PFAS, a threat for food safety?

Stefan van Leeuwen, Wageningen Food Safety Research

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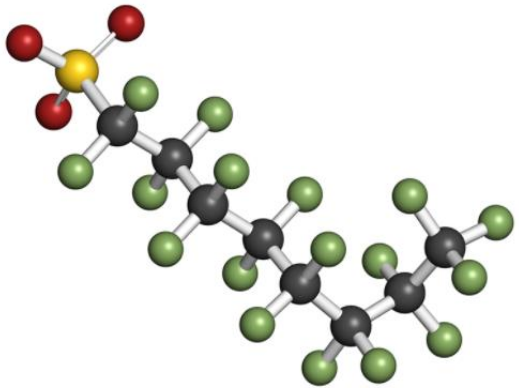
Contents of the talk

- Background on PFAS
- Regulations
- Analytical methods & challenges
- Case of Chemours
- Guidelines and need for standards
- Take home message



Background PFAS

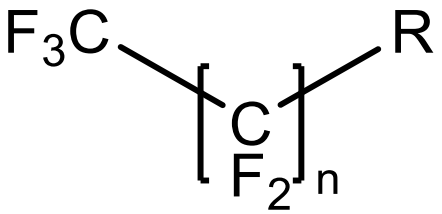
- Persistent compounds, strong C-F bond
- Large diversity of compounds
    - Phys-chem properties
    - Stability
- Applied everywhere in society (households, industry, automotive, medical, etc etc)
- Early reports on PFAS from 2001 onwards

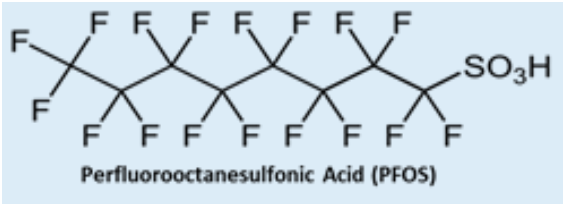
- The PFAS family of >4700 compounds (OECD definition)

What are PFAS?

PFAS is a **collective name** for, mainly, aliphatic compounds of which (part of) the hydrogen atoms have been replaced by Fluorine:

- Carboxylic acids: R = -COOH
- Sulfonates: R = $-SO_3H$
- Sulfonamides: R = $-SO_2NH_2$
- Telomers: R = $-C_2H_4R'$
- Phosphates: R = $-PO_4H_2$
- …

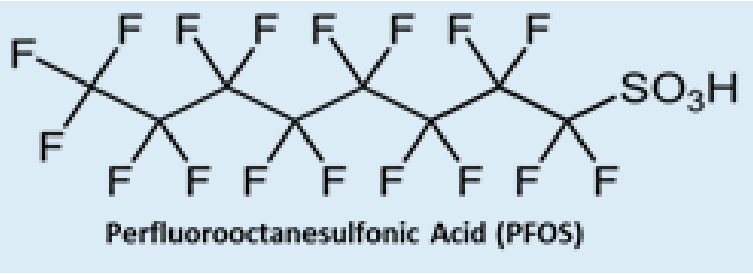




PFOS

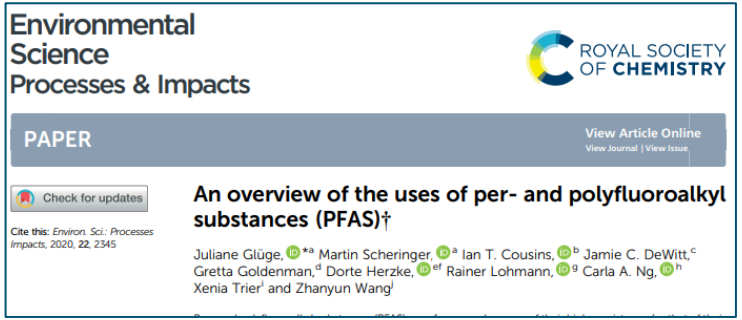
Excellent surfactants

Hydrophobic tail Hydrophilic head



Perfluorooctanesulfonic Acid (PFOS)

- Application as:
- Emulsifiers in fluoropolymer production (e.g. PTFE)
- Aqueous Fire Fighting Foams
- Water/fat/dirt repellent surface treatment (food contact materials, out-door clothing
- ..
- …
- …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An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

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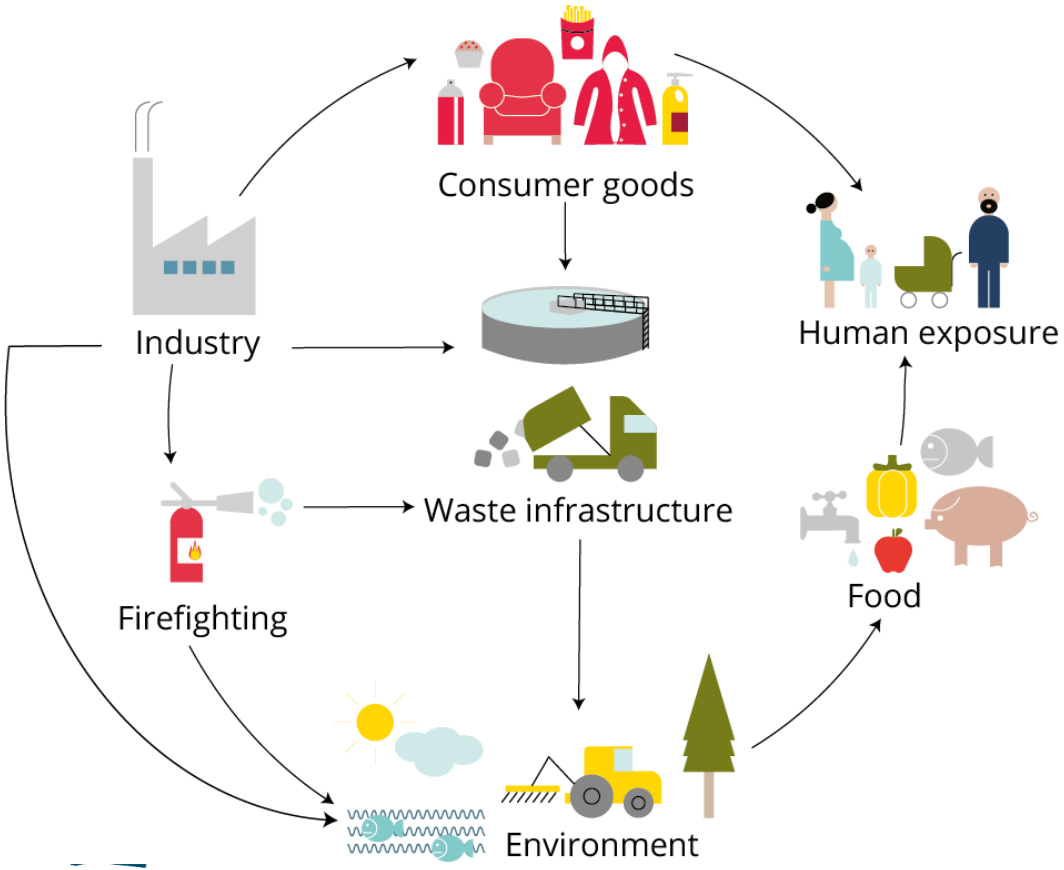
Sources of PFAS in foods

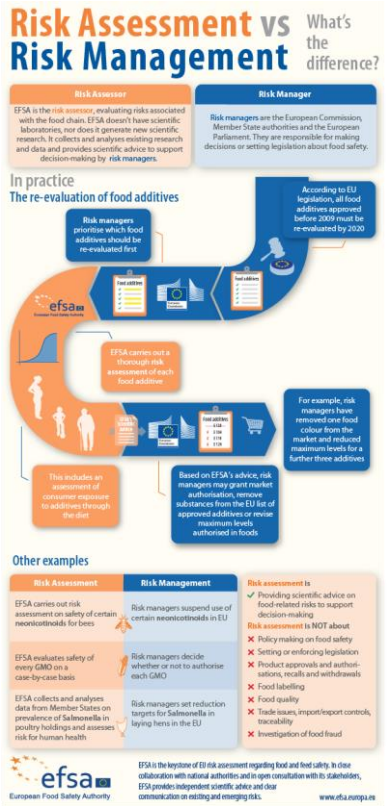


- Indirect pollution of food and drinking water from the environment or processing
- Direct contamination (e.g. through food contact materials)

Risk Assessment & Management of PFAS

Risk Assessment, Management & Enforcement

- Risk Assessment of PFAS
  - European Food safety Authority (EFSA)
- Risk Management of PFAS
  - European Commission
- Enforcement of PFAS regulations
  - Member states
    - NVWA



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Risk Assessment

EU Risk Assessment

- European Food Safety Authority (EFSA), 2020
- Consumers may be at risk at low levels (TWI = 4.4 ng/kg bw per week)
- PFHxS, PFOS, PFOA, PFNA

EFSA - Responsible for risk assessment

European Food Safety Authority

Exposure 4 PFASs (ng/kg bw/week)

Age group	Range of mean dietary exposure (LB-UB) (ng/kg bw per week)		
	Mean LB dietary exposure		
	Minimum	Median	Maximum
Infants	17	34	85
Toddlers	10	21	46
Other children	6	11	21
Adolescents	3	6	11
Adults	4	6	9
Elderly	5	6	15
Very elderly	3	6	22
Age group	95th percentile LB dietary exposure		
	Minimum	Median	Maximum
Infants			
Toddlers			
Children			
Adolescents			
Adults			
Elderly			
Very elderly			

- TWI: 4.4 ng/kg bw/week for sum of 4 PFAS
- Higher intake infants included in deriving TWI
- For mean exposures, nearly all age groups exceed TWI

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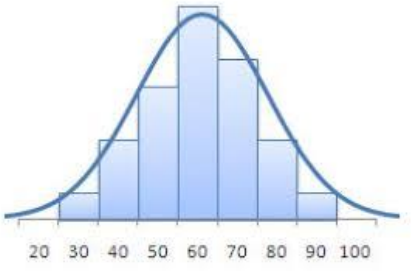
Adolescents	3	6	11
Adults	4	6	9
Elderly	5	6	15
Very elderly	3	6	22
Age group	95th percentile LB dietary exposure		
	Minimum	Median	Maximum
Infants	32	96	195
Toddlers	23	53	96
Children	19	29	68
Adolescents	9	15	37
Adults	9	16	35
Elderly	12	17	39
Very elderly	9	16	70

- TWI: 4.4 ng/kg bw/week
- At 95% percentile, all age groups exceed TWI



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Risk Management

Risk Assessment

- European Food Safety Authority (EFSA), 2020
- Consumers may be at risk at low levels (TWI = 4.4 ng/kg bw per week)
- PFHxS, PFOS, PFOA, PFNA

Risk Management

- Discussions EC & Member states legislative measures
- Limits in food & drinking water

EC - Responsible for risk management

European Commission

efsa
European Food Safety Authority

Risk management of PFAS

Setting maximum limits for PFAS in selected foods where PFAS contamination needs to be regulated

Recommendation for monitoring for foods with limited knowledge on PFAS contamination

Capacity building: improving the capabilities of laboratories to measure PFAS in food

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Risk Management of PFAS

- Commission Recommendation (EU) 2022/1431 of 24 August 2022 on the monitoring of perfluoroalkyl substances in food
- Commission Implementing Regulation (EU) 2022/1428 of 24 August 2022 laying down methods of sampling and analysis for the control of perfluoroalkyl substances in certain foodstuffs
- Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs

2022/1431: monitoring of perfluoroalkyl substances in food - compounds

- Commission Recommendation
- MS should test for PFOS, PFOA, PFHxS, PFNA
- MS should also consider to test for emerging PFAS like F53B, GenX, ADONA, Capstone A + B and Flourotelomer alcohols
- MS should, if possible, also test for PFBA, PFPeA, PFHxA, PFHpA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFPS, PFHpS, PFNS, PFDS, PFUnDS, PFDoDS, PFTrDS, FOSA

2022/1431: monitoring of perfluoroalkyl substances in food - commodities

- The monitoring should include a wide variety of foodstuffs reflecting consumption habits, including fruits, vegetables, starchy roots and tubers, seaweed, cereals, nuts, oilseeds, food for infants and young children, food of animal origin, non-alcoholic drinks, wine and beer. Some specific criteria:
    - for products from different production types, incl organic
    - for animal products (indoor and outdoor rearing, wild and farmed species)
    - for potatoes (peeled, unpeeled, different varieties) and for for fungi, for wild and farmed fungi.

2022/1431: monitoring of perfluoroalkyl substances in food - LOQs

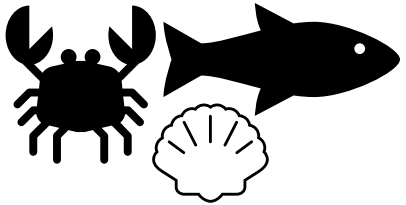
- LOQs should be low (0.001 to 0.5 ug/kg), depending on compounds and food type
- Indicative levels: searching for the source of contamination, when the indicative levels are exceeded
    - (0.005-1,5 ug/kg), depending on compounds and food type

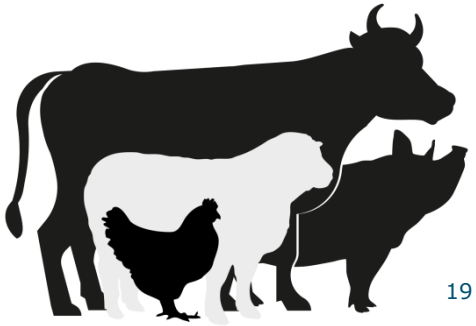
2022/1428: methods of sampling and analysis for the control of perfluoroalkyl substances in food

- Methods for sampling defined
- Methods of chemical analysis defined
    - Precautions to reduce impact of background contamination
    - Performance criteria (precision, trueness, LOQ)
    - Reporting of results
- Reference to EU Reference Laboratory Guidance Document on Analytical Parameters for determination to PFAS

Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs

- Maximum Levels for PFAS in food will become into force 01/01/2023
- For 4 PFAS and the sum of 4
- Foods include animal products
- Not for feed





European activities - food

EU Risk Assessment

- European Food Safety Authority (EFSA), 2020
- Consumers may be at risk at low levels (TWI = 4.4 ng/kg bw per week)
- PFHxS, PFOS, PFOA, PFNA

Setting limits in food

- Ongoing discussion legislative measures
- Limits in food & drinking water

Are we up to the task?

- Method development
- Sensitivity is key
- Control of backgrounds is key

efsa
European Food Safety Authority

The analysis of PFAS in food & feed

Essential backgrounds

- Little information about PFAS in feed
- PFAS can be found in all foods (vegetable, animal, drinks)
- 20+ compounds, of which 4 will become part of legislation for food
- Liquid chromatography coupled to mass spectrometry

Analytical challenges

- Diverse nature of the PFAS
    - Short chain (water soluble) to long chain (bioaccumulative)
- Wide variety of matrices (drinking water, dairy, meats, fish, offal, fruits & vegetables)
- Sensitivity improvement, down to low ppt (10-12) level
- Blanks: PFAS are everywhere in society, also in the lab
- Interferences: interfering compounds that may compromise PFOS accuracy

Selection of PFAS compounds

- Table: commonly analysed PFAS
  - Sulfonic acids
  - Carboxylic acids
- List includes 4 analytes marked by EFSA in their risk assessment

Acronym	Molecular formula
PFBA	$C_4HF_7O_2$
PFPeA	$C_5HF_9O_2$
PFHxA	$C_6F_{11}O_2^-$
PFHpA	$C_7F_{13}O_2^-$
PFOA	$C_8F_{15}O_2^-$
PFNA	$C_9F_{17}O_2^-$
PFDA	$C_{10}F_{19}O_2^-$
PFUnDA	$C_{11}F_{21}O_2^-$
PFDoDA	$C_{12}F_{23}SO_3^-$
PFTrDA	$C_{13}F_{25}SO_3^-$
PFTeDA	$C_{14}F_{27}SO_3^-$

Acronym	Molecular formula
PFBuS	$C_4F_9SO_3^-$
PFHxS	$C_6F_{13}SO_3^-$
PFHpS	$C_7F_{15}SO_3^-$
PFOS	$C_8F_{17}SO_3^-$
PFDS	$C_{10}HF_{21}\ SO_3^-$
PFUnDS	$C_{11}HF_{23}\ SO_3^-$
PFDoDS	$C_{12}HF_{25}\ SO_3^-$
PFTrDS	$C_{13}HF_{27}\ SO_3^-$

Acronym	Molecular formula
GenX	$C_{13}HF_{27}\ SO_3^-$

In addition, PFAS replacement chemicals, e.g. DONA, F53B

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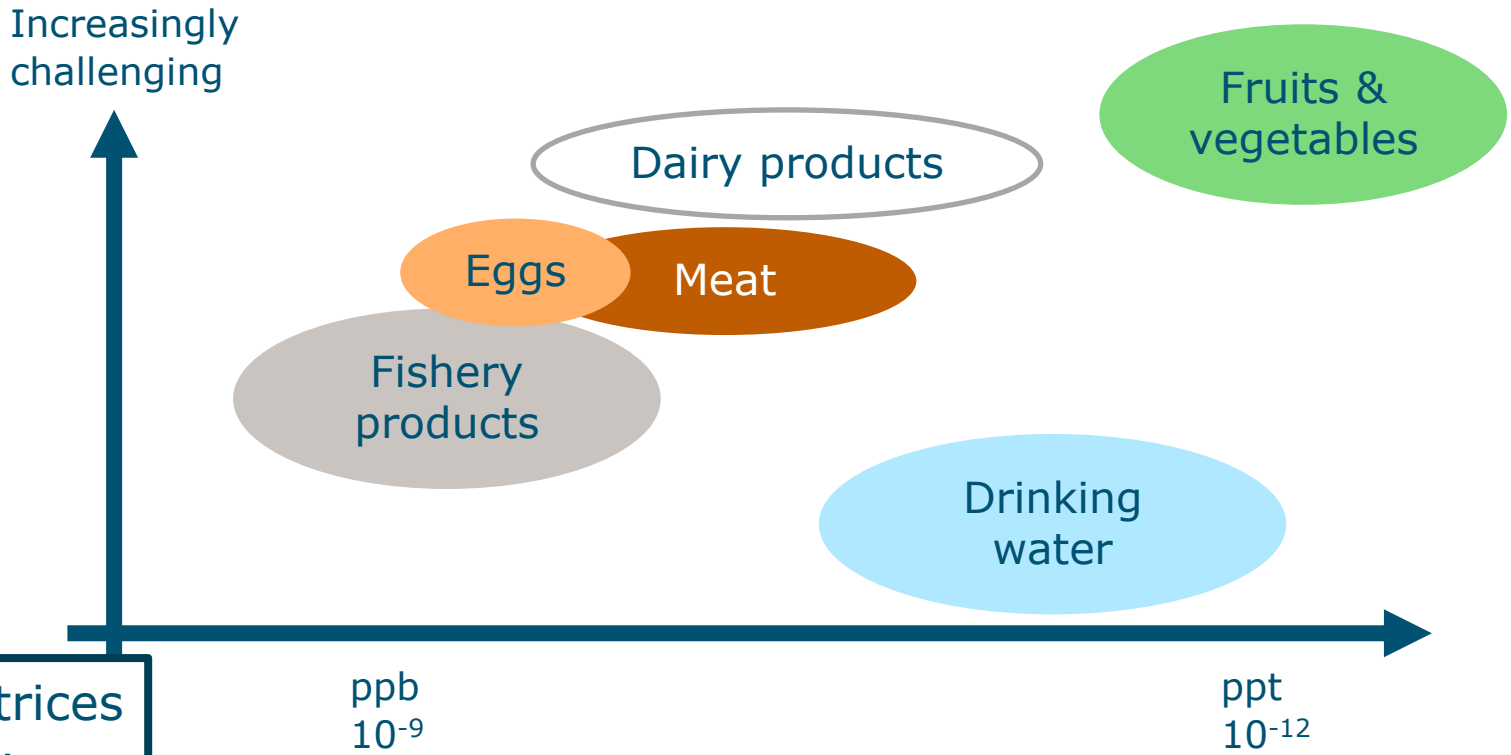
Matrix type vs analytical challenge



Diversity of matrices
Method sensitivity
Level of experience

Methodology – Extraction & Clean-up

Sample intake

Isotope labels, blanks, spikes

Extraction

Clean-up

Final extract

Instrumental analysis

Methodology – Instrumental analysis

- UPLC or HPLC
    - Most ionic PFAS are not GC emendable
- MS/MS, QTOF, HRMS
    - Two transitions or similar identification potential for specificity (interferences)
- Prevent PTFE of other fluoropolymers

Sciex 7500 UPLC-MS/MS

QA\QC: Blank issues

- PFAS are used everywhere – so beware of blanks
  - Dust in the lab
  - Solvents, reagents
  - Instrument (LC-MS/MS)

- Which blanks to run?
  - Method blanks
  - Instrument (solvent) blanks

FTFE tubing

Studie volkstuintjes nabij Chemours

- Chemours is chemische fabriek die PFAS maakt
- Historische uitstoot via lucht en water naar de omgeving
- Volkstuintjes in de regio Sliedrecht vervuild met PFAS
- Kunnen eigen groenten gegeten worden?

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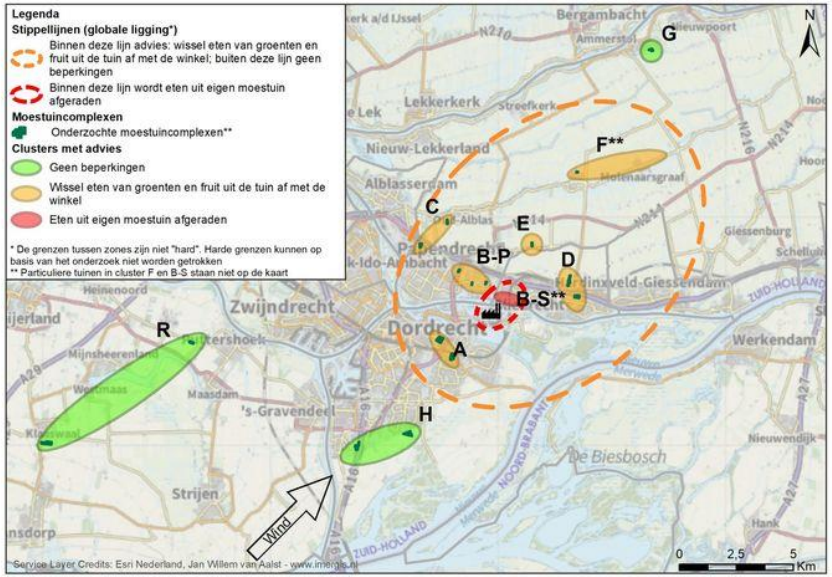
Studieresultaat

- WFSR: analyse groenten- en fruitmonsters
- RIVM: risicobeoordeling



- Advies: vermijd/beperk consumptie uit eigen tuin in nabijheid van de fabriek

How to get started

- Equip your laboratory with resources (machines, human capital, standards, materials)
- Establish the methods, and take care of blanks, sensitivity, interferences etc
- Accreditation
- Monitor the QA\QC, and participate in proficiency tests (e.g. FAPAS, QUASIMEME, EURL)

How about equipment, labware, reference standards...

- Instrumental analysis can be run on commercial systems
    - Some plumbing may be needed to remove PTFE
- Consumable suppliers in recent years paid more attention to ‘PFAS-free’ SPE, sorbents, tubes, chemicals etc etc
- Reference standards are commercially available for the most common PFAS, as well as many (13C) labelled analogues

Standards available?

- ISO standards available for (drinking) water
  - ISO 21675:2019 & ISO 25101:2009
- No CEN/ISO standards available for food (or feed)
  - Need to support future legislation on maximum levels in food
- European Reference Laboratories (EURL) network has worked on guidelines (next slide)

Standardisation of PFAS analysis in food/feed?

- No standard available yet

- To support future implementation of limits, dietary exposure assessment, (inter)national trade and ultimately (human) health.
- Agree on priorities (#PFAS, #matrices, #method characteristics, timelines)

At the European scale – capacity building

- European working group (hosted by EURL-POPs) setting guidelines for analysis of PFAS
- Improving an EU-wide testing infrastructure
- Food and feed
- Performance criteria, not a standard
- Analysis, excluding sampling
- Animal origin/plant origin
- Published recently

EURL POPs

CVUA Freiburg, Germany

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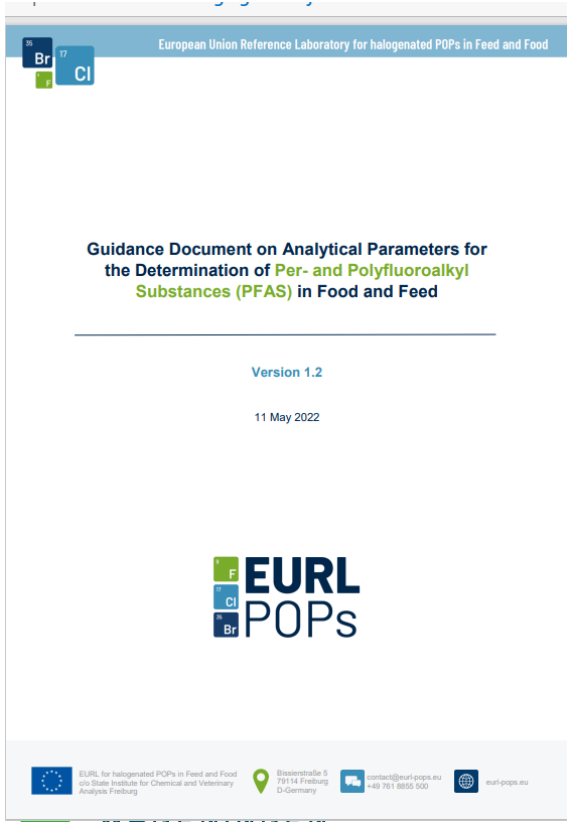
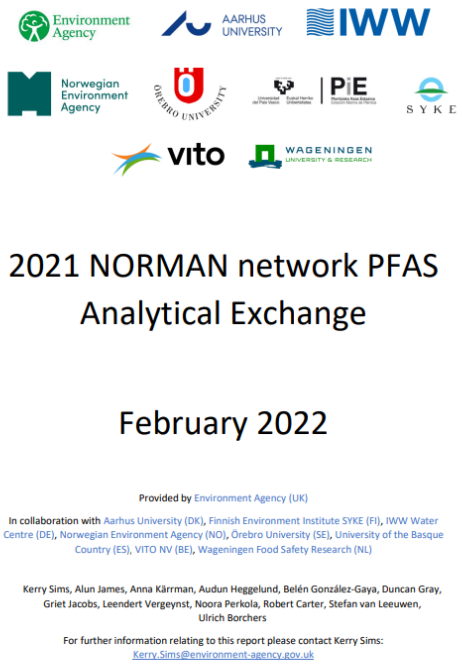
At the European scale – Guidance document



- Version 1.2, 11 May 2022
- Performance based criteria on analysis
- Check updates on
- https://eurl-pops.eu/

European inventory of analytical methods



- NORMAN - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances
- Published Feb 2022
- Summary of analytical approaches on PFAS in environmental matrices (incl. water and biota)
- https://www.norman-network.net/?q=Home

Take home message

- PFAS face global scientists, laboratories and regulators with big challenges
- PFAS are a threat to human health and safe foods
- There is a good basis on PFAS analytical tools for targeted PFAS analysis, but further progress is needed
- Standardisation of PFAS analysis in foods is not in place, but is needed

Acknowledgements

- EURL – Core working group on PFAS analysis for stimulating discussions while preparing the guidelines
- Various funding sources
- @WFSR: Technicians, co-workers and students
    - Ron Hoogenboom, Bjorn Berendsen, Ruben Kause, Rens Leontien de Pagter, Bob van Dooren, Rens Keppels, Niels Pouwels, Menno Duits, and many more....

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Thank you for your attention

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