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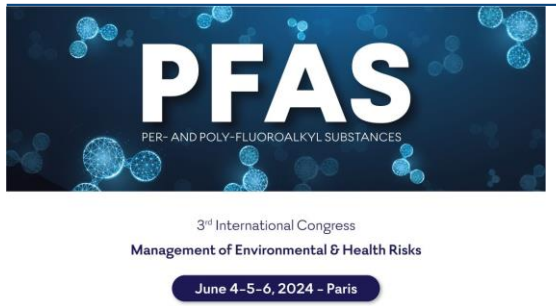
Better Food. Better Health. Better World.

PFAS in firefoams

Situation framing and analytical approach

Paris 4 June 2024



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PFAS and ECHA restriction proposal

February 2023: the European Chemicals Agency (ECHA) announced its **proposed restrictions on per- and polyfluoroalkyl substances (PFASs)**, a unique family of approximately **10,000 substances** which are very persistent in the environment.

Prepared by Denmark, Germany, the Netherlands, Norway and Sweden

POSSIBLE NEXT STEPS from ECHA
2026/27 RESTRICTION TO BECOME EFFECTIVE

Focus on firefoams

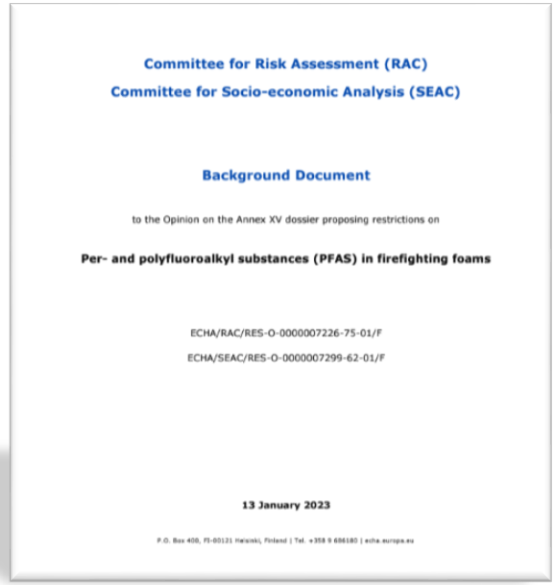
ECHA's decisions concerning PFAS includes all materials and articles, including firefoams.

Firefoams were made and in some case are still made with PFAS.
Fire-fighting foams are the cause of many cases of PFAS contamination in Europe and in the US, both of soil and drinking water.

There is a particular **proposal of restriction** on the placing on the market, use and formulation of **PFAS in firefoam.**

This takes into account available alternatives (10 YEARS TRANSITION PERIOD) and the balance between the restriction's benefits and costs to society.

Next steps: proposal to the Commission, REACH amendment, vote and adoption.


Committee for Risk Assessment (RAC)
Committee for Socio-economic Analysis (SEAC)

Background Document

to the Opinion on the Annex XV dossier proposing restrictions on

Per- and polyfluoroalkyl substances (PFAS) in firefighting foams

ECHA/RAC/RES-O-0000007226-75-01/F
ECHA/SEAC/RES-O-0000007299-62-01/F

13 January 2023

PFAS already regulated

REGULATED BY STOCKHOLM CONVENTION

- **PFOS** and its derivates
- **PFOA**, its salts and related compounds
- **PFHxS**, its salts and related compounds
- *Long-chain perfluorinated carboxylic acids (C9-21 PFCAs) are being considered for inclusion.*

REACH RESTRICTIONS

A number of PFAS are on the REACH Candidate List of substances of very high concern (SVHC). This conclusion is based on persistence, mobility and toxicity.

In addition, several PFAS are on the list for evaluation over the coming years or have already been evaluated.

DEROGATION FOR FIREFOAMS

The use of PFOA, its salts and related compounds shall be permitted until 4 July 2025 in fire-fighting foams already installed in systems, but they shall not be used:

- in training activities
- for testing purposes unless the releases are totally segregated

Main foam concentrates containing PFAS

AFFF (Aqueous Film Forming Foam)
the most common type of fluorine-based foam, often used as a synonym for all PFAS-based foam concentrates.

FFFP (Film Forming Fluoroprotein) foam
Like AFFF, it forms a water film.

FP (Fluoroprotein)
Fluoroprotein foam concentrates were actually the first fluorine-containing foam concentrates to be developed.

European manufacturers are currently offering a new generation of high-performance fluorine-free foams (FFF/3F) suitable for various applications.

A LABORATORY ANALYSIS IS REQUIRED TO DETERMINE THE PFAS CONTENT IN A FOAM CONCENTRATE

It is **not possible to say in general which PFAS** are contained in what concentration in a specific foam concentrate. The **ingredients can vary** and, **there can be a contamination if the tank was not properly cleaned** when switching from AFFF to a fluorine-free foam concentrate.

From fire fighting foams to airports

Le Monde reported that decontamination of water for the civilian population living near Dusseldorf airport cost EUR 100 million; EUR 18 billion would be needed to clean up European airports.

American airports have web info pages on PFAS, about their monitoring plan and any remediation carried out, or environmental commitments.

AUSTRALIAN PFAS Airports Investigation Program

The Australian Government is investigating civilian airports where PFAS-containing foams were used.

The Program aims to determine the nature and extent of PFAS contamination through testing, and to develop robust management plans to address any identified risks.

The Pilot Program was completed in June 2023. The main Program has commenced, and is expected to be completed by 30 June 2027.

SOIL and WATER TESTING TO IDENTIFY THE RISK

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Analytical approach: target analysis

PFAS chemicals contained in firefoams may seep underground and pollute nearby sources:

- water systems that rely on rivers and streams
- wells
- soil including microbiota and plants

These matrices can be tested for PFAS presence with different approaches.

TARGET ANALYSIS

Technologies:
LC\MS\MS and LC-HRMS
GC\MS\MS
Carbon ranges: C2-C18
Concentration limits: 0.5 ppt (PFOA and PFOS) 2.5 - 1000 ppt
Almost ~ 100 PFAS

Absorbable Organic Fluorine (AOF)

For the trace level **determination AOF in water**, the sample must first be passed through a mixed-mode weakanion exchange solid-phase extraction (SPE) cartridge thereby adsorbing the PFAS compounds.

AOF is then determined by eluting the contents of the SPE cartridge with NaOH in methanol, evaporating and reconstituting the extract, and finally determining the fluoride.

By measuring the AOF content in water samples as an initial screening step, a quick overview of the actual amount of organic fluorinated compounds present can be obtained.

- Good as initial screening: step fast overview of the actual amount of organic fluorinated compounds present (simpler, faster, and more robust than targeted methods)
- This can be followed by targeted analyses of individual PFASs if indicated by higher AOF concentrations

Loq =0,5 µg/l

WEAKNESS: Fluorine from PFAS and also from pesticide (for example)

From July 2023 AOF mandatory measure in wastewater (LOQ 100 ng/l selective PFAS)

Draft method EPA 1621 for use in the **Clean Water** Act (CWA) as a screening method to estimate the concentration of adsorbable organic fluorine (AOF) in aqueous matrices by combustion ion chromatography (CIC).

The method reported possibile issues:

- Low recoveries for long chain compounds
- Stratification in the walls of the samples's container
- Interferences for cross-contamination

Total Fluorine and Total Organic Fluorine

Total fluorine of the entire sample, independent of original material thickness, **is measured by integrated direct combustion.**

Samples are contained in ceramic boats and are introduced into the furnace where pyrohydrolysis occurs at 900–1000 ˚C in a humid, O2-rich environment. Carbon-fluorine bond breaking and the vapours are sparged through an absorption solution using Ar. The HF evolved from combustion of organic fluorine dissociates to form H + and F ions in the absorption solution.

The samples are then transferred to the ion chromatograph for analysis where fluoride is measured.

Combined with a separate measurement of a sample subjected to water extraction of inorganic fluorine prior to combustion **total, organic, and inorganic fluorine can be measured**.

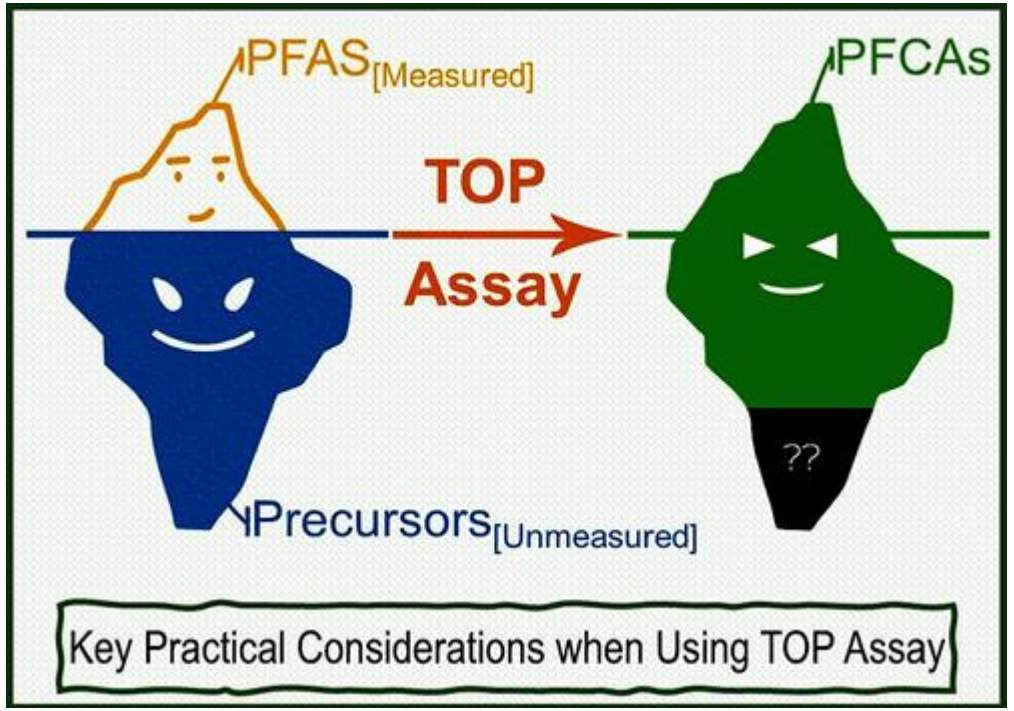
- Fast, accurate, high sensitivity analysis
- Destructive to sample
- Technique referenced in Clean Production Action's firefighting foam standard (Ecolabel to confirm fluorine-free* firefighting foam products) —1 ppm total organic fluorine threshold requirement for certification

TOP Assay

This method can look at many PFAS precursors, which may be converted into related PFAS chemicals through oxidation: **the total oxidizable precursor (TOP) assay** can **oxidize unknown PFAS precursors and intermediates and convert them into stable PFASs with established analytical standards.**

To be used for water or after extraction in solids or firefoam

- Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay.
- Under the conditions of the assay, it is expected that fluorotelomer sulfonates are broken down to shorter chain carboxylates by cleavage of the non-fluorinated portion of the molecule. Perfluorinated carboxylates and sulfonates are stated to remain intact under the conditions of the assay.



Total Oxidizable Precursor (TOP) Assay—Best Practices, Capabilities and Limitations for PFAS Site Investigation and Remediation
Mohamed Ateia, Dora Chiang, Michaela Cashman, and Carolyn Acheson
Environmental Science & Technology Letters **2023** *10* (4), 292-301
DOI: 10.1021/acs.estlett.3c00061

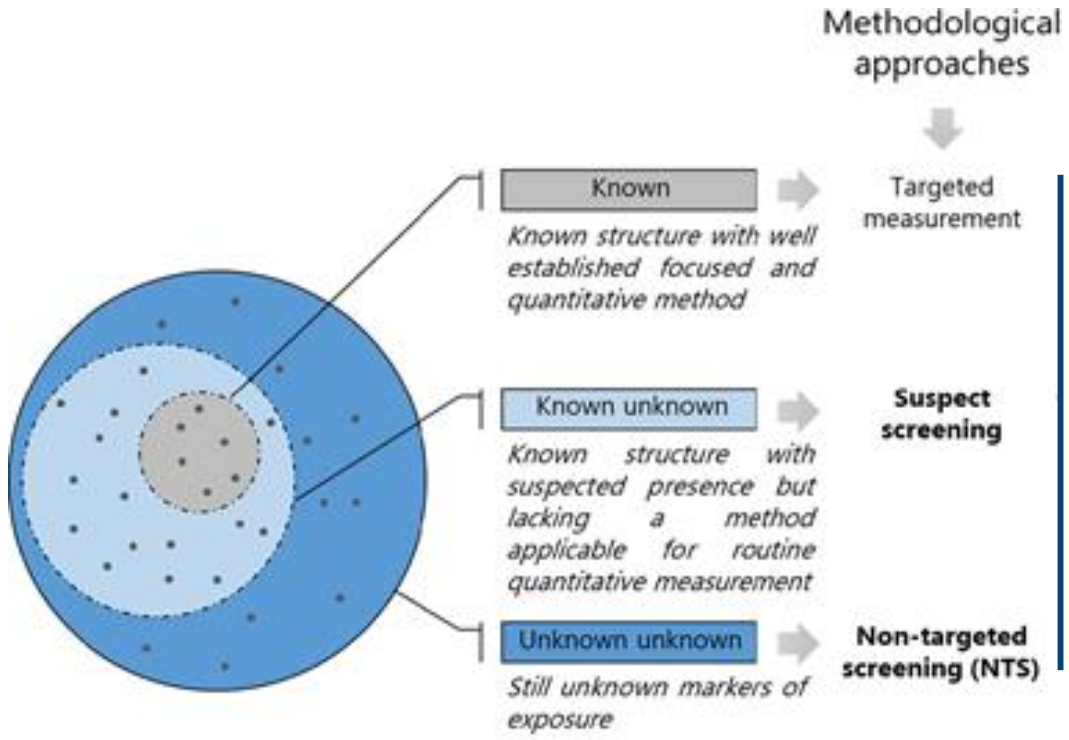
Suspect screening: a possible alternative

TARGETED ANALYSIS
- Restricted list of compunds, specific but not comprehensive of all possible PFAS

TOTAL FLUORINE
- Non specific, can overestimate

SUSPECT SCREENING:
It is focused on analysing so-called **“known unknowns”** whose names and structures are clearly defined and suspected to be present in the sample.

Suspect screening is not restrictive in terms of the preselection of the analytes to consider, but **among the thousands of features pinpointed in the analysis, only those corresponding to the interest or suspect list will be given priority to be evaluated and identified** at a higher or lower confirmation level.



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TARGETED ANALYSIS RESULTS

PFAS THAT ARE DETECTED IN THE SAMPLE

acide n-perfluorobutanoïque [PFBA] (375-22-4)
acide n-perfluoropentanoïque [PFPeA] (2706-90-3)
acide n-perfluorohexanoïque [PFHxA] (307-24-4)
acide perfluoroheptanoïque [PFHpA] (375-85-9)
acide n-perfluorooctanoïque [PFOA] (335-67-1)
acide n-perfluorononanoïque [PFNoA] (375-95-1)
acide n-perfluorodécanoïque [PFDA] (335-76-2)
acide n-perfluoroundécanoïque [PFUnA] (2058-94-8)
acide n-perfluorododécanoïque [PFDoDA] (307-55-1)
acide n-perfluorotridécanoïque [PFTrDA] (72629-94-8)
acide n-perfluorotétradécanoïque (PFTeDA) (376-06-7)
acide perfluorobutane sulfonique [L-PFBS] (375-73-5)
acide perfluorododécanesulfonique [L-PFDoS] (79780-39-5)

Sum of Targeted PFAS < AOF

PFAS THAT ARE NOT DETECTED IN THE SAMPLE

Acide perfluoro(2-((6-chlorohexyl)oxy)éthanesulfonique) [9CL-PF3ONS] (756426-58-1)
acide n-perfluorohexadécanoïque (PFHxDA) (67905-19-5)
acide n-perfluorooctadécanoïque (PFODA) (16517-11-6)
acide perfluoropentane sulfonique [L-PFPeS] (2706-91-4)
acide perfluorohexanesulfonique [L-PFHxS] (355-46-4)
acide perfluoroheptanesulfonique [L-PFHpS] (375-92-8)
acide L-perfluorooctane sulfonique [L-PFOS] (1763-23-1)
acide perfluorononane sulfonique [L-PFNS] (68259-12-1)
acide perfluorodécanesulfonique [L-PFDS] (335-77-3)
acide perfluoroundécane sulfonique [L-PFUnDS] (749786-16-1)
acide perfluorotridécane sulfonique [L-PFTrDS] (791563-89-8)
acide undécafluoro-2-méthyl-3-oxahexanoïque (acide dimère HFPO) (13252-13-6)
cC604 sous forme de sel d'ammonium (1190931-27-1)
4:2 acide fluorotélomère sulfonique (4:2 FTS) (757124-72-4)
acide 1H,1H,2H,2H-perfluorooctanosulfonique [6:2 FTS] (27619-97-2)
1H,1H,2H,2H-Perfluoro-1-octanol [6:2 FTOH] (647-42-7)
8:2 acide sulfonique fluorotélomère (8:2 FTS) (39108-34-4)
1H,1H,2H,2H-Perfluoro-1-decanol [8:2 FTOH] (678-39-7)
perfluorooctanesulfonamide [PFOSA] (754-91-6)
acide dodécafluoro-3H-4,8 dioxanononoïque (Adona) (919005-14-4)
Acide 11-chloroeicosafluoro-3-oxaundécane-1-sulfonique [11CL-PF3OUDS] (763051-92-9)

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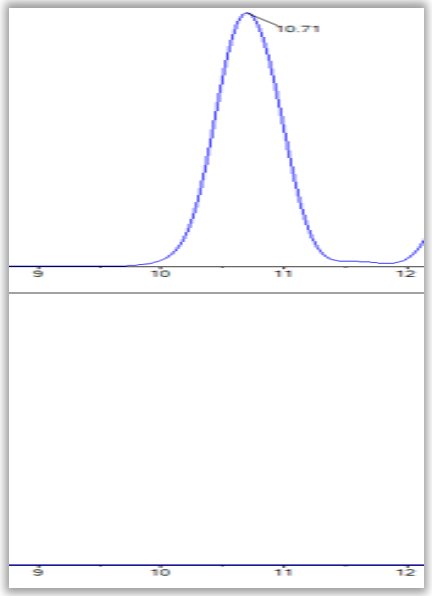
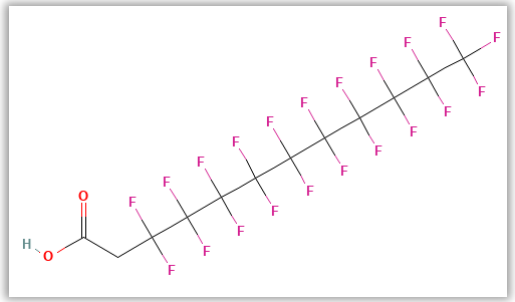
SUSPECT SCREENING RESULTS

Suspect Screening Result Example: 1° Additional PFAS found
(hypothesis to be confirmed with certified reference material)



HRMS **Sample**
Chromatogram
(576,9719 m/z)

HRMS **Blank**
Chromatogram
(576,9719 m/z)



Name: 2-(Perfluorodecyl)ethanoic acid
CAS: 53826-13-4

SUSPECT SCREENING
of known-potential contaminants

List of compounds

Instrumental analysis

Results to be confermed
with standards

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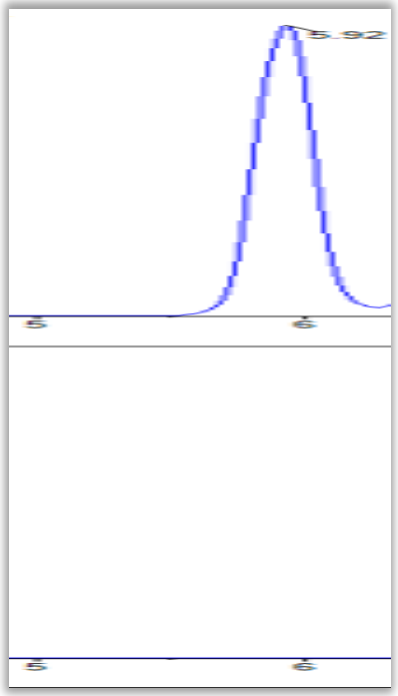
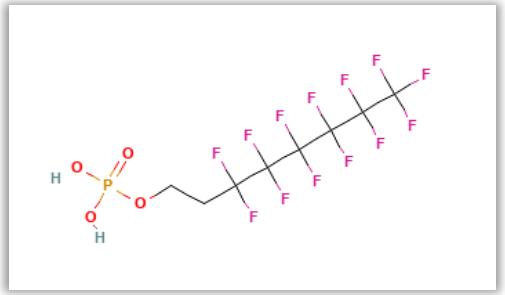
SUSPECT SCREENING RESULTS

Suspect Screening Result Example: 2° Additional PFAS found
(hypothesis to be confirmed with certified reference material)



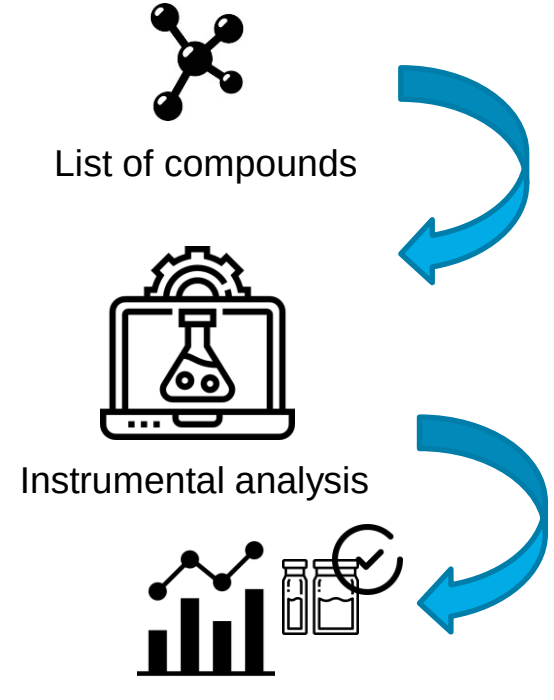
HRMS **Sample**
Chromatogram
(442,9723 m/z)

HRMS **Blank**
Chromatogram
(442,9723 m/z)



Name: 6:2 Fluorotelomer phosphate monoester
CAS: 57678-01-0

SUSPECT SCREENING
of known-potential contaminants



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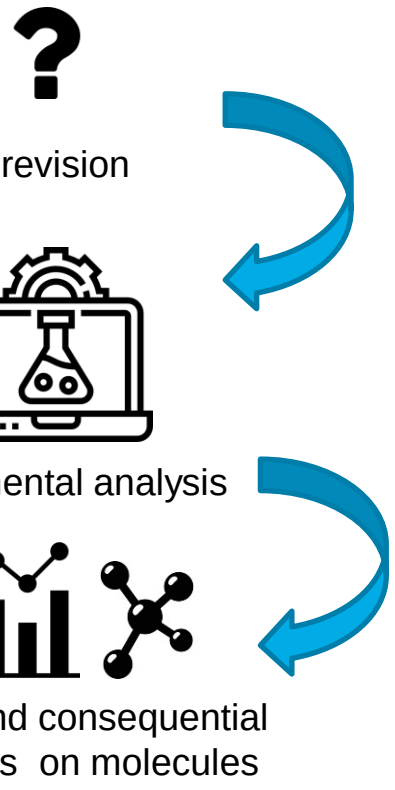
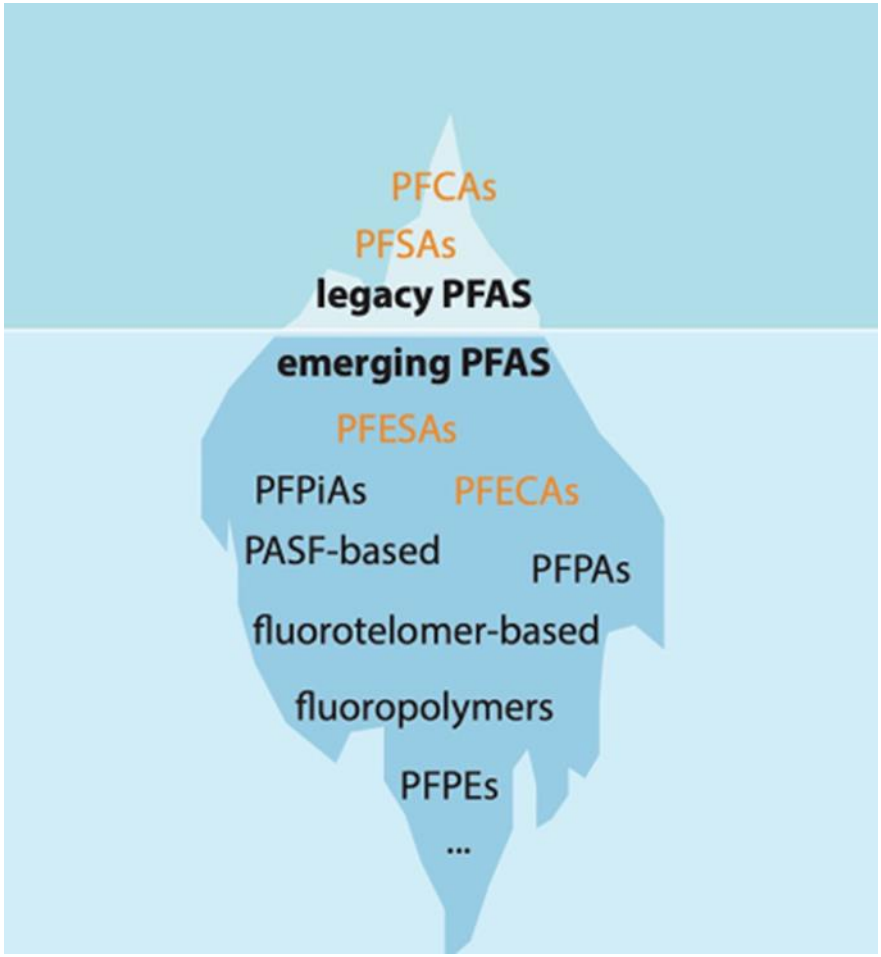
NON TARGETED SCREENING

WORK IN PROGRESS

NON- TARGETED ANALYSIS





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Thank you

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