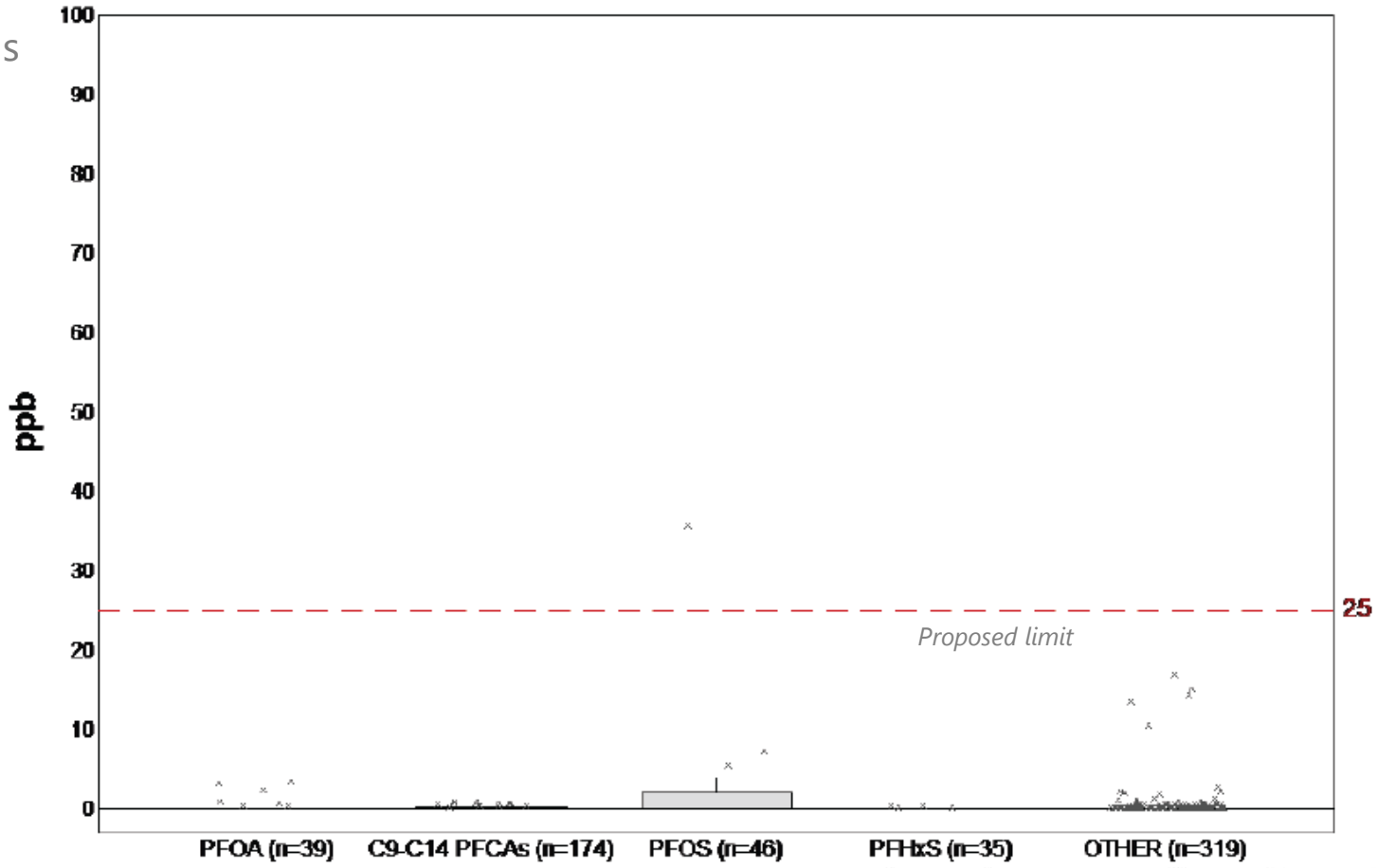
- limited data, pronounced variability caused by uneven sampling, extraction and analysis protocols
- significant acquisitions < detection limit
- range: < detection limit - >2,000 mg/kg

Max values (ppb)

- PFOA: 3.46
- C_9-C_{14} PFCA: 0.84
- PFOS: 35.5
- PFHxS: 0.34
- Other: 16.9

Total PFAS
(sum of median values): 0.36 ppb

PFAS concentration (ppb) and composition
Plastic waste



Source: Pivato et al., 2024

Presence of PFAS in waste - EU

EU framework

Bibliographic review of the most relevant product classes: paper, plastics, leather and textiles, metals

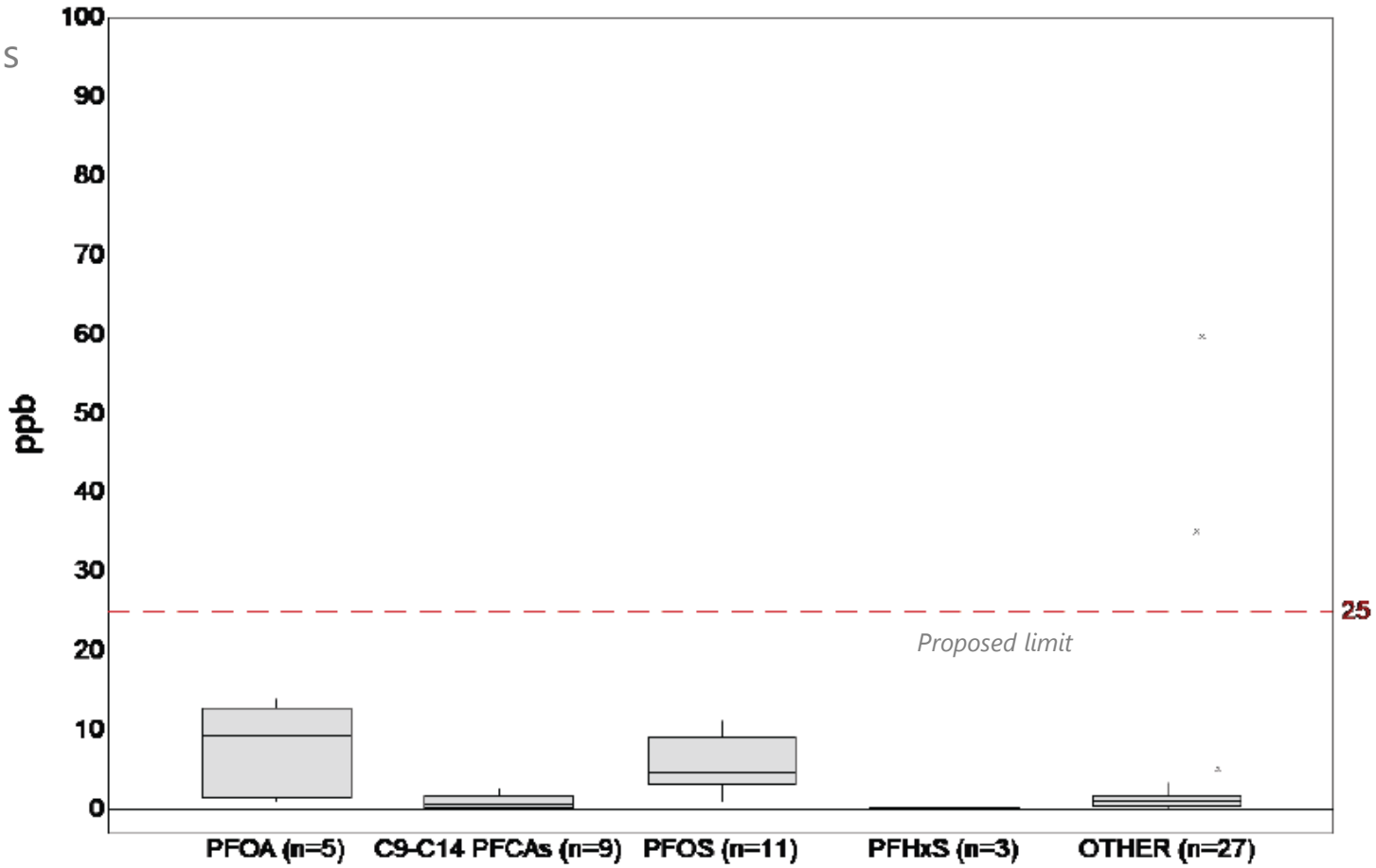
- limited data, pronounced variability caused by uneven sampling, extraction and analysis protocols
- significant acquisitions < detection limit
- range: < detection limit - >2,000 mg/kg

Max values (ppb)

- PFOA: 14
- C_9-C_{14} PFCA: 2.7
- PFOS: 11.3
- PFHxS: 0.21
- Other: 5,065.6

Total PFAS
(sum of median values): 16.01 ppb

PFAS concentration (ppb) and composition
Metal waste and metal scraps



Source: Pivato et al., 2024

General aspects of PFAS thermal treatment

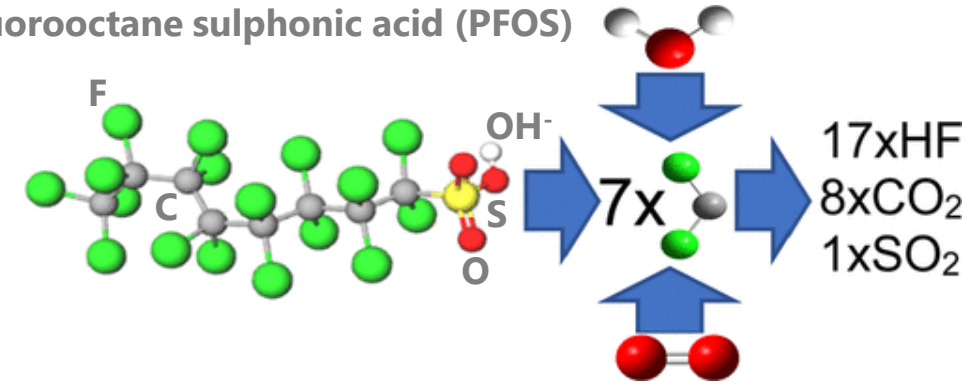
Theoretical aspects (modeling reaction mechanisms) and experimental findings in lab-scale/pilot plants

Complete destruction of PFAS -> mineralization or complete defluorination (up to CO_2, HF, small hydrocarbons)

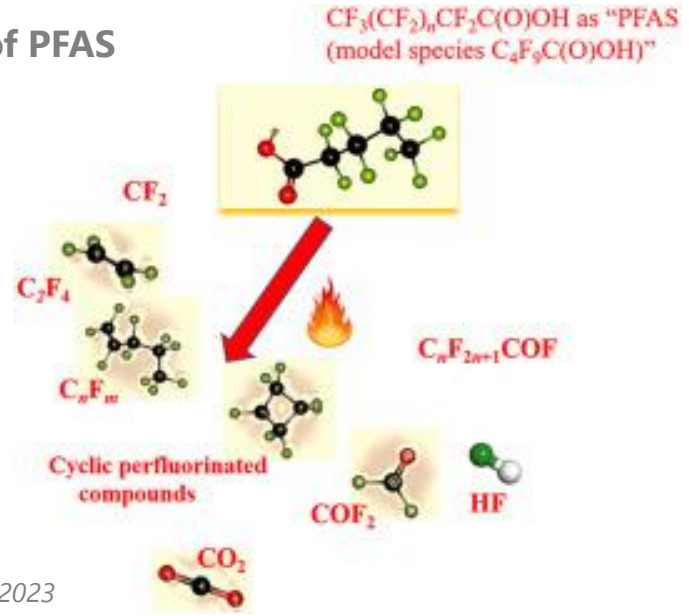
PFAS conversion

- easy conversion of branched-chain intermediates (fewer C-F bonds) / hard conversion of short-chain products (higher number of F atoms increases molecular stability) / formation of Products of Incomplete Combustion (PICs)
- difficult interpretation of analytical results (limitations and inhomogeneity of protocols / identification-quantification of PICs)
- limited number of studies and focused on shorter-chain PFAS (not a proxy for more abundant, longer-chain PFAS)
- desorption/thermal decomposition activation temperature levels:
  a. low - perfluorocarboxylic acids (PFCA): 150°C-300°C
  b. medium - fluoropolymers: 250-500°C
  c. high - perfluoroalkanes (450-550°C) and perfluoroalkenes (350-550°C)

Perfluorooctane sulphonic acid (PFOS)



Possible products of PFAS conversion



Source: Khan et al., 2020; Altarawneh, 2021; Weber et al., 2021; Altarawneh et al., 2022; Krug et al., 2022; Blotevogel et al., 2023; Wang et al., 2023; Weber et al., 2023

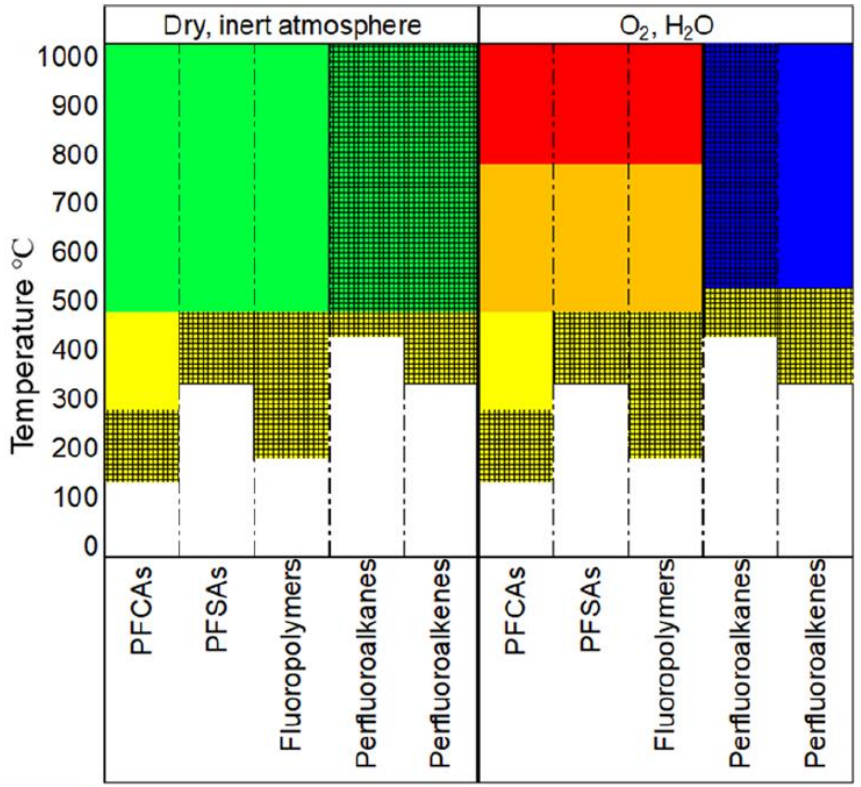
General aspects of PFAS thermal treatment

Theoretical aspects (modeling reaction mechanisms) and experimental findings in lab-scale/pilot plants

Complete destruction of PFAS -> mineralization or complete defluorination (up to CO_2, HF, small hydrocarbons)

Perfluorooctanoic acid (PFOA) and Perfluorooctane sulphonic acid (PFOS)

- destruction levels of 99% at T ≥ 650°C and 99.99% at T > 800°C for t ≥ 2 sec (conditions representative for **MSW WtE plants** - grate furnace or fluidized bed reactor)
- destruction efficiencies of 99.9999% at T ≥ 1,200°C for t ≥ 2 sec (conditions representative for **hazardous waste incineration plants** - rotary drum+post combustor)



Volatile OrganoFluorine (VOF): very stable and hard to further defluorinate

Defuorination >80%: condition quite close to complete mineralization

VOF (CF_4, C_2F_6, C_2F_4), charred residual, cyclic compounds formed

>80% defluorination

~50~80% defluorination

<50% defluorination

Not studied

Thermal decomposition initializes

Thermally stable

Source: Khan et al., 2020; Altarawneh, 2021; Weber et al., 2021; Altarawneh et al., 2022; Krug et al., 2022; Blotevogel et al., 2023; Wang et al., 2023; Weber et al., 2023

PFAS emissions from Waste-to-Energy plants

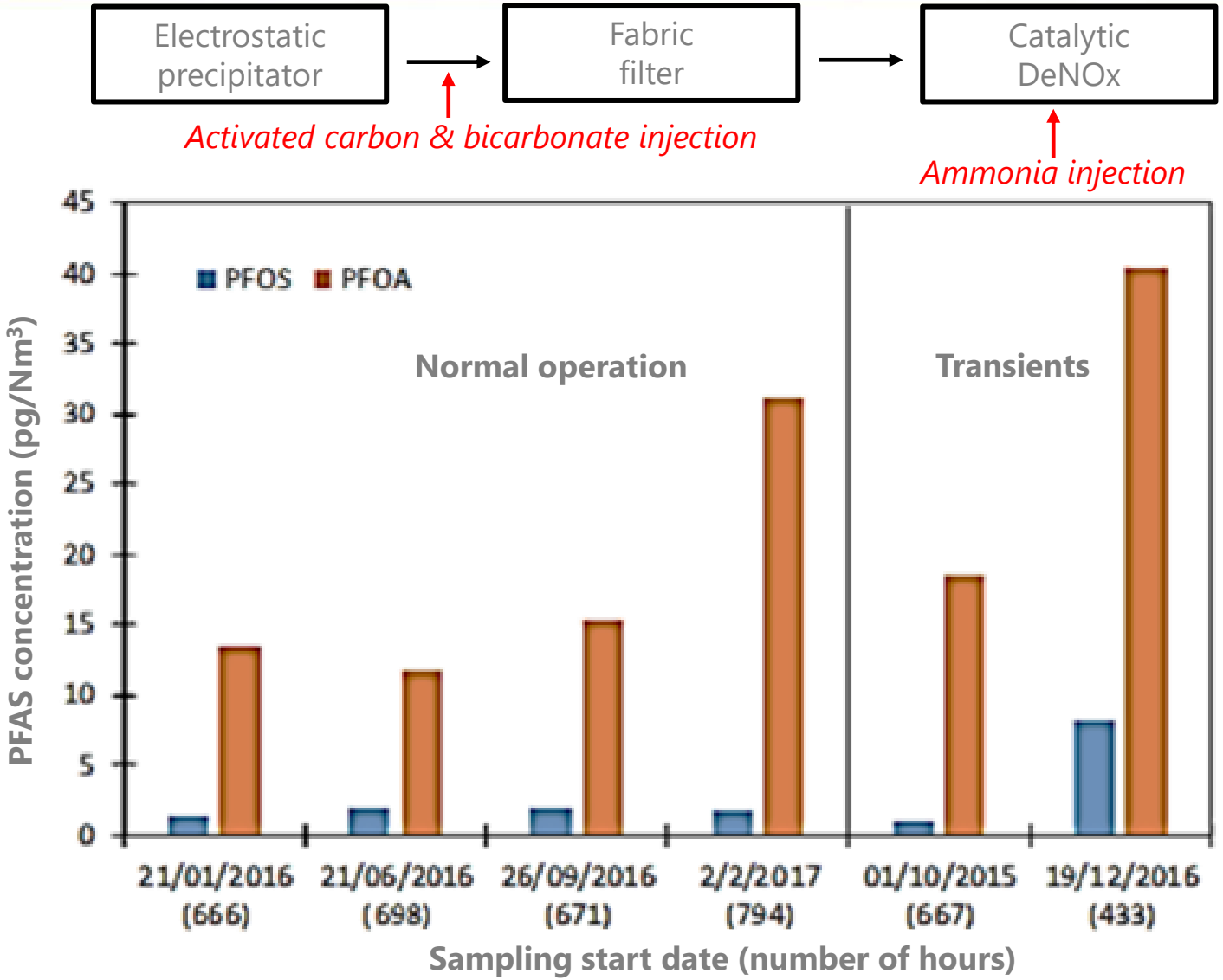
WtE plant - Netherlands

Stack sampling

- plant capacity: 230,000 t/year (municipal solid waste, bulky waste, pre-treated waste)
- dry flue gas treatment line (ESP + FF+ SCR)
- long-term stack sampling (430 - 800 hours) including ignition and shutdown transients

Main findings

- Perfluorooctane sulphonic acid (PFOS) above the detection limit only during the shutdown transient (8.2 pg/Nm^3)
- PFAS always present: 11.8÷40.4 pg/Nm^3 (average 20.9 pg/Nm^3)



Source: Arkenbout, 2018

PFAS emissions from Waste-to-Energy plants

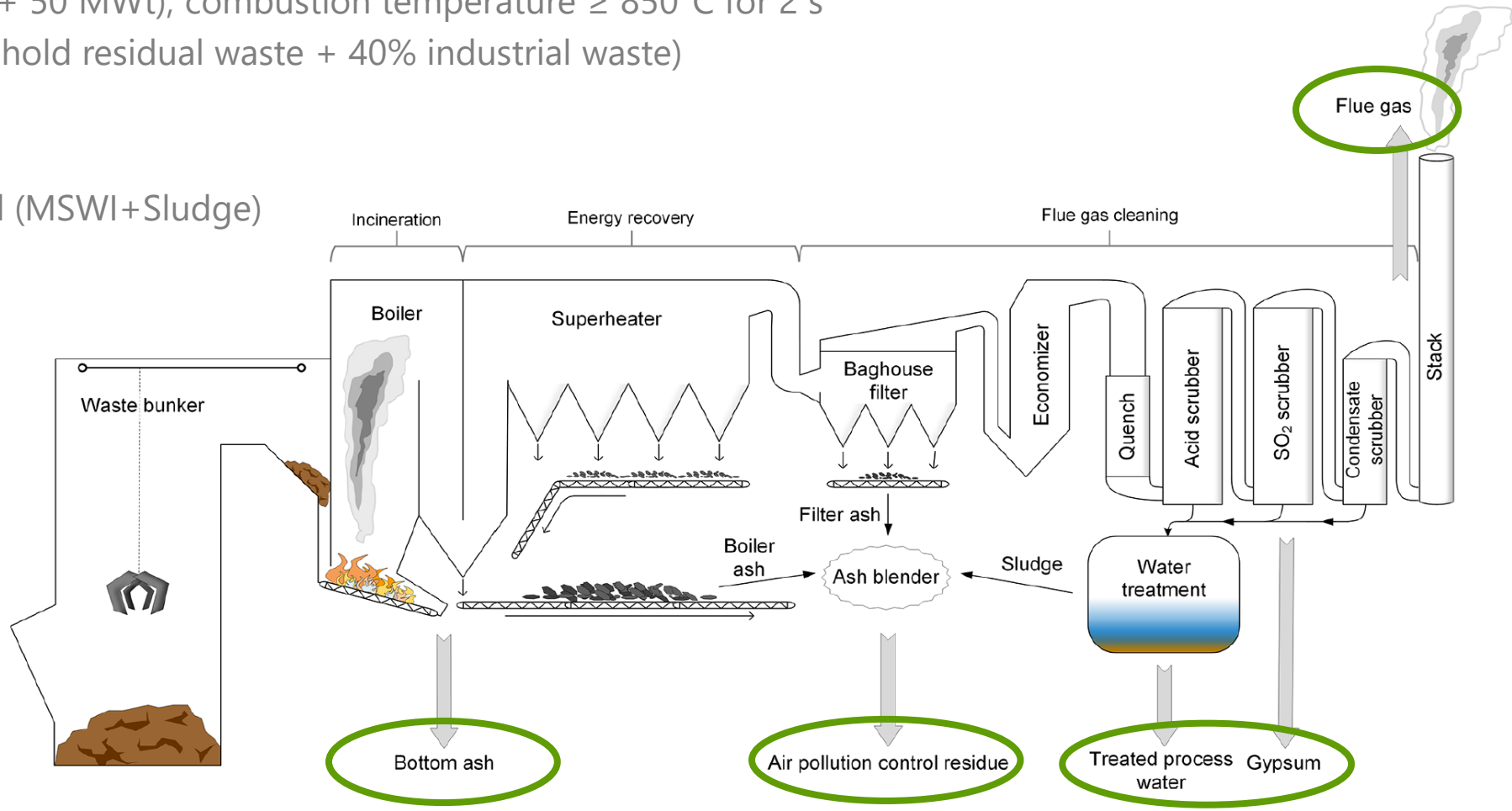
WtE plant - Sweden

Full-scale WtE plant to understand the transport and distribution of PFAS inside the WtE

- Moving grate boiler (15 MWe + 50 MWt), combustion temperature ≥ 850°C for 2 s
- Waste feed: 20 t/h (60% household residual waste + 40% industrial waste)
- Two experimental campaigns:
  1. only MSWI feed (MSWI)
  2. MSWI+WWT sludge feed (MSWI+Sludge)

Flue gas treatment line

- injection of activated carbon
- fabric filtration
- wet scrubber (reduction of HCl, NH_3, and Hg)
- scrubber with injection of $Ca(OH)_2$ (SO_2 reduction)
- condensation scrubber (flue gas moisture reduction)



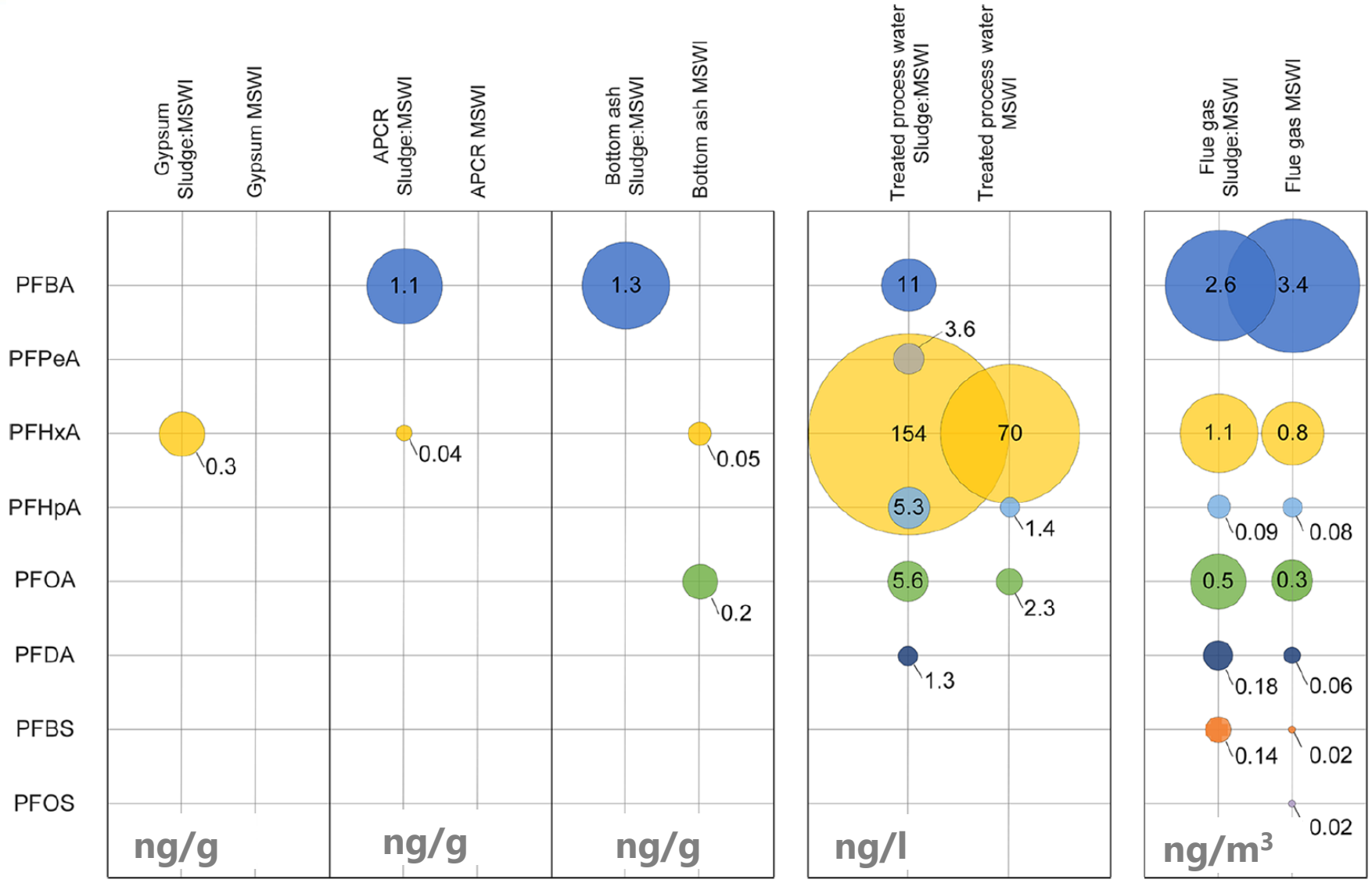
Source: Björklund et al., 2023; Björklund et al., 2024

PFAS emissions from Waste-to-Energy plants

WtE plant - Sweden

PFAS distribution in investigated streams

- higher concentrations in the case of co-incineration with sludge
- higher levels in treated process water
- presence of only PFCA and PFSA
- speciation detected in all residue streams for both feeding situations, except in gypsum and flue gas cleaning residues in waste-only campaigns

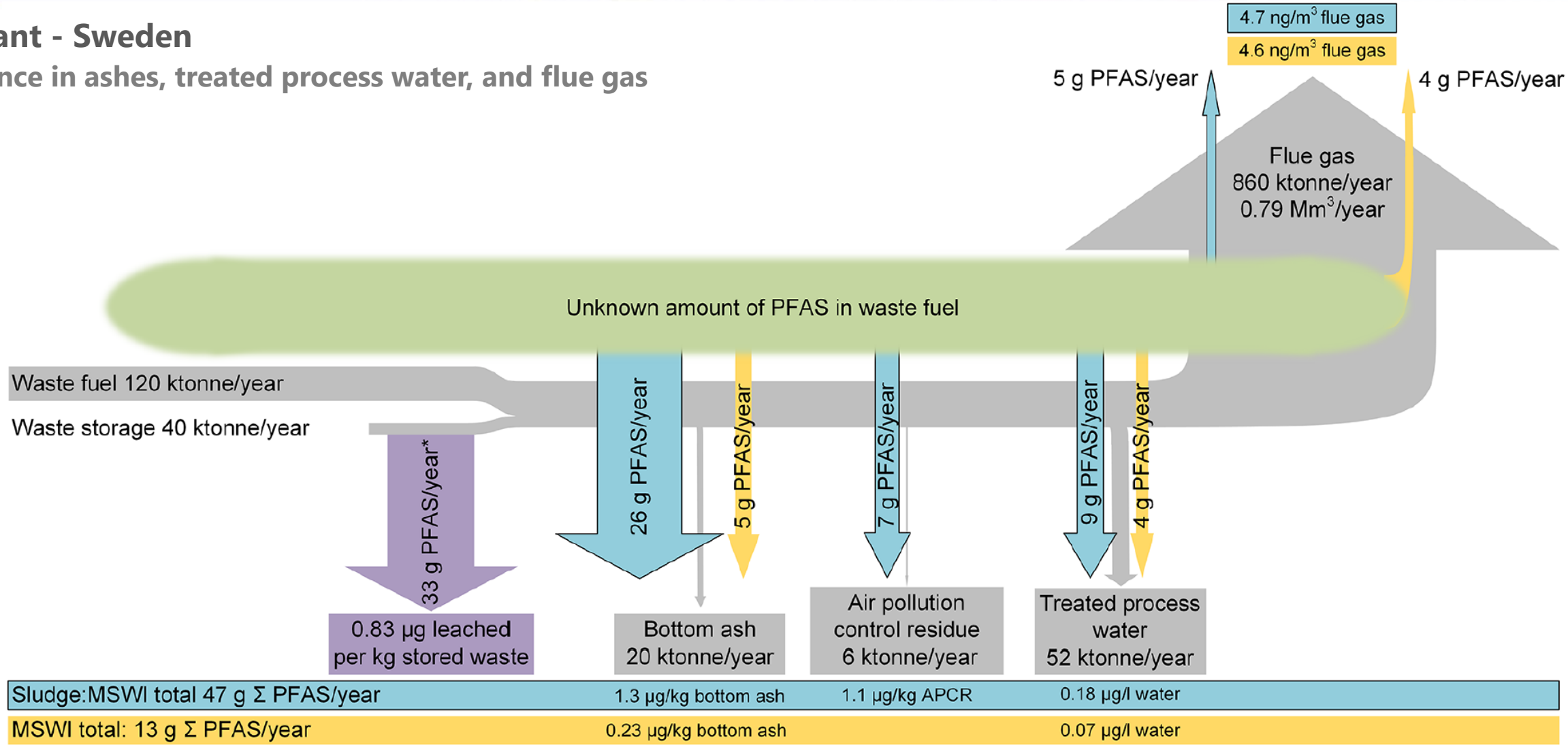


Source: Björklund et al., 2023; Björklund et al., 2024

PFAS emissions from Waste-to-Energy plants

WtE plant - Sweden

Occurrence in ashes, treated process water, and flue gas



Source: Björklund et al., 2023; Björklund et al., 2024

PFAS emissions from Waste-to-Energy plants

WtE plant - Sweden

Focus on flue gas

- stack emissions with overall PFAS levels fully comparable between the two feed situations (4.6-4.7 ng/Nm^3)
- presence of untreated gases from boiler outlet about double for MSWI+Sludge feeding (14 ng/Nm^3) compared to MSWI only (7.3 ng/Nm3), almost entirely attributable to PFHxA
- average removals from raw flue gas (boiler outlet) between 35% (21%-42% - MSWI only) and 66% (59%-70% - MSWI+Sludge)

	MSWI Day 1	MSWI Day 2	MSWI Day 3	Sludge:MSWI Day 1	Sludge:MSWI Day 2	Sludge:MSWI Day 3	
Gaseous							
Untreated gas	7.3	5.2	9.5	11	19	12	ng m^{-3}
Flue gas stack*	4.2	4.1	5.6	3.4	5.6	4.9	

Estimated emission factors

- MSWI only: 0.07-0.1 µg/kg$_{input\ waste}$ with flows equally divided between slag, treated water and flue gas
- MSWI+Sludge: 0.07-0.4 µg/ kg$_{input\ waste}$ with predominantly slag flows

Flue gas treatment can capture some PFASs and transfer them into WtE residues

Source: Björklund et al., 2023; Björklund et al., 2024

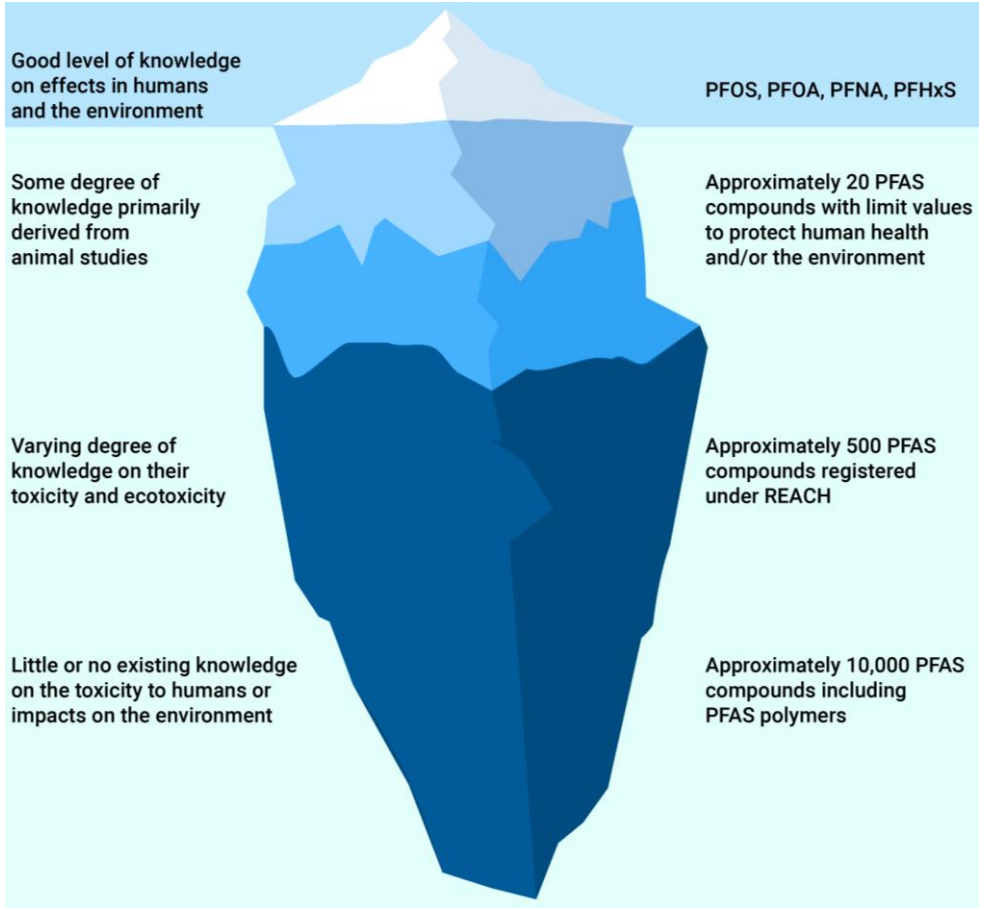
Conclusions

- The presence of **C-F bonds** in **PFAS** makes **complete mineralisation** by combustion almost impossible
- During incomplete destruction phases, **products of incomplete combustion** (PICs) and **secondary derivatives** are formed, with significant effects on the availability and effectiveness of suitable analytical methods
- Any **thermal conversion** operation does not appear able to guarantee the **complete destruction** of PFAS.
- Experimental measurements on **full-scale plants** are totally lacking, especially for gaseous emissions. **No established standard protocols** for residual measurements (PICs, secondary components), especially for gaseous emissions.
- **WtE plants** for municipal waste with modern BAT configurations (operation at T ≥ 850°C and gas residence times of at least 2 sec.) show **target PFAS destruction efficiencies** (perfluorooctane sulphonic acid - PFOS, perfluorooctanoic acid- PFOA) **~99.99%**, reducing analytically assessable PFAS emissions to levels aligned with risk minimization.
- **Incineration plants** for hazardous waste (T ≥ 1,100°C, residence time ≥ 2 sec) show lower uncertainties in achieving **higher destruction rates** (**~99.9999%**).
- **PFAS mass balance** in WtE systems requires **complex sampling** and analysis techniques, some still under development, including **total fluorine detection** and alternative techniques beyond Gas Chromatografy/Mass Spectrometry.
- **PFAS concentrations in residues** are typically **very low**, requiring **complex extraction** and **concentration procedures** for analysis.

Conclusions

Research needs

- **analytical methods** capable of measuring a **wider range** of PFAS compound
- **studies** investigating the fate of PFAS in WtE with a **complete mass balance** to estimate the total release of PFAS



THANK YOU
FOR YOUR ATTENTION!

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