Workshop 5: Exploring how non-target screening can support environmental monitoring of diffuse soil pollution

Policy

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Reference lab

Commercial lab

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vision on technology

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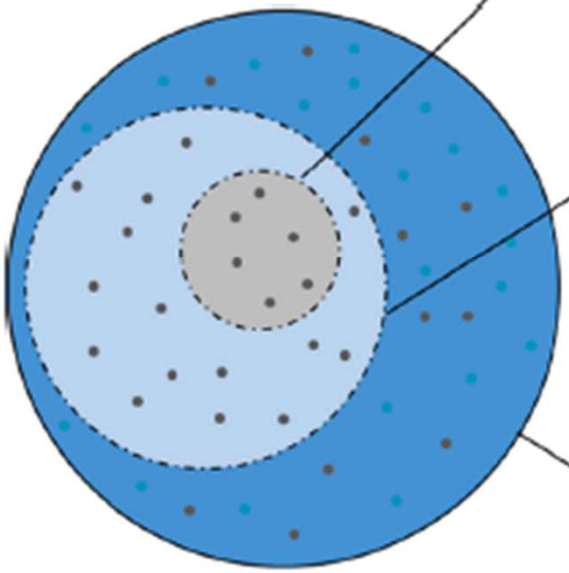
Let’s talk the same language

More than 1 analytical method – emerging contaminants



	Methodological approaches	Objectives
Known *Known structure with well established focused and quantitative method*	Targeted measurement	Unambiguous identification and quantification
Known unknown *Known structure with suspected presence but lacking a method applicable for routine quantitative measurement*	**Suspect screening**	Qualitative detection rates or semi-quantitative data
Unknown unknown *Still unknown markers of exposure*	**Non-targeted screening (NTS)**	Detection of new exposure markers of concern

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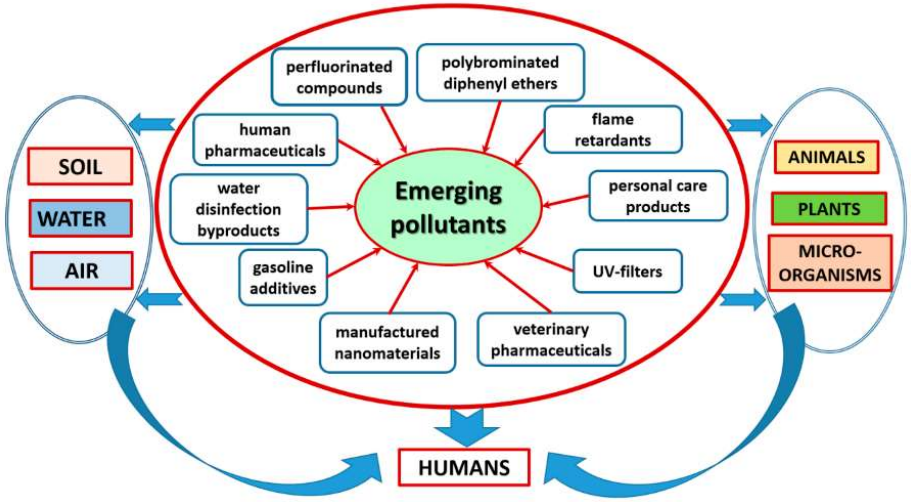
Pourchet et al. 2020

Emerging contaminants



https://doi.org/10.3390/w13020181

Pollutants that have been detected in environmental monitoring samples, that may cause ecological or human health impacts, and typically are not regulated under current environmental laws;

- PFAS
- BFR's
- ....

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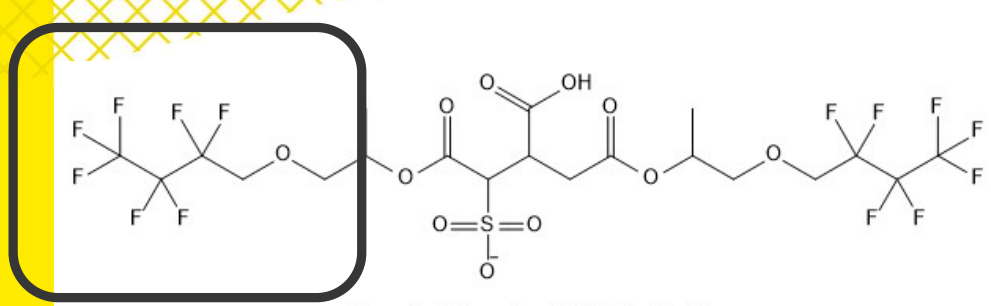
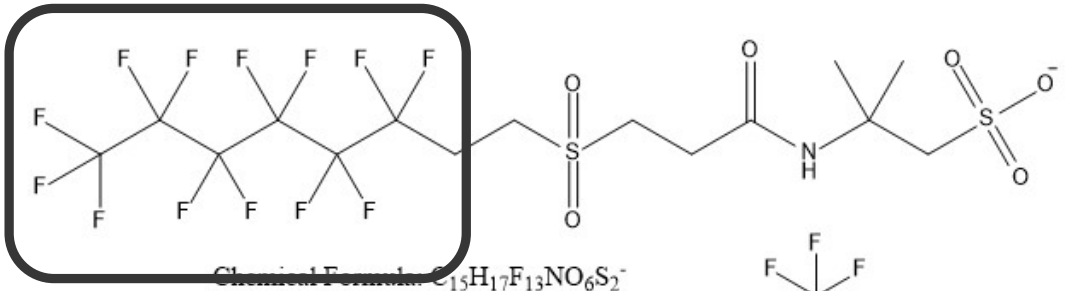
Target or NTA ?



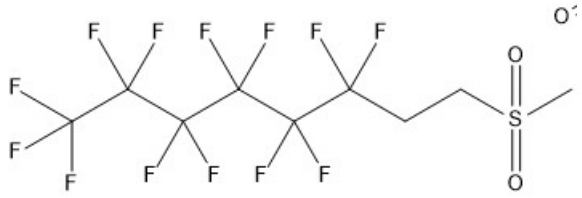
PFBA-precursor

Chemical Formula: $C_{20}H_{21}F_{14}O_{11}S^-$
Exact Mass: 735,0587

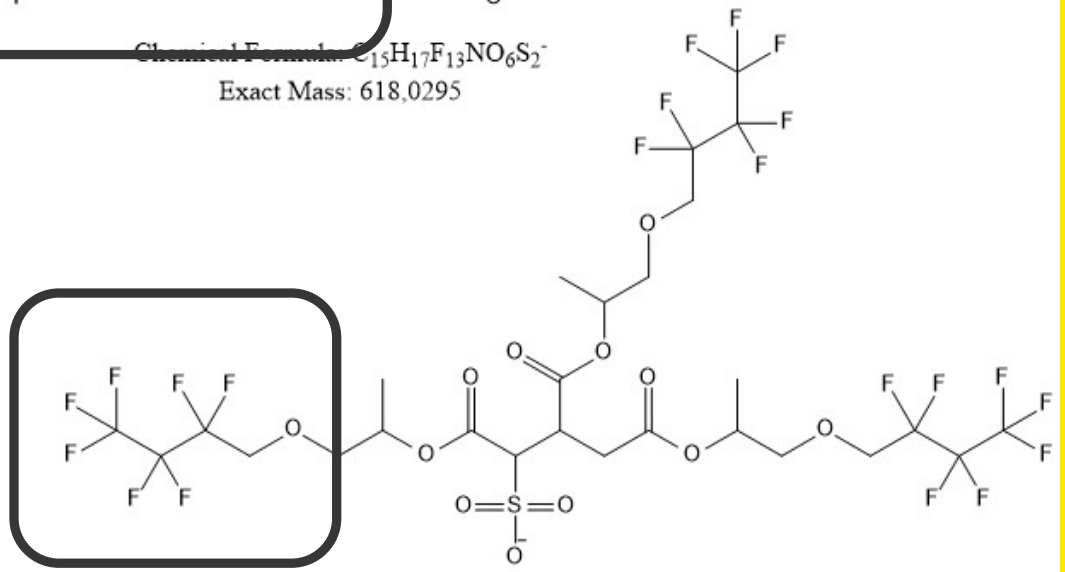


Chemical Formula: $C_{15}H_{17}F_{13}NO_6S_2^-$
Exact Mass: 618,0295

Chemical Formula: $C_{27}H_{28}F_{21}O_{12}S^-$
Exact Mass: 975,0972



Chemical Formula: $C_{11}H_{10}F_{13}O_4S^-$
Exact Mass: 485,0098
Acetate adduct



Chemical Formula: $C_{27}H_{28}F_{21}O_{12}S^-$
Exact Mass: 975,0972

Caveats and restrictions

- **Knowing what to measure & count → > 6000 PFAS**
- **Specificity matters**
- **Isomers – linear vs branched**
- **Qualitative analysis → identity + present or not (LOD)**
  - → How to identify?
- **Quantitative analysis → identity + mass fraction (amount)**
  - → How to identify?
  - → How to quantify? → calibration – **reference (SI-traceable)** – reproducible data (comparison)

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More than 1 analytical method

Intended for
NORDIC WORKING GROUP FOR CHEMICALS, ENVIRONMENT, AND HEALTH (NKE)

Document type
Final Report

Date
December 2023

ANALYSIS OF NEEDS FOR ENFORCEMENT OF PFAS IN ARTICLES AND CHEMICAL PRODUCTS

RAMBØLL vito

Section 2.1

Total fluorine content

- CIC
- LIBS
- WDXRF
- PIGE
- INAA
- HR-CS-GF-MAS
- XPS

All fluorinated compounds
No individual identification/quantification

Section 2.2

Non-targeted and suspect screening analysis *via* HRMS

- LC- and GC-MS(MS)
- MALDI
- IM-MS
- SPE-coupling
- DART
- ICP-MS
- direct infusion ESI
- FT-ICR

High sensitivity and specificity

Section 2.4

Structural analysis & additional methods

- ^{19}F-NMR
- XANES
- FTIR
- MIP-OES
- SERS

High specificity

Section 2.3

Targeted analysis

- LC- and GC-MS
- SFC-MS
- Sensors
- pyr-GC-MS
- Sensors
- TOPA

High sensitivity and specificity

➔ **quantification possible**
... if reference compounds available

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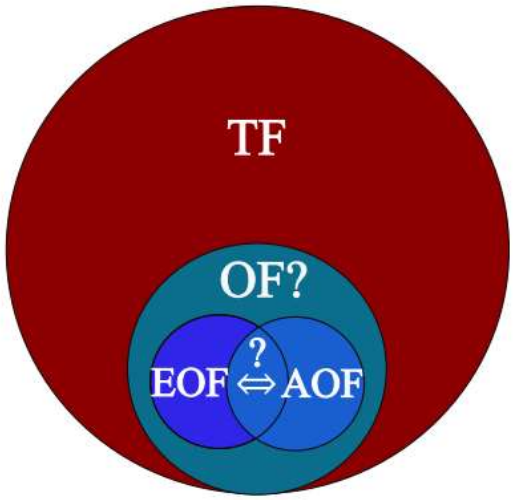
NTA – TOTAL (ORGANO)FLUORINE



The GOOD

- Measuring total F
- EOF and AOF vs inorganic fluorine
- Can give a quick idea of the total fluorine content
- ISO standard is under development (AOF)

The BAD

- Organic vs inorganic F (false positives)
- The limit of F detection µg-mg/L range
- Molecular technique vs SI-data reporting
- Not (yet) wide-spread in commercial labs
- CIC and HR-CS-GF-MAS are available (sample preparation is needed)
- Ultrashort-chain PFAS remain a blind spot

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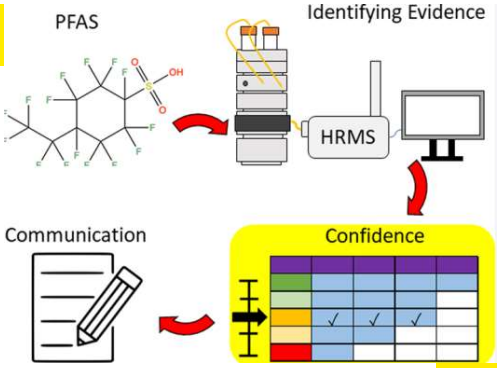
NTA – SUSPECT & NON-TARGET SCREENING



The GOOD

- HRMS allows identification of new and suspected PFAS
- HRMS can measure both multiple known and unknown analytes in a single analysis
- LOD vs target analysis
- Developments for high-throughput ongoing
- Results will direct future developments of target methods

The BAD

- High cost of technology acquisition, operation and maintenance
- High training and experience level of scientists
- Large datasets
- Slower process than target analysis
- Not (yet) assimilated in commercial labs

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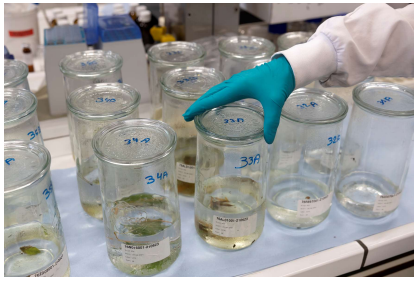
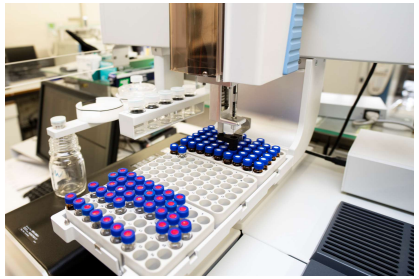
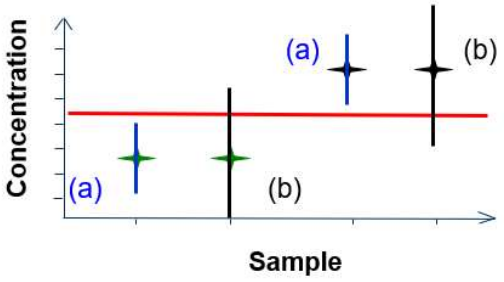
Measurement uncertainty

> *"Uncertainty is unpleasant, but certainty is absurd"*
> Voltaire (1694-1778)

Caveats and restrictions

sampling – preparation – measurement – data interpretation

Analytical result: x ± U

Meta-data

5 %

20 %

50 %

fit-for-purpose measurement uncertainty

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Caveats and restrictions

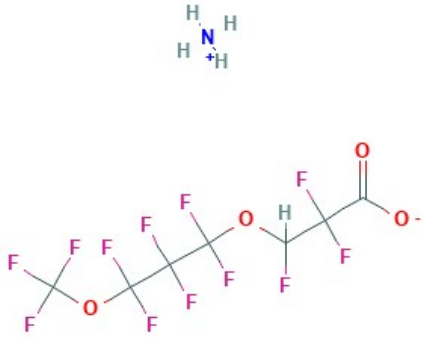
- **The curious case of PFOA and it salts according to [Delegated regulation - 2020/784 - EN - EUR-Lex (europa.eu)]**

"Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds" means the following:

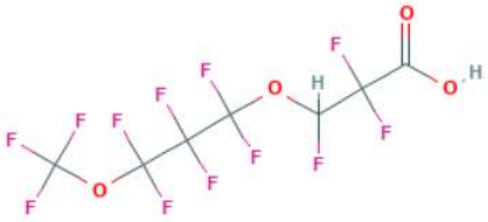
- **Perfluorooctanoic acid, including any of its branched isomers;**
- **Its salts**
- **PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C7F15)C as one of the structural elements.**

Caveats and restrictions

- **The curious case of DONA – ADONA – NaDONA**



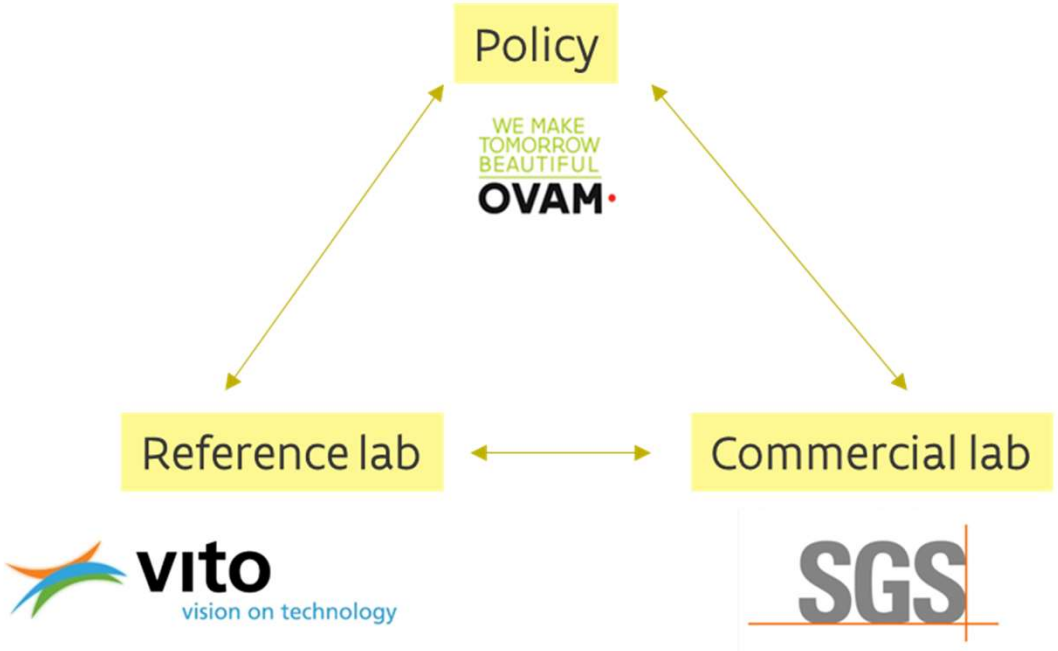
Ammonium 4,8-dioxa-3H-perfluorononanoate
DONA



4,8-Dioxa-3H-perfluorononanoic acid
ADONA

LS0

Different stakeholders, different roles, objectives, expectations, …



be EU
belgium24.eu

Slide 16

LS0 Ik denk dat er eerst nog een paar slides moeten zijn over de methodes - kort zodat iedereen toch mee kan in de discussies achteraf
Laetitia Six; 2024-02-26T13:37:42.179

Starting from OVAM's tasks

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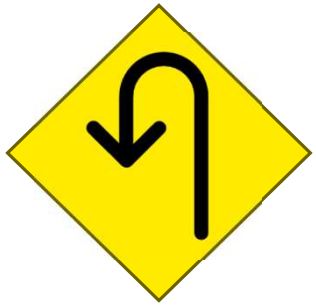
By 2050 we reduce soil contamination and ameliorate the soil quality in Flanders with a positive impact on human and environmental health

Soil CARE and CURE

- → Monitoring of soil contamination in Flanders
- → Protective measures for soil and groundwater
- → Soil and ground water remediation

Which contaminants to monitor?

Can we turn this around?



Contaminant → related activities? → inventory of potentially impacted locations → **Action**

Literature, permits, etc.

NTA data from potentially impacted locations → presence/absence contaminant? → **Action**

New insights on (eco)toxicity,
Persistency, new substances in focus…

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Reference lab - VITO

Flemish Reference Laboratory Erkende laboratoria | EMIS (vito.be)

Link between government and routine labs

- Matrix Soil -> CMA methods Compendium voor monsterneming en analyses van afvalstoffen en bodem (CMA) | EMIS (vito.be)
- Matrix Water -> WAC methods Compendium voor de monsterneming, meting en analyse van water (WAC) | EMIS (vito.be)
- Matrix Air -> LUC methods Compendium voor de monsterneming, meting en analyse van lucht (LUC) | EMIS (vito.be)

Referenc labo - VITO

International harmonization

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Role of commercial labs

- **Generate analytical data allowing enforcer or problem owner to act**

- **Assurance of reliable results**
  - → Acting according robust analytical methods vs acceptable pricing

- **Being a connection with integrity**
  - → Between legislator and client

Commercial challenges

- **Investments are substantial & shareholders want benefit**

- **Target vs Screening analytics requires different approach**
  - → AOF/EOF ←→ PFAS compounds

- **Diffuse vs source identification makes a (huge) difference**

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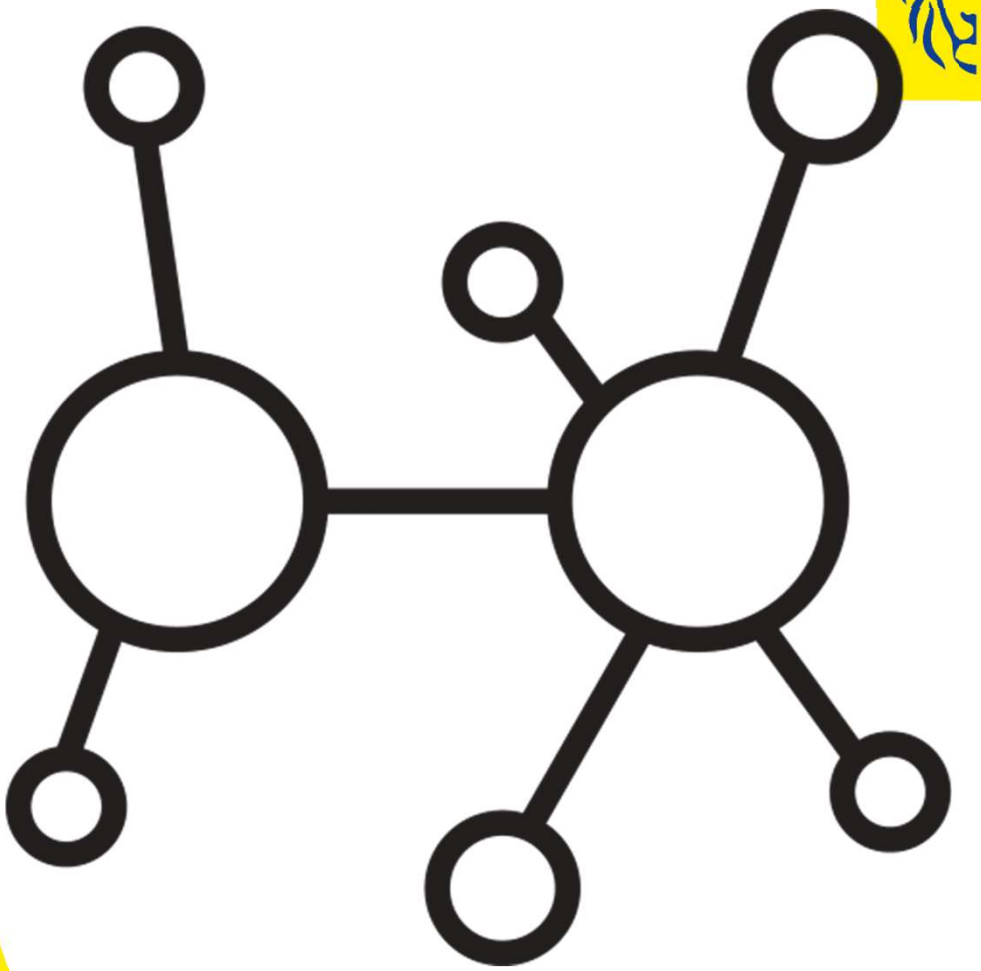
PFAS as a case study to identify challenges



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Slide 23

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Laetitia Six; 2024-02-26T13:37:42.179

Example - PFAS

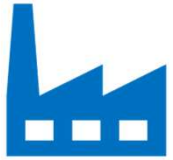
First call (July, 2021): Use of fire extinguishing foam

- Fire fighting training site
- Fire fighting facilities (industry)
- Fire extinguishing calamities
- Military training areas and airports
- Civil airports

→ **826** locations (fire fighting training sites & calamities)

Second call: PFAS processing or producing industry

Risk activities as determined in the study of 2018:
textile industry, paper industry, galvanic industry, ...



→ more than **4000** locations

Screening and prioritisation in ongoing

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Challenges

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Current approach:

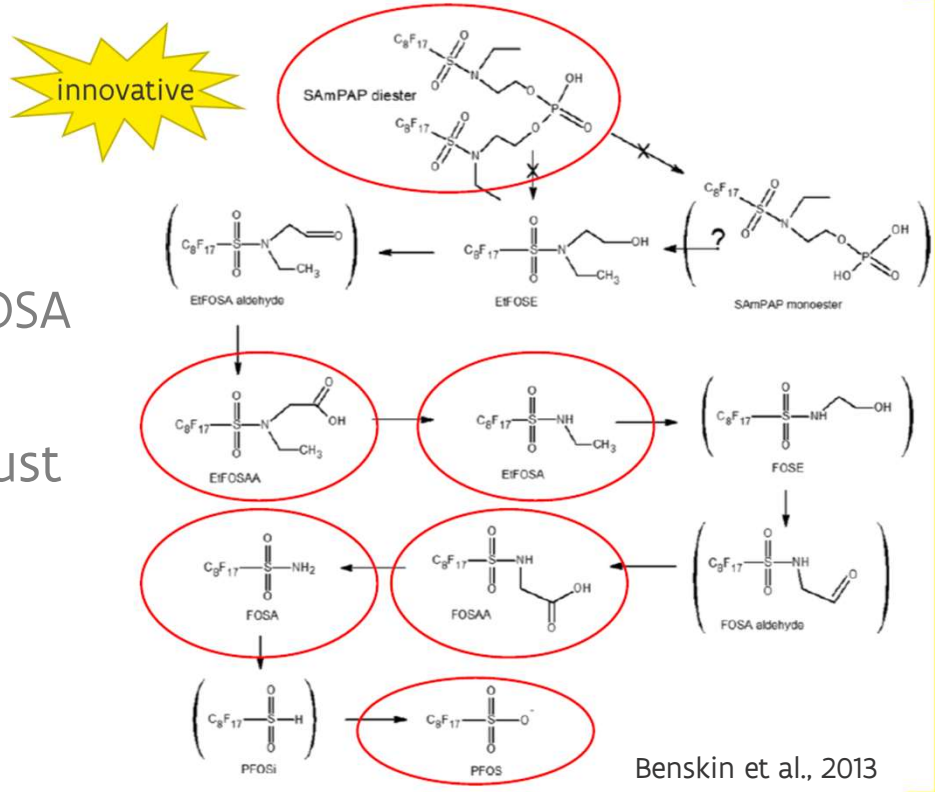
- Starting from activities to identify locations for measurements
- Limited to set of about 40 PFAS in target analysis (WAC and CMA)

Limitations of current approach?

- Do we miss out on important impacted sites?
- What about the other 1000's of PFAS that we are not measuring?
- What with new insights? Do we need to go back to the field to sample?

Suspect screening of PFAS in house dust and soil

- Suspect screening showed contamination with diSAmPAP.
  - → PFAS compound associated to the paper industry
  - → Can break down to EtPFOSAA, PFOSAA, PFOSA and PFOS
  - → Direct link between PFAS found in house dust and the historic activities nearby



Benskin et al., 2013

Obstacles for commercial labs

Continuously changing guidelines

- → EU Directives drinking water / Fire Fighting Foams, …
- → OVAM terms / CMA / WAC
- → What about EU / Belgian inter-regional approach from an analytical point of view

Analytical approach

- → Target/USC/AOF/TOP/…
- → Changing LOD/LOQ's
- → New components enter the scene
- → Storage on data cfr U turn

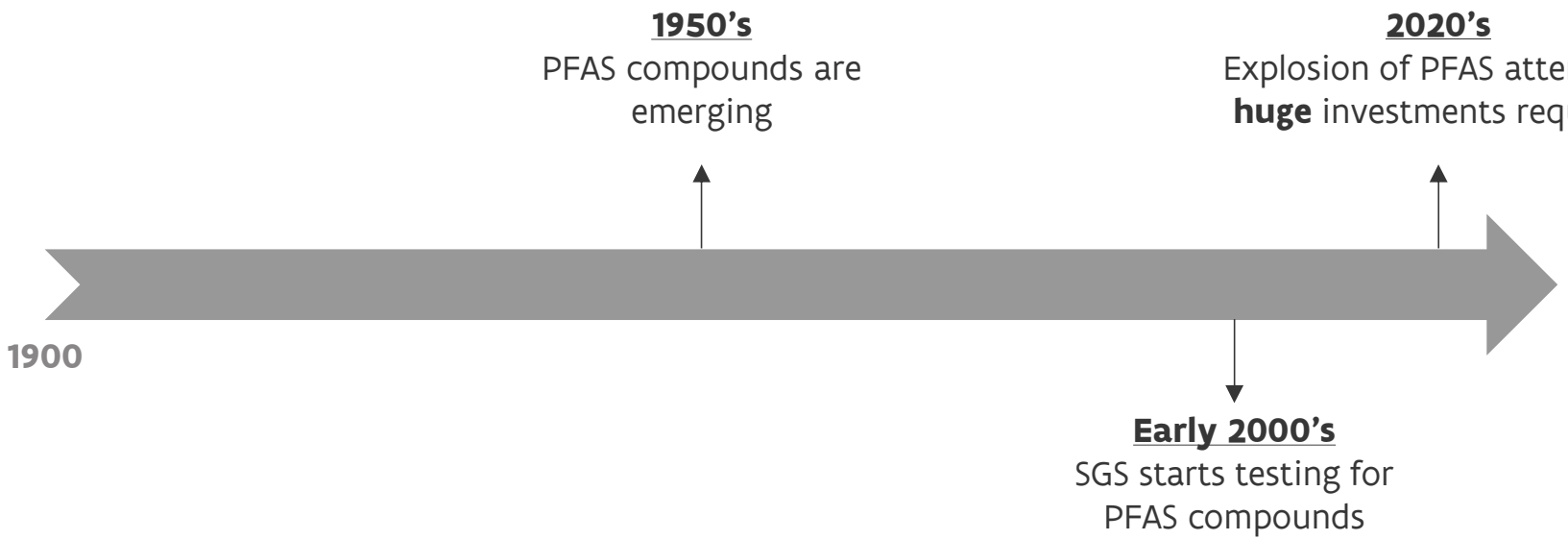
Daily challenge on implementation of guidelines

- **Application of the measurement uncertainty**
- **Sum of PFAS results**
  → different in every region?
- **AFFF analysis and data interpretation**
- **Walloon PFAS compounds ≠ Flanders**

Commercial investment vs Timeline

New insights

Example: PFAS timeline

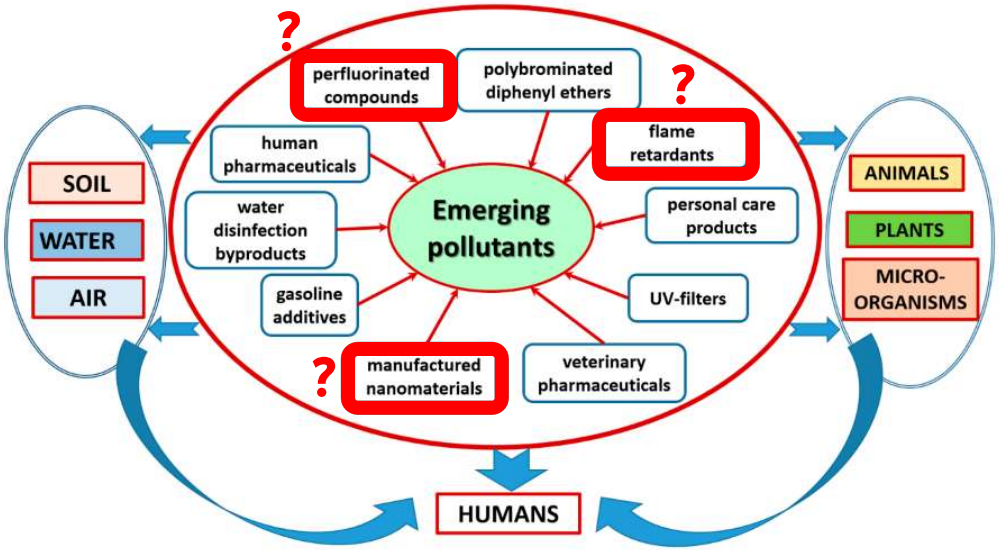


Commercial challenge

New insights lead to?

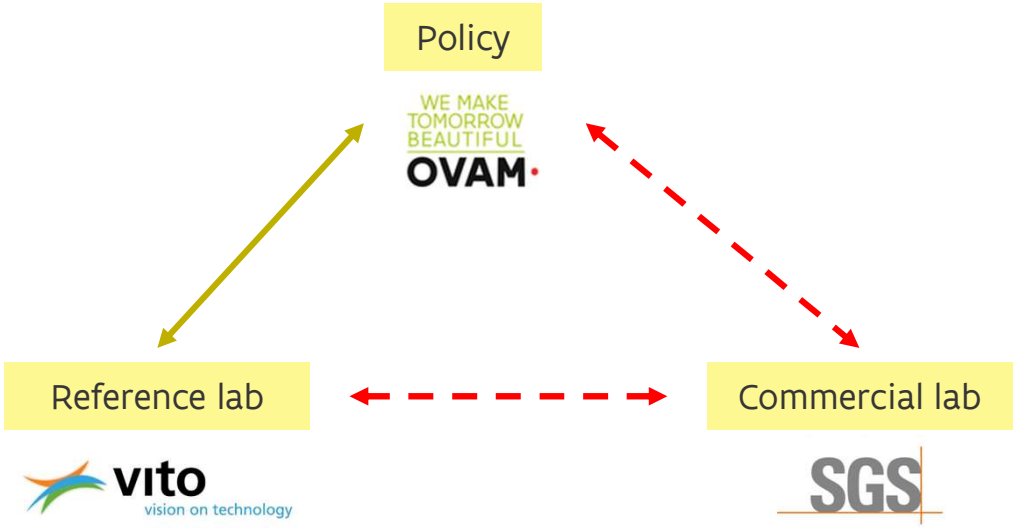
Where's the main focus ?

What should labs invest in?



Interaction with commercial stakeholders (labs)

- **Alignment: legislation ←→ commercial labs**
  - → Technical feasability to avoid conflicting interests
  - → Labs are often invited late to the party (EPA → PFOA < 0,004 ng/l ??)



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Contributions of commercial labs

- **Sustainability (ESG)**
  - → Commercial labs are key players

- **Important role in development of new methods**
  - → PFASafe® (CIC + LC-MSMS + QTOF)
  - → PPCP's (?)
  - → BFR's (?)

“Analytical chemistry is an exact science, as long as it is exact enough”

“Results should always be interpreted according to the conditions under which the analysis was performed”

Wrap- up

Pro's and con's for NTA and SS in environmental monitoring

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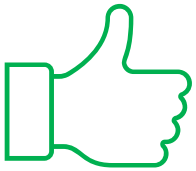
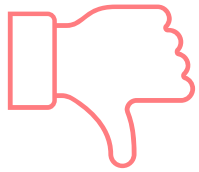


- Detection and identification of new emerging compounds, transformation and break-down products
- Retrospective analysis and trend analysis of NTA data when kept in digital platform
- First screening to identify contaminants of interest, prior target analysis
- Quicker and potential to be cost-efficient
- ...



- Not routine at analytical labs, harmonisation needed
- Get grip on accuracy, margin of error – how to deal with uncertainty?
- Reduce costs if used as routing – role of models, big data and AI?
- Legal implications?

Discussion

Q1 : Only zero tolerance can save our future? True or not true?

Q2: A measurement uncertainty of 50% is unacceptable?

Q3: Are analytical methods the limiting factor for reliable assessment?

Q4: We need to characterize all substances of concern to make assessment possible?

Thank you!!