federal public service
HEALTH, FOOD CHAIN SAFETY AND ENVIRONMENT

PFAS: wat, eigenschappen, toepassingen en toxiciteit. Europees, federaal en internationaal beleidskader.

PFAS: Definition, Properties, Uses and Toxicity. European, federal and international policy framework

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Minaraad, Webinar PFAS, 16/10/2020

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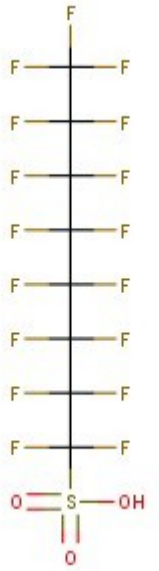
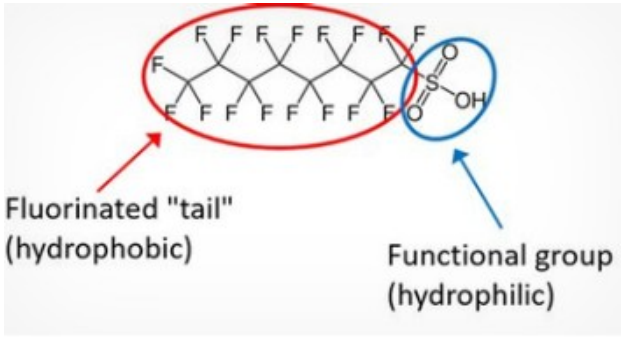
What are the PFAS?



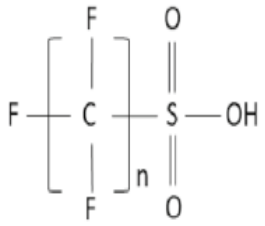
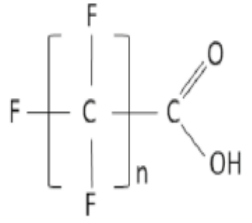
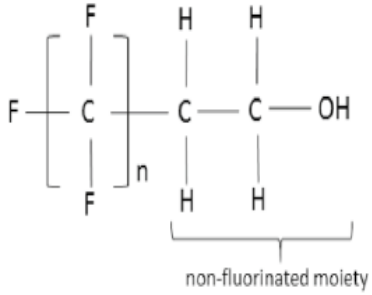
- A Belgian story: Swarts's reaction (1892) very important for fluorine chemistry. Large-scale production of many PFASs started between the 1940s and 1970s and increased
- Per- and poly-fluoroalkyl substances
  - Composed of alkyl chains with fluorine substitutions and functional groups attached to them (e.g. carboxylic, sulfonic acids)
  - Per: fully fluorinated chain
  - Poly: partly fluorinated chain
  - Fluorinated polymers
- Very large group of substances, work ongoing towards unified terminology and inventory, >4700 in OECD list, >6800 in ECHA list
- Common chemicals characteristics: organic compounds (carbon) with a high content in C-F links (carbon-fluorine). Very strong links giving many of the specific properties of the group together with the length of the chain and the functional groups attached to it (thermal & chemical stability, persistence, water-oil-grease repelency, surfactants,etc)

What are the PFAS?

- Some examples of important groups for the environnement:



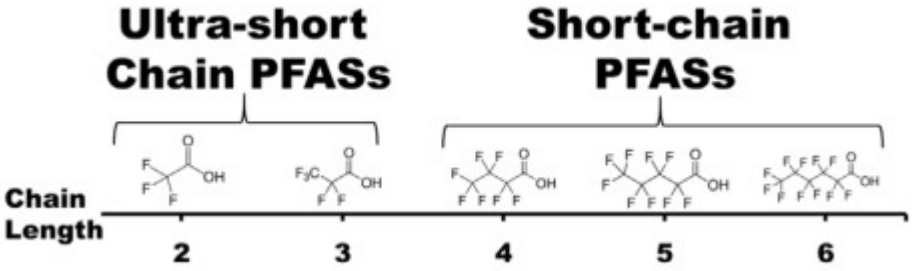
- Gives properties for applications (eg firefighting foams) but also e.g. protein binding in blood
- Industry shift from long-chain to short-chain PFAS

Perfluoroalkane sulfonic acids Long-chain: n ≥ 6 Short-chain: n < 6 Example short-chain representative: PFBS (n = 4)	
Perfluoroalkyl carboxylic acids Long-chain: n ≥ 7 Short-chain: n < 7 Example short-chain representatives: PFBA (n = 3), PFHxA (n = 5)	
Example of short-chain precursors 4:2 fluorotelomer alcohol (n = 4) 6:2 fluorotelomer alcohol (n = 6)	

Brendel & al, 2018

What are the PFAS?

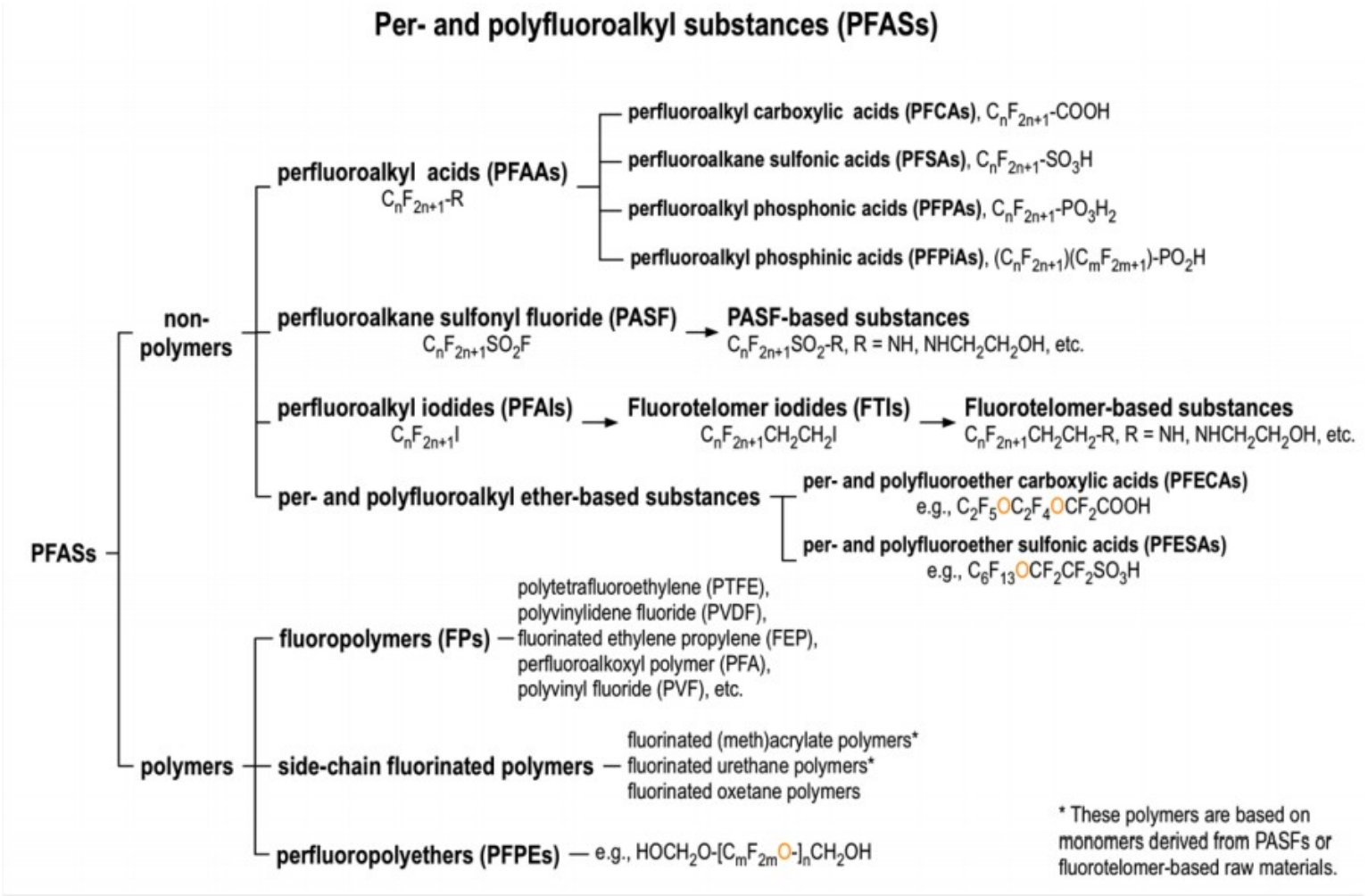
- Recent emphasis on ultrashort PFAS:



Ex:
Bjoornsdotter 2019
Alteia 2019
Chen 2019
Barzen 2015

What are the PFAS?

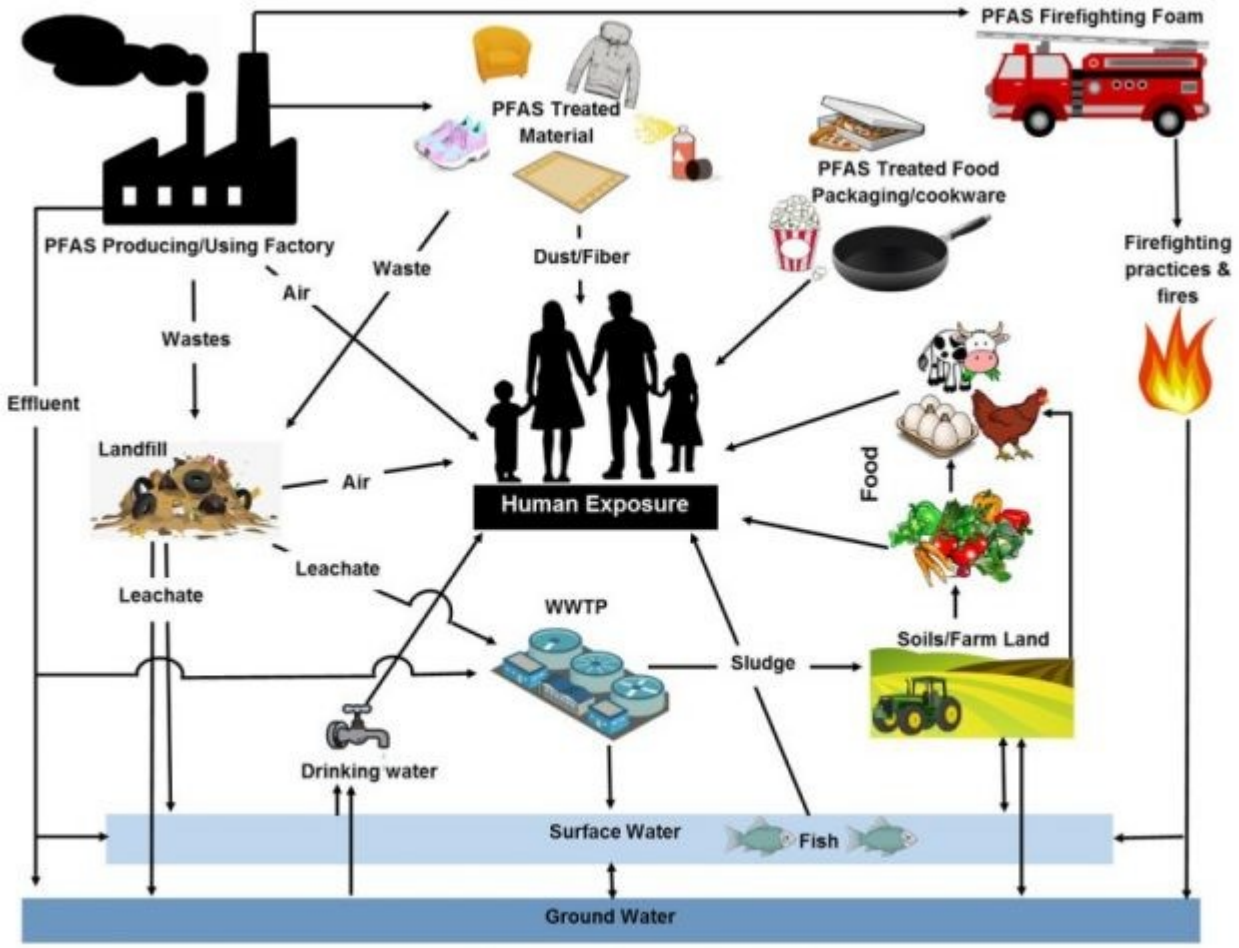
- OECD (2020) work ongoing:



PFAS uses and applications

- Used in a huge number of applications and kinds of products (professional, consumer, industrial uses, intermediates, in mixtures, etc).
- Examples:
  - Sectors: Aerospace, Apparel, Auto, Building & Construction, Chemicals & Pharmaceuticals, Electronics, Energy, First Responder Safety, Healthcare & Hospitals, Oil & Gas, Scientific Studies, Semiconductors, … (http://accfc.sachsdigital.com/applications/)
  - Most usually (OECD, 2020) where extremely low surface energy or surface tension and/or durable water- and oil-repellency is needed, e.g., chromium metal plating, various fire-fighting foams, or for surface treatment of textiles, carpets and papers.
- Current debate in the EU is about defining which are the essential uses and managing the whole group together (see below). Cousins et al, 2019; Kwiatkowski,2020 present this concept.

PFAS fate and exposure



Human Exposure and sources of PFAS
Image: DWP, adapted from Oliaei et al. 2013.

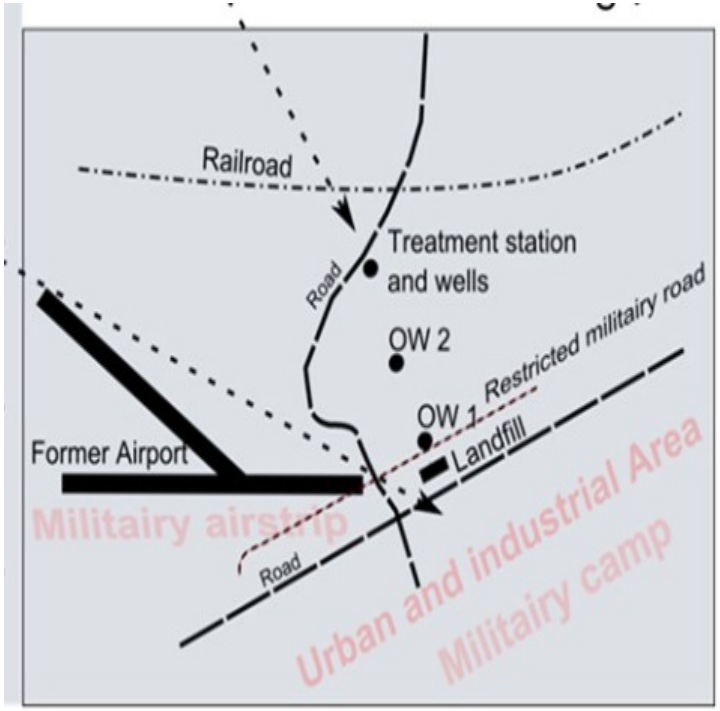
PFAS fate and exposure

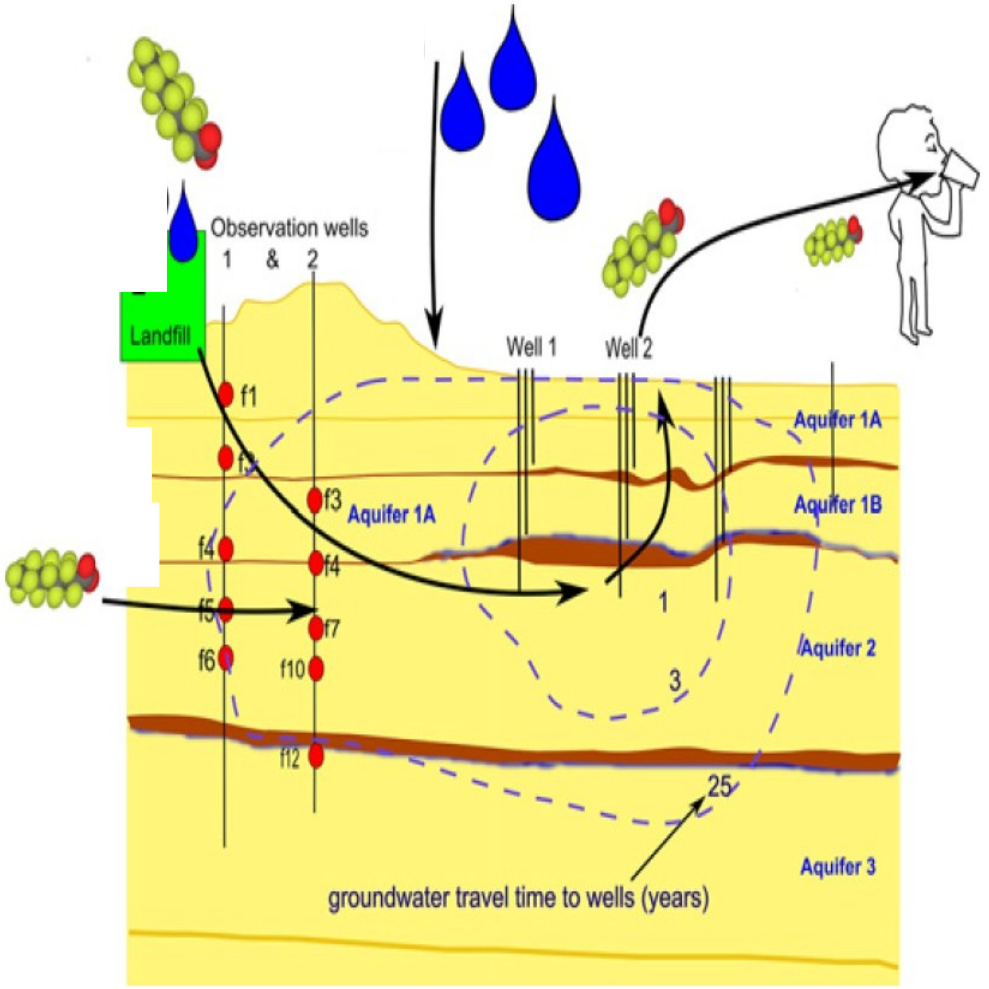
Some examples

- Industrial effluents (PFAS production and use) → water
- Consumer goods → dust, WTP e.g. clothes
- Landfill → air and leachate
- Soil → groundwater
- Sludge application from WTP
- Pesticides (as surfactants)
- Rain, air deposition
- AFFF

PFAS fate and exposure

- Data in the Netherlands, drinking water and landfill (Eschauzier, 2013)





PFAS concerns

- For many of the PFASs other than PFCAs, PFSAs, and their major precursors, public information on their hazardous properties, environmental fate and transport, exposure, and toxic effects is still very limited, and in the public domain they remain largely unassessed and unregulated (Ritscher et al 2018).
- Recognized hazards for individual PFAS and substantiated concerns for the group are on the table
- Costly or impossible to remediate at large scales either in situ or for water treatment
- Poorly reversible exposure → depends e.g. on half-live in groundwater, half-life in serum, molecule, etc
- Existing monitoring shows ubiquity
- Possible enormous liabilities (presently 3 billions in the USA for the US air force)
- Enormous corpus of research but slow to translate into regulation until recently, and and in-depth knowledge of toxicity and ecotoxicity of such a number of substances cannot realistically be expected
- Regrettable substitutions within the group are possible
- A case-by-case risk assessment (and management) is impossible for 4000 to >6000 substances

PFAS concerns

Growing field in environment and health publications, slow translation into regulation until recently (adapted from Grandjean et al, 2018)

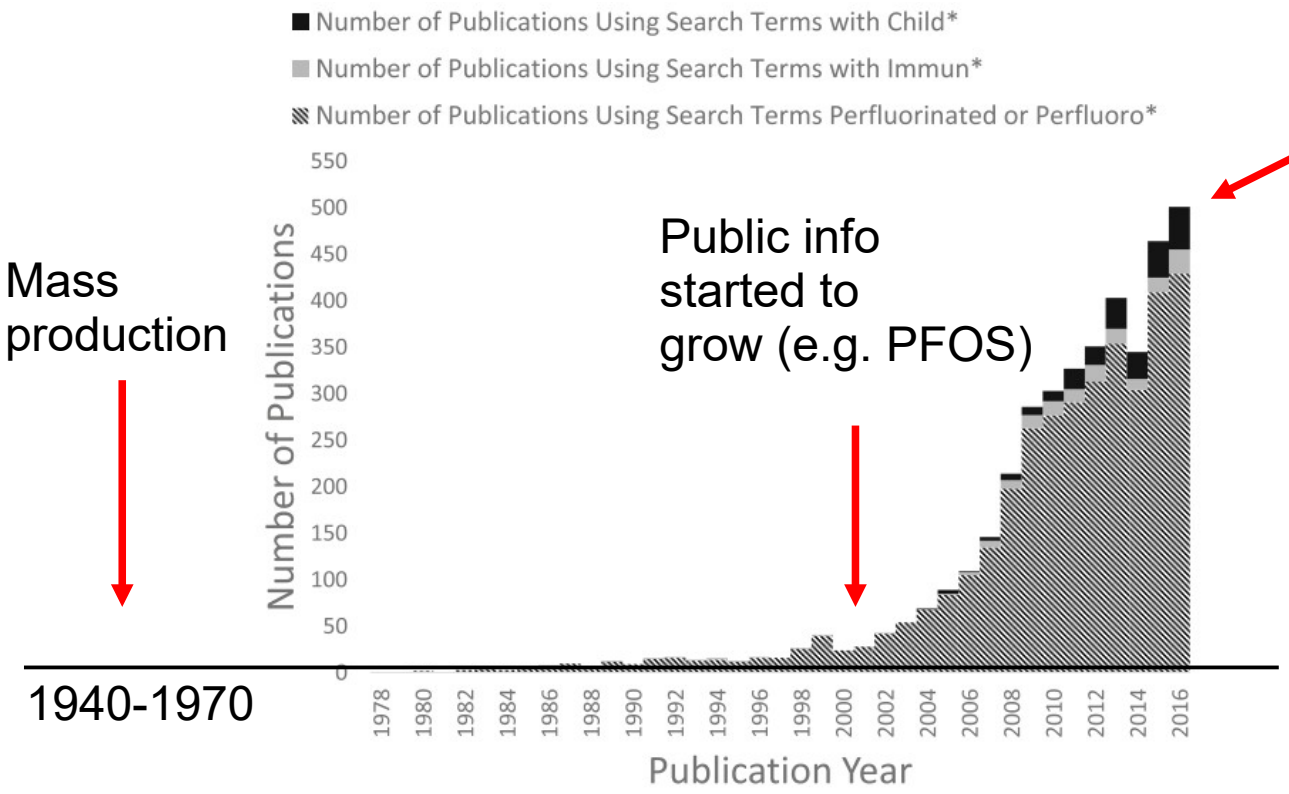


Fig. 1 Number of publications on PFASs over time, according to the Web of Science database (between 1978 and 2017), using the search terms "perfluorinated or perfluoro"* and restricting to environmental sciences, toxicology, or public, environmental, and occupational health categories. This search was further refined using the search terms "immun*" and "child*"

PFAS hazards

Legally recognized hazards already for some substances:

- **PBT/vPvB/POP**
  - PFHxS, PFOA, Several C9-C14 in the REACH candidate list
  - POP - Stockholm Convention : PFOS, PFOA
- **CLP Harmonised classifications** (possibly not exhaustive), various long-chain :
  - presumed developmental toxicants , PFNA and PFDA are harmonised also as Repr. 2 (Suspected of damaging fertility)
  - perfluorooctane sulfonic acid + potassium perfluorooctanesulfonate (PFOS); and related diethanolamine perfluorooctane sulfonate; ammonium perfluorooctane sulfonate; ammonium heptadecafluorooctanesulfonate; lithium perfluorooctane sulfonate; lithium heptadecafluorooctanesulfonate
    → Carc. 2, **Repr. 1B**, Lact., Acute Tox. 4 *, Acute Tox. 4 *, **STOT RE 1 liver**, Aquatic Chronic 2
  - PFDA, PFD-A, PFD-S → Carc2, **repr 1B**, Lact.
  - PFNA, PFN-S, PFN-A (perfluorononan-1-oic acid; perfluorononan-1-oic acid sodium salts; perfluorononan-1-oic acid ammonium salts)
    → Carc. 2; **Repr. 1B**; Lact.; Acute Tox. 4; Acute Tox. 4; **STOT RE 1**; Eye Dam. 1
  - perfluorooctanoic acid (PFOA)
    → Carc. 2, **Repr. 1B**, Lact., Acute Tox. 4, Acute Tox. 4, STOT RE 1, Eye Dam. 1
- **ELOC** (equivalent level of concern under REACH)
  - PFBS
  - GENx : SVHC recognised (basis : weight og evidence, art.57f, persistent, mobile, LRT, some tox, no remediation, exposure unavoidable, irreversibility, etc)

PFAS hazards

- Growing scientific evidence of hazards for many members of the PFAS group, e.g. :
  - Biomonitoring data (see presentation today on the biomonitoring in Flanders). And German HBM Commission (Apel, 2017) : PFOS, PFOA → rates as well proven, relevant, and significantly associated: 1. Fertility and pregnancy 2. Weight of newborns at birth 3. Lipid metabolism 4. Immunity after vaccination, immunological development 5. Hormonal development, age at puberty/menarche 6. Thyroid metabolism 7. Onset of menopause.
  - Additive effet between PFAS (Wolf et al. 2014)
    - mixtures of PFOA and either PFNA, PFHxA, PFOS or PFHxS tested
    - in vitro response addition and concentration addition at low concentration
  - Immunotoxicity and developmental concerns (Liew, 2018, Grandjean,2018 ; DeWitt, 2019)
  - Children chronic respiratory impairment (Qin, 2017 ; Timmermann,2017)
  - Endocrine disruptors (see e.g. ENDO 2020 abstracts : obesity)
  - Accumulation in some edible plants (Brendel, 2018)

PFAS hazards and COVID-19

- Growing concerns that PFAS may act by increasing the occurrence of COVID-19 risk factors because :
  - Immunotoxicants : correlations to diminished vaccine antibody response to vaccines (Grandjean, 2017, Looker et al., 2014) ; may reduce infectious disease resistance (NTP, 2016)
  - Endocrine disruptors (obesity, diabetis,…)

PFAS policy: International aspects

- Perfluorinated Chemicals were identified as an emerging policy issue by the Third session of the International Conference on Chemicals Management (ICCM3) in 2012.
- Efforts on this emerging policy issue are focused on gathering and exchanging information on perfluorinated chemicals and to support the transition to safer alternatives.
- This work has been coordinated by the Global Perfluorinated Chemicals Group, which is supported by the Organisation for Economic Cooperation and Development (OECD) and UNEP.
- A web-portal has been developed for information exchange purposes and is one of the OECD's contributions to implement the Strategic Approach in this area (http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/)

PFAS policy: International aspects

- PFOS, its salts and perfluorooctane sulfonyl fluoride were liste under annex B of the Stockholm Convention on POP with acceptable purposes (no time limitation) and specific exemptions (time limitation) in 2009 (decision SC-4/17). In 2019, this decision was amended (decision SC-9/4) – several acceptable purposes and specific exemptions were removed.
- PFOA, its salts and related compounds were listed under annex A of the Stockholm Convention on POP with specific exemptions in 2019 (decision SC-9/12). Encouraging Parties not to replace fire-fighting foam that contains PFOA with short-chain PFASs due to their persistency and mobility, potential negative environmental, human health and socioeconomic impacts
- Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds are considered as POP candidates.
  - At its thirteenth, fourteenth and fifteenth meetings, the POPs Review Committee,completed the risk profile and risk management evaluation .
  - The Committee adopted a decision recommending that the Conference of the Parties (COP) consider listing PFHxS, its salts and PFHxS in Annex A to the Convention without specific exemptions (decision POPRC-15/1) at the next COP (in 2021).
  - In order to support Parties and observers and to facilitate the identification of substances, an initial indicative list of PFHxS, its salts and PFHxS-related compounds has been prepared as set out in document UNEP/POPS/POPRC.15/INF/9.

PFAS policy: International aspects

PFAS are now politically and juridically sensitive:

- Press and public scandal in NL (GENX)
- USA, e.g. industry settling a case in Minnesota (2018) for $850 millions (indictment included suppression of scientific research, failure to report data to the authorities)
- Press reported tensions between US defense and risk assessment at ATSDR

PFAS policy: European aspects

- Since 2016: a group of MS experts and ECHA (with BE participation) developed the possibility of risk management of PFAS using an “arrow-head approach” where all the substances related to a final degradation product are considered together -> makes restrictions of several 100ds of substances possible
- 2017: DE pushing the PMT and vPvM concepts (persistency, mobility toxicity as complementary criteria to PBT/vPvB
- 2017-2019: REACH showed too slow action when actions where on individual substances, gradually ECHA and MS shifted to a groups approach (ECHA, 2020)
- 2019: a group of 10 MS designed a proposal for a PFAS strategy that was submitted to the Commission (at Ministers level, included BE, regulatory and non-regulatory aspects)
- 2019: EU Council conclusions: UNDERLINES the increasing health and environmental concerns posed by highly persistent chemicals; NOTES in specific the growing evidence for adverse effects caused by exposure to highly fluorinated compounds (PFAS), the evidence for wide spread occurrence of PFAS in water, soil, articles and waste and the threat this may cause to our drinking water supplies; CALLS on the Commission to develop an action plan to eliminate all non-essential uses of PFAS.
- 2020: European green deal → chemicals strategy for sustainability published 14/10/2020 → PFAS action plan, essential uses, sustainable by design (green chemistry principles → avoid P substances), mixture effects

PFAS policy: European aspects

- REACH/CLP work in progress: you can check work by MS and ECHA through the Public activities coordination tool (https://echa.europa.eu/fr/pact)
- Case-by-case development of an ELOC approach in REACH for PFAS (e.g. GENX, PFHxA) = equivalent level of concern compared to CMR or PBT/vPvB substances, as defined in article 57(f). Reasoning similar to vPvB: (i) the level of uncertainty in identifying long-term effects cannot be estimated with sufficient accuracy (vB) and (ii) consequences of an underestimation of adverse effects are not easily reversible by regulatory action (vP), i.e., the effect is occurring or is likely to occur at a certain point in time, and even if there is immediate regulatory action to prevent further emission, the adverse effects will continue.
- NL,DE,NO,DK,SE working on a general REACH restriction of PFAS (RMOA)
- Several restriction intentions under the arrow head approach, overlapping with the now proposed general restriction on PFAS
  - PFHxS & related, PFOA & related, PFNA PFDA PFUnDA PFDoDA PFTrDA PFTDA & related, C9-C14 & related). Status?
  - DE restriction on PFHxA ongoing
  - COM/ECHA working on restrictions on AFFF and textiles, upholstery, leather, apparel and carpets (TULAC). Status?
- BE involved in 4 substance evaluations (=asking more data and understanding), EC700-403-8 is on hold while scope of PFHxA restriction is defined (common degradation product -> arrow head approach, but caution if not same hasards/exposures), EC473-390-7 and perfluamine are on going, and AFS (a surfactant) conclusions are in final phase.
- BE CLH dossier ongoing for PFHpA Repr. 1B, STOT RE 1 (liver)

PFAS policy: European aspects

- Drinking water directive: criteria choice between sum of selected PFAS (max 0,5µg/l) and total PFAS (max 0,1µg/l), technical guidelines to be proposed by the COM. However: Based on immunotoxicity, US agency of toxic substances (ATSRD) considered for some time stricter limits in drinking water than the new EU ones (but for selected PFAS only: PFOS, PFOA, PFNA, PFHxS). Moreover, some provisions states that monitoring is not necessary if the substances are not likely to be present in a give water supply → to me this appears to be unlikely since mobility is a fact form many PFAS (air deposition, water, etc).
- Need of action upstream (=REACH) to comply with the new future criteria in the driking water directive → synergies between regions and federal levels in BE.
- Groundwater Directive : emmerging concern, monitoring, PFAS as possible substances considered in the future Groundwater Dir. Review
- Waste Water reuse regulation, sludge directive
- Plant protection products: debate not started yet
- Contaminants in food: EFSA work on PFOS,PFOA (a considerable part of the population exceeds the TWI), and short chain PFAS
- Stockholm PFOA → more stringent than REACH restriction thus → POP regulation
- PFAS are a very important topic for waste and circular economy (avoiding toxic cycles

PFAS policy: Federal and national aspects

- The federal level involvement:
  - Representing & negotiating for BE at EU and international levels in various fora(cfr above)
  - Implementing EU regulations in BE (CLP, REACH, food, pesticides, etc) + enforcement, some aspects are managed by the regions
  - Scientific expertise (CLH and substance evaluations, restrictions preparations, SVHC identification, PBT expert group, PFAS working group, ED expert group,etc)
- Information exchange and cooperation on through CCIEM, BCR, CIMES:
  - ministers of env. & health from BE (e.g. → asking a PFAS plan to the COM)
  - Discussions on REACH actions and BE positions
- Defense / firefighting foams in proposed or foreseen restrictions
- On 2018 BE Senat adopted an information report on endocrine disruptors, recommending a national action plan.
- Work on the action plan for endocrine disruptors (is ongoing federal/regions/communities, within the EU framework → https://www.health.belgium.be/en/endocrine-disruptors

Conclusions

- Information is available on unacceptable costs and effects that are likely if generalized use of PFAS continues. Drinking water is a particular concern. EU Commission is right to invoke the precautionary principle, indeed the PFAS case involves *[decisions] when scientific information is insufficient, inconclusive, or uncertain and where there are indications that the possible effects on the environment, or human, animal or plant health may be potentially dangerous and inconsistent with the chosen level of protection* [COM/2000/0001 final].
- PFAS policy in the EU is taking the direction of an increased protection of health and environment, within a circular economy with non-toxic lifecycles
- Important to continue synergies between regulations (e.g. REACH and drinking water directive). Upstream measures, grouping, precautionary approach, safe by design and essential uses definition are appropriated tools because a substance-by-substance approach for risk assessment/management of PFAS is not feasible while regrettable substitutions are possible. However, there is already a legacy of pollution to manage, for which monitoring will be needed for many years, and use conditions and environmental permits have also a role for minimizing releases from accepted essential uses until substitutes are developed. Monitoring in the environment is also useful for ensuring that the upstream measures are working.
- Within the proposed measures, a particular attention is needed to imported articles (thus analytical methods and enforcement) for ensuring a level playing field for EU industry
- Building and sharing expertise, collaboration and making investments in green/sustainable chemistry is crucial for correct substitution of PFAS uses. Environmental, health ans sustainability criteria are to be used for orienting those investments.

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