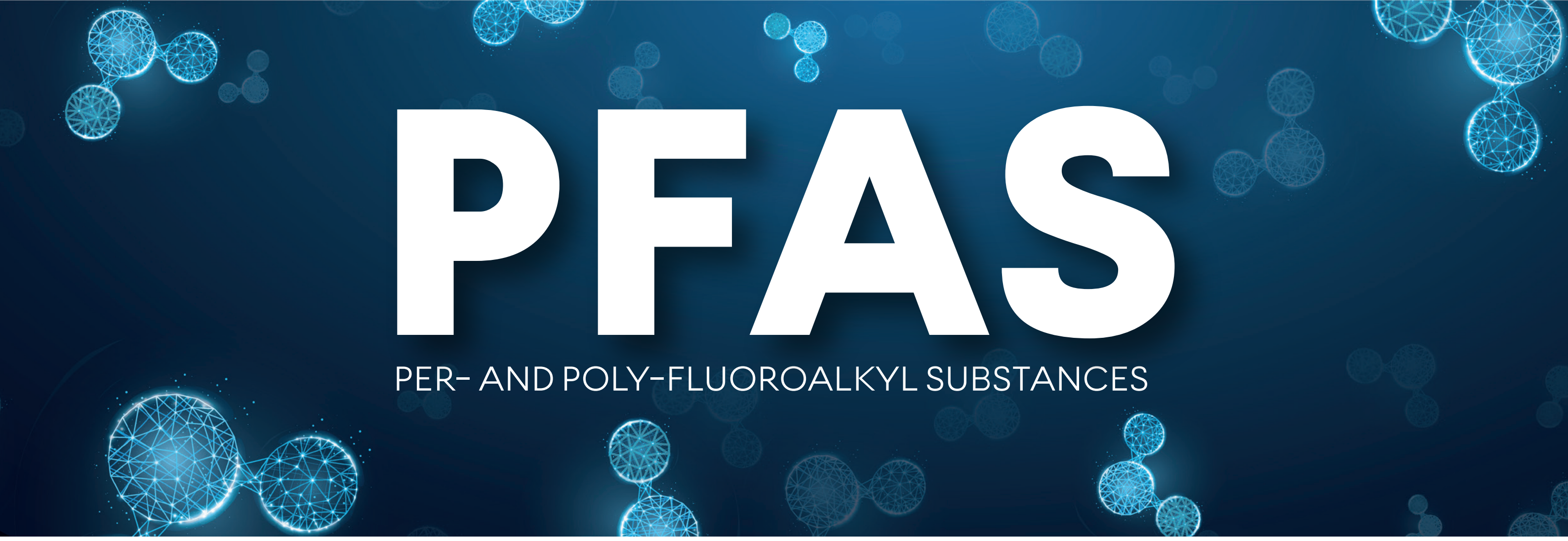

PFAS

PER- AND POLY-FLUOROALKYL SUBSTANCES

3rd International Congress

Gestion des Risques Environnementaux & Sanitaires
Management of Environmental & Health Risks

4-5-6/06/2024 - Paris

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ARET Association pour la Recherche en Toxicologie
ABE Alliance Bretonne de l'Environnement
SFSE Société Francophone de Santé et Environnement – La rigueur scientifique au service des publics

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Mardi 4 juin 2024

08h45
Accueil des participants

Présidents :
- *Laurence Lanoy, Avocate en Droit de l'Environnement - Laurence Lanoy Avocats, France*
- *Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne*

Contexte règlementaire international

09h15
Discours de bienvenue & introduction au congrès
Dr. Frank Karg, Organisation et Président du Congrès International PFAS

09h30
Les PFAS et la politique de santé publique
Dr. Cyrille Isaac-Sibille, Secrétaire de la commission des Affaires Sociales, Député Ouest et Sud de la Métropole de Lyon

09h45
L'actualité du cadre juridique concernant les substances PFAS : les axes d'évolution
Laurence Lanoy, Avocat associé, Spécialiste en droit de l'environnement - Laurence Lanoy Avocats, France

10h15
Valeurs seuils pour les PFAS dans la réglementation européenne : incohérences et pistes d'ajustement
Elodie Bouhoulle, Chef de projets - ISSeP, Institut Scientifique de Service Public, Belgique

10h45
Pause café & thé

11h15
L'articulation de l'action publique en matière d'environnement et de santé lors de la crise Wallonne des PFAS de 2023
Bénédicte Heindrichs, Directrice générale - Service Public de Wallonie - Agriculture, Ressources naturelles et Environnement - SPW ARNE, Belgique

11h45
Dernières tendances en matière de tests et de réglementations PFAS : du ppb au ppq dans l'eau, le sérum et au-delà
Mike Chang, Responsable du développement commercial - Restek Corporation, Etats-Unis

12h15
L'importance de l'identification et de la différenciation des sources PFAS dans les eaux souterraines via la Multi-Vector-Analyse sur la base de l'Intelligence Artificielle dans le cadre des Expertises judiciaires
Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne

12h45
Déjeuner

Identification & Caractérisation des sources des PFAS

14h00
Vision des industriels de traitement de déchets dangereux (HWE) pour un gestion efficace et vertueuse des déchets contenant des PFAS en Europe
Nicolas Humez, Président - Hazardous Waste Europe (HWE), France

14h30
PFAS dans les mousses d'incendie : cadrage de la situation et approche analytique
Sylvain Mourard, Responsable Commercial France - Eau & Environnement, Mérieux NutriSciences, France

15h00
Substances per- et polyfluoroalkyles dans les biosolides : répartition géographique et données du Québec, Canada
Sébastien Sauvé, Professeur titulaire - Université de Montréal, Québec, Canada

15h30
Pause café & thé

16h00
Enjeux pour la Métrologie environnementale pour une meilleure compréhension des sources et transfert des PFAS dans l'environnement : apports de la R&D
Anne Togola, Chef de projet surveillance environnementale - Bureau de Recherches Géologiques et Minières (BRGM), France

16h30
Etude de la contamination en composé fluorés (PFAS) sur un site d’entrainement d’extinction d’incendies : Présence et mobilité
Quentin Dubois, Doctorant - Environnements et Paléoenvironnements Océaniques et Continentaux (EPOC) - CNRS, Université de Bordeaux, France

17h00
L'intérêt d'un screening des PFAS ainsi que la détermination des chaînes ultra courtes dans le concept PFASafe©
- *Anthony Passador, Référent PFAS - SGS Environmental Analytics, France*
- *Pieter Joos, Expert R&D analytique et qualité - SGS Environmental Analytics, France*

17h30
Valeurs de fond des PFAS dans le sol et les eaux souterraines
Charlotte Colman, Expert sols - Arcadis, Belgique

18h00
Mesures de Substances per- et polyfluoroalkylées (PFAS) en air ambiant en Région Auvergne-Rhône-Alpes
Guillaume Salque-Moreton, Ingénieur-Expert - Atmo Auvergne-Rhône-Alpes, France

18h30
Fin de la première journée

Tuesday, June 4, 2024

08h45
Welcoming participants

Presidents:
- *Laurence Lanoy, Lawyer in Environmental Law - Laurence Lanoy Avocats, France*
- *Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany*

International Legal Context

09h15
Welcome speech & introduction to the congress
Dr. Frank Karg, Organization & President of International PFAS Congress

09h30
PFAS and Public Health Politics
Dr. Cyrille Isaac-Sibille, Secretary of the Social Affairs Committee, Member of Parliament, West and South of Lyon Métropole

09h45
Updates on the legal framework concerning PFAS substances: areas for development
Laurence Lanoy, Associate Lawyer, Specialist in environmental law - Laurence Lanoy Avocats, France

10h15
PFAS thresholds in European regulation: inconsistencies and ways for improvement
Elodie Bouhoulle, Project Manager - ISSeP, Scientific Institute of Public Service, Belgium

10h45
Coffee & Tea break

11h15
The articulation of public actions vis-à-vis environment and health matters during the 2023 Wallonia's PFAS crisis
Bénédicte Heindrichs, General Director - Public Service of Wallonia - Agriculture, Natural Resources and Environment (SPW ARNE), Belgium

11h45
Latest trends in PFAS testing and regulations landscape: from ppb to ppq in water, serum and beyon
Mike Chang, Market Development Manager - Restek Corporation, USA

12h15
The importance of Identifying and Differentiating PFAS Sources in Groundwater via Multi-Vector-Analysis, based on Artificial Intelligence in the context of Forensic Expertise
Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany

12h45
Lunch

Identification & characterization of PFAS Sources

14h00
Vision of the Hazardous Waste Industry (HWE) for an efficient and righteous management of PFAS-containing waste in Europe
Nicolas Humez, Chairman - Hazardous Waste Europe (HWE), France

14h30
PFAS in firefoams: situation framing and analytical approach
Sylvain Mourard, Sales Manager France - Water & Environment, Mérieux NutriSciences, France

15h00
Per- and polyfluoroalkyl substances in biosolids: geographical distribution and data from Quebec, Canada
Sébastien Sauvé, Full Professor - University of Montreal, Quebec, Canada

15h30
Coffee & Tea break

16h00
Challenges for Environmental Metrology for a better understanding of the sources and transfer of PFAS in the environment: contributions from R&D
Anne Togola, Environmental Monitoring Project manager - French Geological Survey (BRGM), France

16h30
Study of the fluorinated compounds (PFAS) contamination at a firefighting training site : Presence and mobility
Quentin Dubois, PhD Student - Oceanic and Continental Environments and Paleoenvironments (EPOC) - CNRS, University of Bordeaux, France

17h00
The role of target screening PFAS and determination of ultra short chain PFAS in the PFASafe©-concept
- *Anthony Passador, Product Manager - SGS Environmental Analytics, France*
- *Pieter Joos, Analytical and Quality R&D Expert - SGS Environmental Analytics, France*

17h30
Background values of PFAS in soil and groundwater
Charlotte Colman, Soil Expert - Arcadis, Belgium

18h00

Measurements of per- and polyfluoroalkyl substances (PFAS) in ambient air in the Auvergne-Rhône-Alpes region

Guillaume Salque-Moreton, Expert Engineer - Atmo Auvergne-Rhône-Alpes, France

18h30

End of day one

LAURENCE LANOY AVOCATS
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Actualities in the legal framework for PFAS substances: evolutions axes

Per- and polyfluoroalkylated substances (PFAS) belong to a large family of endocrine disruptors used in many industrial processes and in the manufacture of everyday objects. Due to their non-stick, heat-resistant and waterproofing properties, these unique substances are persistent and harmful pollutants to the environment and human health, as they are found in drinking water, groundwater, surface water, soil, air and food.

Awareness of these substances and their effects is both recent and significant: measures to monitor and limit PFAS in the environment are beginning to be imposed to restrict the use of these compounds and minimize exposure and risks to human health.

PFAS regulations are evolving rapidly, but differently from one sector to another.

It stands out in the field of water, since the transposition into French law of the European "drinking water" directive of December 16, 2020 reinforces their monitoring and sets limit values in water intended for human consumption for around twenty of these substances, and a ministerial decree of June 20, 2023 provides for the analysis and monitoring of PFAS substances in the aqueous discharges of Classified Installations for Environmental Protection (ICPE). The French Ministry for Ecological Transition and Territorial Cohesion is pursuing this approach through its 2024 national action program for the inspection of classified installations, with the aim of requiring operators to eliminate or, failing that, reduce PFAS discharges once the inventory has been completed. France is further committed to strict regulation of PFAS substances, with the adoption of a law proposal on April 4, 2024. The French government also published its interministerial action plan on PFAS on April 5, 2024.

European Union moves forward about PFAS regulation in the field of packaging with the adoption the 27 April, 2024 by the European Parliament of a new regulation. In parallel, the procedure of the proposal to restrict all PFAS substances presented to ECHA in context of REACH regulation by five European countries (Germany, Denmark, the Netherlands, Sweden and Norway) continues. However, the revision of the REACH, which concern PFAS, does not feature in the 2024 work program published by the Commission on October 17, 2023.

Laurence Lanoy, a lawyer specializing in environmental law, will give an overview of evolutions in the regulatory framework for these substances of concern, and present the issues involved in managing them for the industrial sector.

* * *

A lawyer since 1990 and holder of a doctorate in law, Laurence Lanoy developed an in-depth practice in environmental law before founding Laurence Lanoy Avocats in 2005. She advises and assists national and international companies, public authorities and international law firms, notably in environmental and sustainable development law, mining law and energy law.

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L'actualité du cadre juridique concernant les substances PFAS : les axes d'évolution

Les substances per- et polyfluoroalkylées (PFAS) appartiennent à une grande famille de perturbateurs endocriniens utilisés dans de nombreux processus industriels et la fabrication d'objets de la vie quotidienne. En effet, par leurs propriétés antiadhésives, résistantes aux fortes chaleurs et imperméabilisantes, ces substances uniques constituent des polluants persistants et nocifs pour l'environnement et la santé humaine puisqu'elles se retrouvent dans les eaux potables, souterraines ou de surface, les sols, l'air ou encore l'alimentation.

La prise de conscience relative à ces substances et leurs effets est à la fois récente et majeure : des mesures de surveillance et de limitation des PFAS dans l'environnement commencent à s'imposer afin de restreindre l'usage de ces composés et de réduire au maximum l'exposition et les risques pour la santé humaine.

La règlementation des PFAS évolue rapidement mais différemment selon les secteurs.

Elle se démarque en matière d'eau, puisque d'une part la transposition en droit français de la directive européenne du 16 décembre 2020 dite « eau potable » renforce leur suivi et fixe des valeurs limites dans l'eau destinées à la consommation humaine pour une vingtaine de ces substances, et d'autre part un arrêté ministériel du 20 juin 2023 prévoit l'analyse et la surveillance des substances PFAS dans les rejets aqueux des ICPE. Le ministère de la transition écologique et de la cohésion des territoires poursuit cette démarche à travers son programme d'actions nationales 2014 pour l'inspection des installations classées dans l'objectif une fois cet inventaire réalisé d'imposer aux exploitants de supprimer ou, à défaut, réduire ces rejets en PFAS.

En revanche, l'ambitieuse proposition de restriction REACH de toutes les substances PFAS présentée à l'ECHA par cinq pays européens (Allemagne, Danemark, Pays-Bas, Suède et Norvège) avec le soutien de la France n'a pas été suivie puisque la révision de la réglementation sur les substances chimiques ne figure pas dans le programme de travail 2024 que la Commission a publié le 17 octobre 2023.

Laurence Lanoy, avocat spécialiste en droit de l'environnement, effectuera un tour d'horizon des évolutions du cadre réglementaire concernant ces substances préoccupantes, en présentant les enjeux relatifs à leur gestion pour le secteur industriel.

* * *

Avocat depuis 1990 et Docteur en droit, Laurence Lanoy a développé une pratique approfondie en droit de l'environnement avant de fonder en 2005 le cabinet Laurence Lanoy Avocats. Elle conseille et assiste des entreprises nationales et internationales, des collectivités publiques et des cabinets d'avocats internationaux notamment en droit de l'environnement et du développement durable, en droit minier et en droit de l'énergie.

PFAS thresholds in European regulation: inconsistencies and ways for improvement

BOUHOULLE Elodie
Project manager/Researcher

Cellule Environnement-Santé / *Environmental Health Unit*
Institut Scientifique de Service Public / *Public Service Scientific Institute*
Rue du Chéra, 200 - 4000 Liège, Belgique

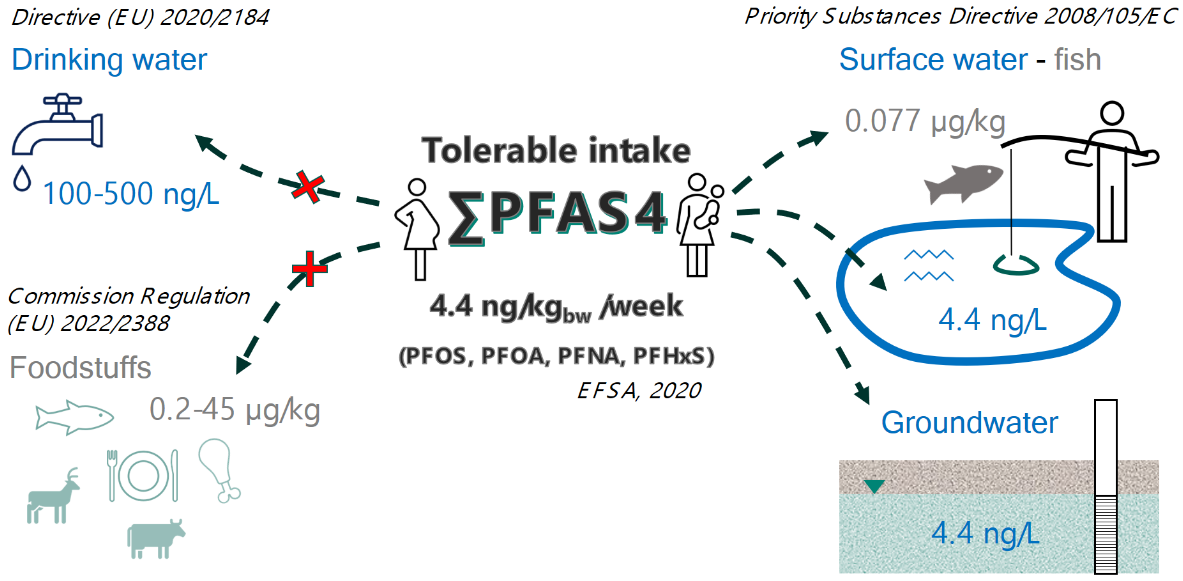
Authors: Elodie Bouhoulle, Jussi Reinikainen, Jaana Sorvari.

Acknowledging the fact that per- and polyfluoroalkyl substances (PFAS) are persistent and ubiquitous contaminants, and therefore present risks to human health, the European Commission has adopted a number of regulatory measures for their management. We carried out a comparative analysis of the thresholds recently set for PFAS in the EU in surface water, groundwater, drinking water and in certain foodstuffs. The analysis covers the quality standards of the Drinking Water Directive (EU) 2020/2184, the environmental quality standards proposed under the Water Framework Directive and its daughter Directive 2008/105/EC on priority substances, the maximum levels in certain foodstuffs in accordance with Commission Regulation (EU) 2022/2388 and the new tolerable weekly intake recommended by EFSA in 2020.

The results show that the principles on which the threshold values for PFAS are founded vary considerably between these different regulations, and that the regulatory texts lack transparency on the rationale used to establish these threshold values. This is likely to confuse the common understanding of the toxicity and health risks of PFAS.

We put forward several solutions that could feed into and facilitate the dialogue needed between scientists and the European authorities to improve the consistency of regulatory decisions and support the One-Substance One-Assessment approach desired in the European Chemical Strategy for Sustainability. We also identify some research needs at the interface with regulatory needs for the risk assessment of chemicals.

The study was carried out as part of the European Partnership for Chemical Risk Assessment (PARC) supported by the Horizon Europe research and innovation program under Grant Agreement No. 101057014 and received co-funding from the Finnish Environment Institute (SYKE) and the Walloon Public Service (SPW).



The articulation of public actions vis-à-vis environment and health matters during the 2023 Wallonia's PFAS crisis

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In the spring of 2021, what will later be named the "PFAS crisis" broke out in Flanders due to revelations regarding the 3M company in Zwijndrecht, in the Antwerp suburbs. Simultaneously, the Walloon Administration was warned about the existence of PFAS levels in the water distributed within the US military base of Chièvres, levels which were exceeding the standards in force in the USA. Finally, in October 2023, a report on the French-speaking Belgian public Tv channel revealed the existence of a PFAS problem in Wallonia to the public.

Back in 2021, the Walloon Administration had already put in place a programme aimed at establishing an inventory and proposals for action. However, the large-scale media dissemination of this issue led to a political-media crisis which required the establishment of a reactive management structure by public authorities aimed at responding to the crisis generated both in aspects linked to the environment but also to public health.

The newly-created structure brought together the SPW ARNE, the ISSeP (Scientific Institute of Public Service), the SWDE (Société wallonne des Eaux), and the ministerial cabinets involved. Many challenges had to be faced. The first one was to have a complete overview of the water quality situation in the 641 zones of the Walloon distribution network – all that in a very short amount of time. This large-scale analysis campaign began in September 2023 and all the results were available by mid-December 2023. Four zones out of the 641 did not comply with the future European standard of 100 ng/l.

The second challenge was to establish a register of PFAS-polluted sites. Sites that were identified as such were the subject of an investigation programme in targeted areas called ZIP (priority investigation zones). A four-phased investigation was developed:

1) A search for PFAS in surface water and groundwater to determine the contaminated area;

2) Analysis of soils in the contaminated area to identify polluted lands responsible for water pollution or contaminated following the use of water well;

3) Analysis of the "living": vegetables, fruits and eggs that may be contaminated by the use of contaminated water in the area;

4) The implementation of biomonitoring for people who have consumed contaminated tap water or well water.

Albeit there were no official PFAS standards for tap water – as the European standard of 100 ng/l was not expected to come into force until 2026, Wallonia decided to resort to this standard from 2024 on.

The third challenge faced by the administration was to respond to the legitimate concerns of the population who consumed water with worrying levels of PFAS. The structure put in place had to demonstrate great agility by setting up a specific biomonitoring programme in PFAS-affected areas andby answering a series of questions such as finding volunteer candidates and carrying out analyses with non-extensible technical capacities, and analytical methods which were not developed yet in Wallonia.

Regarding the biomonitoring, it must also be emphasized that experiments were already underway before the PFAS-crisis occurred. This biomonitoring, which also considered some PFAS, complements that which was put in place.

The structure can rely on the expertise of an independent scientific committee which can provide support on health-related aspects of PFAS, given the few existing standards in this area.

The fourth challenge was communication. How to communicate and transmit results? Who gets to know first? What message should be released? How to taylor the message to the targeted audience: citizens, local authorities, environmental associations...? Agility and creativity were key for the crisis structure. Information sessions were held, and professional mediators and facilitators were hired to navigate through these uncertain times.

Finally, and aside from crisis management itself, this PFAS-crisis shed light on the need for longer-term actions. It is now obvious that some normative bills need to be re-written, such as some sectoral conditions related to the legislation on environmental permitting.

Latest Trends in PFAS Testing and Regulations Landscape: from ppb to ppq in Water, Serum and beyond

Mike Chang
Restek Corporation
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Bellefonte, PA 16823

Among many PFAS destruction technologies for remediation project, formation of byproducts is often ignored and quantitation of ultrashort-chain PFAS can play a critical role in understanding the missing mass Fluorine balance study. Majority of detected PFAS is highly dominated in the form of ultrashort-chain and short chain PFAS, yet, testing of those compounds is untouched. In addition, emerging PFAS compounds are even more susceptible to forming ultrashort-chain and short chain PFAS byproducts.

Accurate quantitation of ultrashort-chain and short chain PFAS in various water matrices (tap water, bottled water, wastewater) and serum samples will be presented. Critical tips and tricks in ultrashort-chain PFAS analysis will be discussed as well.

L'importance de l'identification et de la différenciation des Sources PFAS dans les eaux souterraines via la Multi-Vector-Analyse sur la base de l'Intelligence Artificielle dans le cadre des Expertises judiciaires

The importance of Identifying and Differentiating PFAS Sources in Groundwater via Multi-Vector-Analysis, based on Artificial Intelligence in the context of Forensic Expertise

Frank KARG[1], Philippe GIRARD[2], Ulrike HINTZEN[3], Lucie ROBIN-VIGNERON[4]

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1. Introduction

Since the 1960s, PFAS monomers (Per- & Polyfluoro-Alkyl Substances) have gradually become a major environmental and public health problem in industrialized countries, due to their multiple and wide-ranging applications (historical and still current). This threat to the environment and to public health has been gradually coming to the fore since the 2010s and will be considered to a greater extent in 2022 - 2024. As a result, PFAS are now found in the soil at polluted sites, in groundwater, in food, drinking water, in soil gas and in ambient air (volatile PFAS, e.g. FTOH: Fluorotelomer alcohols, etc.). Between 9,000 and 12,000 synthetic PFAS pollutants have been produced, with some publications indicating as many as 15,000 molecules.

Polymeric PFASs such as Teflon (or PFTE etc.) are not very bioavailable and are therefore much less toxic than monomeric PFASs. These monomeric PFAS are the subject of the work presented below. PFASs are known for their toxicological effects as endocrine disruptors, hepatotoxicity, immunotoxicity, effects on fetal development and, in some cases, carcinogenicity (e.g. PFOA).

An important characteristic of PFASs is their behavior in Environmental Chemistry, since only polyfluorinated PFASs are modified by microbiological bio-transformation into perfluorinated PFASs, which remain totally stable and non-degradable, and even bio-accumulable.

Particularly in the case of groundwater pollution by PFAS, it is becoming increasingly important to identify and, above all, differentiate the contribution of each PFAS source to pollution plumes. This need for clarification regarding the contribution of each PFAS source to pollution, e.g. in the vicinity of drinking water wells, etc., is becoming crucial for the protection of water resources, (shared) responsibilities and the search for the (multiple) origins of pollution in the context of legal court expertises.

Sources of pollution by PFAS are varied and can be found on industrial sites that have used these products, sites that have suffered fires or fire training sites where fire-fighting foams have been used. **(AFFF : Anti Fire Fighting Foams or Aqueous Film Forming Foam, e.g. at airports)** have been used. Agricultural land is also a source of PFAS pollution, due to the input of sewage sludge, which contains accumulated PFAS.

The following (historical) activities may be the source of PFAS pollution:

- Fire-fighting training,
- Airport or air base on a military site,
- Fire site and use of AFFF,
- Electrochemical galvanisation,
- Production of waxed paper and cardboard,
- Manufacture of waterproof textiles,
- Sprays, paints, waterproofing lacquers,
- Production and application of Teflons (PTFE, etc.),
- Petroleum and chemical industry sites and/or production and application of paints, dyes, inks, pigments, chemical waxes and polishing products,
- Solvent applications (garages, dry cleaners, laundries, etc.),
- Landfill sites and former municipal landfill sites, etc. (ISDD, ISDND, ISDD, etc.),
- Dyeing & Tanning,
- Carpets, rugs, fabrics and plastics with flame retardants,
- Production of objects and furniture containing surfaces,
- Production of cleaning products,
- Photographic chemistry (laboratories, paper and film production, etc.),
- Production of electronic components,
- Production and application of pesticides and biocides,
- Production of cosmetics,
- Sites receiving WWTP sludge.

2. Environmental chemistry

The environmental chemistry of PFAS is particularly important and complicated. There is no group of pollutants with a more complex environmental chemistry than PFAS. In particular, there are **more than 9,000 PFAS substances**, divided into **33 categories of substances**.

The best known are Perfluoroalkane sulphonic acids (PFASs), Perfluoroalkyl carboxylic acids (PFCAs), Perfluoroalkyl phosphates and their esters, Fluorotelomer alcohols (**FTOH**), etc. (including more than 29 other groups …). Some of them, such as the **PFOA :** Perfluorooctanoic acid and **PFOS** : Perfluoro-octane-sulphonate (see Fig. 1) are banned (and **prohibited in EC and USA & Canada**) by the **Stockholm Convention** in the category of **POPs** : Persistent Organic Pollutants. PFOA is carcinogenic. **Commercial products** mainly contain **mixes**.

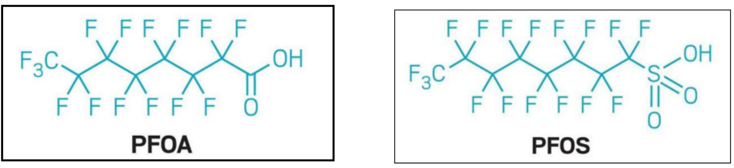


Fig. 1 : Structural formulae for PFOA & PFOS

The reason for the high solubility in water, associated with lipophilicity, is based on the fact that **PFAS** :

- **Anionics** (e.g. sulphonates, sulphates, carboxylates and phosphates),
- **Cationics** (e.g. quaternary ammonium),
- **Amphoteric** (e.g. betaines and sulpho-betaines): base + acid and
- **Non ionic** (e.g. polyethylene glycols, acrylamide oligomers).

It is very important to emphasize that poly-fluorinated PFAS that are not fully fluorinated (‘precursors’) can be converted by bio-transformation into persistent, fully fluorinated chemicals, per-fluorinated PFAS. The complete microbiological degradation of PFAS has not yet been demonstrated.

Figs. 2a & 2b show an example of the biotransformation of 6 :2-FTAB & 6 :2-FTS in soil and water to volatile Fluorotelomer Alcohols (FTOHs) which then migrate into soil gas (vapor) and ambient air. FTOHs are then microbiologically transformed into stable per-fluorinated PFASs. For example, 6:2-FTOH is biotransformed into PFHxA, PFPeA and PFBA and 8:2-FTOH into PFOA, PFHpA, PFHxA, PFPeA and PFBA.

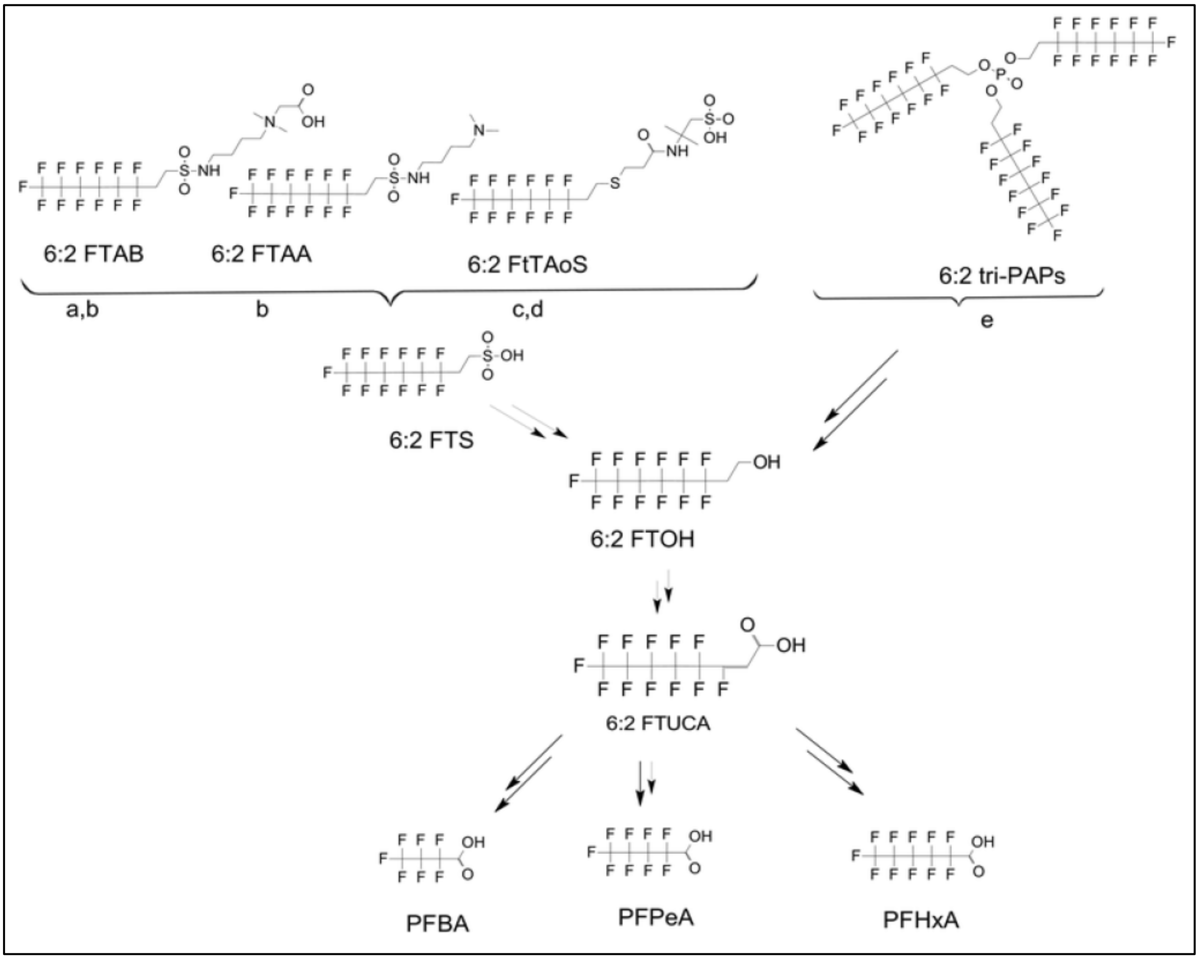


Fig. 2a : Biotransformation scheme of polyfluorinated PFAS (Precursors): Example: 6 :2 FTAB and its degradation via 6 :2 FTS and 6 :2 FTOH to per-fluorinated PFAS PFBA, PFPeA and PFHxA (LaFond et al. 2023, D.M.J. Shaw et al. 2019,Ying Shi, 2018 and V. Mendeza et. al. 2022)

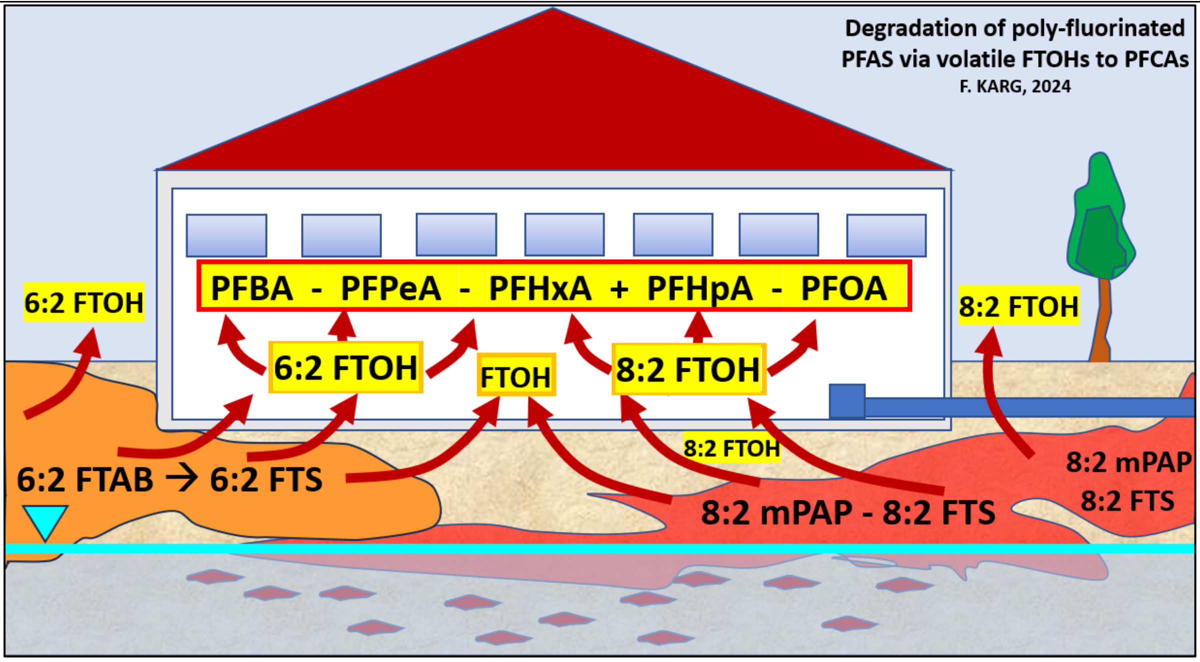
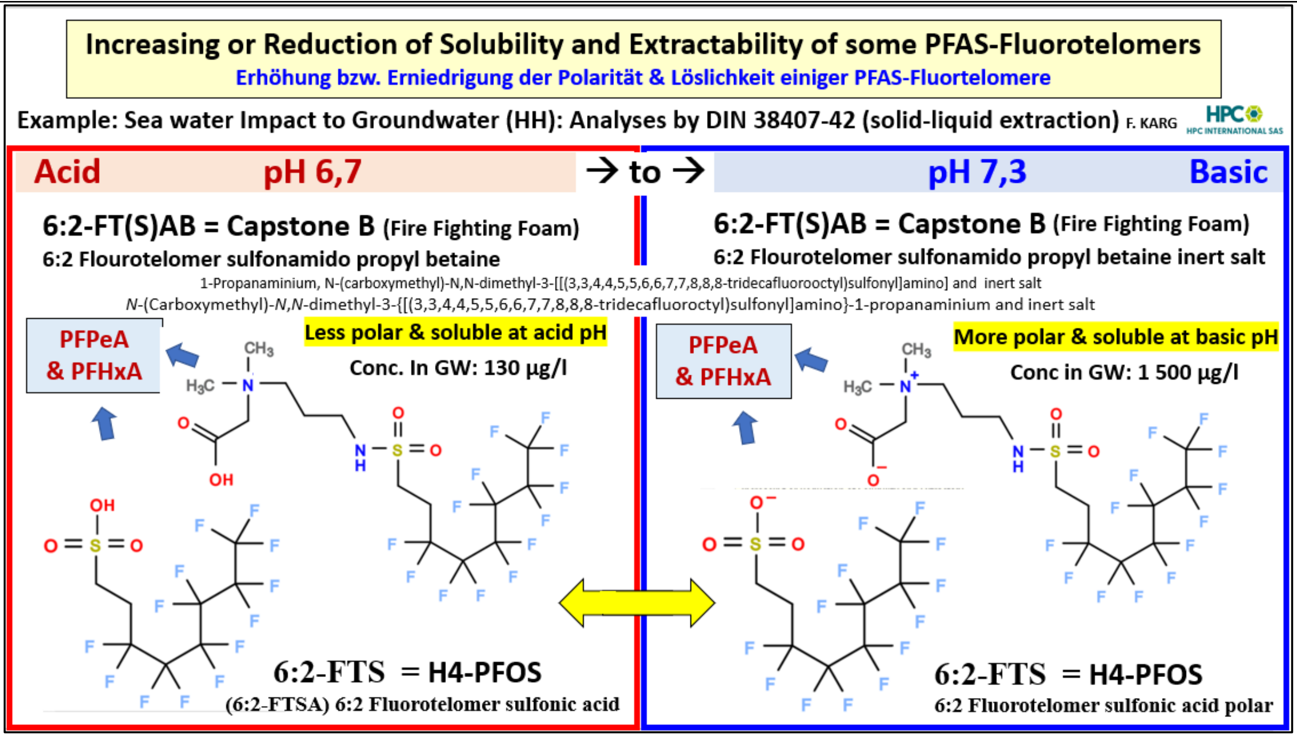


Fig. 2b : Example of the biotransformation of 6 :2 FTAB, 6 :2 FTS, 8 :2 FTS and polyfluorinated alkyl phosphates (PAP) in soil and water to Fluorotelomer alcohols (FTOH) and per-fluorinated PFAS, e.g. to PFOA, PFHpA, PFHxA, PFPeA and PFBA (L. KOPF / HPC, 2017 and F. KARG, 2022 & 2024).

In the event of a change in pH, some PFAS may become more or less soluble, which also has an impact on emissions of volatile fluorinated telomers such as FTOH, etc. in soil gas (vapor). Certain precursors could change their solubility (and their extractable properties during chemical analysis procedures). For example, the intrusion of seawater into the aquifer could result in an increase in the basic pH and therefore in the solubility of Capstone B. This was observed in 2022 in the port area of Hamburg/Germany following seawater flooding and groundwater intrusion (see Fig. 3). These effects could result in groundwater concentrations more than 10 times higher than before seawater intrusion into the soil and groundwater.



Increasing or Reduction of Solubility and Extractability of some PFAS-Fluorotelomers
Erhöhung bzw. Erniedrigung der Polarität & Löslichkeit einiger PFAS-Fluortelomere

Example: Sea water Impact to Groundwater (HH): Analyses by DIN 38407-42 (solid-liquid extraction) F. KARG

Acid pH 6,7	→ to →	pH 7,3 Basic
6:2-FT(S)AB = Capstone B (Fire Fighting Foam) 6:2 Flourotelomer sulfonamido propyl betaine		6:2-FT(S)AB = Capstone B (Fire Fighting Foam) 6:2 Flourotelomer sulfonamido propyl betaine inert salt
PFPeA & PFHxA Less polar & soluble at acid pH Conc. In GW: 130 µg/l		PFPeA & PFHxA More polar & soluble at basic pH Conc in GW: 1 500 µg/l
6:2-FTS = H4-PFOS (6:2-FTSA) 6:2 Fluorotelomer sulfonic acid		6:2-FTS = H4-PFOS 6:2 Fluorotelomer sulfonic acid polar

1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino] and inert salt
N-(Carboxymethyl)-*N*,*N*-dimethyl-3-{[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino}-1-propanaminium and inert salt

Fig. 3 : solubility of PFAS according to pH (example: before and after seawater intrusion into an aquifer and change to a slightly alkaline pH)

3. Identification and differentiation of sources of PFAS pollution

Pollution of soil, groundwater and surface water by PFAS is frequently a mixture of several sources of commercial products and sources of pollution. It is possible to carry out complete screening of individual PFAS substances in order to identify between 9,000 and 12,000 molecules, but in the day-to-day management of pollution in the environment this is not applicable due to the limits of technical and economic feasibility.

For this reason, it is necessary to reduce the number of PFAS compounds to be analysed during environmental assessments by means of **the chemical signature** of commercial products suspected of being the source of contamination. As PFAS are a family of more than 9,000 compounds, it would be impossible to quantify them all.

Typical sources of pollution caused by PFAS include, for example, applications of fire-fighting foams (AFFF = Aqueous Film Forming Foam or Anti Fire Fighting Foams), for example during fire drills and fires at airports, refineries and oil depots, industries involved in the production and processing of PFAS polymers, galvanizing activities such as chromium plating, the agricultural application of sewage WWTP sludge or fertilizers containing PFAS, the application of water-repellent coatings to paper, cardboard and textiles, etc. , but also when they are used as flame retardants in the electrical and electronics industries... The list of sources of PFAS in the environment is long, and there are also volatile PFAS pollutants that can enter indoor air via soil gases, such as fluorotelomer alcohols (FTOH).

One of the current challenges in managing environmental problems linked to PFAS is to identify the various sources of pollution caused by PFAS or their commercial products, for example in the case of major contamination of groundwater by PFAS.

Experience and assessments of more than 800,000 PFAS analyses in soil, groundwater and surface water show the presence of various PFAS clusters and substances, such as perfluorinated carboxylic acids (PFCAs), perfluorinated sulphonic acids (PFSAs) and others, which are typical of certain industrial sectors. Other important PFAS groups are fluorotelomer sulphonic acids (FTS), fluorotelomer alcohols (FTOH) and fluorinated sulfo-betaines (FTAB), from a total of 33 different PFAS groups.

When identifying and differentiating PFAS sources, various relative concentration distributions, relationships with perfluorinated carboxylic acids (PFCAs) and with various poly-fluorinated PFASs as 'precursors', as well as various statistical distribution models, are taken into account.

Commercial PFAS products are examined using non-target analyses to identify as many individual PFAS substances as possible present in PFAS products. To this end, percolation tests to simulate the ageing of 'fresh' commercial PFAS products are being carried out on lysimeters, with bacteriological degradation allowing the biotransformation of poly-fluorinated PFAS (precursors) to per-fluorinated PFAS, and to identify the chromatographic effects of soils (F. Karg et al.: 2023 and 2024).

The purpose is to record the resulting mixtures of individual PFAS molecules by HR-MS (high-resolution mass spectrometry). The results obtained are typical fingerprints of fresh and degraded commercial PFAS products for the complete database of parent mixtures of PFAS products.

PFAS sources can be identified from this database using standard analyses and a multivariate statistical identification program. Multi-Vector-Analysis (MVA) is carried out in several dimensions using artificial intelligence (machine learning), so that PFAS sources can also be determined in the event of groundwater pollution containing a mixture of several different PFAS sources.

In addition to the use of standard environmental analyses of polluted sites for MVA identification of the different sources of PFAS pollution, other analytical tools may also be applicable, such as the 'Top Assay' (Houtz & Sedlak: 2012, Glöckner et al.: 2021) to best determine the mass of poly-fluorinated precursors present, which can be oxidised to perfluorinated carboxylic acids (PFCAs) (see Fig. 4). In addition, measurements of isotope ratios between PFAS source areas and plume areas can be carried out to determine PFAS sources (Quian et al. 2023), as well as the use of comprehensive 'untargeted analyses', in which hundreds of individual PFAS molecules can be identified and at least semi-quantified.

Such applications are more time-consuming and expensive than the normal standard PFAS analysis for polluted sites, which is mainly used to identify PFAS sources. The MVA application can avoid this and be more cost-effective.

More than 9,000 PFAS have been polluting the environment and our health for decades. This also includes volatile PFAS, such as fluorotelomer alcohols (6:2 or 8:2 FTOH, etc.). The problem in investigating PFAS-contaminated sites lies mainly in the huge quantity of poly-fluorinated PFASs, which are biotransformed into per-fluorinated PFASs over time. Individual poly-fluorinated PFASs may also be relatively resistant in the environment and transform only very slowly into perfluorinated PFASs (such as Capstone B - FTAB, FTS or FTOH). In order to improve transparency and knowledge of this large number of PFAS pollutants, there are several approaches to the investigation, risk assessment and remediation of PFAS.

An important characteristic of PFASs is their chemical behavior in the environment, as poly-fluorinated PFASs (precursors) are converted to stable perfluorinated PFASs by biotransformation. The risk assessment of individual cases via a QSRA* (or RRA*) can estimate the future risks of most of the "precursors", since an analysis based on 28 to 70 individual PFASs is carried out before and after examination by the 'Top Assay' test (see Fig. 4). In the Top Assay, poly-fluorinated PFAS are converted into stable per-fluorinated PFAS by oxidation via persulphate, into which they are generally biotransformed after a certain residence time in the environment (see also Figs. 2a & 2b). Thanks to the 'Top Assay' test, investigations and risk assessments include almost all transformable 'precursors' as well as the remaining per-fluorinated PFAS end products.

(*EQRS & *ARR: Quantitative Health Risk Assessment and Residual Risk Analysis).

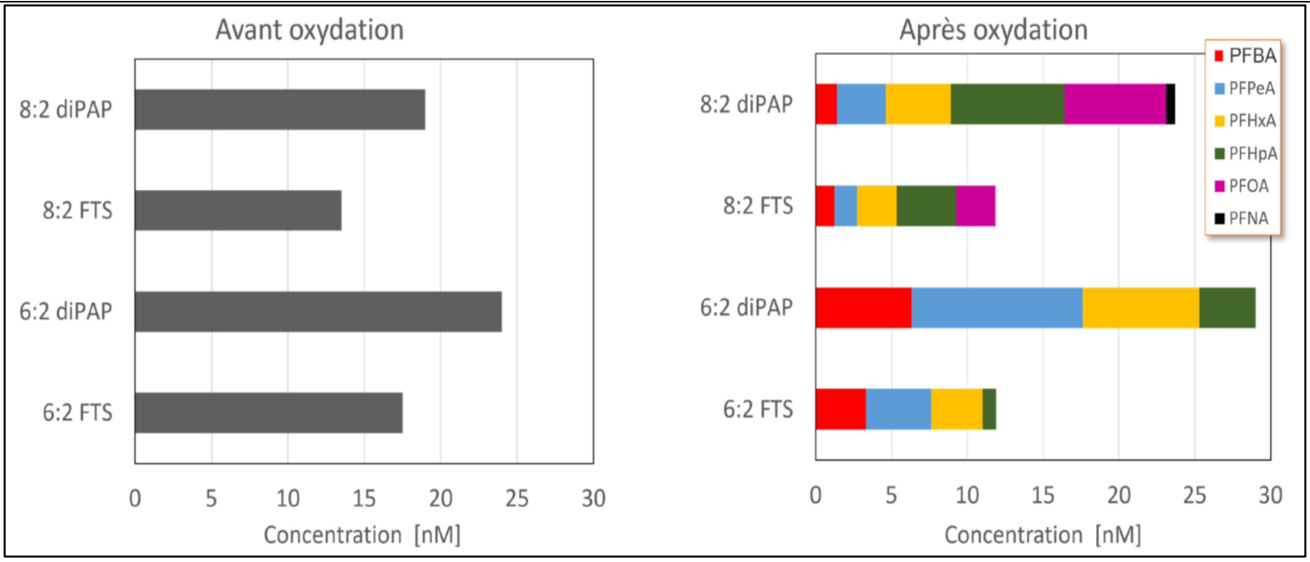


Fig. 4 : *Top Assay (Total Oxidizable Precursor method) to quantify oxidizable poly-fluorinated PFAS, transformable into per-fluorinated carboxylic acids (Houtz & Sedlac 2012, Glöckner et al.: 2021).*

The following examples illustrate some of the ways in which sources of PFAS can be identified and differentiated using certain standard analyses, taking into account experience of MVA (Multi-Vector-Analysis) applications based on artificial intelligence in Europe (EU) and the United States.

Typical sources of PFAS include areas that have experienced fire and fire training events, civil and military airports (anti fire-fighting foams / AFFF), but other activities can also cause PFAS contamination in soils and groundwater.

These activities include, for example, the spreading of sewage sludge from wastewater treatment plants, galvanic chromium plating, landfill leachates, paper production, textile impregnation, the electrical and electronics industries, paint companies, cleaning products and fluor-polymer production, etc.

Various statistical analyses and visualizations, based on experiments and PFAS clusters from over 800,000 soil and groundwater analyses (NAS: 2023, F. Karg: 2024), help to identify PFAS sources.

The methodology for differentiation of PFAS sources can be divided into three main categories:

I. Analysis of data and (historical) information available that can be used to identify potential sources of PFAS at different sites (specific industrial sites airports, landfills, etc.).

II. Laboratory methods for analyzing PFAS in environmental samples.

III. Advanced forensic investigations to identify potential sources of PFAS more precisely.

Category I. includes the following phases :

- Historical investigation of potential sources of PFAS from suspect areas. The objective is to list and map the areas of potential sources of PFAS pollution.
- Study the hydrogeological zones above the suspected areas to determine whether there are (or have been) activities that use (or have used) PFAS.

- To obtain a detailed understanding of the geology, hydrogeology, hydrology, stormwater infrastructure and surface water run-off of the sites. This also includes the nature of the soil, the location and depth of nearby wells, and the depth and direction of surface and groundwater flow.
- Prepare a conceptual plan of the site concerning PFAS sources, transfer paths and exposure paths to targets.

Categories II and III focus on :

- Evaluation of PFAS chemical analysis data as a screening step to determine whether indications or evidence of source differentiation can be identified.
- Analysis of advanced PFAS forensics on selected samples to differentiate potential sources of PFAS (e.g. by structural isomerism, isotopic studies, Top Assay, MVA applications, etc.).

The general differences between PFAS's commercial products can be identified, for example, through the following distinctions:

- Modern anti fire-fighting foams (AFFF) are based on fluoro-telomers, mainly with C6-PFAS molecules. Although these firefighting foams do not contain PFOA or PFOS, when emitted into the environment they can degrade to other shorter-chain PFAS, such as perfluoro-hexanoic acid (PFHxA), perfluoro-pentanoic acid (PFPeA), buntanonic acid and 5:3 fluorotelomer carboxylic acid (FTCA).
- In the early 2000s (following general requests from the US and European authorities), the chemical industry began to phase out anti fire-fighting foams based on C8-PFAS, as PFOS and PFOA were classified as being “too toxic”. Producers of fluorotelomer-based firefighting foams then turned to the use of short-chain forms of PFAS with six fluorinated carbons (called C6-PFAS), which did not contain PFOS or PFOA (and could not be broken down into these products either). These C6-PFAS firefighting foams can also contain PFHxA, PFPeA and 6:2-fluorotelomersulphonate (6:2-FTS) as well as fluorotelomers, which can be transformed over time into their end groups, perfluoro carboxylic acids with less than six carbon atoms. The exact period of transition from C8-PFAS fire-fighting foams to C6-PFAS fire-fighting foams varies according to the application site (civil or military airports, fire training areas, oil sites, etc.).
- Before 2016, many firefighting foams contained PFAS with eight fluorinated carbon chains. Some of these long-chain firefighting foams, or C8 PFASs, contained PFOS until the early 2000s, and PFOA and other long-chain PFCAs until around 2015, when these products were withdrawn from the market.
- Analyses of the molecular chemical structures of PFASs can be useful in relation to existing information such as origin, period and likely use. Structural differences include, for example, structural isomerism (linear and branched isomers, etc.). For example, if a particular cyclic PFAS with an eight-carbon chain, such as perfluoroethyl-cyclohexane sulphonate (PFECHS: CAS 335-24-0) is observed, it could originate from a corrosion inhibitor used in aircraft hydraulic fluids (MPART: 2020). PFECHS is not known to be a component of fire-fighting foams.
- Specific PFASs can be used as markers in the production of fluoropolymers, food packaging and paper coatings, as well as cosmetics. They are not currently thought to be related to fire-fighting foam products.
- Some PFASs can be chemically biotransformed (i.e. broken down into smaller, stable chemicals), but these poly-fluorinated PFASs (precursors) often transform into other PFASs, particularly per-fluorinated PFAAs.

Identifying the different sources of PFAS:

The standard environmental analyses used during investigations of sites polluted by PFAS can, in principle, be used to identify and differentiate sources of PFAS. Between 28 and 70 individual PFAS substances are analyzed. The analytical data obtained can be very complex due to the presence of many different PFAS in an environmental sample and pose a challenge in interpreting the data. For this reason, a computerized MVA application with artificial intelligence is required.

Because of this complexity, large amounts of data need to be interpreted on the basis of statistical experience gained from large amounts of analysis in multi-vector analysis (MVA or poly-topic analysis) with artificial intelligence, so that the sources of PFAS can be identified and differentiated with a very high probability. This can only be done as part of a parallel analysis of different pieces of evidence, as each analysis on its own is generally not sufficiently significant. The basis for this are ‘target’ (and ‘non-target’) analyses as well as the ‘Top Assay’, total organic fluorine (TOF) or AOF (adsorbable total organic fluorine) and isotopic analyses (see Fig. 5):

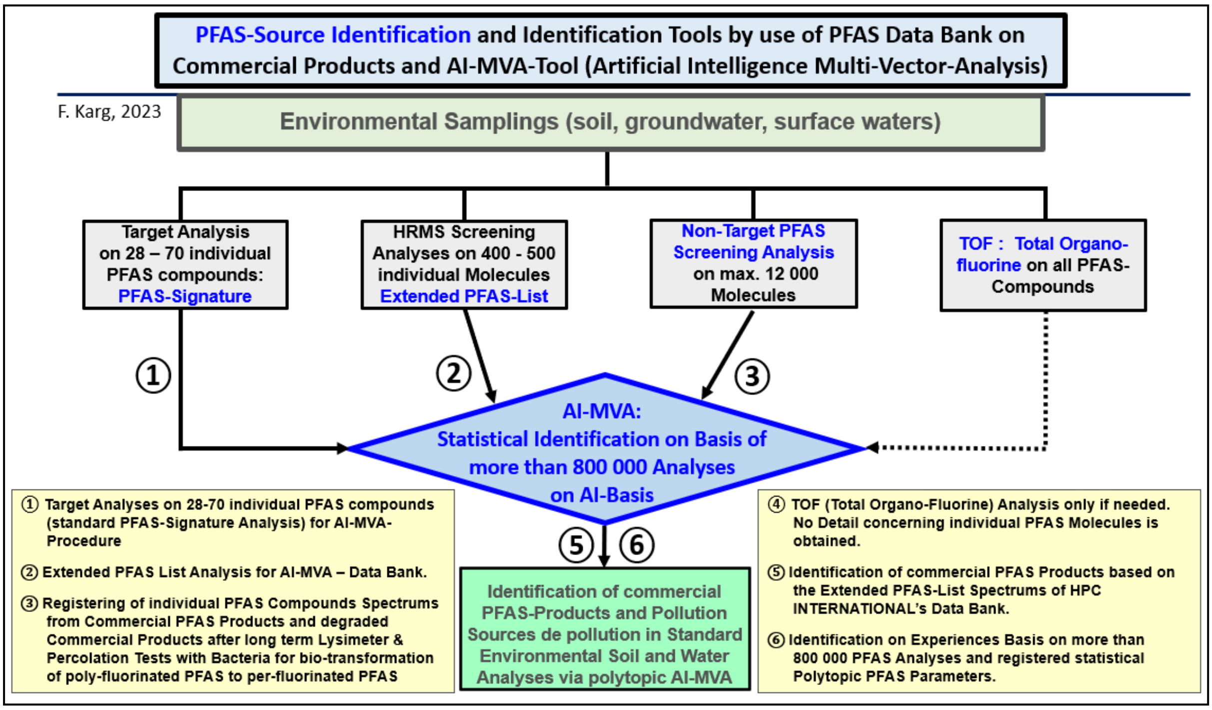
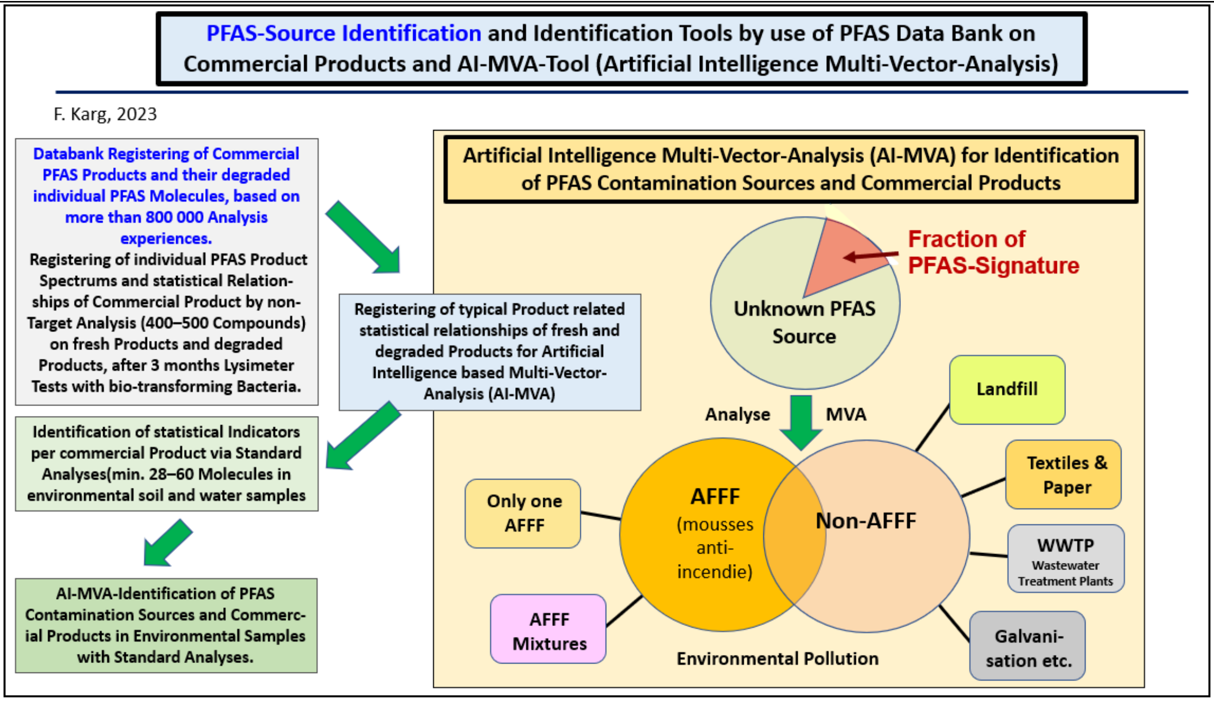


Fig. 5 : Analytical procedures for the identification and differentiation of PFAS sources using multi-vector analysis (MVA or poly-topic analysis) with artificial intelligence (F. Karg et al.: 2023 and 2024)

Figure 6 shows the procedure for identifying and differentiating potential sources of PFAS using MVA based on artificial intelligence (e.g. AFFF fire-fighting foams, sewage sludge, electroplating activities, textile and paper industries, waste dumps, etc.).



PFAS-Source Identification and Identification Tools by use of PFAS Data Bank on Commercial Products and AI-MVA-Tool (Artificial Intelligence Multi-Vector-Analysis)

F. Karg, 2023

Databank Registering of Commercial PFAS Products and their degraded individual PFAS Molecules, based on more than 800 000 Analysis experiences.
Registering of individual PFAS Product Spectrums and statistical Relation-ships of Commercial Product by non-Target Analysis (400–500 Compounds) on fresh Products and degraded Products, after 3 months Lysimeter Tests with bio-transforming Bacteria.

Registering of typical Product related statistical relationships of fresh and degraded Products for Artificial Intelligence based Multi-Vector-Analysis (AI-MVA)

Identification of statistical Indicators per commercial Product via Standard Analyses(min. 28–60 Molecules in environmental soil and water samples

AI-MVA-Identification of PFAS Contamination Sources and Commerc-ial Products in Environmental Samples with Standard Analyses.

Artificial Intelligence Multi-Vector-Analysis (AI-MVA) for Identification of PFAS Contamination Sources and Commercial Products

Fig. 6 : MVA analysis approach based on artificial intelligence to identify and differentiate sources of PFAS (e.g. AFFF fire-fighting foams, sewage sludge, galvanic activities, textile and paper industries, waste dumps, petroleum sites, etc.) (F. Karg et al.: 2023 & 2024).

Because of the many individual PFASs within this chemical family, ‘non-target analysis’ also offers the possibility of identifying unknown molecules, as the result is open-ended without any limitation on a standard list of pre-calibrated pollutants. Hundreds of individual compounds can be identified. The disadvantage is that non-targeted analysis is relatively expensive and time-consuming. Figure 5 shows the differences compared with standard analysis of selected PFAS parameters.

Figures 7 and 8 show PFAS cluster analyses to differentiate between several PFAS sources.

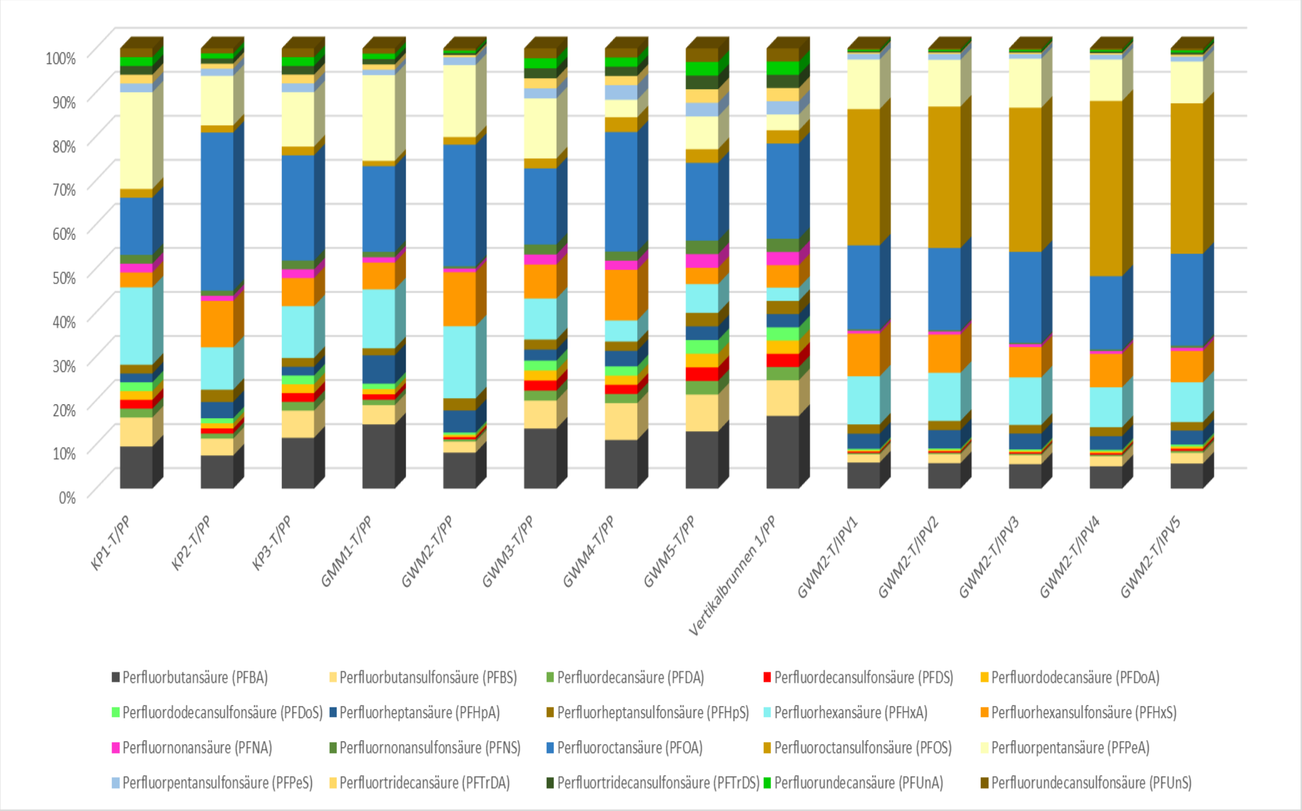


Fig. 7 : Various PFAS clusters identified to determine the sources of PFAS (F. Karg and al., 2023, 2024)

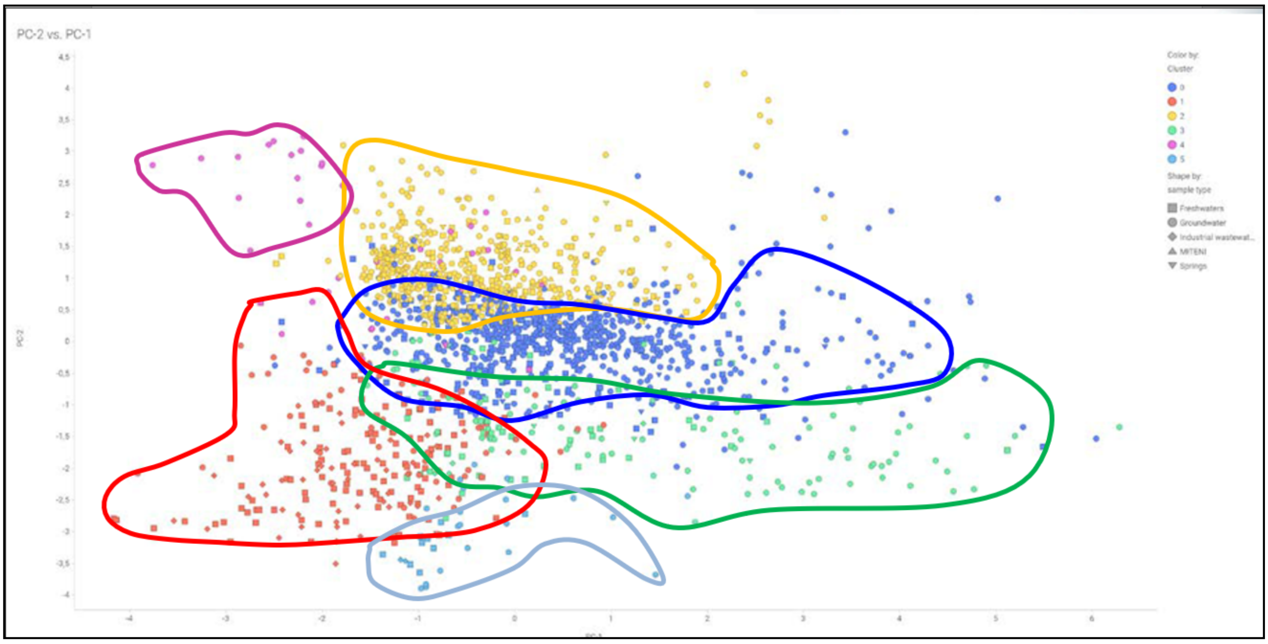


Fig. 8 : Identification and differentiation of 6 different sources of PFAS and commercial PFAS products on the basis of analyses of PFAS clusters (area of 761 ha) on the basis of 472 analyses of groundwater and surface water) in north-east Italy (C. Monti et al.: 2023 & F. Karg: 2023).

The multi-vector analysis (MVA) computer tool with artificial intelligence to identify and differentiate the sources of PFAS clusters was created (and is under continuous development) by HPC-International based on the statistical experience of more than 800,000 environmental analyses.

The basis is, among others, the experiences of the US Airport Cooperative Research Program (ACRP), the Airports Council International - North America (ACI-NA), the American Association of Airport Executives (AAAE), the USA National Academy of Sciences Guide (NAS: 2023), as well as chemical cluster determinations of fresh commercial PFAS products and aged commercial PFAS products (according to degradation procedures applied by HPC International; F. Karg et al. 2023 - 2024) as standards for the MVA-PFAS database. The ageing of commercial PFAS products was carried out using lysimetric tests with exposure to degrading bacteria, which biotransform poly-fluorinated PFAS into per-fluorinated PFAS (F. Karg et al. 2023 – 2024, NAS, 2023).

The analysis of PFAS clusters takes into account the environmental chemistry of PFAS and in particular the metabolism or biotransformation of poly-fluorinated PFAS into stable per-fluorinated PFAS, e.g. the metabolism of poly-fluorinated PFAS into stable per-fluorinated PFAS, for example 6 :2 FTAB → 6:2-FTS → 6:2-FTOH → PFHxA + PFPeA + PFBA etc. to determine the 'precursors' and final products in the event of environmental contamination by mixtures of PFAS through the biotransformation chain.

Site-specific investigations and the identification and differentiation of PFAS sources include the following multi-criteria applied in the MVA tool. All the criteria are always applied at the same time:

A. **Concentration ratios between PFAS:** this is a simple first screening technique, where one or more concentration ratios between two or more different PFAS compounds can be applied. For example, PFHxS/PFOS ratios within a certain range have been used as an indicator of a source of fire-fighting foam (McGuire et al. 2014), and PFHxS/PFOA ratios have been identified as markers of other sources of industrial PFAS production (Guelfo and Adamson 2018).

B. **Circular diagrams and other data visualisations :** These are statistical graphs showing **the relative contribution of several molecules** to the total PFAS concentration in the same study area.

   They can help identify compositional differences between PFAS mixtures in different samples to determine whether there are chemical clues or evidence from different PFAS sources. It can also identify the mixing of different PFAS sources or changes in source signatures along a transport pathway (e.g. migration in groundwater) and also reveal biotransformations and soil chromatography effects.

C. **Isomer ratios:** Individual PFAS can exist in **different isomeric forms** and the relative abundance of different isomers in a sample can be used to infer the source of PFAS (Charbonnet et al. 2021). **The presence of branched isomers (structural isomers) in a sample can be measured using standard methods** (which analyse around 60 to 70 individual substances). **The two different PFAS production processes, ECF (electrochemical fluorination) and telomerisation, result either in a mixture of branched and linear PFAS (ECF) or in isomers of purely linear PFAS.**

   This information could be useful as evidence to identify sources of PFAS. **Branched isomers indicate that PFAS come from the specific electrochemical fluorination (ECF)** manufacturing process**.** The proportion of branched isomers in ECF products falls within a relatively narrow range (ITRC 2022a&b). If the proportion of branched isomers in a sample is below this range, this may indicate that products containing PFAS generated by telomerisation-based manufacturing processes are also present.

   Modern firefighting foams (AFFFs) contain PFASs that are produced solely by telomerisation processes. Older AFFF blends may contain PFAS produced by ECF manufacture or telomerisation. In the USA and somewhat later in Western Europe, the production of AFFF mixes using ECF production was discontinued in the early 2000s.

Another important fact is that branched isomers of some PFAS (e.g. PFOS) propagate more rapidly in groundwater than linear isomers of the same compound (different chromatographic effects in soil) due to the different interactions of the isomers with the soil. This can lead to enrichment of **ramified isomers** in groundwater hydrogeologically downstream of a PFAS source (Nickerson et al. 2020).

D. Analysis of the main components of PFAS and hierarchical classification study of PFAS clusters: These statistical methods are used to analyze data associated with many variables (e.g. measured PFAS) in order to identify differences between clusters of PFAS that can be visualised graphically. This data analysis facilitates the identification of different groups (or clusters) of PFAS mixtures (each of which may come from different sources or commercial PFAS products (see Figs. 7 & 8), which clusters may overlap).

E. Research methods (screening): identification and characterization of sources of PFAS:

- **Frequency of detection:** Experimental statistics (from over 800,000 individual analyses from different PFAS source locations) on the relative detection of individual PFAS (in each analysis data set) help to distinguish between different PFAS sources. The absence (or low frequency of detection) of specific PFAS in samples from one type of site can also be used in the same way. Experiments with over 800,000 individual analyses of samples from various PFAS source locations show very clearly these differences depending on the PFAS source (NAS: 2023).

- **Concentration distributions:** These data help to determine the relative distribution of individual PFAS found in environmental samples from different locations. The average concentration of individual PFAS from the samples examined is used in the MVA assessment (see Fig. 7a - d). These data provide information on the relative proportion of different PFAS sources in a given site type, as well as the relative presence of PFAS associated with different sources.

- **PFAS composition ratios:** These ratios show the general distribution of PFAS within the sample groups. This includes the percentage of perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulphonic acids (PFSAs) and non-perfluoroalkyl acids (non-PFAAs) relative to the total of overlapping PFAS mixtures (e.g. present in groundwater). The application of this methodology also includes the quantification of concentration ratios between frequently detected individual PFASs.

- **Statistics for identifying and characterizing sources of PFAS using multi-vector analysis (MVA):**

The results of the PFAS source determination are presented in five different types of statistical visualizations of PFAS source categories. These five types of MVA are:

- **MVA1 : PFAS composition circular diagrams,**
- **MVA2 : Boxplot distribution of concentrations and PFAS histograms,**
- **MVA3 : Average PFAS concentrations and detection frequency: Heat-Maps,**
- **MVA4 : Average PFAS concentration and detection frequency: 'Cross-plots',**
- **MVA5 : Report of PFAS logarithmic average concentrations: Relative and radial point diagrams.**

Some examples of MVA assessments (MVA 2, 4 & 5) :

MVA2 : Distribution of PFAS concentrations in histograms:

The analytically determined PFAS groups are classified on the basis of experience gained from environmental analyses of PFAS. Figures 9a to d show a series of histograms of e.g. PFAS concentrations for four main PFAS source categories (based on experiments on over 800,000 analyzed groundwater, soil and surface water samples, NAS, 2023). For ease of visualization, individual PFAS are placed in the same order on each graph to show the relative magnitude of concentrations associated with each type of site.

The PFAS levels measured at a site are first assigned to one of the MVA assessment categories (for example in Figures 9a to d) to apply some of the parameters for identifying and differentiating PFAS sources.

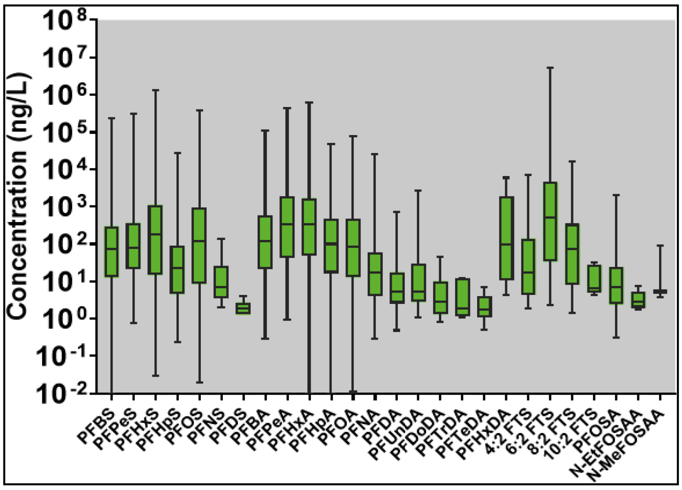


Fig. 9a: Typical distribution of PFAS in environmental samples from airports civils (NAS, 2023).

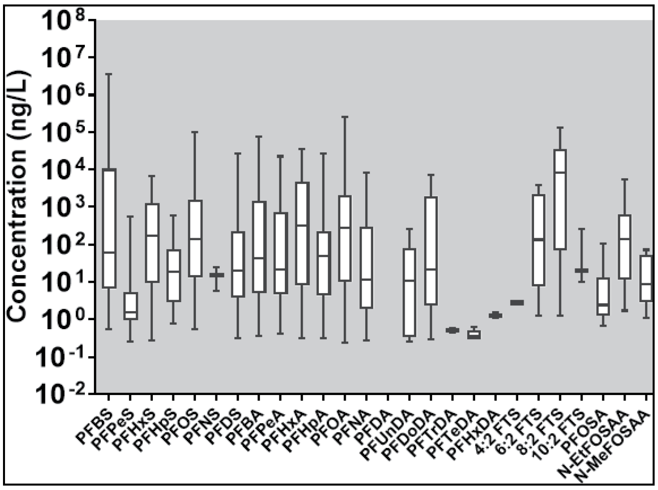


Fig. 9b : Typical distribution of PFAS in environmental samples of sites industrial production of fluoropolymers (NAS, 2023).

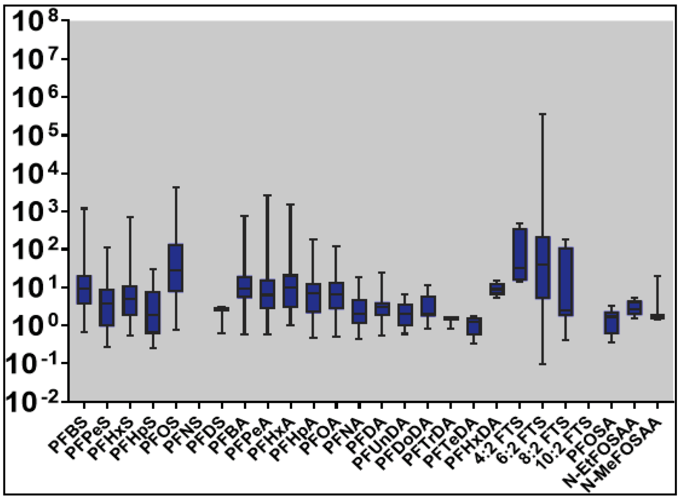


Fig. 9c: Typical distribution of PFAS in environmental samples from galvanizations (chrome plating) (NAS, 2023)

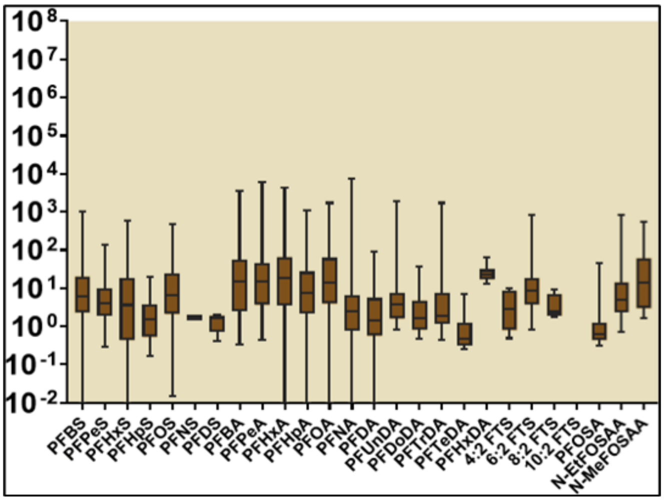


Fig. 9d: Typical distribution of PFAS in environmental samples from household waste landfill sites (NAS : 2023)

MVA4 : Median PFAS concentration and detection frequency : ***Cross Plots*** : Experience (from more than 800,000 environmental analyses of PFAS) on the statistical frequency of the average concentration of individual PFAS compounds can also be summarized in cross plots that serve as a representative PFAS signature for each PFAS source category (see Figures 10a to b, NAS: 2023). Compounds found in the colored area at the top right of each plot represent PFAS that are frequently detected at relatively high concentrations by type of PFAS source (y). For each PFAS molecule, the percentage frequency of detection is given in relation to the average concentration (in ng/l) in all the groundwater samples analyzed (x).

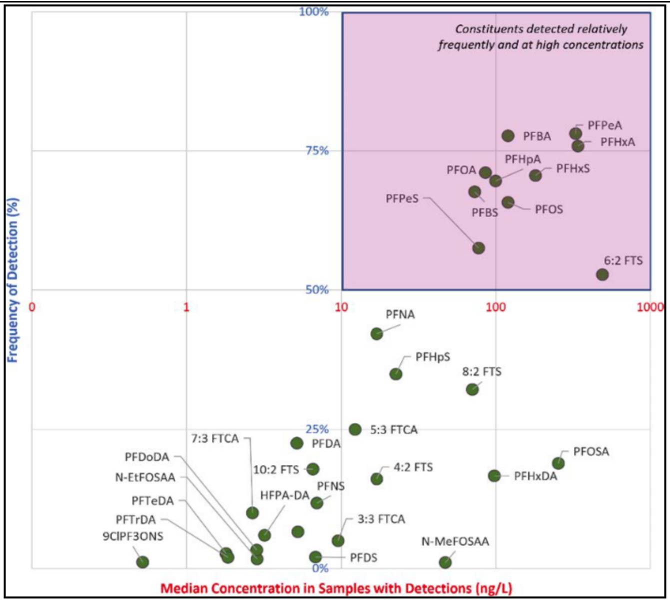


Fig. 10a : Typical distribution of PFAS in of environmental samples of civil airports (NAS : 2023)

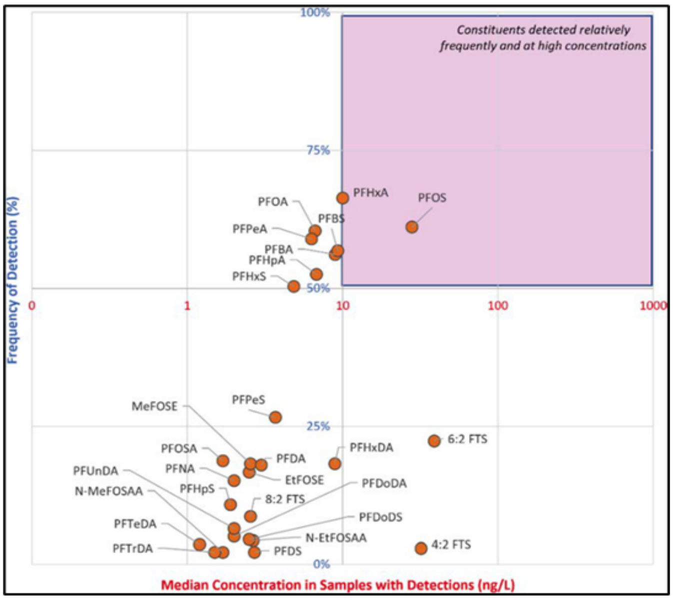


Fig. 10b : Typical distribution of PFAS in galvanisation samples (chrome-plating (NAS : 2023)

MVA5: Ratio of median logarithmic concentrations of PFAS and points and radial plots of ratios : Additional graphical representations of various statistical analyses are useful for checking a set of PFAS analyses for PFAS source associations in more detail. Figures 11 and 12 (NAS: 2023) show the results of a logarithmic analysis of the ratio of median concentrations. The results are evaluated statistically and verified graphically. This approach offers opportunities for a comparative study of PFAS data collected at a site and also illustrates that different visualizations are often appropriate to better communicate complex results from different PFAS sources. In the scatter and radial plots presented in these figures, each symbol represents the median log concentration ratio of the designated PFAS compound pairs.

Table 1 shows the PFAS analysis parameters recommended for MVA. All these assessment steps are carried out in parallel by the MVA-PFAS source identification tool.

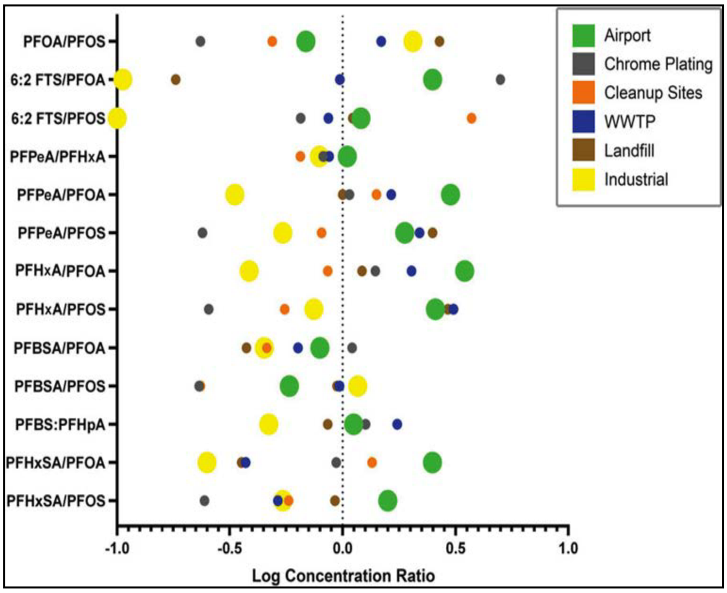


Fig. 11 : Typical distribution of PFAS in environmental samples from different sources in the form of ratio points (NAS, 2023)

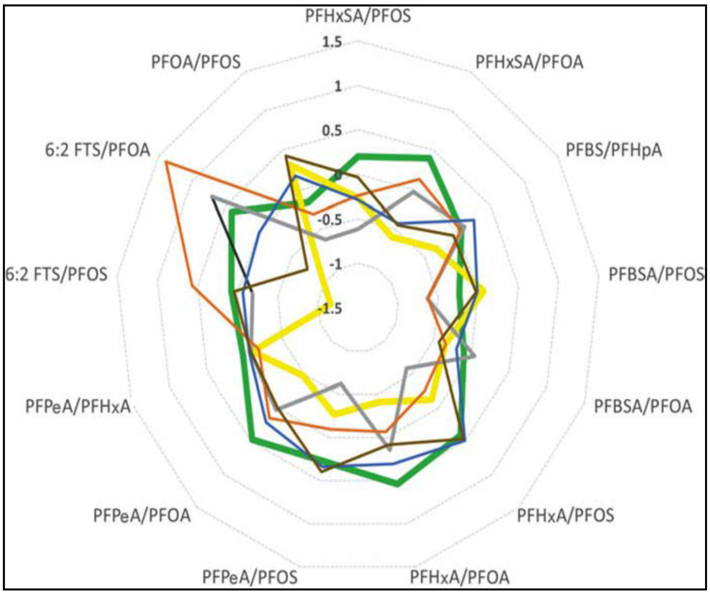


Fig. 12 : Typical distribution of PFAS in environmental Samples from different sources in radial form (NAS, 2023)

Figure 13 shows a summary of the parameters evaluated for the identification and differentiation of AI-MVA (artificial intelligence-based multi-vector analysis) PFAS sources.

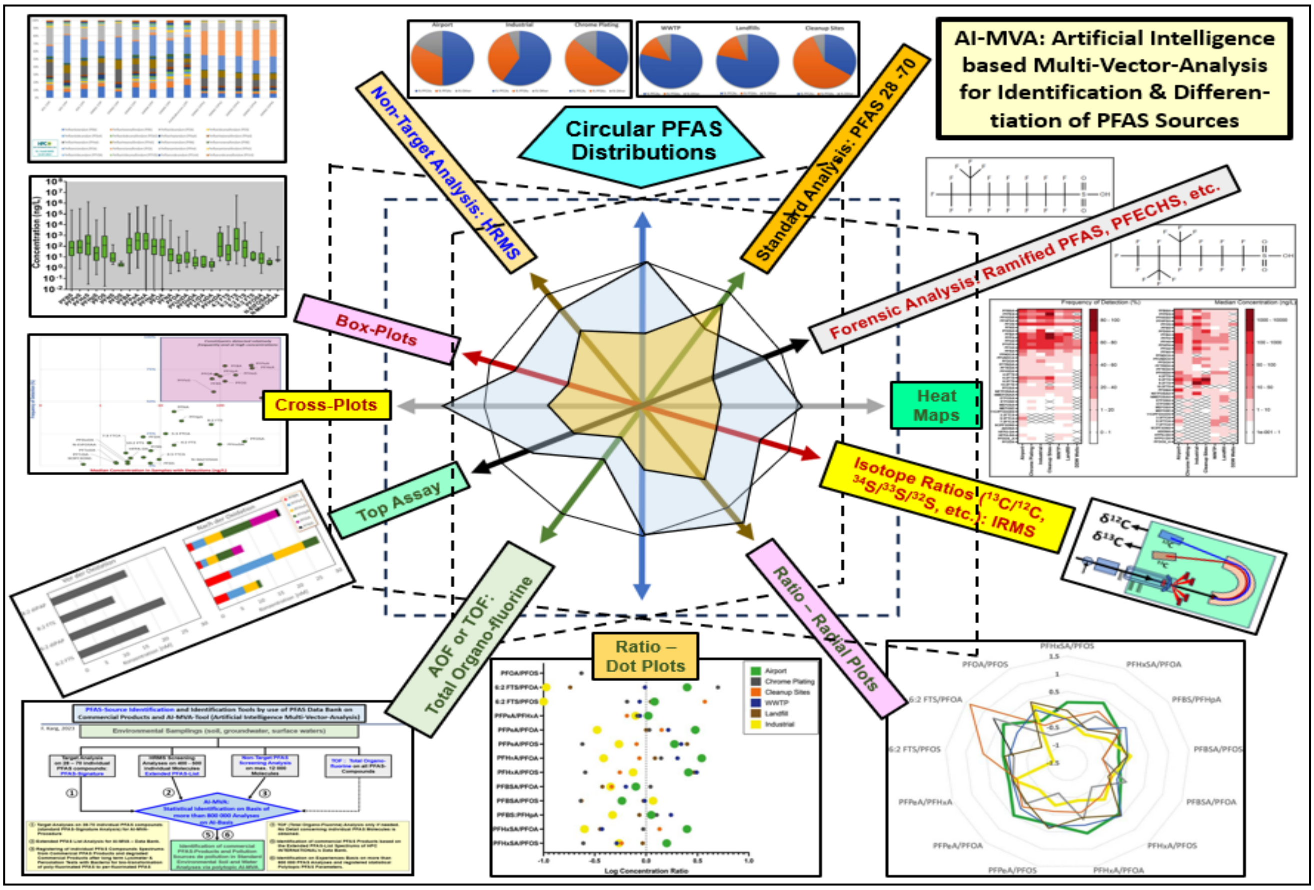


Fig. 13 : Parameters evaluated for the identification and differentiation of PFAS sources using AI-MVA (artificial intelligence-based multi-vector analysis).

Table 1 : Recommended standard analysis parameters for using the multi-vector analysis (MVA) computer tool with artificial intelligence to identify and differentiate sources of PFAS.

Table 1a: Recommended standard analysis parameters for using the multi-vector analysis (MVA) computer tool with artificial intelligence to identify and differentiate sources of PFAS.

PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
PFBA (acide perfluorobutanoique)	ng/l	1	375-22-4	🟩	🟩	🟩
PFPeA (acide perfluoropentanoique)	ng/l	5	2706-90-3	🟩	🟩	🟩
PFHxA (acide perfluorohexanoique)	ng/l	1	307-24-4	🟩	🟩	🟩
PFHpA (acide perfluoroheptanoique)	ng/l	1	375-85-9	🟩	🟩	🟩
PFOA linéaire (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟩	🟩
PFOA ramifié (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFOA totale (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFNA (acide perfluorononanoique)	ng/l	1	375-95-1	🟩	🟩	🟩
PFDA (acide perfluorodecanoique)	ng/l	1	335-76-2	🟩	🟩	🟩
PFUnDA (acide perfluoroundecanoique)	ng/l	1	2058-94-8	🟩	🟩	🟩
PFDoDA (acide perfluorododecanoique)	ng/l	2	307-55-1	🟩	🟩	🟩
PFTrDA (acide perfluorotridecanoique)	ng/l	1	72629-94-8	🟩	🟩	🟩
PFTeDA (acide perfluorotetradecanoique)	ng/l	1	376-06-7	🟩	🟥	🟩
PFHxDA (acide perfluorohexadecanoique)	ng/l	2	67905-19-5	🟩	🟥	🟩
PFODA (acide perfluorooctadecanoique)	ng/l	1	16517-11-6	🟩	🟥	🟩
PFBS (acide perfluorobutane sulfonique)	ng/l	1	375-73-5	🟩	🟩	🟩
PFPeS (acide perfluoropentane sulfonique)	ng/l	1	2706-91-4	🟩	🟩	🟩
PFHxS linéaire (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟩	🟩	🟩
PFHxS ramifié (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟥	🟥	🟥
PFHxS totale	ng/l	1	355-46-4	🟥	🟥	🟥
PFHpS (acide perfluoroheptane sulfonique)	ng/l	1	375-92-8	🟩	🟩	🟥
PFOS linéaire (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟩	🟩	🟥
PFOS ramifié (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFOS totale (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFDS (acide perfluorodecane sulfonique)	ng/l	1	335-77-3	🟩	🟩	🟥
4:2 FTS (acide 4:2 fluorotelomer sulfonique) H4-PFOS	ng/l	1	757124-72-4	🟩	🟥	🟥
6:2 FTS (acide 6:2 fluorotelomer sulfonique)	ng/l	1	27619-97-2	🟩	🟥	🟥
8:2 FTS (acide 8:2 fluorotelomer sulfonique)	ng/l	1	39108-34-4	🟥	🟥	🟥
10:2 FTS (acide 10:2 fluorotelomer sulfonique)	ng/l	1	120226-60-0	🟥	🟥	🟥
MePFOSAA (acide N-méthylperfluorooctane sulfonamide acétique)	ng/l	1	2355-31-9	🟥	🟥	🟥
EtFOSAA (acide N-éthylperfluorooctane sulfonamide acétique)	ng/l	1	2991-50-6	🟥	🟥	🟥
PFOSA linéaire (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟩	🟥	🟥
PFOSA ramifié (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
PFOSA totale (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
MeFOSA linéaire (N-méthylperfluorooctanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥

Table 1b: Recommended standard analysis parameters for using the multi-vector analysis (MVA) computer tool with artificial intelligence to identify and differentiate sources of PFAS.

PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
MeFOSA ramifié (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
MeFOSA totale (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
8:2 DiPAP (8:2 polyfluoroalkyl phosphate diester)	ng/l	1	678-41-1	🟥	🟥	🟥
HFPO-DA (acide hexafluoropropyleneoxide dimer) Gen X	ng/l	1	13252-13-6	🟥	🟥	🟩
EtFOSA linéaire (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA ramifié (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA totale (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
MeFBSAA (perfluorobutanesulfonamide(N-méthyl)acetate)	ng/l	5	159381-10-9	🟥	🟥	🟥
9Cl-PF3ONS (acide 9-chlorohexadecafluoro-3-oxanonane-1-sulfonique)	ng/l	1	73606-19-6	🟥	🟥	🟥
4H-PFUnDa (acide 2H,2H,3H,3H,-perfluoro undécane)	ng/l	5	34598-33-9	🟥	🟥	🟥
8:2 FTUCA (acide 2H-perfluoro-2-décenoique)	ng/l	1	70887-84-2	🟥	🟥	🟥
DONA (acide 4,8-dioxa-3H-perfluorononanoique)ADONA	ng/l	1	919005-14-4	🟩	🟥	🟩
MeFBSA (n-méthylperfluorobutanesulfonamide)	ng/l	1	68298-12-4	🟥	🟥	🟥
PFBSA (perfluorobutanesulfonamide)	ng/l	1	30334-69-1	🟥	🟥	🟥
PFECHS (acide perfluoro-4-éthylcyclohexanesulfonique)	ng/l	1	646-83-3	🟥	🟥	🟥
PFNS (acide perfluorononane sulfonique)	ng/l	1	68259-12-1	🟩	🟩	🟩
PFDoDS (acide perfluorododecane sulfonique)	ng/l	1	79780-39-5	🟩	🟩	🟩
6:2 diester de phosphate fluorotélomérique. 6:2 diPAP	ng/l	10	57677-95-9	🟥	🟥	🟥
6:2 8:2 diester de phosphate fluorotélomérique. 6:2 8:2 diPAP	ng/l	10	943913-15-3	🟥	🟥	🟥
PFHxSA (perfluorohexanesulfonamide)	ng/l	1	41997-13-1	🟥	🟥	🟥
PFUnDS (acide perfluoroundecane sulfonique)	ng/l	2	749786-16-1	🟩	🟩	🟩
PFTrDS (acide perfluorotridecane sulfonique)	ng/l	2	791563-89-8	🟩	🟩	🟩
EtFOSE (2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	1691-99-2	🟥	🟥	🟥
MeFOSE (2-(N-methylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	24448-09-7	🟥	🟥	🟥
NFDHpA (Nonafluoro-3,6-dioxaheptanoic acid)	ng/l	1	151772-58-6	🟥	🟥	🟥
PFMPA (Perfluoro-3-methoxypropanoic acid)	ng/l	1	377-73-1	🟥	🟥	🟥
PFMBA (perfluoro-4-methoxybutanoic acid)	ng/l	1	863090-89-5	🟥	🟥	🟥
C6O4 (Perfluoro([5-methoxy-1,3-dioxolan-4-yl]oxy)acetic acid)	ng/l	10	1190931-41-9	🟩	🟥	🟩
6:2-FTOH (6:2 fluorotelemer alcohol) FHET	ng/l	20	647-42-7	🟩	🟥	🟩
8:2-FTOH (8:2 fluorotelemer alcohol) FOET	ng/l	10	678-39-7	🟩	🟥	🟩
6:2-FTAB (6 :2 fluorotelomer sulfonamido propyl betaine) Capstone B	ng/l	10	34455-29-3	🟩	🟥	🟩
Parameters for PFAS Source Identification per AI-MVA (Artificial Intelligence Multivector Analysis)						

Summary

In the context of groundwater pollution by PFAS, it is becoming increasingly important to identify and, above all, to differentiate the contribution of each PFAS source to pollution plumes. This need for clarification of the contribution of each PFAS source to pollution, e.g. in the vicinity of catchments (for drinking water, etc.), is becoming increasingly crucial for the protection of water resources, (shared) responsibilities and the search for the (multiple) origins of pollution in the context of legal expertise.

To conclude, it is now possible (using comprehensive statistical, graphical and chemical-mathematical studies) to use multi-vector analysis (MVA) in several dimensions (and with the help of artificial intelligence) to identify and differentiate the sources of PFAS pollution in soils, groundwater and surface water, and in some cases even to identify the commercial PFAS products causing the pollution.

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L'importance de l'identification et de la différenciation des Sources PFAS dans les eaux souterraines via la Multi-Vector-Analyse sur la base de l'Intelligence Artificielle dans le cadre des Expertises judiciaires

The importance of Identifying and Differentiating PFAS Sources in Groundwater via Multi-Vector-Analysis, based on Artificial Intelligence in the context of Forensic Expertise

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1. Introduction

Dans les pays industrialisés, les monomères des PFAS : Per- & Polyfluoro-Alkyl Substances sont devenus progressivement depuis des années 1960 un problème environnemental majeur, également pour la Santé Publique, en raison de leur application multiple et vaste (historique et toujours actuelle). Cette menace pour l'environnement et la Santé Publique commence à être prise en compte petit à petit depuis les années 2010 et plus fortement en 2022 - 2024. Par conséquent, les PFAS se retrouvent aujourd'hui dans les sols de certains sites pollués, certaines nappes d'eaux souterraines, les aliments et l'eau potable ainsi que dans les gaz du sol et l'air ambiant (PFAS volatils, comme par ex. les FTOH : Fluorotélomère-alcools). Entre 9 000 et 12 000 polluants synthétiques de PFAS ont été produits et certaines publications indiquent même jusqu'à 15 000 molécules.

Les PFAS polymères du type « Teflon » (ou PFTE) etc. ne disposent pas d'une bonne biodisponibilité et sont par conséquent beaucoup moins toxiques que les PFAS monomères. Ces PFAS monomères font l'objet des travaux présentés ci-après. Les PFAS sont connus notamment pour leurs effets toxicologiques de perturbateurs endocriniens, d'hépatotoxicité, d'Immunotoxicité, leurs effets sur le développement des fœtus et pour certains, de cancérogénicité (par ex. le PFOA).

Une caractéristique importante des PFAS est leur comportement dans la Chimie Environnementale, car seuls les PFAS polyfluorés sont modifiés par bio-transformation microbiologique en PFAS perfluorés, qui demeurent totalement stables et non-dégradables, voire même bioaccumulables.

Notamment dans le cadre des pollutions des eaux souterraines par les PFAS, il est de plus en plus important d'identifier, et surtout de différencier la part de l'attribution de chaque source de PFAS aux panaches des pollutions. Ce besoin de clarification concernant la contribution de chaque source de PFAS aux pollutions, par ex. au droit des captages (d'eau potable, etc.) devient crucial pour la protection des ressources en eaux, les responsabilités (partagées) et la recherche des origines (multiples) des pollutions dans le cadre des expertises judiciaires.

Les sources de Pollutions par PFAS sont multiples et notamment présentes sur les sites industriels qui ont utilisé ces produits, les sites ayant subi des incendies ou les sites d'entrainement anti-incendie où des mousses anti-incendie **(AFFF : Aqueous Film Forming Foam ou Anti Fire Fighting Foams, par ex. sur des aéroports)** ont été utilisées. Les terrains agricoles sont aussi des sources de pollution par les PFAS, en raison de l'apport de boues de STEP (Stations d'Epuration) qui contiennent des PFAS accumulés.

Les activités (historiques) suivantes peuvent être à l'origine de pollutions par des PFAS :

- Entrainements anti-incendie,
- Aéroport ou base aérienne de site militaire,
- Site d'incendie et utilisation des AFFF,
- Galvanisation électrochimique,
- Production de papiers ou cartons « cirés »,
- Production de Textiles imperméables,
- Sprays, peintures, laques d'imperméabilisation,
- Production et application de Teflons (PTFE, etc.),
- Sites pétroliers et de l'industrie chimique et/ou production et application de peintures, de teintures, d'encres, de pigments, de cires chimiques et de produits de polissage,
- Applications de solvants (garages, pressings, blanchisseries, etc.),
- Décharges et anciennes décharges municipales, etc. (ISDD, ISDND, ISDD, etc.),
- Teintureries & Tanneries,
- Moquettes, tapis, tissus et plastiques avec des retardateurs de flammes,
- Production d'objets et meubles contenant des surfaces,
- Production de produits de nettoyage,
- Chimie photographique (laboratoires, et production des papiers et films, etc.),
- Production d'éléments électroniques,
- Production et applications de pesticides et biocides,
- Production de produits cosmétiques,
- Sites ayant reçus des Boues de STEP.

2. Chimie environnementale

La Chimie environnementale des PFAS est particulièrement importante et compliquée. Il n'existe aucun groupe de polluants montrant une chimie environnementale plus complexe que les PFAS. En particulier, il faut constater qu'il existe **plus que 9 000 substances PFAS**, divisées en **33 catégories de substances**.

Les plus connues sont les Acides perfluoroalkane-sulfoniques (PFASs), les Acides perfluoroalkyliques-carboxyliques (PFCA), les Perfluoroalkyliques-phosphates & leurs esters, les Fluorotélomère-alcools (**FTOH**), etc. (dont plus de **32 autres groupes**…). Certains d'entre eux, comme par ex. le **PFOA :** Acide perfluoro-octanoïque et le **PFOS** : Perfluoro-octane-sulfonate (cf. Fig. 1) sont bannis (et **interdit en CE et USA & Canada**) par la **Convention de Stockholm** dans la catégorie des **POPs** : Persistent Organic Pollutants. Le PFOA est cancérigène. Les **produits commerciaux** contiennent principalement des **mélanges**.

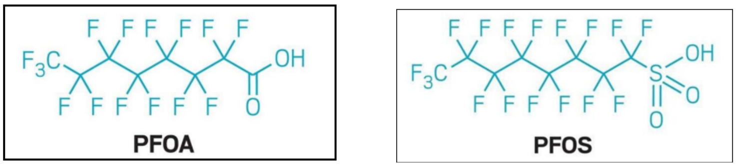


Fig. 1 : Formules structurelles des PFOA & PFOS

La raison de la forte solubilité dans l'eau, associée à une lipophilie, est basée sur le fait qu'il existe des **PFAS** :

- **Anioniques** (par ex. les sulfonates, les sulfates, les carboxylates et les phosphates),

- **Cationiques** (par ex. ammonium quaternaire),
- **Amphotères** (par ex. betaines et sulfo-betaines) : base + acide et
- **Non ioniques** (par ex. polyéthylène glycols, oligomères d'acrylamide).

Il est très important de souligner, que les PFAS poly-fluorés non entièrement fluorés (« Précurseurs ») peuvent être convertis par bio-transformation en produits chimiques persistants et entièrement fluorés, les PFAS per-fluorés [87 - 94]**. La dégradation complète microbiologique des PFAS n'a pas encore été démontrée.**

Les schémas Fig. 2a & 2b montrent un exemple de biotransformation du 6 :2-FTAB & 6 :2-FTS dans les sols et les eaux vers les Fluorotélomère alcools (FTOH) volatils qui migrent par la suite dans les gaz du sol et vers l'air ambiant. Par la suite, les FTOH sont transformés microbiologiquement en PFAS per-fluorés stables. Par exemple ; le 6:2-FTOH est bio-transformé en PFHxA, PFPeA et PFBA et le 8:2-FTOH en PFOA, PFHpA, PFHxA, PFPeA et PFBA.

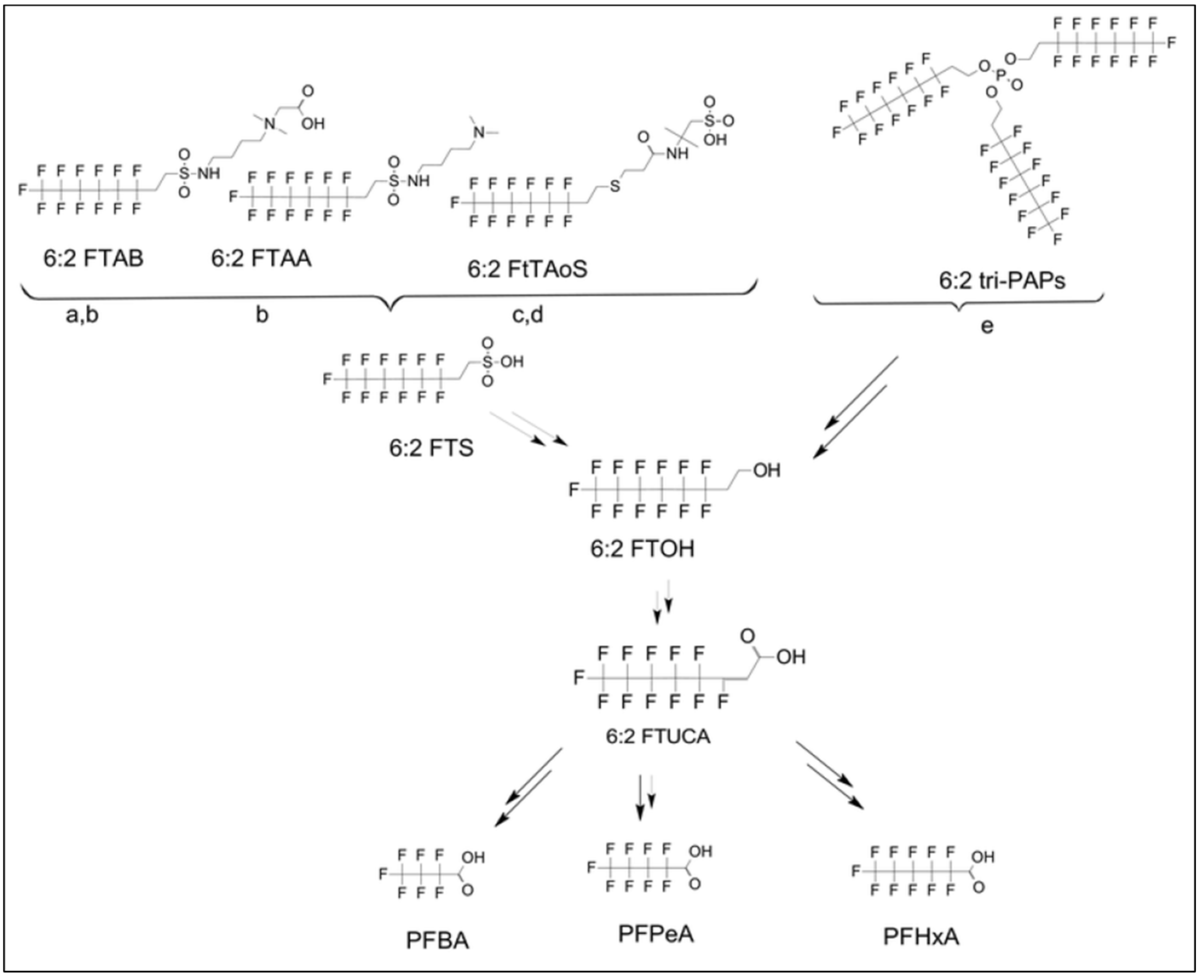


Fig. 2a : Schéma de biotransformation des PFAS polyfluorés (Précurseurs) : Exemple : 6 :2 FTAB et sa dégradation via le 6 :2 FTS et le 6 :2 FTOH vers les PFAS per-fluorés PFBA, PFPeA et PFHxA (LaFond et al. 2023, D.M.J. Shaw et al. 2019,Ying Shi, 2018 et V. Mendeza et. al. 2022)

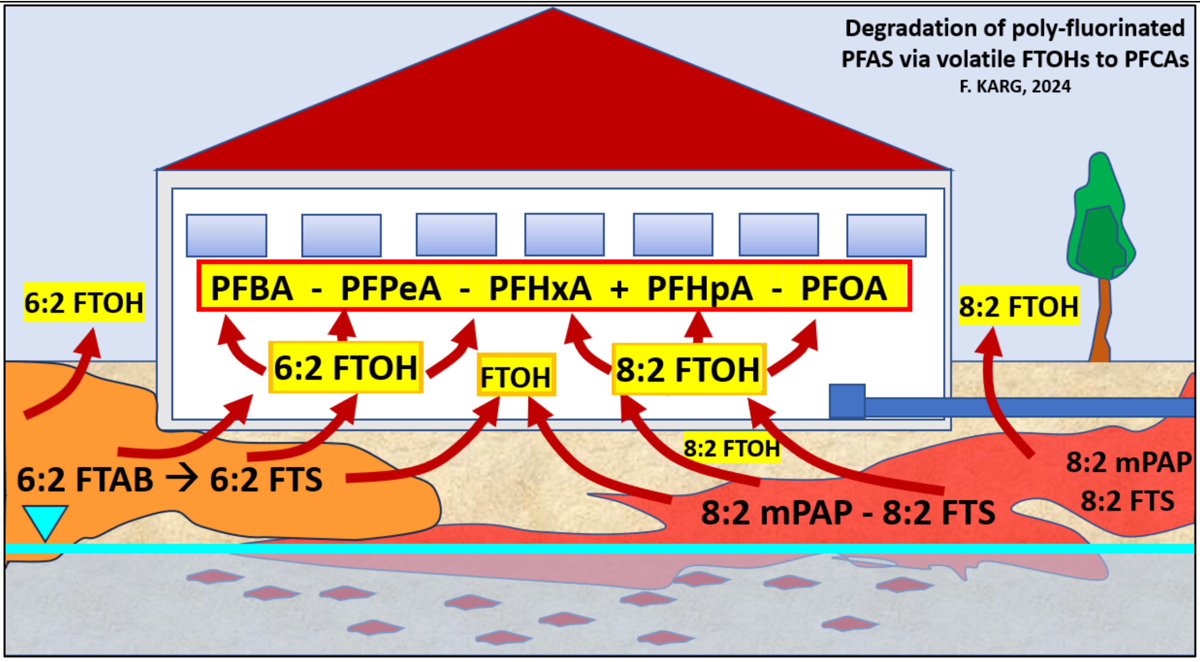
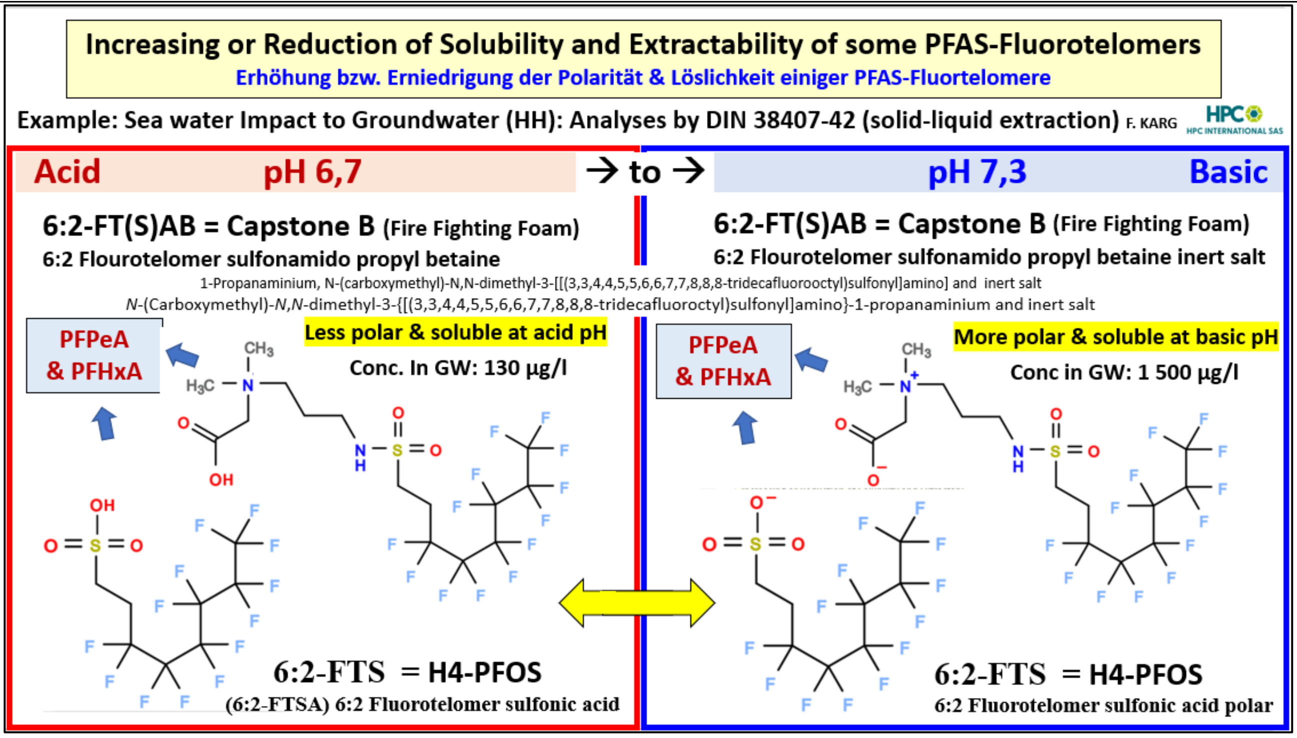


Fig. 2b: Exemple de biotransformation des 6 :2 FTAB, 6 :2 FTS, 8 :2 FTS et les alkyl phosphates polyfluorés (PAP), dans les sols et eaux vers le Fluorotelomer alcools (FTOH) et les PFAS per-fluorés, par ex. vers le PFOA, PFHpA, PFHxA, PFPeA et PFBA (L. KOPF / HPC, 2017 et F. KARG, 2022 & 2024)

En cas de changement de pH, certains PFAS pourraient devenir plus ou moins solubles, ce qui a également un impact sur les émanations de télomères fluorés volatils comme le FTOH, etc. dans les gaz du sol. Certains précurseurs pourraient modifier leurs solubilités (et leur propriété extractible lors des procédures d'analyse chimique). Par ex. l'intrusion d'eau de mer dans l'aquifère pourrait entraîner une augmentation du pH basique et donc de la solubilité de Capstone B. Cela a été observé en 2022 dans la zone portuaire de Hambourg / Allemagne suite aux inondations par l'eau de mer et l'intrusion dans les eaux souterraines (cf. Fig. 3). Ces effets pourraient entraîner des concentrations plus de 10 fois plus élevées dans les eaux souterraines qu'avant l'intrusion de l'eau de mer dans les sols et les eaux souterraines.



Increasing or Reduction of Solubility and Extractability of some PFAS-Fluorotelomers
Erhöhung bzw. Erniedrigung der Polarität & Löslichkeit einiger PFAS-Fluortelomere

Example: Sea water Impact to Groundwater (HH): Analyses by DIN 38407-42 (solid-liquid extraction) F. KARG

Acid pH 6,7 → to → pH 7,3 Basic

6:2-FT(S)AB = Capstone B (Fire Fighting Foam)
6:2 Flourotelomer sulfonamido propyl betaine

6:2-FT(S)AB = Capstone B (Fire Fighting Foam)
6:2 Flourotelomer sulfonamido propyl betaine inert salt

1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino] and inert salt
N-(Carboxymethyl)-*N*,*N*-dimethyl-3-{[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino}-1-propanaminium and inert salt

PFPeA & PFHxA
Less polar & soluble at acid pH
Conc. In GW: 130 µg/l

PFPeA & PFHxA
More polar & soluble at basic pH
Conc in GW: 1 500 µg/l

6:2-FTS = H4-PFOS
(6:2-FTSA) 6:2 Fluorotelomer sulfonic acid

6:2-FTS = H4-PFOS
6:2 Fluorotelomer sulfonic acid polar

Fig. 3 : solubilités des PFAS selon le pH (exemple : avant et après l’intrusion de l’eau de mer dans un aquifère et changement vers un pH légèrement alcalin)

3. Identification et différenciation des sources de pollution par les PFAS

Les pollutions des sols, eaux souterraines et eaux superficielles par les PFAS sont fréquemment des mélanges à l’origine de plusieurs sources de produits commerciaux et de sources de pollution. Il est possible de réaliser des screening complets des substances PFAS individuelles afin d’identifier entre 9 000 à 12 000 molécules, mais dans la gestion au quotidien des pollutions dans l’environnement ceci n’est pas applicable du fait de la limite de faisabilité technico-économique.

Pour cette raison il est nécessaire de réduire le nombre de composés PFAS à analyser lors des diagnostics environnementaux **grâce à la signature chimique** des produits commerciaux suspectés d'être à l'origine de la contamination. En effet, les PFAS étant une famille de plus de 9 000 composés, il serait impossible de tous les quantifier.

Les sources typiques de pollutions causées par les PFAS comprennent, par exemple, les applications des mousses anti-incendies (AFFF = Aqueous Film Forming Foam), par exemple lors d'exercices d'incendie et d'incendies dans les aéroports, les raffineries et les dépôts pétroliers, les industries impliquées dans la production et la transformation de polymères PFAS, les activités de galvanisation telles que le chromage, l'application agricole de boues d'épuration ou d'engrais contenant des PFAS, l'application de revêtements hydrofuges sur le papier, les cartons et textiles etc., mais également lorsqu'elles sont utilisées comme retardateur de flammes dans les secteurs électriques et l’industrie électronique... La liste des sources de PFAS dans l'environnement est longue et il existe également des polluants volatils PFAS qui peuvent pénétrer dans l'air intérieur via les gaz du sol, tels que les alcools fluoro-télomères (FTOH).

L’un des défis actuels de la gestion des problèmes environnementaux liés aux PFAS est de déterminer quelles sont les différentes sources de pollution causées par les PFAS ou leurs produits commerciaux, par exemple dans le cas de contaminations majeures des eaux souterraines par les PFAS.

Les expériences et évaluations de plus de 800 000 analyses PFAS dans les sols, les eaux souterraines et les eaux de surface montrent la présence de divers groupes (clusters) et substances PFAS, tels que les acides perfluoro-carboxyliques (PFCA) ou les acides perfluoro-sulfoniques (PFSA) et autres, qui sont typiques de certains secteurs industriels. D'autres groupes PFAS importants sont les acides sulfoniques fluoro-télomères (FTS), les alcools fluoro-télomères (FTOH) ainsi que les sulfobétaïnes fluorés (FTAB). parmi un total de 33 groupes PFAS différents.

Lors de l'identification et de la différenciation des sources de PFAS, diverses distributions de concentrations relatives, relations par rapport aux acides perfluoro-carboxyliques (PFCA) ainsi qu'avec divers PFAS poly-fluorés comme « précurseurs », ainsi que divers modèles de distributions statistiques, sont pris en compte.

Les produits PFAS commerciaux sont examinés à l'aide d'analyses non ciblées (*non-target*) pour identifier le plus grand nombre possible de substances PFAS individuelles présentes dans les produits PFAS. Pour cela, des tests de percolation pour simuler un vieillissement des produits commerciaux PFAS « frais » sont réalisés sur des lysimètres, avec une dégradation bactériologique permettant la biotransformation des PFAS poly-fluorés (précurseurs) vers les per-fluorés ainsi que pour identifier les effets chromatographiques des sols (F. Karg et al. : 2023 et 2024).

L'objectif est d'enregistrer les mélanges résultants des molécules de PFAS individuelles par HR-MS (spectrométrie de masse à haute résolution). Les résultats obtenus sont des empreintes typiques de produits PFAS commerciaux frais et dégradés pour la base de données complète des mélanges parents des produits PFAS.

L'identification des sources de PFAS peut être effectuée à partir de cette base de données, par le biais d'analyses standards et par l'application d'un programme d'identification statistique multivarié. L'analyse multi-vecteur (MVA : *Multi-Vector-Analysis*) est réalisée en plusieurs dimensions à l'aide de l'intelligence artificielle (machine learning), afin que les sources de PFAS puissent également être déterminées en cas de pollutions des eaux souterraines contenant un mélange de plusieurs sources de PFAS différentes.

En plus de l'utilisation d'analyses environnementales standards des sites pollués pour l'identification MVA des différentes sources de pollution causées par les PFAS, d'autres outils analytiques peuvent également être applicables, tels que le « *Top Assay* » (Houtz & Sedlak : 2012, Glöckner et al. : 2021) pour déterminer au mieux la masse de précurseurs poly-fluorés présents, qui peuvent être oxydés en acides carboxyliques perfluorés (PFCA) (voir Fig. 4). En outre, des mesures des rapports isotopiques entre les zones sources de PFAS et les zones de panaches peuvent être effectuées pour déterminer les sources de PFAS (Quian et al. 2023), ainsi que l'utilisation « d'analyses non ciblées » complètes, dans lesquelles des centaines de molécules individuelles de PFAS peuvent être identifiés et au moins semi-quantifiés.

De telles applications prennent plus de temps et sont plus coûteuses que l'analyse standard normale des PFAS relative aux sites pollués, qui est principalement utilisée pour identifier les sources de PFAS. L'application MVA peut éviter cela et être plus économe.

Plus de 9 000 PFAS polluent l'environnement et la santé depuis des décennies. Cela inclus également les PFAS volatils, tels que les alcools fluoro-télomères (6:2 ou 8:2 FTOH, etc.). Le problème des investigations sur les sites contaminés par les PFAS réside principalement dans la quantité énorme de PFAS poly-fluorés, qui sont biotransformés en PFAS per-fluorés au fil du temps. Les PFAS poly-fluorés individuels peuvent également être relativement résistants dans l'environnement et se transformer que très lentement en PFAS perfluorés (comme les Capstone B - FTAB, les FTS ou les FTOH). Afin d'améliorer la transparence et la connaissance relative à ce grand nombre de polluants PFAS, il existe plusieurs approches d'investigations, d'évaluation des risques et de dépollution des PFAS.

Une caractéristique importante des PFAS est leur comportement chimique dans l'environnement, car les PFAS poly-fluorés (précurseurs) sont convertis en PFAS perfluorés stables par biotransformation. L'évaluation des risques de cas individuels via une EQRS* (ou ARR*) peut estimer les risques futurs de la plupart des « précurseurs », puisqu'une analyse basée sur 28 à 70 PFAS individuels est effectuée avant et après un examen par le test « *Top Assay* » (cf. Fig. 4). Par le test « *Top Assay* », les PFAS poly-fluorés sont convertis en PFAS per-fluorés stables par oxydation via le persulfate, dans lesquels ils sont généralement biotransformés après un certain temps de séjour dans l'environnement (cf. aussi les Fig. 2a & 2b). Grâce au test « *Top Assay* », les investigations et évaluations des risques intègrent presque toutes les « précurseurs » transformables ainsi que les produits finaux PFAS per-fluorés restants.

(*EQRS & *ARR : Evaluation Quantitative des Risques Sanitaires et Analyse des Risques Résiduels).

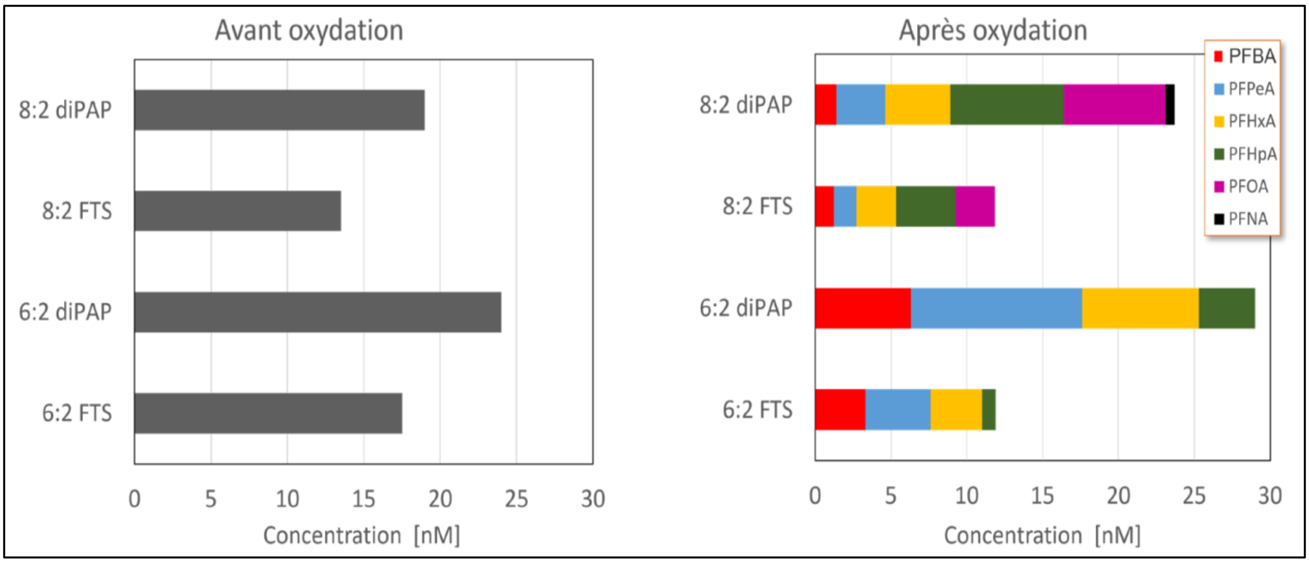


Fig. 4 : *Top Assay* (méthode Total Oxidizable Precursor) pour quantifier les PFAS poly-fluorés oxydables, transformables en acides carboxyliques per-fluorés (Houtz & Sedlac 2012, Glöckner et al. : 2021).

Les exemples suivants démontrent quelques possibilités d'identification et de différenciation des sources de PFAS avec certaines analyses standards, en tenant compte des expériences d'applications MVA (*Multi-Vector-Analysis*) basées sur l'intelligence artificielle en Europe (UE) et aux États-Unis.

Des sources typiques de PFAS existent dans les zones ayant subi des événements d'incendie et d'entraînement aux incendies, dans les aéroports civils et militaires (mousses anti-incendie / AFFF), mais d'autres activités peuvent également être à l'origine d'une contamination par les PFAS dans les sols et les eaux souterraines.

Ces activités comprennent, par exemple, l'épandage de boues d'épuration provenant des stations d'épuration, le chromage galvanique, les lixiviats de décharge, la production de papier, l'imprégnation textile, les industries électriques et électroniques, les entreprises de peintures, de produits de nettoyage et de production des fluor-polymères, etc.

Diverses analyses statistiques et visualisations, basées sur les expériences et les clusters PFAS de plus de 800 000 analyses de sols et d'eaux souterraines (NAS : 2023, F. Karg : 2024), aident à identifier les sources de PFAS.

La méthodologie de différenciation des sources de PFAS peut être divisée en trois catégories principales :

I. Examen des données et informations (historiques) disponibles qui peuvent être utilisées pour identifier les sources potentielles de PFAS sur différents sites (sites industriels spécifiques, aéroports, décharges, etc.).

II. Méthodes d'analyse des PFAS en laboratoire sur des échantillons environnementaux.

III. Investigations « forensiques » avancées pour différencier plus précisément les sources potentielles de PFAS.

La catégorie I. comprend les étapes suivantes :

- Le diagnostic historique des sources potentielles de PFAS provenant des zones suspectes. L'objectif est de répertorier et cartographier les zones de sources potentielles de pollutions de PFAS.
- Évaluer les zones hydrogéologiques en amont des zones suspectées pour déterminer s'il y a (ou a eu) des activités qui utilisent (ou ont utilisé) des PFAS.
- Parvenir à une compréhension détaillée de la géologie, de l'hydrogéologie, de l'hydrologie, des infrastructures de traitement des eaux pluviales et du ruissellement des eaux de surface des sites. Cela concerne également la nature du sol, l'emplacement et la profondeur des puits à proximité ainsi que la profondeur et le sens d'écoulement des eaux de surface et des eaux souterraines.
- Préparer un schéma conceptuel du site concernant les sources de PFAS, les voies de transfert et les voies d'exposition aux cibles.

Les catégories II et III se concentrent sur :

- L'évaluation des données des analyses chimiques de PFAS comme étape de sélection pour déterminer si des indications ou des preuves de différenciation des sources peuvent être identifiées.

- L'ad'analyses de la forensie avancée de PFAS sur des échantillons sélectionnés pour distinguer les sources potentielles de PFAS (par exemple, par l'isomérie structurelle, les études isotopiques, les tests *Top Assay*, les applications MVA, etc.).

Les différences générales entre les produits commerciaux de PFAS peuvent être identifiées, par exemple à travers les différenciations suivantes :

- Les mousses anti-incendie modernes (AFFF) sont à base de fluoro-télomères, principalement avec des molécules C6-PFAS. Bien que ces mousses anti-incendie ne contiennent pas de PFOA ou de PFOS, lorsqu'elles sont émises dans l'environnement, elles peuvent se dégrader en d'autres PFAS à chaîne plus courte, tels que l'acide perfluoro-hexanoïque (PFHxA), l'acide perfluoro-pentanoïque (PFPeA), l'acide buntanonique et l'acide fluorotélomère carboxylique 5:3 (FTCA).

- Au début des années 2000 (à la suite de demandes générales des autorités américaines et européennes), l'industrie chimique a commencé à abandonner progressivement les mousses anti-incendie sur une base de C8-PFAS, car le PFOS et le PFOA étaient classés comme ayant une toxicité trop élevée. Les producteurs de mousses anti-incendie à base de fluoro-télomères se sont alors tournés vers l'utilisation de formes de PFAS à chaîne courte avec six carbones fluorés (appelés C6-PFAS), qui ne contenaient pas de PFOS ou du PFOA (et ne pouvaient pas être décomposés non plus en ces produits). Ces mousses anti-incendies C6-PFAS peuvent également contenir du PFHxA, du PFPeA ainsi que du 6:2-fluorotélomersulfonate (6:2-FTS) ainsi que des fluorotélomères, qui peuvent se transformer au fil du temps en leur groupe terminal, les acides perfluoro-carboxyliques à moins de six atomes de carbone. La période exacte de passage des mousses anti-incendie C8-PFAS aux mousses anti-incendie C6-PFAS varie en fonction du lieu d'application (aéroports civils ou militaires, zones d'entraînement incendie, sites pétroliers, etc.).

- Avant 2016, de nombreuses mousses anti-incendie contenaient des PFAS à huit chaînes de carbone fluoré. Certaines de ces mousses anti-incendie à longue chaîne ou PFAS C8 contenaient du PFOS jusqu'au début des années 2000, du PFOA et d'autres PFCA à longue chaîne jusqu'en 2015 environ, date à laquelle ces produits ont ensuite été retirés du marché.

- Les analyses des structures chimiques moléculaires des PFAS peuvent être utiles par rapport aux informations existantes telles que l'origine, la période et l'utilisation probable. Les différences structurelles incluent, par exemple, l'isomérie structurelle (isomères linéaires et isomères ramifiés, etc.). Par exemple, si un PFAS cyclique particulier à chaîne de huit carbones, tel que le perfluoroéthyle-cyclohexane sulfonate (PFECHS : CAS 335-24-0) est observé, il pourrait provenir d'un inhibiteur de corrosion utilisé dans les fluides hydrauliques d'avions (MPART : 2020). Le PFECHS n'est pas connu pour être un composant des mousses anti-incendie.

- Des PFAS spécifiques peuvent être utilisés comme marqueurs pour la production de polymères fluorés, d'emballages alimentaires et de revêtements de papier, ainsi que de produits cosmétiques. Il n'est actuellement pas supposé qu'ils soient liés aux produits en mousse anti-incendie.

- Certains PFAS peuvent être chimiquement biotransformés (c'est-à-dire décomposés en produits chimiques plus petits et stables), mais ces PFAS poly-fluorés (précurseurs) se transforment souvent en d'autres PFAS, en particulier les PFAA per-fluorés.

Identification des différentes sources de PFAS :

Les analyses environnementales standards utilisées lors des investigations des sites pollués par les PFAS peuvent, en principe, être utilisées pour identifier et différencier les sources de PFAS. 28 à 70 substances PFAS individuelles sont analysées. Les données analytiques obtenues peuvent être très complexes en raison de la présence de nombreux PFAS différents dans un échantillon environnemental et posent un défi dans l'interprétation des données. Pour cette raison, une application informatisée MVA dotée d'intelligence artificielle est nécessaire.

En raison de cette complexité, de grandes quantités de données doivent être interprétées sur la base de l'expérience statistique issue de grandes quantités d'analyses en analyse multi-vecteur (MVA ou analyse poly-topique) avec l'intelligence artificielle, de telle manière que les sources de PFAS puissent être identifiées et différenciées avec une probabilité très élevée. Cela ne peut se faire que dans le cadre d'une analyse parallèle de différents éléments de preuves, car chaque analyse isolément n'est généralement pas suffisamment significative. La base pour cela sont les analyses « cibles » (et « non cibles ») ainsi que le « Top Assay », le fluor organique total (TOF) ou l'AOF (fluor organique total adsorbable) ainsi que les analyses isotopiques (voir Fig. 5) :

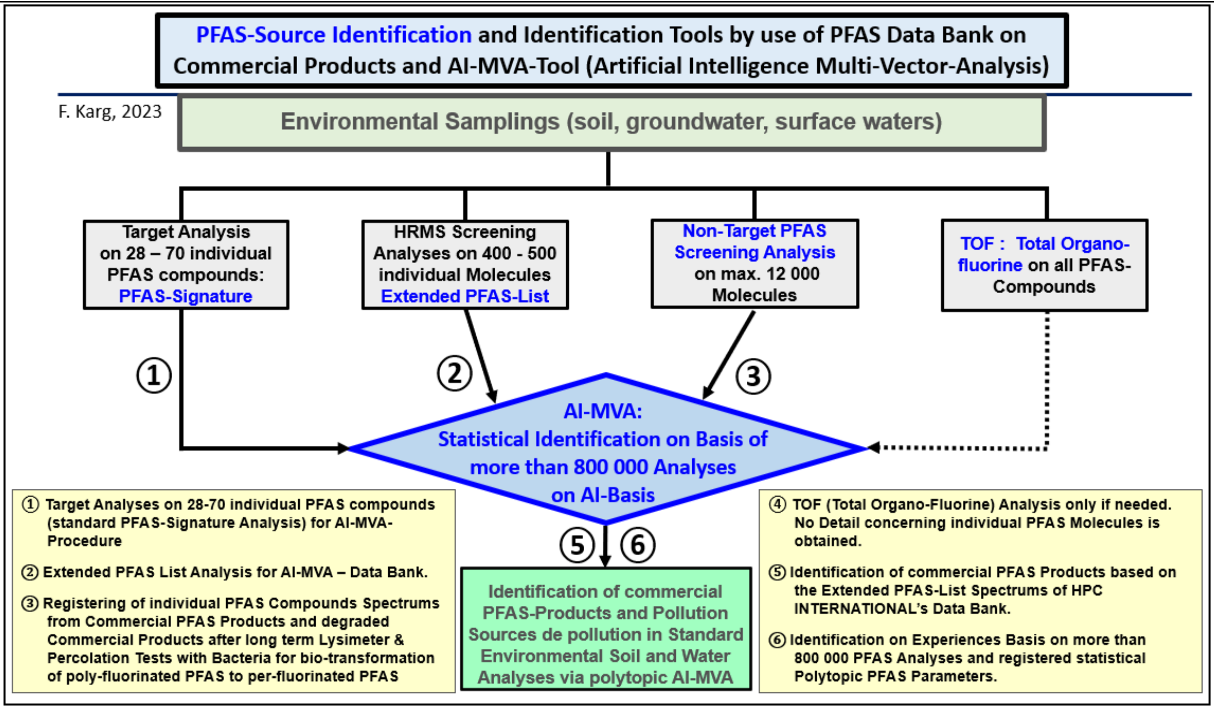


Fig. 5 : Procédures analytiques pour l'application de l'identification et de la différenciation des sources de PFAS par analyse multi-vecteur (MVA ou analyse *poly-topic*) avec intelligence artificielle (F. Karg et al. : 2023 et 2024).

La figure 6 montre la procédure d'identification et de différenciation des sources potentielles de PFAS à l'aide d'une analyse MVA basée sur l'intelligence artificielle (par exemple, mousses anti-incendie AFFF, boues d'épuration, activités de galvanoplastie, industries textiles et papetières, décharges de déchets, etc.).

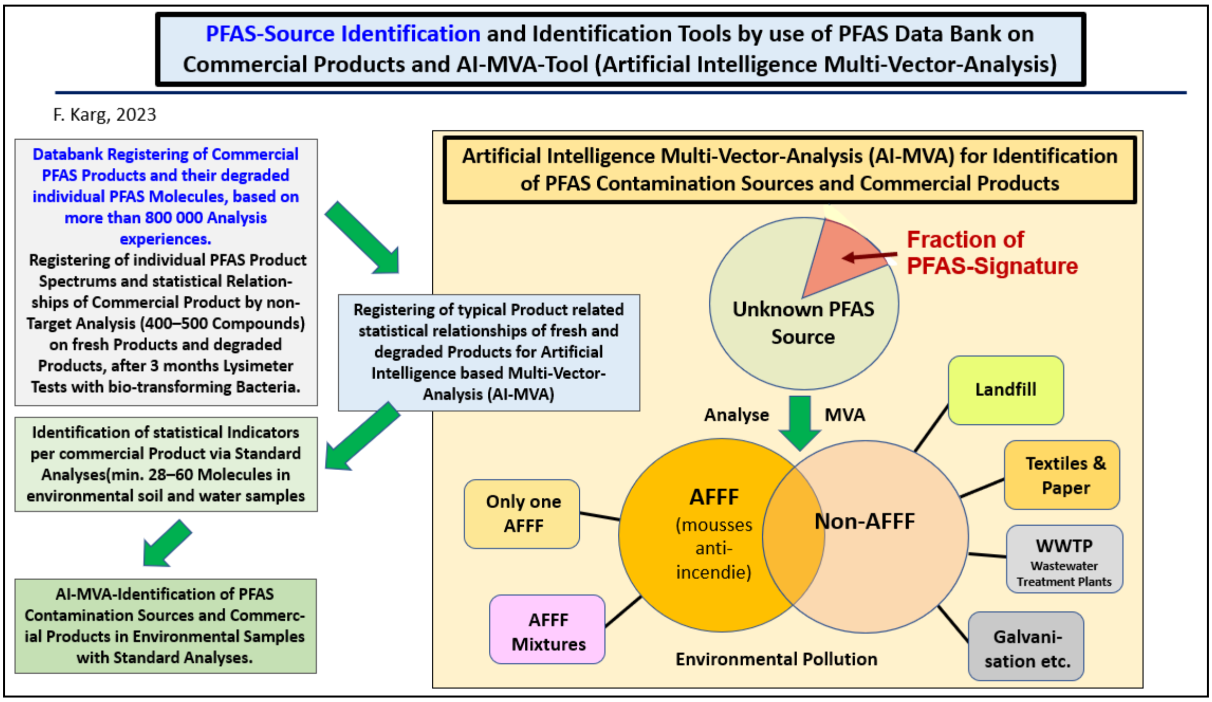


Fig. 6 : Approche d'analyse MVA basée sur l'intelligence artificielle pour identifier et différencier les sources de PFAS (par exemple, mousses anti-incendie AFFF, boues d'épuration, activités galvaniques, industries textiles et papetières, décharges de déchets, sites pétrôliers, etc.) (F. Karg et al.: 2023 & 2024).

En raison des nombreux PFAS individuels au sein de cette famille chimique, « l'analyse non ciblée » (*non-target*) offre également la possibilité d'identifier des molécules inconnues, car le résultat est ouvert sans aucune limitation sur une liste standard de polluants préalablement calibrés. Des centaines de composés individuels peuvent être identifiés. L'inconvénient est que l'analyse non-ciblée est relativement coûteuse et prend du temps. La figure 5 montre les différences par rapport à l'analyse standard de certains paramètres PFAS sélectionnés.

Les figures 7 et 8 montrent les analyses de cluster PFAS pour différencier plusieurs sources PFAS.

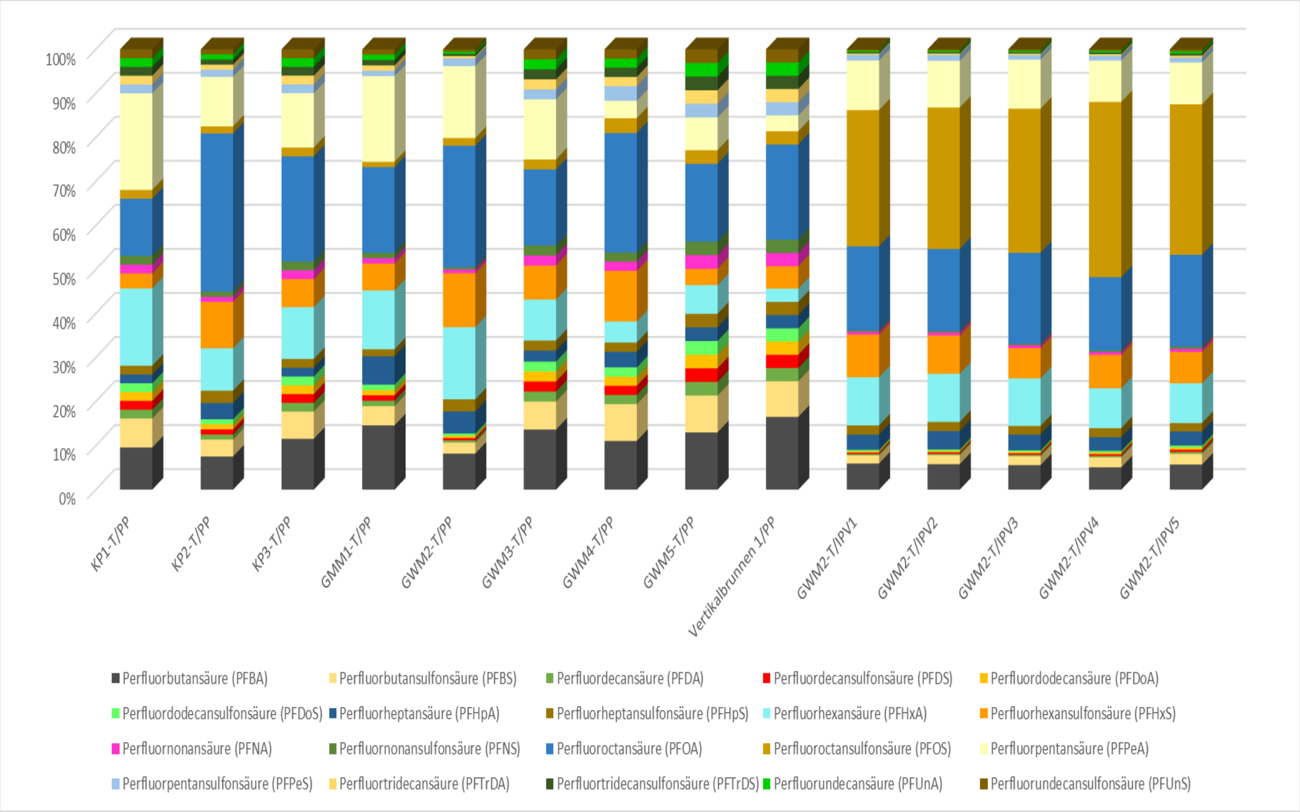


Fig. 7 : Divers clusters de PFAS identifiés pour différencier les sources de PFAS (F. Karg et al., 2023, 2024)

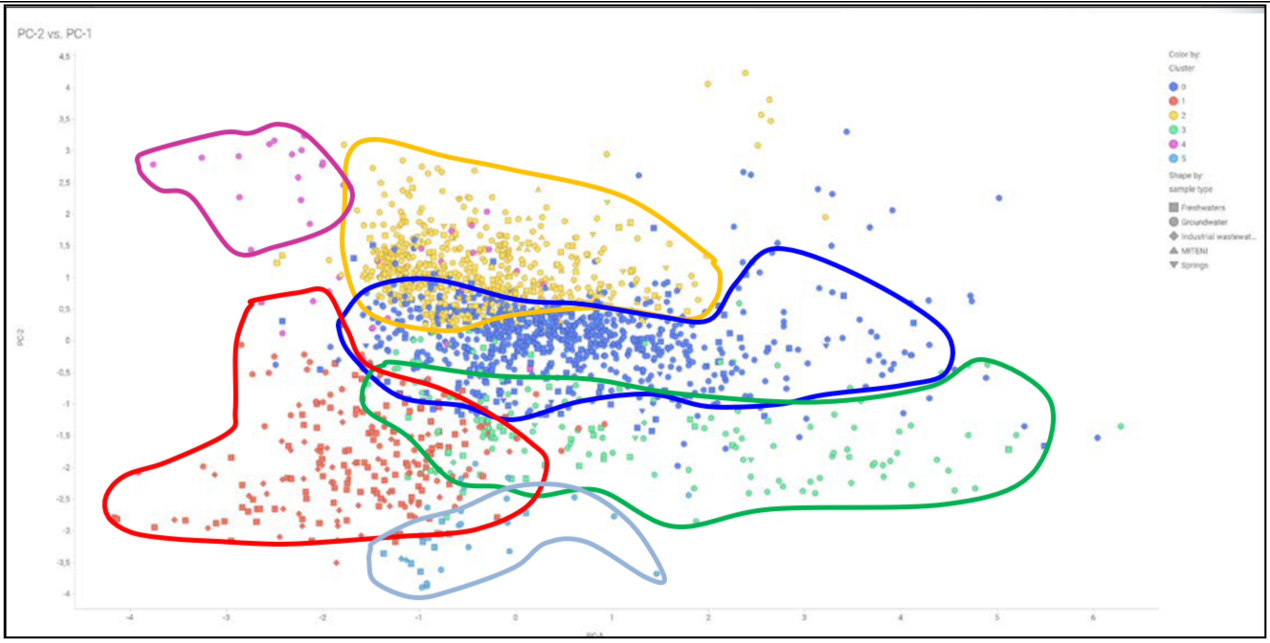


Fig. 8 : Identification et différenciation de 6 sources différentes de PFAS et de produits commerciaux de PFAS sur la base des analyses des clusters de PFAS (superficie de 761 ha) sur la base de 472 analyses des eaux souterraines et des eaux de surface) dans le nord-est de l'Italie (C. Monti et al. : 2023 & F. Karg : 2023).

L'outil informatique d'analyse multi-vecteur (MVA) avec intelligence artificielle pour identifier et différencier les sources de clusters de PFAS a été créé (et est en développement continu) par HPC-International sur la base de l'expérience statistique de plus de 800 000 analyses environnementales. La base est, entre autres, les expériences du US Airport Cooperative Research Program (ACRP), de l'Airports Council International - North America (ACI-NA), de l'American Association of Airport Executives (AAAE), du USA National Academy of Sciences Guide (NAS : 2023), ainsi que les déterminations de clusters chimiques de produits PFAS frais commerciaux et de produits PFAS commerciaux vieillis (selon des procédures de dégradation appliquées par HPC International ; F. Karg et al. 2023 - 2024) comme étalons de la banque de données MVA-PFAS. Le vieillissement des produits PFAS commerciaux a été réalisé à l'aide de tests lysimétriques avec exposition à des bactéries dégradantes, qui biotransforment les PFAS poly-fluorés en PFAS per-fluorés (F. Karg et al. 2023 - 2024).

L'analyse des clusters de PFAS prend en compte la chimie environnementale des PFAS et en particulier le métabolisme ou la biotransformation des PFAS poly-fluorés en PFAS per-fluorés stables, par ex. B. : 6 :2 FTAB → 6:2-FTS → 6:2-FTOH → PFHxA + PFPeA + PFBA etc. afin de déterminer les « précurseurs » et produits terminaux en cas de contamination environnementale par des mélanges de PFAS à travers la chaîne de biotransformation.

Les investigations spécifiques d'un site ainsi que l'identification et la différenciation des sources de PFAS incluent les multicritères suivants appliqués dans l'outil MVA. Tous les critères sont toujours appliqués en même temps :

A. **Rapports de concentrations entre PFAS :** c'est une première technique de sélection simple, où un ou plusieurs rapports de concentration entre deux ou plusieurs composés PFAS différents peuvent être appliqués. Par exemple, les ratios PFHxS/PFOS dans une certaine plage ont été utilisés comme indicateur d'une source de mousse anti-incendie (McGuire et al. 2014), et les ratios PFHxS/PFOA ont été identifiés comme marqueurs d'autres sources de production industrielle de PFAS (Guelfo et Adamson 2018).

B. **Diagrammes circulaires et autres visualisations de données :** il s'agit de graphiques statistiques qui montrent la **contribution relative de plusieurs molécules** à la concentration totale de PFAS dans la même zone d'étude.

Ils peuvent aider à visualiser les différences de composition entre les mélanges de PFAS dans différents échantillons afin de déterminer s'il existe des indices chimiques ou des preuves provenant de différentes sources de PFAS. Cela permet également d'identifier le mélange de différentes sources de PFAS ou les changements dans les signatures des sources le long d'une voie de transport (par exemple lors de la migration dans les eaux souterraines) et également de révéler les biotransformations et les effets de la chromatographie du sol.

C. **Rapports d'isomères :** Les PFAS individuels peuvent exister sous **différentes formes isomères** et l'abondance relative des différents isomères dans un échantillon peut être utilisée pour en **déduire la source des PFAS (Charbonnet et al. 2021). La présence d'isomères ramifiés (isomères structuraux) dans un échantillon peut être mesurée** à l'aide de méthodes standard (qui analysent environ 60 à 70 substances individuelles). Les **deux processus de production différents des PFAS, l'ECF (fluoration électrochimique) et la télomérisation, aboutissent soit à un mélange de PFAS ramifiés et linéaires (ECF), soit à des isomères de PFAS purement linéaires.**

Ces informations pourraient être utiles comme preuve pour distinguer les sources de PFAS. **Les isomères ramifiés indiquent** que les PFAS proviennent du procédé de **fabrication spécifique de la fluoration électrochimique (ECF).** La proportion d'isomères ramifiés dans les produits ECF se situe dans une fourchette relativement étroite (ITRC 2022a&b). Si la proportion d'isomères ramifiés dans un échantillon est inférieure à cette plage, cela peut indiquer que des produits contenant des PFAS générés par des processus de fabrication à base de télomèrisation sont également présents.

Les mousses anti-incendie modernes (AFFF) contiennent des PFAS qui sont produits uniquement à l'aide de processus de télomérisation. Les mélanges AFFF plus anciens peuvent contenir des PFAS produits par fabrication d'ECF ou télomérisation. Aux États-Unis et un peu plus tard en Europe occidentale, la production de mélanges AFFF utilisant la production ECF a été interrompue au début des années 2000.

Un autre fait important est que les isomères ramifiés de certains PFAS (par exemple le PFOS) se propagent plus rapidement dans les eaux souterraines que les isomères linéaires du même composé (effets chromatographiques différents dans le sol) en raison des différentes interactions des isomères avec le sol. Cela peut entraîner un **enrichissement en isomères ramifiés** dans les eaux souterraines hydro-géologiquement en aval d'une source de PFAS (Nickerson et al. 2020).

D. **Analyse des composants principaux des PFAS et étude de classification hiérarchique des clusters de PFAS :** Ces méthodes statistiques sont utilisées pour analyser les données associées à de nombreuses variables (par exemple, les PFAS mesurées) afin d'identifier les différences entre les clusters de PFAS visualisables graphiquement. Cette analyse de données facilite l'identification des différents **groupes (ou clusters) de mélanges de PFAS** (chacun pouvant provenir de différentes sources ou de produits PFAS commerciaux (cf. Fig. 7 & 8), lesquels clusters pouvant se chevaucher).

E. Méthodes de recherche (dépistage) : identification et différenciation des sources de PFAS :

➢ **Fréquence de détection :** Les statistiques d'expériences (sur plus de 800 000 analyses individuelles provenant de différents emplacements de sources de PFAS) sur la détection relative de PFAS individuels (dans chaque ensemble de données d'analyse) aident à distinguer les différentes sources de PFAS. L'absence (ou la faible fréquence de détection) de PFAS spécifiques dans les échantillons provenant d'un type de site peut également être utilisée de la même manière. Les expériences de plus de 800 000 analyses individuelles d’échantillons provenant de divers emplacements de sources de PFAS montrent très clairement ces différences en fonction de la source de PFAS (NAS : 2023).

- **Distributions des concentrations :** Ces données aident à déterminer la distribution relative des PFAS individuels trouvés dans des échantillons environnementaux provenant de différents endroits. La concentration moyenne de PFAS individuels provenant des échantillons examinés est utilisée dans l'évaluation MVA (voir Fig. 7a – d). Ces données fournissent des informations sur la proportion relative de différentes sources de PFAS dans un type de site donné, ainsi que sur la présence relative de PFAS associées à différentes sources.

- **Ratios de composition des PFAS :** Ces ratios montrent la répartition générale des PFAS au sein des groupes d'échantillons. Cela inclut le pourcentage d'acides perfluoroalkyl-carboxyliques (PFCA), d'acides perfluoroalkyl-sulfoniques (PFSA) et d'acides non perfluoro-alkyliques (non-PFAA) par rapport au total des mélanges de PFAS qui se chevauchent (par exemple présents dans les eaux souterraines). L’application de cette méthodologie comprend également la quantification des rapports de concentration entre les PFAS individuels fréquemment détectés.

- **Statistiques d’identification et de différenciation des sources de PFAS par analyse multi-vectorielle (MVA) :**

Les résultats de la détermination des sources de PFAS sont présentés dans cinq types différents de visualisations statistiques des catégories de sources de PFAS. Ces cinq types de MVA sont les suivants :

- **MVA1 : Diagrammes circulaires de répartition de la composition des PFAS,**
- **MVA2 : Distribution des concentrations en « *Boxplot* » et histogrammes de PFAS,**
- **MVA3 : Concentrations moyennes de PFAS et fréquence de détection : *Heat-Maps* »,**
- **MVA4 : Concentration moyenne de PFAS et fréquence de détection : « *Cross-plots* »,**
- **MVA5 : Rapport des concentrations logarithmiques moyennes de PFAS : Diagrammes de points relatifs et radiaux.**

Quelques exemples d’évaluations MVA (MVA 2, 4 & 5) :
MVA2 : Distribution des concentrations de PFAS en histogrammes :

Les groupes de PFAS déterminés analytiquement sont classés sur la base de l'expérience acquise par les analyses environnementales de PFAS. Les figures 9a à d montrent une série d’histogrammes de concentrations de PFAS par ex. pour quatre grandes catégories de sources de PFAS (à partir des expériences sur plus de 800 000 échantillons d’eaux souterraines, de sols et d’eaux de surface analysés, NAS, 2023). Pour faciliter la visualisation, les PFAS individuels sont placés dans le même ordre sur chaque graphique pour montrer l’ampleur relative des concentrations associées à chaque type de site.

Les niveaux de PFAS mesurés sur un site sont attribués en premier lieu à l'une des catégories de l'évaluation MVA (par exemple sur les figures 9a à d) pour appliquer certains des paramètres d'identification et de différenciation des sources de PFAS.

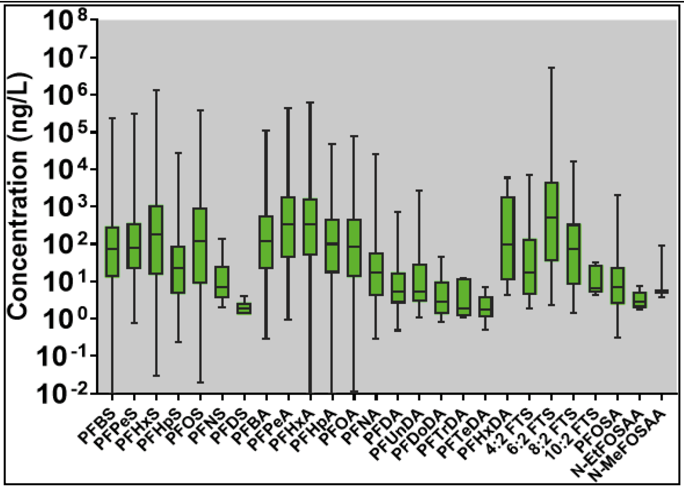


Fig. 9 a: Distribution typique de PFAS dans échantillons environnementaux des aéroports civils (NAS, 2023).

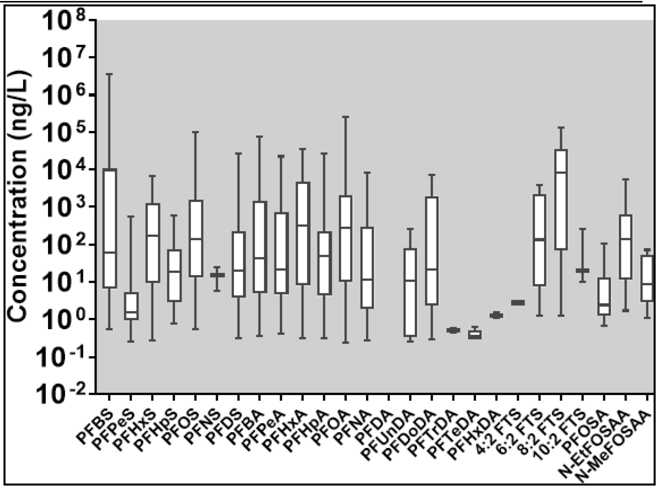


Fig. 9b : Distribution typique de PFAS dans des échantillons environnementaux des sites industriels de production des fluoro-polymères (NAS, 2023).

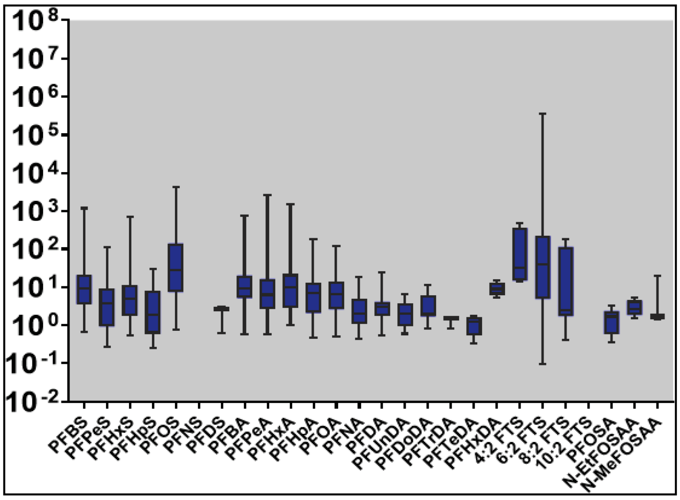


Fig. 9c : Distribution typique de PFAS dans les échantillons environnementaux de galvanisations (installations de chromatage) (NAS, 2023)

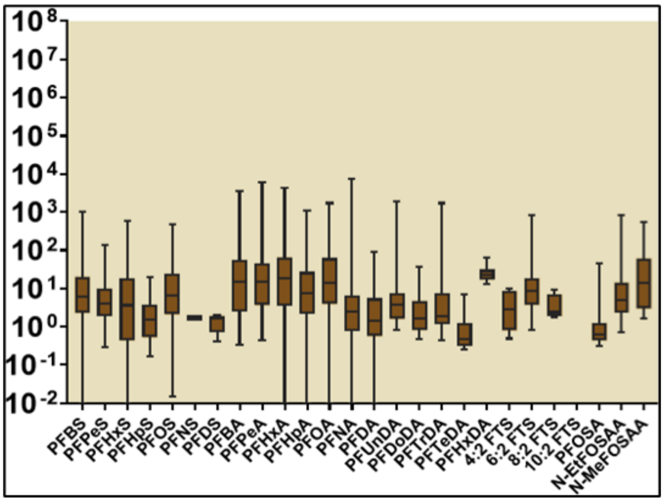


Fig. 9d : Distribution typique de PFAS dans les échantillons environnementaux de décharges d'ordures ménagères (NAS : 2023)

MVA4 : Concentration médiane de PFAS et fréquence de détection : ***Cross Plots*** : L'expérience (à partir de plus de 800 000 analyses environnementales de PFAS) sur la fréquence statistique de la concentration moyenne de composés individuels de PFAS peut également être résumée dans des graphiques croisés (*Cross plots*) qui servent de signature représentative des PFAS pour chaque catégorie de sources de PFAS (voir figures 10a à b, NAS : 2023). Les composés trouvés dans la zone colorée en haut à droite de chaque graphique représentent les PFAS qui sont détectés fréquemment à des concentrations relativement élevées par type de source de PFAS (y). Pour chaque molécule de PFAS, le pourcentage de fréquence de détection est donné par rapport à la concentration moyenne (en ng/l) dans tous les échantillons d'eaux souterraines analysées (x).

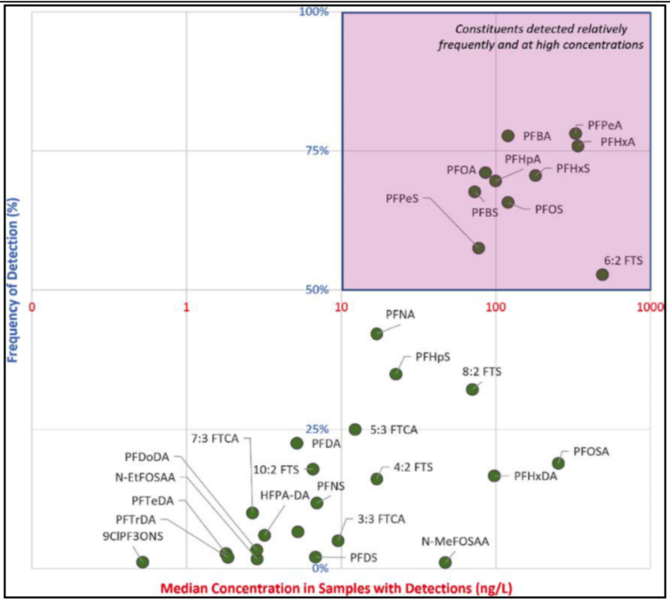


Fig. 10a : Distribution typique de PFAS dans les échantillons environnementaux des d'aéroports civils (NAS : 2023)

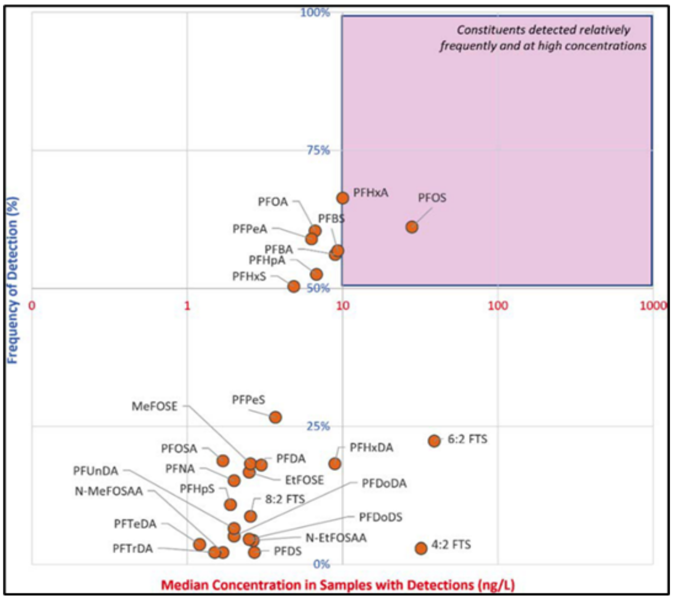
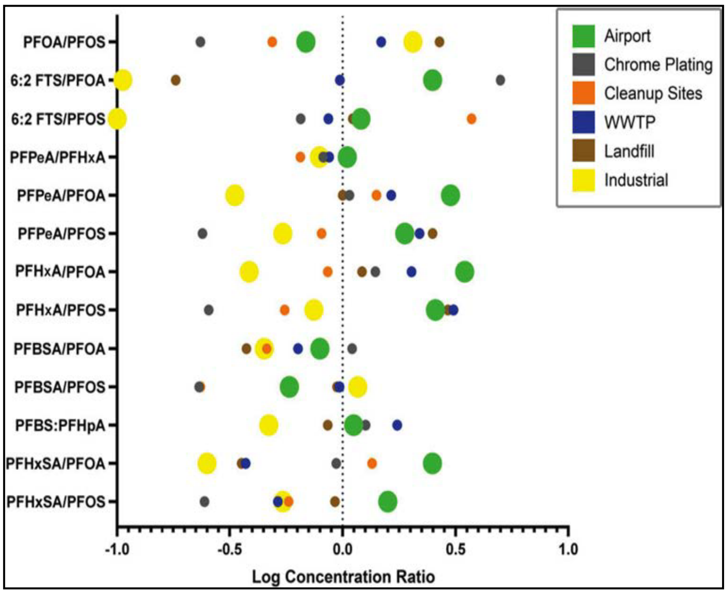


Fig. 10b : Distribution typique de PFAS dans les échantillons des galvanisations (chromage) (NAS : 2023)

MVA5 : Rapport de concentrations logarithmiques médianes de PFAS et points et tracés radiaux des ratios : Des représentations graphiques supplémentaires de diverses analyses statistiques sont utiles pour vérifier plus en détail un ensemble d'analyses PFAS pour les associations de sources PFAS. Les figures 11 et 12 (NAS : 2023) montrent les résultats d'une analyse logarithmique du rapport des concentrations médianes. Les résultats sont évalués statistiquement et vérifiés graphiquement. Cette approche offre des opportunités pour une étude comparative des données PFAS collectées sur un site et illustre également que différentes visualisations sont souvent appropriées pour mieux communiquer des résultats complexes provenant de différentes sources de PFAS. Dans les diagrammes de dispersion et radiaux présentés sur ces figures, chaque symbole représente le rapport de concentration logarithmique médian des paires de composés PFAS désignées.

Le tableau 1 présente les paramètres d'analyse PFAS recommandés pour la réalisation de la MVA. Toutes ces étapes d'évaluation sont réalisées en parallèle par l'outil d'identification de source MVA-PFAS.



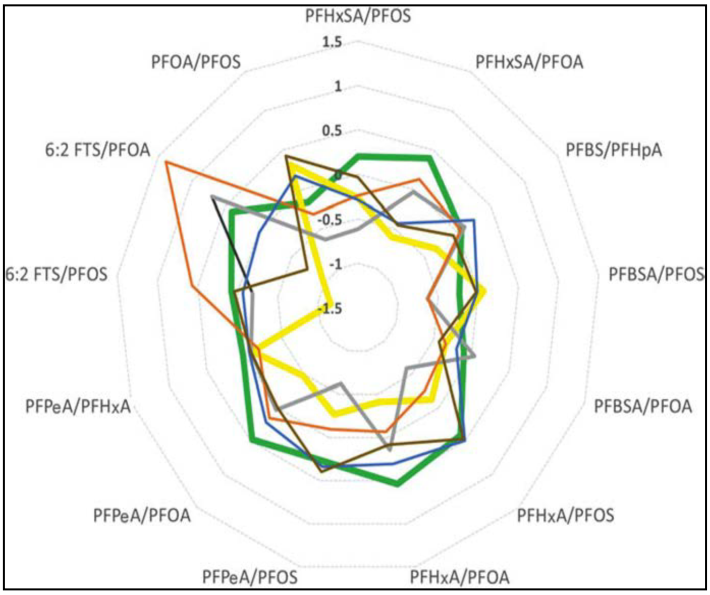


Fig. 11 : Distribution typique de PFAS dans les échantillons environnementaux de différent sources sous forme Points des ratios.(NAS, 2023)

Fig. 12 : Distribution typique de PFAS dans les échantillons environnementaux de diffèrent sources sous forme sous forme radiale (NAS, 2023)

La figure 13 montre un résumé des paramètres évalués pour l'identification et la différenciation des sources de PFAS AI-MVA (analyse multi-vecteur basée sur l'intelligence artificielle).

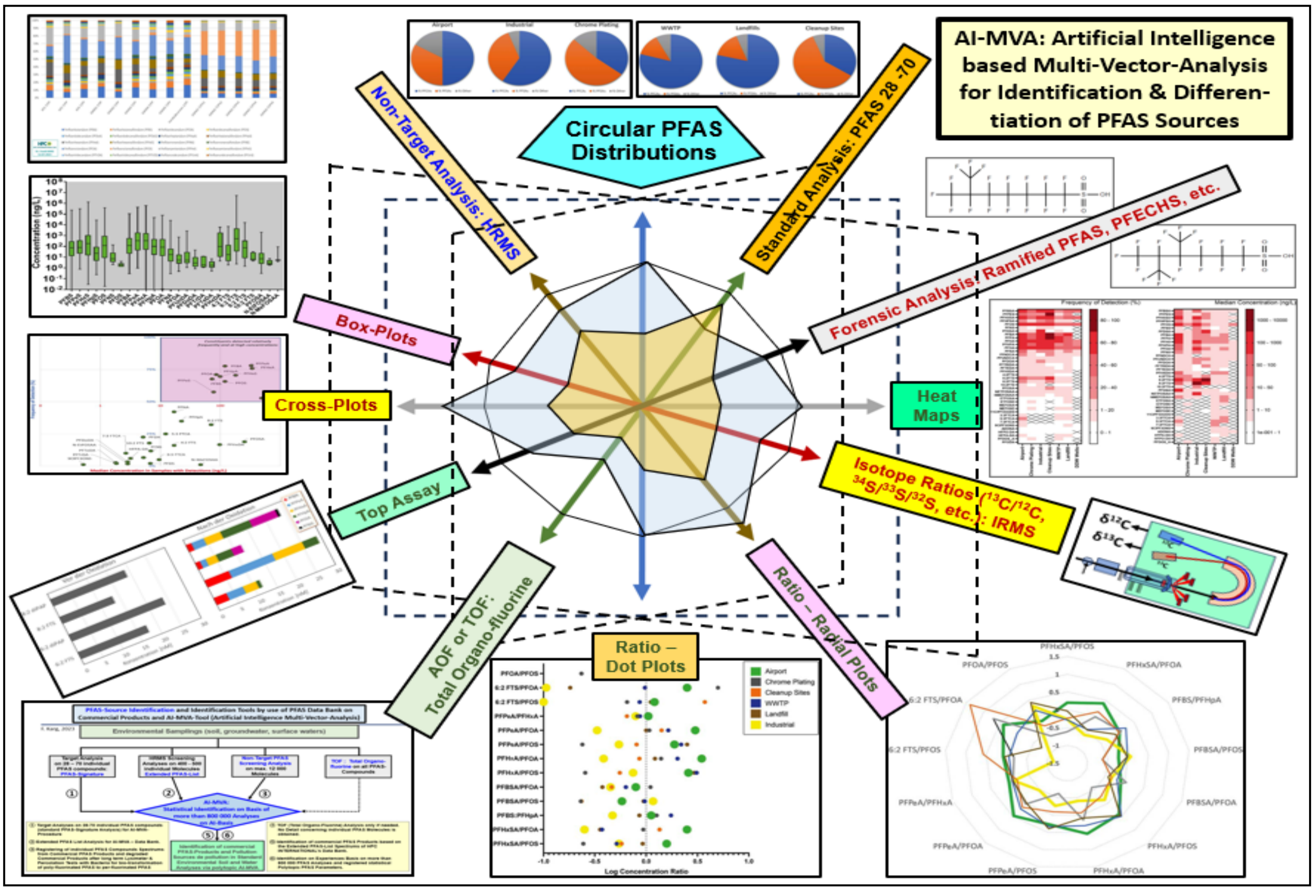


Fig. 13 : Paramètres évalués pour l'identification et la différenciation des sources de PFAS via l'AI-MVA (analyse multi-vecteurs basée sur l'intelligence artificielle).

Tableau 1 : Paramètres d'analyse standard recommandés pour l'utilisation de l'outil informatique d'analyse multi-vecteur (MVA) avec intelligence artificielle pour identifier et différencier les sources de PFAS.

Tableau 1a : Paramètres d'analyse standard recommandés pour l'utilisation de l'outil informatique d'analyse multi-vecteur (MVA) avec intelligence artificielle pour identifier et différencier les sources de PFAS.

PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
PFBA (acide perfluorobutanoique)	ng/l	1	375-22-4	🟩	🟩	🟩
PFPeA (acide perfluoropentanoique)	ng/l	5	2706-90-3	🟩	🟩	🟩
PFHxA (acide perfluorohexanoique)	ng/l	1	307-24-4	🟩	🟩	🟩
PFHpA (acide perfluoroheptanoique)	ng/l	1	375-85-9	🟩	🟩	🟩
PFOA linéaire (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟩	🟩
PFOA ramifié (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFOA totale (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFNA (acide perfluorononanoique)	ng/l	1	375-95-1	🟩	🟩	🟩
PFDA (acide perfluorodecanoique)	ng/l	1	335-76-2	🟩	🟩	🟩
PFUnDA (acide perfluoroundecanoique)	ng/l	1	2058-94-8	🟩	🟩	🟩
PFDoDA (acide perfluorododecanoique)	ng/l	2	307-55-1	🟩	🟩	🟩
PFTrDA (acide perfluorotridecanoique)	ng/l	1	72629-94-8	🟩	🟩	🟩
PFTeDA (acide perfluorotetradecanoique)	ng/l	1	376-06-7	🟩	🟥	🟩
PFHxDA (acide perfluorohexadecanoique)	ng/l	2	67905-19-5	🟩	🟥	🟩
PFODA (acide perfluorooctadecanoique)	ng/l	1	16517-11-6	🟩	🟥	🟩
PFBS (acide perfluorobutane sulfonique)	ng/l	1	375-73-5	🟩	🟩	🟩
PFPeS (acide perfluoropentane sulfonique)	ng/l	1	2706-91-4	🟩	🟩	🟩
PFHxS linéaire (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟩	🟩	🟩
PFHxS ramifié (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟥	🟥	🟥
PFHxS totale	ng/l	1	355-46-4	🟥	🟥	🟥
PFHpS (acide perfluoroheptane sulfonique)	ng/l	1	375-92-8	🟩	🟩	🟥
PFOS linéaire (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟩	🟩	🟥
PFOS ramifié (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFOS totale (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFDS (acide perfluorodecane sulfonique)	ng/l	1	335-77-3	🟩	🟩	🟥
4:2 FTS (acide 4:2 fluorotelomer sulfonique) H4-PFOS	ng/l	1	757124-72-4	🟩	🟥	🟥
6:2 FTS (acide 6:2 fluorotelomer sulfonique)	ng/l	1	27619-97-2	🟩	🟥	🟥
8:2 FTS (acide 8:2 fluorotelomer sulfonique)	ng/l	1	39108-34-4	🟥	🟥	🟥
10:2 FTS (acide 10:2 fluorotelomer sulfonique)	ng/l	1	120226-60-0	🟥	🟥	🟥
MePFOSAA (acide N-méthylperfluorooctane sulfonamide acétique)	ng/l	1	2355-31-9	🟥	🟥	🟥
EtFOSAA (acide N-éthylperfluorooctane sulfonamide acétique)	ng/l	1	2991-50-6	🟥	🟥	🟥
PFOSA linéaire (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟩	🟥	🟥
PFOSA ramifié (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
PFOSA totale (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
MeFOSA linéaire (N-méthylperfluorooctanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥

Tableau 1b : Paramètres d'analyse standard recommandés pour l'utilisation de l'outil informatique d'analyse multi-vecteur (MVA) avec intelligence artificielle pour identifier et différencier les sources de PFAS.

PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
MeFOSA ramifié (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
MeFOSA totale (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
8:2 DiPAP (8:2 polyfluoroalkyl phosphate diester)	ng/l	1	678-41-1	🟥	🟥	🟥
HFPO-DA (acide hexafluoropropyleneoxide dimer) Gen X	ng/l	1	13252-13-6	🟥	🟥	🟩
EtFOSA linéaire (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA ramifié (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA totale (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
MeFBSAA (perfluorobutanesulfonamide(N-méthyl)acetate)	ng/l	5	159381-10-9	🟥	🟥	🟥
9Cl-PF3ONS (acide 9-chlorohexadecafluoro-3-oxanonane-1-sulfonique)	ng/l	1	73606-19-6	🟥	🟥	🟥
4H-PFUnDa (acide 2H,2H,3H,3H,-perfluoro undécane)	ng/l	5	34598-33-9	🟥	🟥	🟥
8:2 FTUCA (acide 2H-perfluoro-2-décenoique)	ng/l	1	70887-84-2	🟥	🟥	🟥
DONA (acide 4,8-dioxa-3H-perfluorononanoique)ADONA	ng/l	1	919005-14-4	🟩	🟥	🟩
MeFBSA (n-méthylperfluorobutanesulfonamide)	ng/l	1	68298-12-4	🟥	🟥	🟥
PFBSA (perfluorobutanesulfonamide)	ng/l	1	30334-69-1	🟥	🟥	🟥
PFECHS (acide perfluoro-4-éthylcyclohexanesulfonique)	ng/l	1	646-83-3	🟥	🟥	🟥
PFNS (acide perfluorononane sulfonique)	ng/l	1	68259-12-1	🟩	🟩	🟩
PFDoDS (acide perfluorododecane sulfonique)	ng/l	1	79780-39-5	🟩	🟩	🟩
6:2 diester de phosphate fluorotélomérique. 6:2 diPAP	ng/l	10	57677-95-9	🟥	🟥	🟥
6:2 8:2 diester de phosphate fluorotélomérique. 6:2 8:2 diPAP	ng/l	10	943913-15-3	🟥	🟥	🟥
PFHxSA (perfluorohexanesulfonamide)	ng/l	1	41997-13-1	🟥	🟥	🟥
PFUnDS (acide perfluoroundecane sulfonique)	ng/l	2	749786-16-1	🟩	🟩	🟩
PFTrDS (acide perfluorotridecane sulfonique)	ng/l	2	791563-89-8	🟩	🟩	🟩
EtFOSE (2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	1691-99-2	🟥	🟥	🟥
MeFOSE (2-(N-methylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	24448-09-7	🟥	🟥	🟥
NFDHpA (Nonafluoro-3,6-dioxaheptanoic acid)	ng/l	1	151772-58-6	🟥	🟥	🟥
PFMPA (Perfluoro-3-methoxypropanoic acid)	ng/l	1	377-73-1	🟥	🟥	🟥
PFMBA (perfluoro-4-methoxybutanoic acid)	ng/l	1	863090-89-5	🟥	🟥	🟥
C6O4 (Perfluoro([5-methoxy-1,3-dioxolan-4-yl]oxy)acetic acid)	ng/l	10	1190931-41-9	🟩	🟥	🟩
6:2-FTOH (6:2 fluorotelemer alcohol) FHET	ng/l	20	647-42-7	🟩	🟥	🟩
8:2-FTOH (8:2 fluorotelemer alcohol) FOET	ng/l	10	678-39-7	🟩	🟥	🟩
6:2-FTAB (6 :2 fluorotelomer sulfonamido propyl betaine) Capstone B	ng/l	10	34455-29-3	🟩	🟥	🟩
Parameters for PFAS Source Identification per AI-MVA (Artificial Intelligence Multivector Analysis)						

Résumé

Dans le cadre des pollutions des eaux souterraines par les PFAS, il est de plus en plus important d'identifier, et surtout de différencier la part de l'attribution de chaque source de PFAS aux panaches des pollutions. Ce besoin de clarification concernant la contribution de chaque source de PFAS aux pollutions, par ex. au droit des captages (d'eau potable, etc.) devien de plus en plus crucial pour la protection des ressources en eaux, les responsabilités (partagées) et la recherche des origines (multiples) des pollutions dans le cadre des expertises judiciaires.

En résumé, on peut affirmer qu'il est désormais possible (grâce aux études statistiques, graphiques et chimico-mathématiques complètes) de réaliser via une analyse multi-vecteur (MVA) en plusieurs dimensions (et avec l'aide de l'intelligence artificielle), l'identification et la différenciation des sources de pollutions par les PFAS dans les sols, les eaux souterraines et les eaux de surface, voire d'identifier dans certains cas les produits PFAS commerciaux à l'origine des pollutions.

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Vision of the Hazardous Waste Industry (HWE) for an efficient and righteous management of PFAS-containing waste in Europe

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Hazardous Waste Europe (HWE) is the trade association for the treatment and recovery of hazardous waste in Europe. Its members operate 175 treatment facilities in 11 European countries, representing a vast type of processes and a total treatment capacity of 10 millions tons per year.

HWE (Hazardous Waste Europe) aims to promote proper management of hazardous waste treatment, environmental protection, and worker safety. Their principles are traceability of waste, non-dilution of hazardous substances, and decontamination to remove hazardous substances from waste.

HWE welcomes the proposed REACH restriction on PFAS (per- and polyfluoroalkyl substances) and emphasises the need to account for PFAS persistence and potential toxicity. Persistence can increase a substance's hazardousness by allowing it to accumulate to toxic levels over time.

There is a major lack of data on the thousands of PFAS that could end up in waste streams from products. Only a small portion are currently regulated (e.g. PFOA, PFOS under the POP regulation). The "no data, no market" principle should apply to track all PFAS throughout product life cycles.

Measurement standards and regulations for PFAS in waste and emissions are currently lacking, hindering effective monitoring and treatment. There are no specific PFAS measurement regulations for waste treatment processes like incineration, landfilling, recycling, etc.

HWE members intend to address the treatment of PFAS waste in an holistic approach in order to answer specificities in terms of type of waste and appropriate treatment routes. Some technologies and processes aimed at retaining PFAS before discharge to the environment (water bodies and soils), others are dedicated to the mineralisation of PFAS and finally permanent storage should not be excluded. Nevertheless, it is important to ensure complementarity of the different routes and the high performances of retention or mineralisation according to the nature of the waste to be treated.

However, additional treatments may be needed for residues concentrated in PFAS from waste treatment plants. Research is ongoing to identify effective technologies for PFAS-containing waste streams.

HWE calls for:

- Defining PFAS thresholds in waste to indicate if special treatment/decontamination is needed, especially for a circular economy and material cycles where wastes are reintroduced in the loop,
- Setting emission limit values for PFAS discharges from waste treatment plants at the EU level,
- Regulating PFAS similarly to persistent organic pollutants (POPs) to stop environmental dispersion.

In summary, while waste treatment technologies exist, the lack of PFAS data, measurement standards and clear regulations hinders full accountability and treatment of the diverse PFAS family. HWE advocates responsible PFAS management through better tracking, thresholds, limits and regulations.

Key words: PFAS, hazardous waste, decontamination, circular economy, identification and characterisation, traceability

PFAS IN FIREFOAMS: SITUATION FRAMING AND ANALYTICAL APPROACH

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Almost every foam concentrate contains a whole range of fluorine surfactants as impurities: sometimes they are not active substances but by-product of production. The presence of PFAS in fire-fighting foams constitutes a hazard in terms of site pollution and wastewater contamination, as well as occupational exposure for firefighters or personnel at military sites or airports.

In Europe, some PFAS molecules are regulated under REACH and POPs Regulation; European Union is planning a general ban on PFAS in foam concentrate, as ECHA’s Committee for Socio-Economic Analysis (SEAC) has adopted its final opinion supporting this ban.

Separately, at the beginning of 2023 the ECHA announced its proposed restrictions on all PFAS, almost 10.000 molecules.

In the US, where PFAS contamination around military airports was strongly denounced, at least 12 states including California and Connecticut have banned or introduced laws to ban the chemicals for firefighting purposes.

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 due to contamination, foam concentrates that should be fluorine-free can also contain PFAS, if the tank was not properly cleaned when switching from one product to another. For this reason, a laboratory analysis is required to determine the PFAS content in a foam concentrate.

We will present a case study in which, in the absence of knowledge about PFAS present in some fire foam samples, the first step included a general screening at high dilution. This study was preparatory to specific analyses, also at higher concentration, which aimed to target PFAS of concern.

A contemporary deep analysis on the site (soil, waste water, etc.) is also useful to understand if a contamination from fire foams has occurred.

Per- and polyfluoroalkyl substances in biosolids: geographical distribution and data from Quebec, Canada

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Innovation: Compilation and characterization of PFAS in biosolids and discussion of risks and pathways to propose regulatory guidelines.

ABSTRACT

Applying sewage sludge and biosolids to agricultural lands has become an increasingly essential aspect of sustainable waste management and circular economy as it contributes positively to nutrient recycling, soil fertility and environmental health. Due to the widespread presence of per and poly-fluoroalkyl substances (PFAS) globally, wastewater treatment plants have become a sink for PFAS. PFAS resist degradation by conventional wastewater treatment processes and are usually adsorbed to sewage sludge and biosolids. However, there have been significant concerns that land application of sewage sludge and biosolids could become a probable pathway for PFAS to enter the food chain. We assessed the global sewage sludge/biosolids generation and country-to-country management methods through a systematic review. The global occurrence, distribution and prevalence of different classes of PFAS were assessed. We also evaluate the factors influencing PFAS contamination in sewage sludge/biosolids and the existing regulations on the upper limit of PFAS in biosolids before their disposal or application to farmland (or other usages). We have complemented this literature review with analyses from over 100 biosolids, sewage sludge and composts samples from the province of Quebec (Canada). While most studies focused on legacy PFAS detection, recent studies and our own data have revealed the prevalence of diPAPs in high concentrations in sewage sludge and biosolids, contributing from 40 to 95% of the total PFAS concentration. Due to documented PFAS contamination in agricultural lands, rigorous regulations are being instituted to govern the application of these biowastes on agricultural lands. However, several countries lack data on the level of PFAS in the sewage sludges they generate, and there are currently few or no regulations guiding their application to farmlands. Notably, the diPAPs class of PFAS was shown to be present in biosolids and sewage sludge, their inclusion in the list of PFAS required in standardized analytical methods and risks assessment becomes imperative.

Keywords: Sewage sludge, Biosolids, Nutrient recycling, PFAS, Agricultural Land

Enjeux pour la Métrologie environnementale pour une meilleure compréhension des sources et transfert des PFAS dans l’environnement : apports de la R&D

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Les enjeux autour des composés per et polyfluoroalkylés (PFAS) sont actuellement au cœur des préoccupations. En lien avec les enjeux industriels, sanitaires et règlementaires, la métrologie environnementale est un domaine de recherche de premier ordre, qui devra apporter des réponses au plus tôt pour permettre des mesures de gestion pertinentes et efficaces.

Concernant le besoin de connaissances, deux axes majeurs sont actuellement développés : la caractérisation des principales sources de pollution tant d’un point de vue quantitatif que qualitatif et la caractérisation de l’imprégnation des milieux environnementaux, mais aussi de l’alimentation et des populations.

Pour cela, en parallèle des méthodes d’analyses conventionnelles, en constant développement que ce soit par le nombre de PFAS recherchés que par la performance des méthodes, de nouvelles approches montrent leur capacité à répondre à cette problématique complexe. Seront présentées les approches globales, permettant la définition des polluants organiques fluorés et les approches non ciblées permettant d’identifier à la fois de nouveaux composés d’intérêts, mais aussi de mettre en évidence de manière rapide de nouveaux hot-spots, grâce à l’utilisation de banques d’échantillons virtuels. Ces approches seront décrites, leurs avantages et limitations explicités via des exemples d’applications dans le domaine de l’environnement, déployés dans les actions nationales françaises, notamment le plan PFAS ou des actions d’appuis aux politiques publiques comme les travaux du réseau AQUAREF.

Environmental metrology challenges for a better understanding of the sources and transfer of PFAS in the environment: R&D contributions

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The issues of per- and polyfluoroalkyl compounds (PFAS) are at the top of current concerns. In conjunction with industrial, health and regulatory issues, environmental metrology is a key area of research, which must provide answers as early as possible to enable relevant and effective management measures.

With regard to the need for knowledge, two major areas are currently being developed: characterization of the main sources of pollution from both a quantitative and qualitative point of view, and characterization of the impregnation of environmental media, but also of foodstuffs and populations.

To this end, in parallel with conventional analytical methods, which are constantly expanding both in terms of the number of PFAS sought and method performance, new approaches are demonstrating their ability to respond to this complex issue. We will be presenting global approaches, enabling the definition of fluorinated organic pollutants, and non-targeted approaches, enabling the identification of new compounds of interest, as well as the rapid identification of new hot-spots, thanks to the use of virtual sample banks. These approaches will be described, and their advantages and limitations clarified, through examples of applications in the environmental field, deployed in French national actions, notably the PFAS plan, or public policy support actions such as the work of the AQUAREF network.

Study of the fluorinated compounds (PFAS) contamination at a firefighting training site: Presence and mobility

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The aim of this study is to provide an overview of the contamination of a fire training areas that is disused since the end of the 90's. This site is located at a major civil airport and the uses of Aqueous Film Forming Foams (AFFFs) have been confirmed. The study is focused on the spatialization of PFAS contamination; for this purpose, we have investigated 10 sampling points and for each point up to four different soils horizon (0-15, 15-30, 50-70 and 90-110 cm depth).

Targeted analyses were conducted with the following method: first, the samples were freeze-dried, ground and sieved to 2mm. Then, the sample extraction procedure was adapted from a previous study carried out by our group. Soils (25mg-1g, dw) were supplemented with internal standard (8ng each), and the extraction step consisted on a solid-liquid extraction assisted by a microwave, using 10mL solution of methanol amended with 50mM of ammonium acetate (CH_3COONH_4) as extraction solvant. This step was followed by filtration on glass wool and a cleanup step using ENVI-CARB cartridges (250mg).

Two different methods were tested to determine the concentration of unattributed precursors of perfluoroalkyls acids (pre-PFAAs): the total oxidation precursor assay (TOP assay) and the direct Total oxidation precursor assay (dTOP assay). The principle of those methods is the same; we introduce two oxidative agents to generate hydroxyl radical, which can react with pre-PFAAs and generate PFAAs (i.e., carboxylic acids). Using the targeted analysis, it is then possible to quantify the quantity of PFCAs formed upon oxidation; this fraction can be attributed to the presence of unattributed pre-PFAAs.

While the TOP assay relies on the extraction of PFAS before oxidation (i.e. extractible fraction), in the dTOP assay oxidation is directly performed on soil samples. The aim of this study is to compare these two methods to see if they provide equivalent results on the quantity of PFCAs formed and in the oxidation profile. For now, only preliminary results have been obtained so we are not able to provide a complete description of this comparison.

Analyses were performed using liquid chromatography electrospray ionization coupled with tandem mass spectrometry (LC-ESI-MS/MS) on a 1290 LC system interfaced with a 6495 triple quadrupole mass spectrometer (Agilent Technologies, Massy, France). The ESI source was set on fast polarity switching mode for the analysis of zwiterrionic compound such as the 6:2 and 8:2 FTAB. In total, 39 molecules were analyzed on the extracts.

Overall, perfluorooctane sulfonate (PFOS) and 6:2 Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) were the most predominant PFAS on this site, their concentration range between (<0.3-1400ng/g, dw) and (<0.02-3600ng/g, dw) respectively. The maximal concentration found for the total PFAS concentration (∑PFAS, 6000ng/g,dw) was in the 50-70cm depth horizon, at the most contaminated sampling point (Figure). These results show that the contamination on the site is not consistent between all the sampling point and differences in the contamination profile are observed (i.e levels and molecular/vertical patterns).

The preliminary tests conducted on the comparison of the two oxidative methods led to different results in the oxidation profile such as in the quantity of the PFCAs generated. The dTOP assay generate more PFCAs compare to the TOP assay. Furthermore, in the case of the dTOP assay only 20% of the PFCAs formed can be explain by the presence of the pre-PFAAs analyzed in the targeted analysis while in the TOP assay, all the PFCAs formed can be explained by the analyzed pre-PFAAs.

This contribution will i) present the results of the targeted analysis approach (spatial patterns and vertical profiles), ii) make a preliminary comparative analysis of the methods used for the TOP and the dTOP assays, iii) confront targeted analysis and TOP assay.

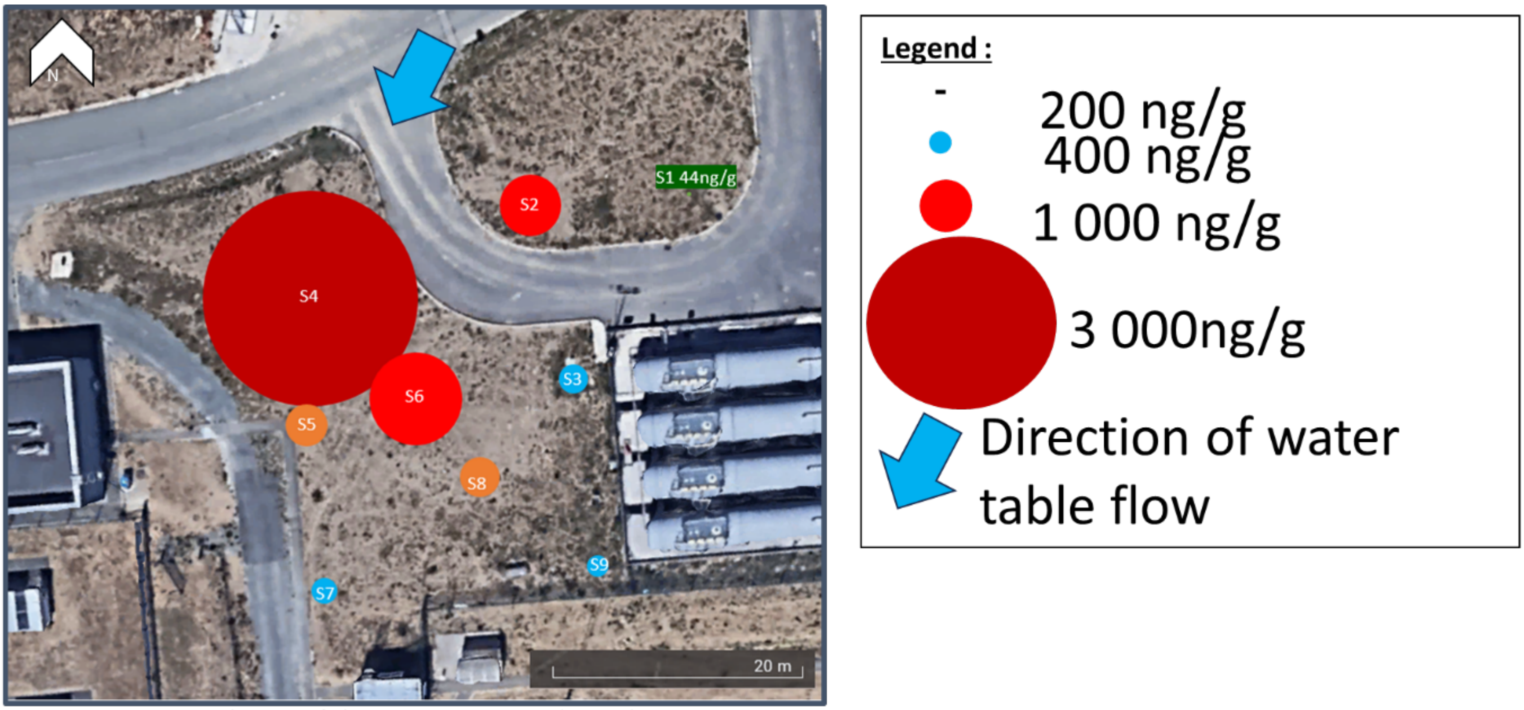

Figure: Aerial view of the training site with total average concentration in PFAS at each sampling point.

Acknowledgments:

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The role of target screening PFAS and determination of ultra short chain PFAS in the PFASafe©-concept

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Although PFAS were used during many decades from the 20th century on, concern about their toxicity grew only since the late nineties of the last century. The two most pronounced examples were perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS), but gradually more and more compounds attracted attention. PFAS are considered as forever chemicals due to the very strong C-F-bond and, hence, their high stability towards degradation in the environment, i.e. most of these compounds can be considered as persistent. Moreover, many of these PFAS contain a lipophilic tail and a hydrophilic head and are thus to be considered as surfactants, which enhance their mobility in the environment. Some of the PFAS congeners tend also to volatilize, which makes long distance transportation possible.

In Buck et al [1] per- and polyfluoroalkyl substances (PFAS) are defined as “the highly fluorinated aliphatic substances that contain one or more C atoms on which all the H-substituents have been replaced by F-atoms, in such a manner that they contain the perfluoroalkyl moiety CnF2n+1–” (where n is equal to or greater than 1, i.e. the structure must contain at least one CF3– group). In 2018, OECD Global PFC Group [2] defined PFAS as chemicals with at least one perfluorocarbon moiety (–CnF2n–), i.e. a PFAS contains at least one CF2-moiety. In the latter 4730 compounds and their CAS-register number were identified, including substances which do not correspond to the definition of Buck et al, i.e. they do not necessarily have a CF3-group at the end. As such, this definition looks more appropriate towards the various number of PFAS- and PFAS-like compounds in literature. In the meanwhile, the database DSSTox of the US Environmental Protection Agency (US EPA) listed 14735 unique PFAS compounds and PubChem even mentions over 6 million of PFAS [3]. Using the definition of the OECD also non-typical compounds like the pesticide fipronil should be considered a PFAS as well, while trifluoromethane is not, as it does not contain a fully fluorinated methyl-moiety. It must be stated that the more ancient term PFC (perfluorinated fluorinated compounds) should be considered as obsolete.

Glüge et al [4] identified more than 200 use categories and subcategories for more than 1400 individual PFAS. In addition to well-known categories such as textile impregnation, fire-fighting foam, and electroplating, the identified use categories also include many categories not described in the scientific literature, including PFAS in ammunition, climbing ropes, guitar strings, artificial turf, and soil remediation and even toilet paper. Hence, people are not only exposed during the production of PFAS (like e.g. at the 3M factory in Zwijndrecht, Flanders), but also during daily use. This widespread of PFAS explains thus the omnipresence in humans. Once released in the environment many PFAS tend to accumulate in the different environmental compartments as discussed above.

The PFASafe® concept was elaborated by SGS incorporating various techniques to determine PFAS in various matrices to cope with the different types of PFAS found in the environment and get an insight in the total amount of organic fluorine in and thus the PFAS risk of a sample. The approach consists of the following steps:

- Adsorbable Organic Fluorine (AOF): determination of organic fluorine in water samples
- Extractable Organic Fluorine (EOF): determination of organic fluorine in solid samples
- PFAS-analysis: classical target analysis of a selected number of classically known PFAS congeners, but also including other, ‘newer’ PFAS, like ultra-short chain (USC) PFAS and volatile PFAS.
- Q-TOF screening: purely qualitative determination of unknown PFAS (no quantitative information)

- Total Oxidizable Precursors (TOP): oxidation of larger PFAS, consisting of weaker bonds and which are then cleaved and after identification result in stable, perfluorinated PFAS.

A full validation study was performed for both the quantitative determination of USC PFAS and for the qualitative non-target screening of PFAS in water. The method of determining USC PFAS is in line with WAC/IV/A/026 [5] and uses direct injection of the sample on a LC-MSMS-instrument. Determination of the different compounds is done using MRM in negative ESI-mode. Validation was carried out according to WAC/VI/A/001 and 002 [6-7] and consists essentially of determining accuracy and precision, resulting in uncertainty of measurement, limit of quantification and linearity of the method for the different USC PFAS. During the presentation the results of this validation study will be shown.

The French government has determined via the 20 June 2023 decree on water emission that 20 compounds must be determined on a regularly base. However, as stated above, many more PFAS have been synthesized in the past and found their way to the environment. Determining all these compounds using classical target analysis is not manageable. Hence, it is a far more efficient to determining which compounds are present in a sample using screening (targeted or non-targeted) methods and subsequently, if these compounds are frequently present and if standards are available to take up these compounds in a quantitative scheme. As many of the PFAS can be determined using LC-MSMS, we started developing a method with this technique using a Q-TOF-analyzer, as this technique is capable of exact mass determination and, consequently, determining molecular formula information. Together with the possibility of creating MSMS-spectra, this technique can give us possible hits for unknown compounds or possible structures can be scanned towards a database of PFAS which is commercially available. In our method we used the Comptox-database [8], consisting of over 400 PFAS-congeners. However, to get an idea of the accuracy of our method, we carried out a validation study. A definition of measurement uncertainty for a qualitative method is not straightforward. Using Bayesian statistical techniques, we will highlight during our presentation what the accuracy is of our method and to get an idea from which concentration limits this method can be used.

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ANTHROPOGENIC BACKGROUNDVALUES OF PFAS IN SOIL AND GROUNDWATER

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A study was conducted to determine anthropogenic background values of PFAS in soil and groundwater in Flanders. As PFAS do not naturally occur in the environment, this refers to the diffuse anthropogenic presence of PFAS in soil and groundwater.

The derivation of anthropogenic background values for PFAS was done based on soil and groundwater sampling at unsuspected locations spread over Flanders, i.e., zones where no known PFAS suspected point sources are present or were present in the past. To select sampling locations spatial data were collected and merged as different map layers into one map image: known zones with PFAS contamination, Inventory of known firefighting training sites and fires, known analytical results for PFAS, PFAS measurement results in wastewater, known landfills in Flanders, land on which PFAS suspicious activities were carried. For determining background values, it is also important to avoid contamination with other substances. Therefore, a map layer of sites with an OVAM file number and locations of sewage treatment plants were also added.

To arrive at a survey with good coverage, 147 monitoring wells were selected across Flanders from the VMM (Flanders Environment Agency) monitoring network. The selected monitoring wells have a filter in the phreatic groundwater and are located a distance more than 100 m from sites with a known OVAM file number, landfills, land with PFAS-suspicious activities, potential hotspot sites for sediments, sewage treatment plants and known discharges of PFAS-containing wastewater .Soil samples were also taken near 73 of these monitoring wells. The selected sites were sampled and analysed from February 2023 to June 2023.

Groundwater

Groundwater was analysed for 34 quantitative PFAS and 8 indicative PFAS. Simultaneously with the sampling commissioned by OVAM, VMM also conducted its annual monitoring program. Results from VMM for the monitoring wells matching above selection criteria were also included in this study.

In total 387 monitoring sites were retained for the derivation of background values of PFAS in groundwater. In 341 of the 387 monitoring wells, at least 1 PFAS component is measured above quantification limit (LOQ). The top 4 most common PFAS in the 387 monitoring wells are listed in Table A. The remaining PFAS compounds are analysed above quantification limit in less than 33% of samples.

Table A: most commonly detected compounds above quantification limit of 1 ng/L

	% measurements above LOQ Frequency of quantification (%)
PFBA	59%
PFBS	57%
PFOA Total	49%
PFOS Total	34%

For the above 4 most common PFAS in unsuspected areas, the P90 value (90 percentile value) was determined. Data was additionally checked for outliers and adjusted where necessary. Table B shows the derived values.

If a component is found in less than half of the sampling locations, it can be said that no general elevated anthropogenic background value is present. PFBA and PFBS were detected in more than half of the sampling sites. For PFOA, this value is approached (49%). Consequently, target values are proposed only for PFBA, PFBS and PFOA.

Table B: Proposed background value for PFBA, PFBS, and $PFOA_{total}$ in groundwater and indicative P90 value for PFOS in groundwater

	P90 in ng/L
PFBA	21,0
PFBS	9,4
PFOAtot	8,0
*PFOStot***	*5,0*

**For PFOS, the P90 is listed for informational purposes only, it is not proposed as a background value.

The current standard for Sum EU DWD20 is 100 ng/L according to the Drinking Water Directive (DWD). It is to be noted that a significant part of this standard has already been filled by the anthropogenic background value of PFBA, (21%).The anthropogenic background value PBFA also exceeds the discharge standard in Flanders (20 ng/L).

If compared to the European Commission's proposed environmental quality standard for groundwater and surface water of 4.4 ng/L PFOA-equivalents, we find that the proposed anthropogenic background values (P90) of PFOA and PFOS, already exceed this value of 4.4 ng/L individually. Although 3 of the 24 components in this sum were not analysed in the present study, the proposed quality standard of 4.4 ng/L is already exceeded in 37% of sampled sites in unsuspected areas.

Soil

At a selection of 73 monitoring sites used for the groundwater sampling, soil samples were also taken and analysed for PFAS. In addition, results from a previous study with the aim of deriving anthropogenic background PFAS values were also taken into account.

The 90-percentile of the samples analysed in the present study and those in the previous study combined, result in an anthropogenic background value of 1.4 µg/kg dw for $PFOS_{tota}$l. This is the same order of magnitude as the current anthropogenic background value in Flanders derived in the previous study (1.5 µg/kg dw). For $PFOA_{total}$, lower values than the current anthropogenic background value derived by VITO (1.0 µg/kg dw) are measured in this study. As a P90 value for $PFOA_{total}$, 0.8 µg/kg dw is calculated. Given the limited differences between the currently published anthropogenic background values for PFOS and PFOA (OVAM, 2021) and the 90-percentile values calculated in this study, it is recommended to keep the existing values for PFOS and PFOA.
For the other PFAS compounds, insufficient data above the reporting limit are available to derive a statistically sound and representative anthropogenic background value.

Recommendations

The samples in the present study originate from agricultural or natural areas and are not necessarily representative for urbanised or industrial areas. Additional research in urban areas and in ambient areas around industrial zones can provide more insight into the extent to which there is an anthropogenic increased diffuse presence of PFAS in these areas.

The results from the present study can be used when interpreting results in a soil investigation. The values can be used as motivation to demonstrate to which extent a contaminant can be assigned with high probability to the investigated source.

Per- and polyfluoroalkyl substances in the atmosphere near a fluoropolymer production plant in an urban area
Mesures de Substances per- et polyfluoroalkylées (PFAS) en air ambiant en Région Auvergne-Rhône-Alpes

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Keywords: PFAS, ambient air, urban background, industrial influence, HV-AAS

Innovation**: First PFAS active sampling measurement campaign in ambient air in the Auvergne-Rhône-Alpes Region.**

Goals: Quantitative measurements of PFAS in ambient air.

Technical abstract:

In recent years, the issue of PFAS has become a growing concern, and the Auvergne-Rhône-Alpes region is home to several PFAS-producing companies. Studies have been carried out by ANSES and DREAL on soil and surface water (Dauchy 2023; DREAL AuRA 2022) in the vicinity of a background site under industrial influence in southern Lyon. These revealed proven PFAS contamination (PFUnDA predominating in the soil (27-73% of 10 PFAS sum in dry weight), and PFTrDA and PFUnDA predominating in dust on the soil surface (23-56 % and 25-34 % respectively of 10 PFAS sum in dry weight)). Ambient air measurements are still complex to set up, as the methodology has not yet been established. However, following an injunction from the public authorities, the first passive sampling measurements in ambient air were carried out by a PFAS producer in southern Lyon (DREAL AuRA, 2022). They concluded that these measurements showed "results well below the most restrictive international benchmark values". However, further investigations are still required, as passive methods are subject to questions regarding desorption artifacts on sampling matrices (Karásková et al. 2018; Lai et al. 2019).

Atmo Auvergne-Rhône-Alpes (Atmo AuRA), the reference for air quality monitoring in the Auvergne-Rhône-Alpes region, is increasingly called upon by its members, local authorities, and citizens to respond to their growing concerns on the subject. In 2023, Atmo AuRA therefore initiated bibliographical work and exchanges with its partners, AASQAs and French metrological authorities to define a methodology.

Active air sampling methods use a wide variety of filters and sorbents, including quartz or glass fiber filters for the particle phase and PUF, XAD2, and PUF/XAD2 combinations for the gaz phase. Other methods like solid phase extraction sorbents, and sorbent-filled thermal desorption tubes are also used. HV-AAS is commonly used for outdoor measurements whereas LV-AAS are most often used to sample indoor air.

Atmo AuRA set-up measurements simultaneously at an urban background site and at a commune hosting PFAS-producing companies in the Lyon area. These samplings were carried out using high-volume air samplers equipped with a sampling head for PM10, and in the first tests with quartz filters for the particulate phase and polyurethane foams for the semi-volatile fraction. These were analysed separately, with the identification of 22 PFAS compounds.

Initials results are encouraging, with a different profile observed at the site close to a PFAS-producing company than at the urban background site. Among the 22 PFAS analysed, from 9 to 16 compounds

were detected and quantified, depending on the site and the sampling support. Perfluoroalkyl carboxylic acids (PFCA), ranging from 45 % to 92%, is the major fraction of the measured PFAS, while (fluorotelomer sulfonic acids) FTSA represent from 7% to 50 % of samples. Perfluoroalkane sulfonic acids (PFSA) and perfluoroalkane sulfonamides (FASA) represent each less than 5% of the measured levels. On average, 6:2 FTS is the most abundant (39%) compound on the background site, whereas PFHxA represents up to 64% on the industrial influence location. Moreover, although PFOA and PFOS are banned for decades, both compounds are still detected in these samples.

When compared to previous studies at this industrial influence site, roughly common profile is found with the passive sampling method, but different partitioning profiles is observed with those of soil and dust samples.

The partitioning between the two supports (Filter and PUF foam) tend to show more compounds found in the PUF foam for PFCA and FASA but to a less extend for PFSA and PFTA depending on the sample. Using different filters or PUF foams might have an influence.

All those questions will further be investigated in 2024 with the test of different methods and at different seasons.

Mercredi 5 juin 2024

08h30
Accueil des participants

Présidents :

- *Dr. Christophe Rousselle, ANSES, SFSE & ARET, France*
- *Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne*

Investigations des sites, Chimie Environnementale et Modélisation des transferts

09h00
L'avenir de la fabrication responsable : une approche à plusieurs volets
Cédric Triquet, Directeur de la Stratégie Groupe de la division Advanced Performance Materials - Chemours International Operations, Suisse

09h30
Leçons tirées des enquêtes en cours sur 16 sites de pompiers
Lars Van Passel, Directeur Technique - RSK Benelux, Belgique

10h00
Etude de la contamination et de l'impact des PFAS dans la zone de Fos-Berre : présentation du projet MATISSE et premiers résultats
Maelys Dijoux, Doctorante CIFRE - ABO-ERG Environnement / Aix-Marseille Université, France

10h30
Pause café & thé

11h00
Mesure PFAS FLUX pour améliorer la gestion et le traitement des eaux souterraines
Erik Bosmans, Chef de projet - iFLUX, Belgique

Evaluation des risques environnementaux et sanitaires, Toxicologie & Épidémiologie

11h30
Exposition des enfants aux PFAS : l'importance de l'exposition in utero, de l'allaitement et de l'alimentation étudiée dans le cadre de la cohorte HELIX, à l'aide de la modélisation pharmacocinétique basée sur la physiologie (PBPK)
Ophélia Gestin, Post-doctorante en modélisation toxicocinétique - Institut National de l'Environnement Industriel et des Risques (INERIS), France

12h00
Déjeuner

13h15
Evaluation des risques toxicologiques (EQRS & ARR) des PFAS par le bon choix des VTR et via l'application du Top Assay, entre autres par l'application du Guide de Gestion des PFAS de la SFSE (F.10)
Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne

13h45
Détermination de teneurs limites sanitaires pour PFOA et PFOS dans les sols combinant données épidémiologiques et modèle multimedia, toxicocinétique et probabiliste à 1 compartiment
Dr. Jérôme Petit, Chargé scientifique principal, Direction des Risques Chroniques / Cellule Environnement-Santé - ISSeP, Institut Scientifique de Service Public, Belgique

14h15
Étude de l'activité endocrinienne des composés per et polyfluorés (PFAS) et développement d'une méthodologie intégrative visant à évaluer la toxicité résiduelle des matrices traitées
Louise Delor, Chargée de projets Risk Assessment - Spuma, France

14h45
Biomonitoring humain spécifique autour des sites des broyeurs à métaux en Wallonie (Belgique)
Ingrid Ruthy, Chargée de projet - ISSeP, Institut Scientifique de Service Public, Belgique

15h15
Pause café & thé

Plans de gestion et objectifs de réhabilitation

15h45
Comparaison de la durabilité des systèmes actifs et passifs de confinement des eaux souterraines pour le traitement des panaches de PFAS
- *Mariangela Donati, Responsable de région - Regenesis, Italie*
- *Frédéric Leveau, Directeur Sites et Sols Pollués - Ramboll, France*

16h15
Destruction des PFAS via un plasma non thermique dans les eaux (usées)
Wouter De Weirdt, Gérant - Tectero, Belgique

16h45

Élimination efficace des substances alkyles per- et polyfluorées des eaux potables et usées grâce aux résines sélectives Lewatit®

Dr. Dirk Steinhilber, Directeur Marketing Technique - Lanxess Deutchland, Allemagne

17h15

Développement d'un procédé pour l'élimination des PFAS à chaîne courte avec une résine échangeuse d'ions

Francis Boodoo, Directeur des Applications - Purolite, an Ecolab Company, Etats-Unis

17h45

Fin de la seconde journée

Wednesday, June 5, 2024

08h30
Welcoming participants

Presidents:
- *Dr. Christophe Rousselle, ANSES, SFSE & ARET, France*
- *Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany*

Site Investigations, Environmental Chemistry and Transfer Modelling

09h00
The future of responsible manufacturing: a multipronged approach
Cédric Triquet, Global Strategy and Avocacy Director Advanced Performance Materials - Chemours International Operations, Swiss

09h30
Lessons learned from on-going investigations at 16 fire department sites
Lars Van Passel, Technical Director - RSK Benelux, Belgium

10h00
Study of the contamination and impact of PFAS in the Fos-Berre area: introduction to the MATISSE project and initial results
Maelys Dijoux, PhD student CIFRE - ABO-ERG Environment / Aix-Marseille University, France

10h30
Coffee & Tea break

11h00
Measures PFAS FLUX for improved groundwater management and treatment
Erik Bosmans, Project Manager - iFLUX, Belgique

Environmental and Health Risk Assessments, Toxicology & Epidemiology

11h30
Children's Exposure to PFAS: the Importance of In Utero Exposure, Breastfeeding and Diet studied through the HELIX Cohort, using Physiologically Based PharmacoKinetic (PBPK) Modelling
Ophélia Gestin, Post-doctoral student in toxicokinetic modeling - French National Institute for Industrial Environment and Risks (INERIS), France

12h00
Lunch

13h15
Human Health Risk Assessment via Toxicological Exposure Risk Quantification (HRA & TERQ) of PFAS by the correct choice of TRVs and via the application of the Top Assay; according the SFSE PFAS Management Guideline (F.10)
Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany

13h45
Determination of sustainable health risk based soils standards for PFOA and PFOS with a combination of epidemiological data and a multimedia, one-compartment toxicokinetic and probabilistic model
Dr. Jérôme Petit, Principal Scientific Officer, Chronic Risks Department / Environment-Health Unit – ISSeP, Scientific Institute of Public Service, Belgium

14h15
Study of the endocrine activity of per- and polyfluorinated compounds (PFAS) and development of an integrative methodology aimed at evaluating the residual toxicity of treated matrices
Louise Delor, Risk Assessment Project Manager - Spuma, France

14h45
Human biomonitoring around the metal shredders targeted on metals and others hazardous chemicals in Wallonia (Belgium)
Ingrid Ruthy, Project manager - ISSeP, Scientific Institute of Public Service, Belgium

15h15
Coffee & Tea break

Remediation Plans and Remediation Goals

15h45
Comparing the sustainability of active and passive groundwater containment systems for the treatment of PFAS plumes
- *Mariangela Donati, District Manager - Regenesis, Italy*
- *Frédéric Leveau, Manager Contaminated Land - Ramboll, France*

16h15
PFAS destruction via nonthermal plasma in (waste)water
Wouter De Weirdt, Owner - Tectero, Belgium

16h45
Efficient removal of per- and polyfluorinated alkyl substances from potable- and waste water with selective Lewatit® resins
Dr. Dirk Steinhilber, Technical Marketing Manager - Lanxess Deutchland, Germany

17h15
Process development for ultra-short chain PFAS using regenerable ion exchange resin
Francis Boodoo, Applications Director - Purolite, an Ecolab Company, USA

17h45
End of Day of Two

The Future of Responsible Manufacturing: A Multipronged Approach for fluoropolymers

Cedric TRIQUET, cedric.triquet@chemours.com, +41.22.719.15.31
Global Strategy and Advocacy Director, Chemours Advanced Performance Materials

Technical summary

Fluoropolymers are high-performance plastics material with a unique combination of properties that makes them the building blocks for an extraordinary range of products and industry applications. Their unique properties—including durability, mechanical strength, inertness, thermal stability, and resistance to chemical, biological, and physical degradation—mean they are used across many sectors where they can withstand the most challenging and high-stress conditions where failure is not an option.

Fluoropolymers are critical to a range of industries, have no suitable alternatives in the majority of uses, do not pose risks to human health and the environment when used for their intended purposes, and are manufactured responsibly.

In the upcoming session, Cedric Triquet explores responsible manufacturing in the context of fluoropolymers. The talk provides a practical look at the use of processing aids, the role that abatement technology plays in current manufacturing practices, and the considerations that need to be made regarding product performance, environmental impact, and residue profile in the end product.

Triquet delves into Chemours' decision-making process when it comes to surfactant or processing aid usage. This illuminates the steps companies can take to balance production and environmental requirements. Alongside this, he will explain the detailed analysis required to manage potential emissions and residues—an increasingly important aspect amidst evolving regulatory standards.
A key part of the talk will be the presentation of real-world examples to illustrate current practices. This will help attendees better understand the practical challenges and solutions within the industry.

In summary, Triquet's session is structured to help attendees understand the complexities of responsible fluoropolymer manufacturing. The talk strips back the theory and offers an in-depth, practical exploration of the actual decision-making processes, challenges, and opportunities that companies face in their pursuit of sustainable manufacturing. This is an ideal session for those interested in industry best practices and the future of responsible manufacturing.

Study of the contamination and impact of PFAS in the Fos-Berre area: introduction to the MATISSE project and initial results

Technical abstract

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I. PFAS handling issues bibliographic study

A literature review of over a hundred scientific publications was carried out, using specific keywords related to stability experiments (*i.e.* stability, integrity, storage, degradation), recovery investigations after sample preparation (*i.e.* loss, filtration, sorption, volatilization), or contamination problems (*i.e.* contamination, blanks, PFAS background).

Contamination from the operator and the material should be investigated and reduced, by avoiding the use of fluoropolymer materials (clothes, laboratory equipment) and by rinsing all materials with methanol before use.

Samples should be stored at low temperature as well as extracted and analysed in the shortest laps time to reduce the degradation and adsorption of PFAS, as samples preservation conditions are still in discussion. Filtration of sample should be avoided since it was shown to retain PFAS, and concentration shouldn't be performed to dryness to avoid the loss through volatilization. Sample transfers during preparation steps should be limited to avoid the loss of compounds, and all containers should be rinsed with methanol to recover sorbed PFAS.

II. Analytical results

1) Sampling campaign

An analytical method has been developed following previously established recommendations to quantify the 30 PFAS of the ISO 21675[1] procedure in tap water.

7 supplementary PFAS belonging to the french PCI[2] regulation published in June 2023 were investigated.

Water samples were collected in pre-washed high-density polyethylene (HDPE) bottles in 5 houses in the Fos-Berre area (Figure 1).

Figure 1: Map of the Fos-Berre area

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[1] PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA, PFBS, PFHxS, PFHpS, PFOS, PFDS, ADONA, HFPO-DA, 6:2 FTS, 8:2FTS, 6:2Cl-PFAES, PFOSA, NEtFOSA, NMeFOSA, NEtFOSAA, NMeFOSAA, 8:2FTUCA, 8:2diPAP

[2] Classified installations for the protection of environment

Powder-free nitrile gloves were worn during the sampling. Water samples were collected after 5mins of water flushing, and ammonium acetate was immediately added to all samples. The samples were placed into polyethylene plastic bags to be labelled. Samples were kept in a cooler at a temperature below 4°C for transport and stored refrigerated before extraction within 2 days after collection. Water samples were preconcentrated using weak anion exchange stationary phase. They were then centrifuged and analysed by LC/MS.

2) Quality assurance and quality control (QA/QC)

- Field blanks were made by handling ultrapure water for the whole sampling and analytical procedure. They were stored in the same containers as samples, exposed to the sampling environment for the time of sampling and underwent the same extraction and analysis procedures.
- Procedural blanks were run to control the potential background contamination from equipment and reagents when solid-phase extraction was used as a sample preparation step. For this, ultrapure water samples were loaded onto the cartridges and the procedure followed was the same as for the field samples.
- Solvent blanks were run before and after each batch of 10 samples to perform analytical blanks and investigate the instrumental background as well as the potential carryover contamination.
- The precision and accuracy of the method were confirmed for each run and monitored by the regular analysis of duplicate samples and quality control solutions.
- Squared coefficient of determination (R^2) for all compound calibration curves were higher than 0,99.

3) Results

The extraction of triplicate samples over 2 days confirmed that the results were consistent.

Over the 37 PFAS investigated, 15 PFAS were detected, 11 PFAS were present in all samples and 14 PFAS were quantified. A careful analysis of blank samples has been performed. Trace amounts of 6:2FTS, PFBA, PFHxS, N-MeFOSAA and 6:2Cl-PFAES have been found both in trip and procedural blanks. The signal obtained was then subtracted to the signal of the corresponding analyte during sample quantification. 6:2FTS, PFOS, PFHxA, PFHxS and PFPeA displayed the highest concentrations among all PFAS.

Sum of total PFAS was about 0.05µg.L^{-1} in sample 1 and ranged from 0.18 to 0.39µg.L^{-1} in samples 2, 3, 4 and 5, which is below the standard value of 0.50µg.L^{-1} of the 2020/2184 Water Framework Directive regulation. However, even though the sum of the 20 regulated PFAS was below the standard value of 0.10µg.L^{-1} for sample 1, they were close to the limit for samples 2, 3, and 4 and about 0.24µg.L^{-1} for sample 5.

The higher concentration of PFAS in samples 2, 3, 4 and 5 than in sample 1 could result from a potential contamination of the groundwater from an air base leachate located between these sampling locations. Indeed, PFCAs and PFSAs such as PFOS or PFHxA were used in aqueous film forming foams (AFFF) until the 2000s, and 6:2FTS was and is still in the composition of more recent AFFF.

However, considering the detection of some PFAS in procedural blanks and trip blanks despite the taken precautions, further investigation of the contamination sources during sampling and sample treatment will be required. In addition, a larger-scale sampling campaign will take place, considering more cities and a larger geographic surface in the Fos-Berre area.

Improved management and treatment of groundwater contamination with the help of PFAS FLUX measurements

Erik Bosmans, project manager iFLUX
Marjan Joris, account expert, iFLUX

At the request of our customer, an expert in soil and groundwater remediation, passive flow samplers were used as part of the characterization of PFAS contamination at an industrial site in France. As the project is confidential, neither the site nor the customer will be mentioned. But the most important thing is that we have the agreement to present the results.

Figure 1: iFLUX passive sampler

The main goal of the study was to determine the spreading of pollutants (measurement of groundwater flow and and mass flux) in order to evaluate the optimal treatment for the contaminated groundwater present in the study area.
The secondary objective was to identify the origin of the PFAS concentrations detected in a drain and ultimately propose a sustainable treatment solution.

Firstly, the investigations made it possible to highlight preferential flow routes and to specify the areas of the site where the dispersion potential is the highest.

The combined results of groundwater fluxes and PFAS mass fluxes made it possible to quantify the effects of geological heterogeneity on groundwater flow and PFAS contamination and they made it possible to quantify the effect of local artificial drainage under buildings on the dispersion of contamination in the downstream part of the site.

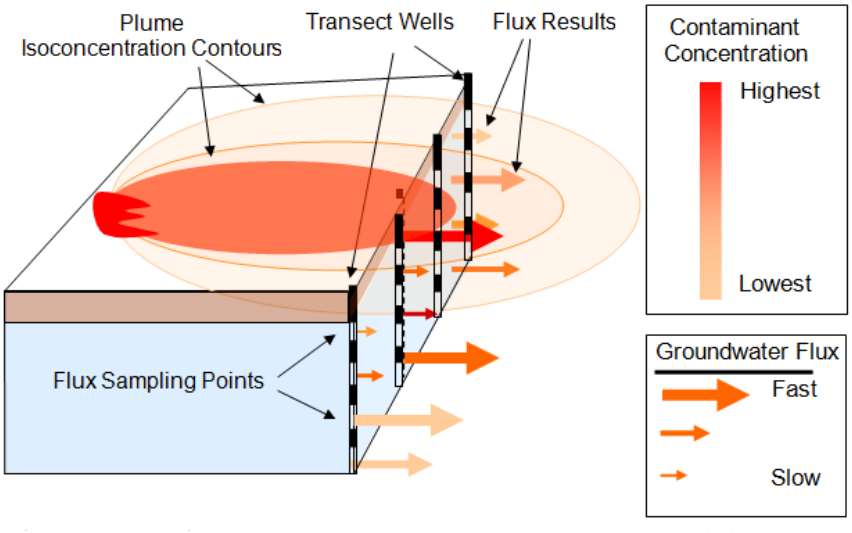

figure 2 : 3D visualization how the presence of contamination and groundwater flux are driving the spreading of the contamination

A longer exposure period compared to the very short sampling time of conventional groundwater sampling, increases the chances of detecting the contaminants of interest present and makes it possible to provide results averaged over time, which exclude high or low peaks. The results are therefore less sensitive to the sometimes-rapid variations in concentrations under the action of the specific hydrogeological characteristics of the site. They are also good measures of exposure for downstream receptors.

During the sampling campaign the exposure time was 31 days. A PFAS compound that had not been detected during traditional groundwater sampling and could perhaps have come from a neighboring site could be identified in an area located hydrogeologically upstream of the site.

Finally, the possibility of measuring flows at different depths in the same structure made it possible to determine vertical flow profiles and refine the conceptual model of the site.

Therefore, the results of the study contributed to better guidance and consequently, the reduction of the costs of carrying out the additional sampling plan necessary for the complete characterization of PFAS contamination before its treatment. Passive flux measurements will also allow targeted monitoring of the effectiveness of remediation, measurements.

Exposure assessment to PFAS of pregnant women and children of the HELIX cohort using physiologically based pharmacokinetic (PBPK) modelling

Ophélia GESTIN (ophelia.gestin@ineris.fr), Post-doctoral researcher in toxicokinetic modelling,
« Toxicologie Expérimentale et Modélisation » Unit, « Milieux et impacts sur le Vivant »
Direction, at l'INERIS (Institut National de l'environnement Industriel et des risques)
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Innovative nature of the proposed work: The overall aim of this work is to provide tools to improve the interpretation of biomonitoring data for sensitive populations, such as the exposure of pregnant women and children to PFAS. The PBPK model developed by Brochot *et al.*, 2019 and Ratier *et al.*, (2024) was applied to four PFAS (PFOA, PFOS, PFHxS and PFNA), in a reverse dosimetry approach to assess the exposure of mothers and children to PFAS. The sum of the predicted dietary intakes estimated for each PFAS, by the PBPK model, was compared with that of the most recent EFSA scientific opinion (2020) to assess the risk of the addition of their exposures in mixture.

Keywords: Sensitive population, Mixtures, Target organs, Prenatal exposure, postnatal exposure, PBPK models.

Aims: This work aims: (i) to determine the exposure of pregnant women and their children in the HELIX cohort to PFHxS and PFNA; and (ii) to assess the risk using the sum of the intake rates of the four PFAS (PFOA, PFOS, PFHxS and PFNA), as recommended by EFSA (2020).

Abstract: Childhood is a critical period for exposure to chemicals such as PFAS. Few studies have used PBPK models that link prenatal and early postnatal exposures for PFAS, and none of them considered maternal and child exposure along a *continuum*. This work aims: (i) to determine the exposure of pregnant women and their children in the HELIX cohort to PFHxS and PFNA; and (ii) to assess the risk using the sum of the intake rates of the four PFAS (i.e. PFOA, PFOS, PFHxS and PFNA), as recommended by EFSA (2020). Plasma concentrations of PFOA, PFOS, PFHxS, and PFNA were available for 1,239 mother-child pairs from a HELIX cohort, at two times of sampling. A lifetime PBPK model was parametrized for the four PFAS, such as half-life and partition coefficients. Firstly, a placental transfer value (from the mother to the fetus) was estimated based on PFAS concentration data in the mothers' serum, and in the umbilical cord serum, on a pool of 52 women from another sub-cohort of HELIX. Dietary intakes for pregnant women and children were estimated using reverse dosimetry in a Bayesian framework based on the measured plasma concentrations of PFAS and individual characteristics obtained from questionnaires. The first results showed that among the six countries of the HELIX cohort, France and Norway had the highest dietary intakes of PFOS and PFOA. To further assess the exposure of the HELIX children, the dietary intake results of the four PFAS investigated were added, as recommended in the latest EFSA scientific opinion (2020). In perspective, the study will then be used to assess the contribution of different sources of exposure to the four PFAS (i.e. *in utero*, breastfeeding and diet) during childhood.

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Human Health Risk Assessment via Toxicological Exposure Risk Quantification (HRA & TERQ) of PFAS by the correct choice of TRVs and via the application of the Top Assay; according the SFSE PFAS Management Guideline (F.10)

Evaluation des risques toxicologiques (EQRS & ARR) des PFAS par le bon choix des VTR et via l'application du Top Assay, en d'autre par l'application du Guide de Gestion des PFAS de la SFSE (F.10)

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1. Introduction

Since the 1960s, PFAS: Per- & Polyfluoro-Alkyl Substances have gradually become a major environmental and Public Health concern, due to their multiple and wide-ranging applications (historical and still current). This threat to the environment and to public health has been gradually coming in fore since the 2010s, and became more acute in 2022 - 2024. As a result, PFAS are now found in soil, groundwater, food and drinking water, as well as in soil gas and ambient air for the volatile PFAS families, e.g. FTOH: Fluorotelomer Alcohols. Between 9,000 and 12,000 synthetic PFAS pollutants have been produced.

Polymeric PFASs such as Teflon (or PFTE) etc. are not very bioavailable and are therefore much less toxic than monomeric PFASs. These monomeric PFAS are the subject of the work presented here. PFASs are known for their toxicological effects as endocrine disruptors, hepatotoxicity, immunotoxicity, effects on foetal development and, in some cases, carcinogenicity (e.g. PFOA) [1 - 84, 184, 185].

An important characteristic of PFASs is their behaviour in Environmental Chemistry, as only polyfluorinated PFASs are modified by microbiological biotransformation into perfluorinated PFASs, which remain totally stable and non-degradable, and even bioaccumulable.

There are **many sources of PFAS pollution**, including industrial sites where these products have been used and former fire or fire training sites where fire-fighting foams (**AFFF: Aqueous Film Forming Foam or Anti Fire Fighting Foams, e.g. at airports**) have been applied. Agricultural land can be also a source of PFAS pollution, in case of sludge use from waste water treatment plants (WWTP), which contains accumulated PFAS.

The following (historical) activities may be the source of PFAS pollution:

- Fire training,
- Airport or military airbase,
- AFFF fire and use site,
- Electrochemical galvanisation,
- Production of waxed paper and cardboard,
- Manufacture of waterproof textiles,
- Sprays, paints, waterproofing lacquers,
- Production and application of Teflons (PTFE, etc.),

- Oil and chemical industry sites and/or production and application of paints, dyes, inks, pigments, chemical waxes and polishes,
- Solvent applications (garages, dry cleaners, laundries, etc.),
- Landfill sites and former municipal landfill sites, etc.,
- Dyeing & Tanning sites,
- Carpets, rugs, fabrics and plastics with flame retardants,
- Production of objects and furniture with glossy surfaces,
- Production of cleaning products,
- Photographic chemistry (laboratories, paper and film production, etc.),
- Production of electronic components,
- Production and application of pesticides and biocides,
- Production of cosmetics,
- Sites receiving sludge from wastewater treatment plants.

2. Environmental chemistry

The environmental chemistry of PFAS is particularly important and complicated. There is no group of pollutants with a more complex environmental chemistry than PFAS. In particular, there are **more than 9,000 PFAS compounds**, divided into **33 substance categories.** The best known are Perfluoroalkyl sulphonic acids (PFSAs), Perfluoroalkyl carboxylic acids (PFCAs), Perfluoroalkyl phosphates & their esters (**mPAP, diPAP, triPAP**), Fluorotelomer alcohols **(FTOHs),** etc. (and more than **29 other groups...).** Some of them, such as **PFOA** (Perfluorooctanoic Acid) and **PFOS** (Perfluorooctane Sulfonate) (see Fig. 1) are banned (and **prohibited in the EC and USA & Canada)** by the **Stockholm Convention as POPs** (Persistent Organic Pollutants). PFOA is carcinogenic. Commercial products mainly contain **mixtures.**

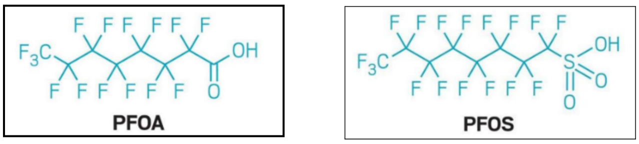


Fig. 1 : Structural formulae for PFOA & PFOS

The reason for the high water solubility associated with lipophilicity is based on the fact that **PFAS**:

- **Anionics** (e.g. sulphonates, sulphates, carboxylates and phosphates),
- **Cationics** (e.g. quaternary ammonium),
- **Amphoteric** (e.g. betaines and sulpho-betaines): base + acid
- **Non ionic** (e.g. polyethylene glycols, acrylamide oligomers).

It is very important to stress that poly-fluorinated PFAS that are not fully fluorinated (‘precursors’) can be converted by bio-transformation into persistent, fully fluorinated chemicals, per-fluorinated PFAS [87-94, 161, 168]. The complete microbiological degradation of PFAS has not yet been demonstrated.

The following schemes (2 - 4) show examples of the biotransformation of 6 :2 FTAB, 6 :2- & 8 :2 FTS and polyfluorinated alkylphosphates (PAP) in soils and groundwater to volatile fluorotelomer alcohols (FTOH), which then migrate into soil gas (vapor) and ambient air. FTOHs are then microbiologically transformed into stable per-fluorinated PFASs. For example, 6:2-FTOH is bio-transformed into PFHxA, PFPeA & PFBA and 8:2-FTOH into PFOA, PFHpA, PFHxA, PFPeA and PFBA (see Fig. below).

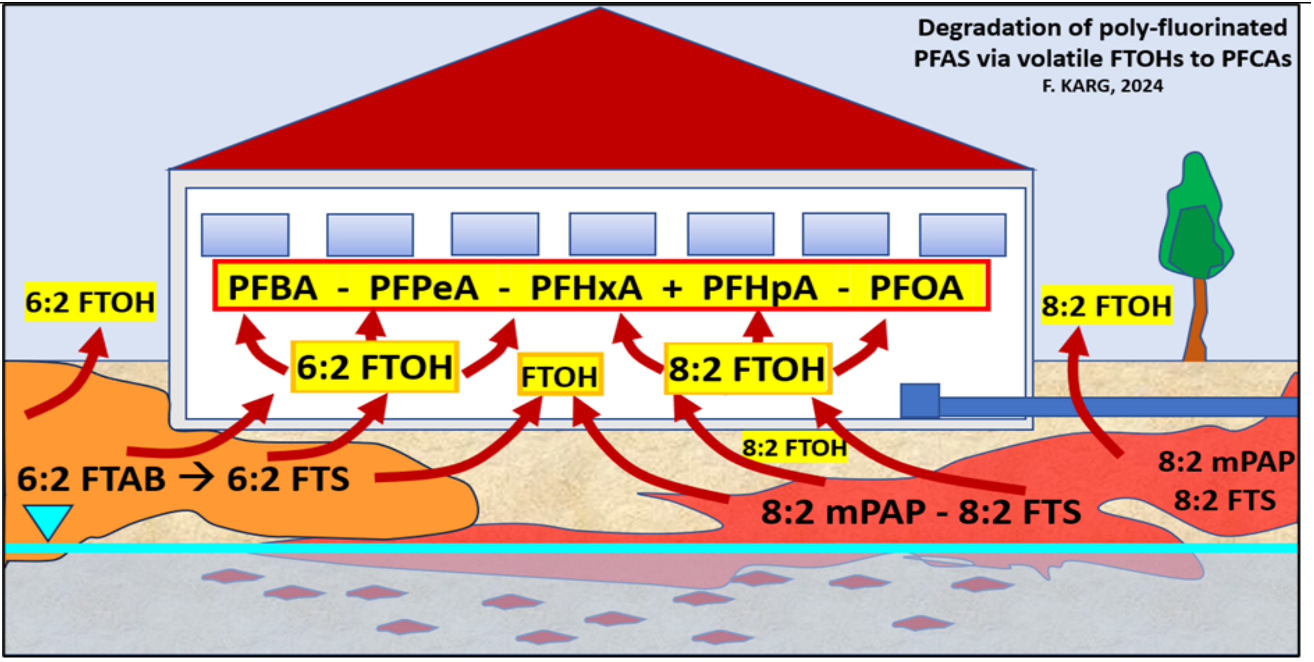


Fig. 2: Example of the biotransformation of 6 :2 FTAB, 6 :2 FTS, 8 :2 FTS and polyfluorinated alkyl phosphates (PAP) in soil and water to Fluorotelomer alcohols (FTOH) and per-fluorinated PFAS, e.g. to PFOA, PFHpA, PFHxA, PFPeA and PFBA (L. KOPF / HPC, 2017 and F. KARG, 2022 & 2024).

The following scheme shows an example of the biotransformation of 8: 2-FTOH ($F(CF_2)_8CH_2CH_2OH$) via metabolites to stable perfluorinated PFASs, such as PFPeA (Perfluoro-pentanonic acid), PFHxA (Perfluoro-hexanonic acid), PFHpA (Perfluoro-heptanonic acid), 2H-PFOA, 7:3 Acid and the carcinogen PFOA (Perfluoro-octanonic acid).

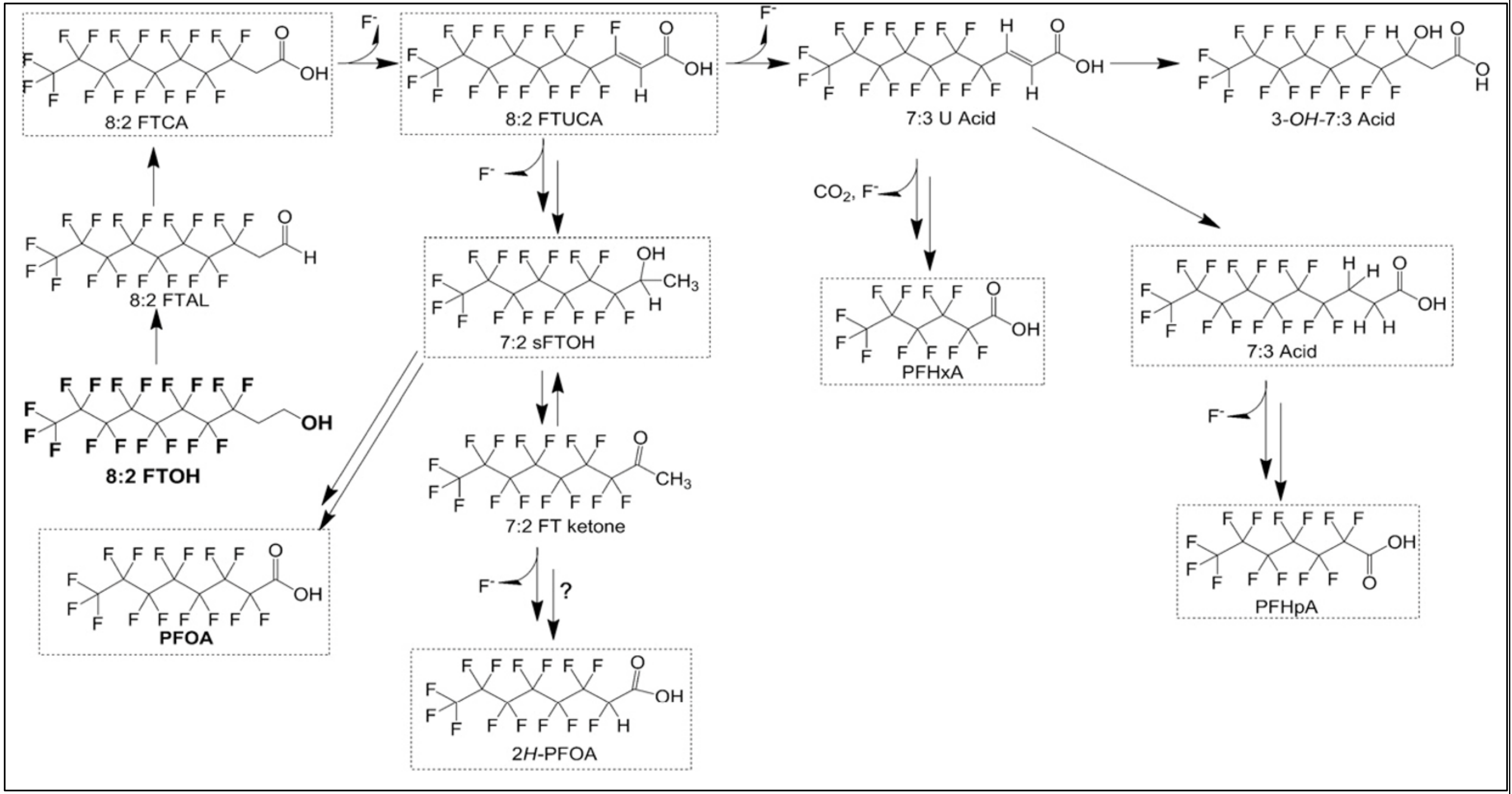


Fig. 3 : Exemple de biotransformation aérobique du 8:2 FTOH ($F(CF_2)_8CH_2CH_2OH$) dans les sols. Des flèches doubles indiquent la formation des substances perfluorés stables (Wang et al. 2009, modifié).

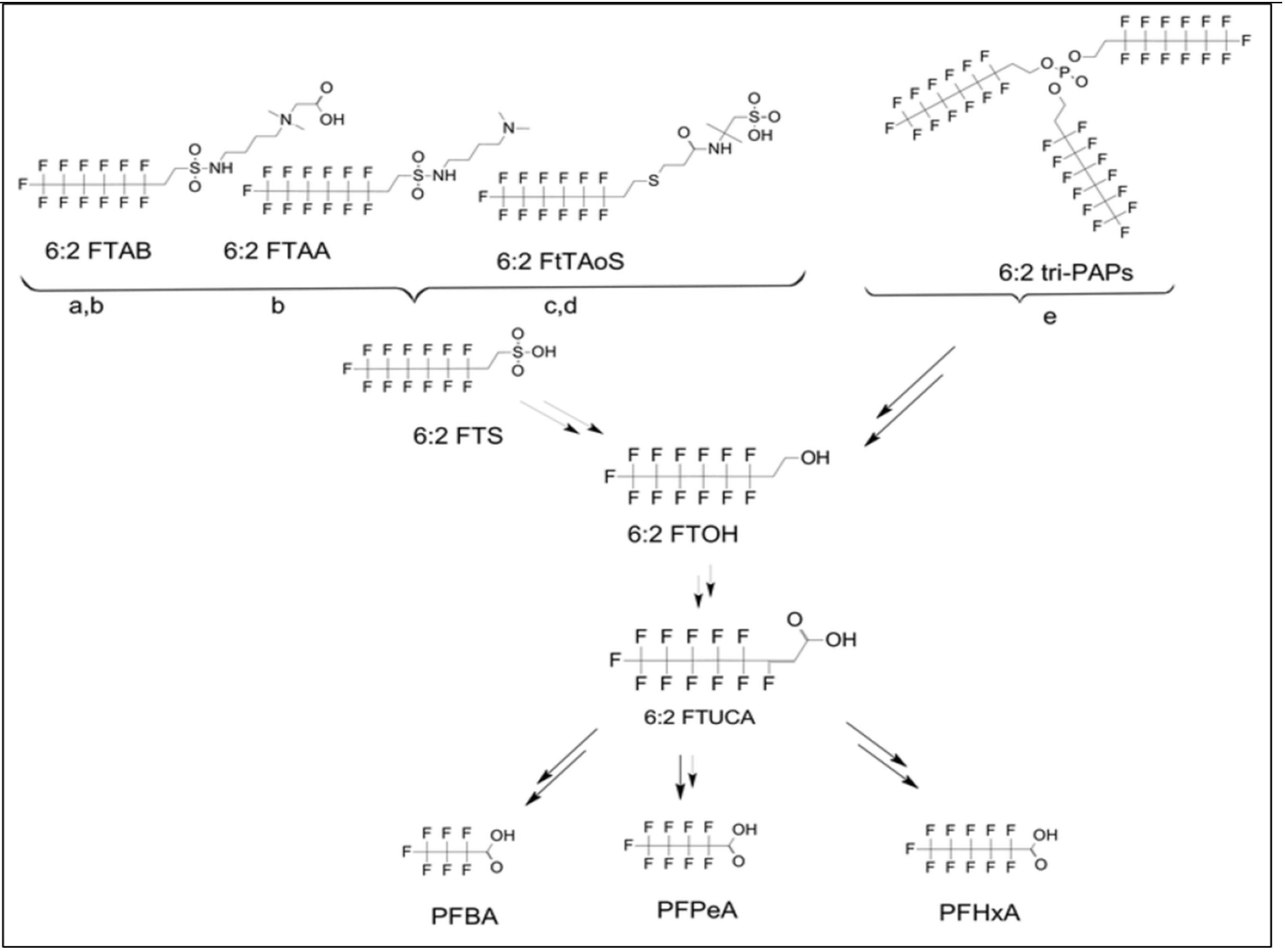


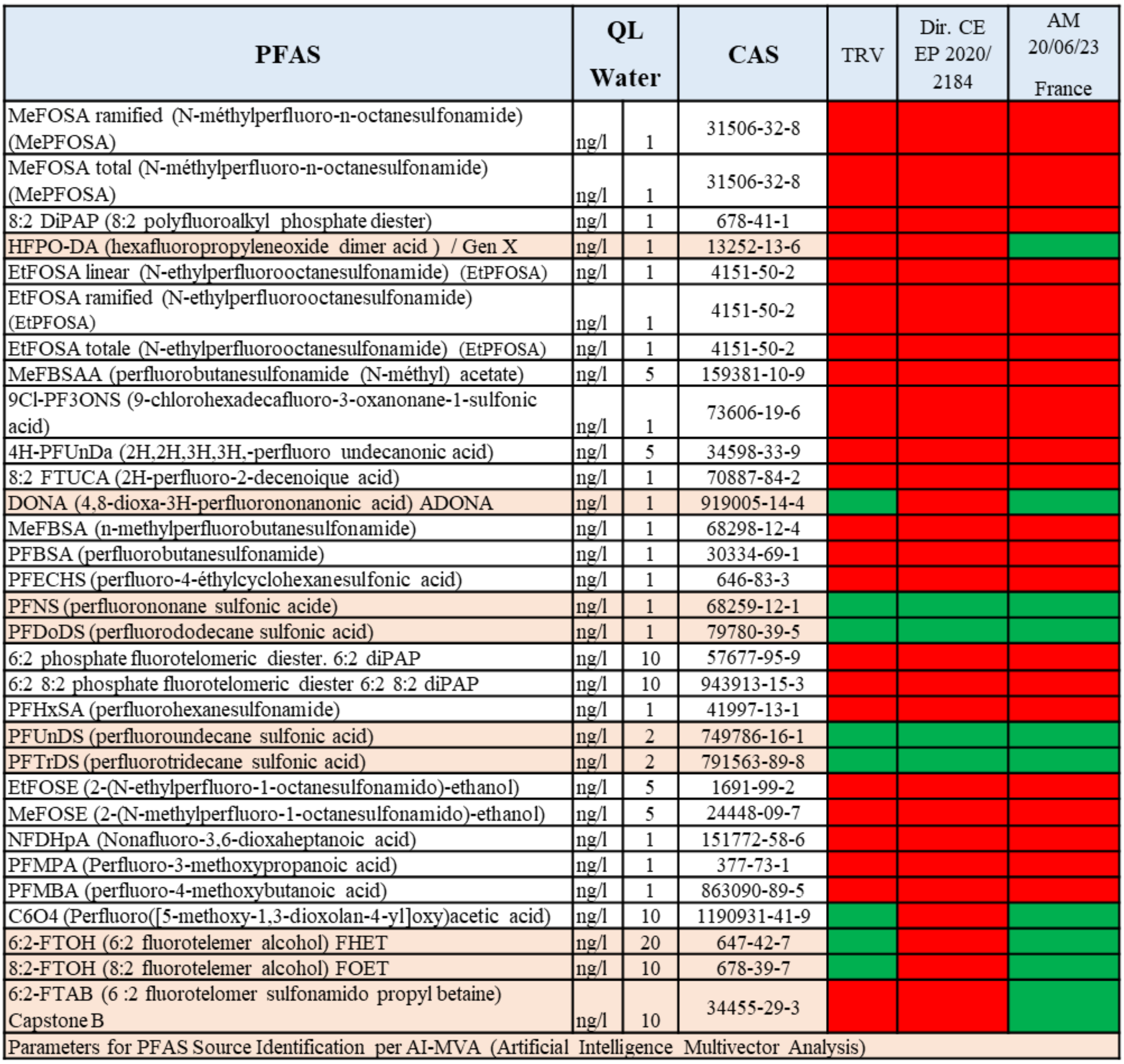
Fig. 4: Biotransformation scheme of polyfluorinated PFAS (Precursors): Example: 6 :2 FTAB and its degradation via 6 :2 FTS and 6 :2 FTOH to per-fluorinated PFAS PFBA, PFPeA and PFHxA (LaFond et al. 2024, D.M.J. Shaw et al. 2019 ,Ying Shi, 2018 and V. Mendeza et. al. 2022)

3. Toxicological Exposure Risk Quantification & Health Risk Assessments (TERQ & HRA)

As a general prerequisite, it is recommended that PFAS contamination diagnoses include at least the pollutants listed in the following tables:

PFAS	QL Water		CAS	TRV	Dir. CE EP 2020/ 2184	AM 20/06/23 France
PFBA (perfluorobutanonic acid)	ng/l	1	375-22-4	🟩	🟩	🟩
PFPeA (perfluoropentanonic acid)	ng/l	5	2706-90-3	🟩	🟩	🟩
PFHxA (perfluorohexanonic acid)	ng/l	1	307-24-4	🟩	🟩	🟩
PFHpA (perfluoroheptanonic acid)	ng/l	1	375-85-9	🟩	🟩	🟩
PFOA lineare (perfluorooctanonic acid)	ng/l	1	335-67-1	🟩	🟩	🟩
PFOA ramified (perfluorooctanonic acid)	ng/l	1	335-67-1	🟩	🟥	🟥
PFOA total (perfluorooctanonic acid)	ng/l	1	335-67-1	🟩	🟥	🟥
PFNA (perfluorononanonic acid)	ng/l	1	375-95-1	🟩	🟩	🟩
PFDA (perfluorodecanonic acid)	ng/l	1	335-76-2	🟩	🟩	🟩
PFUnDA (perfluoroundecanonic acid)	ng/l	1	2058-94-8	🟩	🟩	🟩
PFDoDA (perfluorododecanonic acid)	ng/l	2	307-55-1	🟩	🟩	🟩
PFTrDA (perfluorotridecanonic acid)	ng/l	1	72629-94-8	🟩	🟩	🟩
PFTeDA (perfluorotetradecanonic acid)	ng/l	1	376-06-7	🟩	🟥	🟩
PFHxDA (perfluorohexadecanonic acid)	ng/l	2	67905-19-5	🟩	🟥	🟩
PFODA (perfluorooctadecanonic acid)	ng/l	1	16517-11-6	🟩	🟥	🟩
PFBS (perfluorobutane sulfonic acid)	ng/l	1	375-73-5	🟩	🟩	🟥
PFPeS (perfluoropentane sulfonic acid)	ng/l	1	2706-91-4	🟩	🟩	🟥
PFHxS linear (perfluorohexane sulfonic acid)	ng/l	1	355-46-4	🟩	🟩	🟥
PFHxS ramified (perfluorohexane sulfonic acid)	ng/l	1	355-46-4	🟥	🟥	🟥
PFHxS total	ng/l	1	355-46-4	🟥	🟥	🟥
PFHpS (perfluoroheptane sulfonic acid)	ng/l	1	375-92-8	🟩	🟩	🟥
PFOS linear (perfluorooctane sulfonic acid)	ng/l	1	1763-23-1	🟩	🟩	🟥
PFOS ramified (perfluorooctane sulfonic acid)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFOS total (acide perfluorooctane sulfonic acid)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFDS (perfluorodecane sulfonic acid)	ng/l	1	335-77-3	🟩	🟩	🟥
4:2 FTS (4:2 fluorotelomer sulfonic acid) H4-PFOS	ng/l	1	757124-72-4	🟩	🟥	🟥
6:2 FTS (6:2 fluorotelomer sulfonic acid)	ng/l	1	27619-97-2	🟩	🟥	🟥
8:2 FTS (8:2 fluorotelomer sulfonic acid)	ng/l	1	39108-34-4	🟥	🟥	🟥
10:2 FTS (acide 10:2 fluorotelomer sulfonique)	ng/l	1	120226-60-0	🟥	🟥	🟥
MePFOSAA (N-methylperfluorooctane sulfonamide acetic)	ng/l	1	2355-31-9	🟥	🟥	🟥
EtFOSAA (acide N-ethylperfluorooctane sulfonamide aceticue)	ng/l	1	2991-50-6	🟥	🟥	🟥
PFOSA (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟩	🟥	🟥
PFOSA ramified (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
PFOSA total (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
MeFOSA linear (N-méthylperfluorooctanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥

Fig. 5a: Minimum recommended PFAS analysis parameters



PFAS	QL Water		CAS	TRV	Dir. CE EP 2020/ 2184	AM 20/06/23 France
MeFOSA ramified (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
MeFOSA total (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
8:2 DiPAP (8:2 polyfluoroalkyl phosphate diester)	ng/l	1	678-41-1	🟥	🟥	🟥
HFPO-DA (hexafluoropropyleneoxide dimer acid) / Gen X	ng/l	1	13252-13-6	🟥	🟥	🟩
EtFOSA linear (N-ethylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA ramified (N-ethylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA totale (N-ethylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
MeFBSAA (perfluorobutanesulfonamide (N-méthyl) acetate)	ng/l	5	159381-10-9	🟥	🟥	🟥
9Cl-PF3ONS (9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid)	ng/l	1	73606-19-6	🟥	🟥	🟥
4H-PFUnDa (2H,2H,3H,3H,-perfluoro undecanonic acid)	ng/l	5	34598-33-9	🟥	🟥	🟥
8:2 FTUCA (2H-perfluoro-2-decenoique acid)	ng/l	1	70887-84-2	🟥	🟥	🟥
DONA (4,8-dioxa-3H-perfluorononanonic acid) ADONA	ng/l	1	919005-14-4	🟩	🟥	🟩
MeFBSA (n-methylperfluorobutanesulfonamide)	ng/l	1	68298-12-4	🟥	🟥	🟥
PFBSA (perfluorobutanesulfonamide)	ng/l	1	30334-69-1	🟥	🟥	🟥
PFECHS (perfluoro-4-éthylcyclohexanesulfonic acid)	ng/l	1	646-83-3	🟥	🟥	🟥
PFNS (perfluorononane sulfonic acide)	ng/l	1	68259-12-1	🟩	🟩	🟩
PFDoDS (perfluorododecane sulfonic acid)	ng/l	1	79780-39-5	🟩	🟩	🟩
6:2 phosphate fluorotelomeric diester. 6:2 diPAP	ng/l	10	57677-95-9	🟥	🟥	🟥
6:2 8:2 phosphate fluorotelomeric diester 6:2 8:2 diPAP	ng/l	10	943913-15-3	🟥	🟥	🟥
PFHxSA (perfluorohexanesulfonamide)	ng/l	1	41997-13-1	🟥	🟥	🟥
PFUnDS (perfluoroundecane sulfonic acid)	ng/l	2	749786-16-1	🟩	🟩	🟩
PFTrDS (perfluorotridecane sulfonic acid)	ng/l	2	791563-89-8	🟩	🟩	🟩
EtFOSE (2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	1691-99-2	🟥	🟥	🟥
MeFOSE (2-(N-methylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	24448-09-7	🟥	🟥	🟥
NFDHpA (Nonafluoro-3,6-dioxaheptanoic acid)	ng/l	1	151772-58-6	🟥	🟥	🟥
PFMPA (Perfluoro-3-methoxypropanoic acid)	ng/l	1	377-73-1	🟥	🟥	🟥
PFMBA (perfluoro-4-methoxybutanoic acid)	ng/l	1	863090-89-5	🟥	🟥	🟥
C6O4 (Perfluoro([5-methoxy-1,3-dioxolan-4-yl]oxy)acetic acid)	ng/l	10	1190931-41-9	🟩	🟥	🟩
6:2-FTOH (6:2 fluorotelemer alcohol) FHET	ng/l	20	647-42-7	🟩	🟥	🟩
8:2-FTOH (8:2 fluorotelemer alcohol) FOET	ng/l	10	678-39-7	🟩	🟥	🟩
6:2-FTAB (6 :2 fluorotelomer sulfonamido propyl betaine) Capstone B	ng/l	10	34455-29-3	🟥	🟥	🟩
Parameters for PFAS Source Identification per AI-MVA (Artificial Intelligence Multivector Analysis)						

Fig. 5b: Minimum recommended PFAS analysis parameters

To present day, the analysis of the 20 individual PFAS of the European Directive 2020/2184 can be carried out, but it is not sufficient in all cases.

4. Toxicological Risk Assessment

For health risk assessment, toxicological data (TRVs: Toxicological Reference Values) must be sought and updated at international level on an almost weekly basis. The most recent TRVs are available mainly from the USA (EPA, etc.), ATSDR and EFSA. In 2017, ANSES also published TRVs for PFASs, but given the rapid progress of toxicological studies, most of these TRVs have already been exceeded.

In the case of FTOH present in soil, groundwater and soil gas, it is essential to carry also out investigations of FTOH in the ambient air inside buildings, especially in the case of sensitive use (ERP: Schools, Kindergardens, etc.) or residential buildings, on the basis of quantification thresholds (or at least detection thresholds), of the order of 4 - 8 ng/m3 to ensure a good basis that can be used for a TERQ-HRA: Toxicological Exposure Risk Quantification – Health Risk Assessment.

An initial simplified risk assessment approach is possible using existing limit values or Threshold Levels, such as those in Germany or Switzerland, etc., or those published by the European Community. Germany & Switzerland have limit values for drinking water, soil and groundwater.

The US-EPA considers that most exposure today comes from drinking water, outside polluted sites, due to the lack of monitoring and treatment of PFAS.

Under the European 'Water Framework' Directive (EU) 2013/39/EU (WFD), an Environmental Quality Standard (EQS-MA) of 0.65 ng/l for surface waters and 0.13 ng/l for marine waters (and EQS-MA: Maximum Allowable Concentrations) has been set for PFOS & derivatives (and other priority substances).

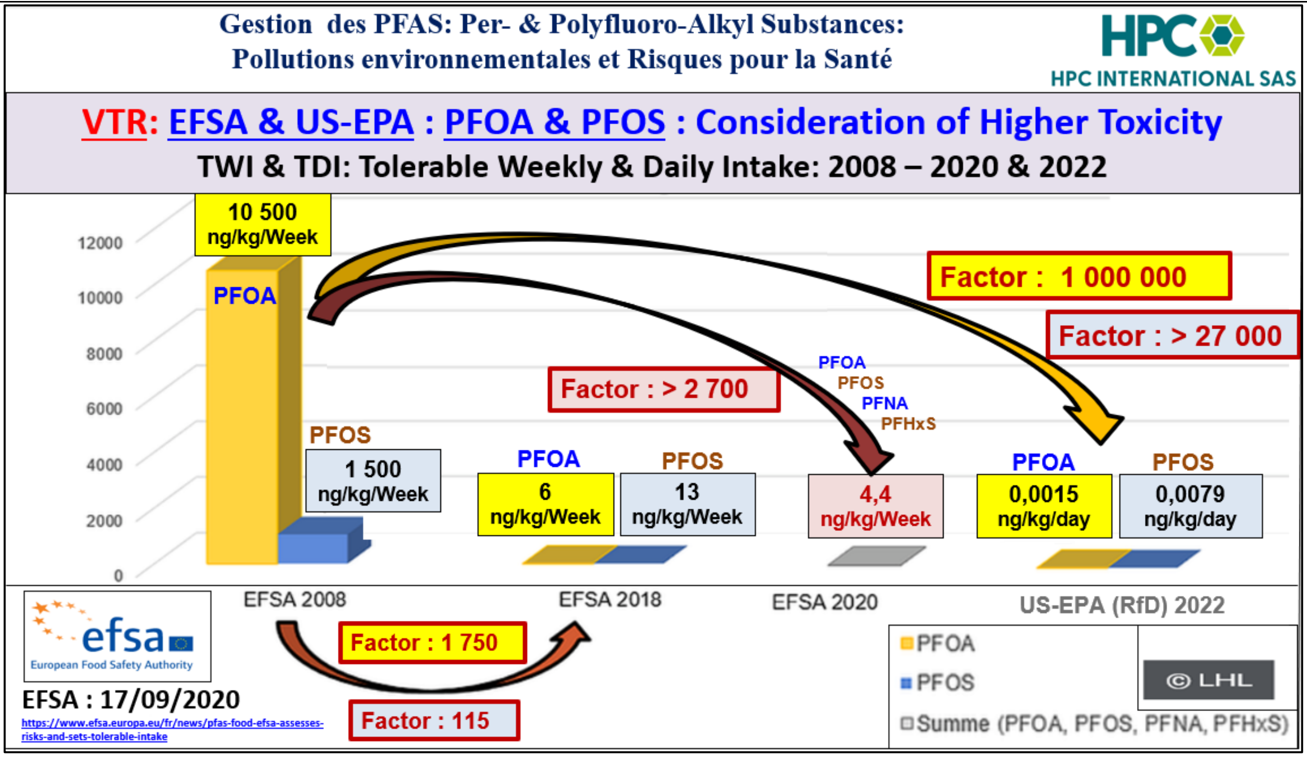
It is important to note that the simple application of generic and individual Limit Values as part of a simplified risk assessment does not consider specific exposure scenarios and exposure to mixtures ('Cocktails') of pollutants with, at the very least, consideration of pollutants risk additivities with the same toxicological targets and effects. Consequently, it is preferable to carry out TERQ - HRA which corresponds well, for ex. to the French Methodology for Management of Polluted Sites, according to the Environmental Ministry Guideline, dated from 19 April 2017.

Another important aspect is that only an TERQ - HRA) will make it possible to define Health Compliance Control Values, in the form of MACs (Maximum Acceptable Concentration) for maximally acceptable Individual Cancer Risk: ICR < 10E-5 or a Systemic Risk of < DTI: Daily Tolerable Intake Dose).

For Quantitative Health Risk Assessment (HRA), the basis is either the measurement of concentrations in exposure media, or the modelling of the transfer of pollutants from one compartment to another (e.g. from pollutants in groundwater or soil to soil gas and ambient air or to feed and food).

An important stage in the TERQ-HRA is the appropriate choice of TRVs (Toxicological Reference Values), as they change rapidly. For example, the 2017 French ANSES PFAS guide includes certain TRVs for PFASs, but in view of the many TRV publications to date, these values are partially out of date, and in particular much more restrictive to date. A Tolerable Weekly Intake (TWI) of 4.4 ng/kg/week (or Tolerable Daily Intake (TDI) of 0.63 ng/kg/day for PFAS: PFOA, PFOS, PFNA & PFHxS) was published by EFSA on 17 September 2020. In 2020, toxicity equivalence factors in relation to PFOA were also published by W. Bil et al. in the form of RPF: Relative Potency Factors.

The choice of TRVs is an important stage in the TERQ-HRA, as they evolve rapidly with regard to PFAS. Today, the published TRVs have become much more restrictive, as shown by the evolution of the TRVs published by EFSA since 2015, see Fig. 6.



Gestion des PFAS: Per- & Polyfluoro-Alkyl Substances:
Pollutions environnementales et Risques pour la Santé

HPC INTERNATIONAL SAS

VTR: EFSA & US-EPA : PFOA & PFOS : Consideration of Higher Toxicity

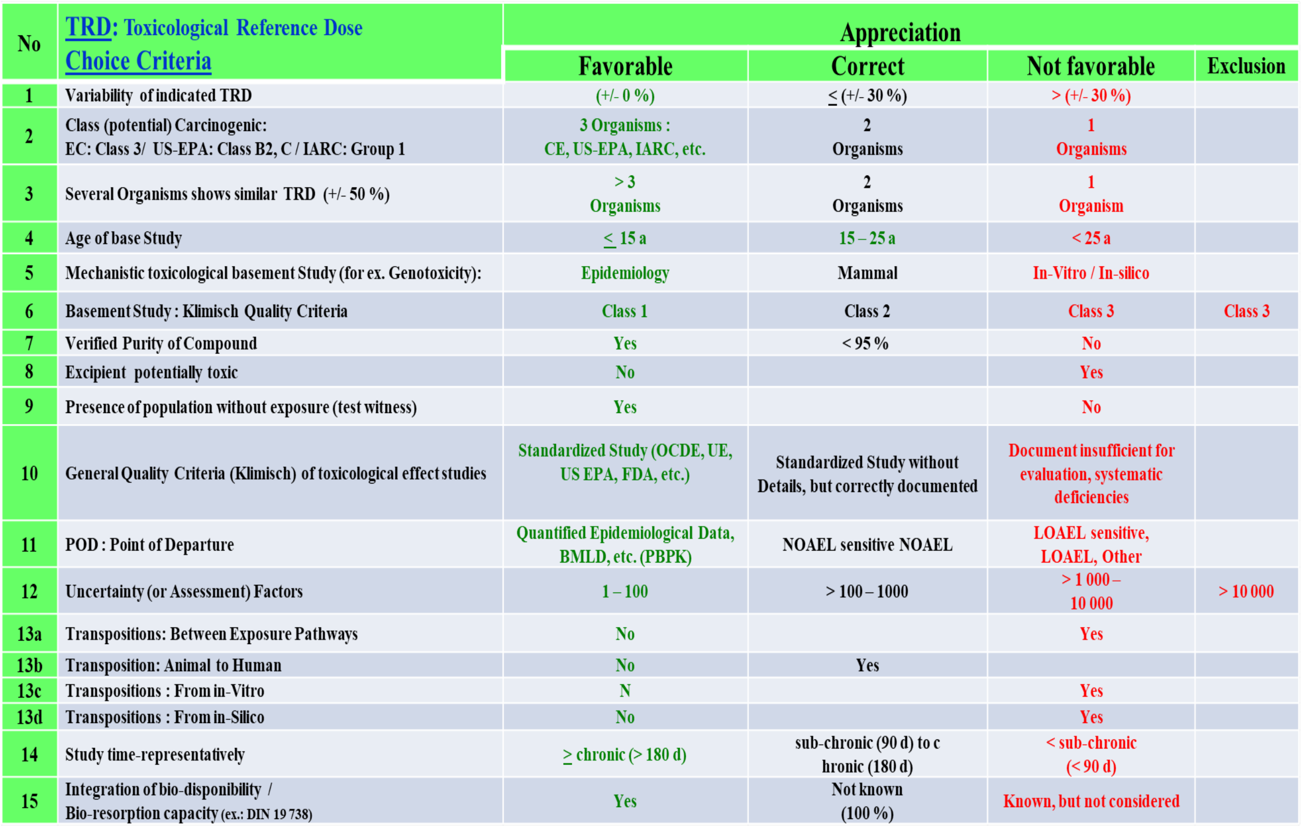
TWI & TDI: Tolerable Weekly & Daily Intake: 2008 – 2020 & 2022

EFSA : 17/09/2020

https://www.efsa.europa.eu/fr/news/pfas-food-efsa-assesses-risks-and-sets-tolerable-intake

Fig. 6: Trends in TRVs for PFOA & PFOS and PFNA & PFHxA, based on EFSA TWI & TDI (2020) and US-EPA RfD (2022), (F. KARG 2023a & b)

In order to ensure the correct choice of TRVs for PFAS, it is recommended that scientific selection criteria be applied rather than national criteria. The following figure shows the selection criteria for the applicable TRVs, in order to take into account, the best toxicological knowledge concerning the dose-effect relationships of PFASs.



No	TRD: Toxicological Reference Dose Choice Criteria	Appreciation			
		Favorable	Correct	Not favorable	Exclusion
1	Variability of indicated TRD	(+/- 0 %)	≤ (+/- 30 %)	> (+/- 30 %)	
2	Class (potential) Carcinogenic: EC: Class 3/ US-EPA: Class B2, C / IARC: Group 1	3 Organisms : CE, US-EPA, IARC, etc.	2 Organisms	1 Organisms	
3	Several Organisms shows similar TRD (+/- 50 %)	> 3 Organisms	2 Organisms	1 Organism	
4	Age of base Study	≤ 15 a	15 – 25 a	< 25 a	
5	Mechanistic toxicological basement Study (for ex. Genotoxicity):	Epidemiology	Mammal	In-Vitro / In-silico	
6	Basement Study : Klimisch Quality Criteria	Class 1	Class 2	Class 3	Class 3
7	Verified Purity of Compound	Yes	< 95 %	No	
8	Excipient potentially toxic	No		Yes	
9	Presence of population without exposure (test witness)	Yes		No	
10	General Quality Criteria (Klimisch) of toxicological effect studies	Standardized Study (OCDE, UE, US EPA, FDA, etc.)	Standardized Study without Details, but correctly documented	Document insufficient for evaluation, systematic deficiencies	
11	POD : Point of Departure	Quantified Epidemiological Data, BMLD, etc. (PBPK)	NOAEL sensitive NOAEL	LOAEL sensitive, LOAEL, Other	
12	Uncertainty (or Assessment) Factors	1 – 100	> 100 – 1000	> 1 000 – 10 000	> 10 000
13a	Transpositions: Between Exposure Pathways	No		Yes	
13b	Transposition: Animal to Human	No	Yes		
13c	Transpositions : From in-Vitro	N		Yes	
13d	Transpositions : From in-Silico	No		Yes	
14	Study time-representatively	≥ chronic (> 180 d)	sub-chronic (90 d) to c hronic (180 d)	< sub-chronic (< 90 d)	
15	Integration of bio-disponibility / Bio-resorption capacity (ex.: DIN 19 738)	Yes	Not known (100 %)	Known, but not considered	

Fig. 7: Criteria for selecting TRVs (F. KARG 2022)

On the basis of these selection criteria, it is possible to define, for example, the TRVs shown in the following figure. It is important to bear in mind that the administrations of certain US states are very advanced in toxicological research and the publication of TRVs for PFAS, due to their strong presence of chemical and petroleum industries (with the strong historical uses of AFFF) or the strong presence of large industrial landfill sites (and the associated environmental pollution). These include the states of Texas, Michigan and New Jersey. These TRVs often form the basis of the US-EPA's TRV publications for PFAS.

Substance	Cancerogene / not cancerogene	Chronic toxicological value			Species	Sigle	Security Factor	Organization
		Exposure path	Target organ	Value				
PFBA	NC	oral	Hepatic	1 µg/kg/d	Rate	RFD	NOAEL / 2400	TCEQ 2023
		inhalation	Hepatic	3,5 µg/m³	Rate	RFC	From oral value	TCEQ 2023
PFPeA	NC	oral	Hepatic	0,5 µg/kg/d	Rate	RFD	Same than PFHxS LOAEL/(263*300)	TCEQ 2023
PFHxA	NC	oral	Hepatic	0,5 µg/kg/d	Rate	RFD	Same than PFHxS LOAEL/(263*300)	TCEQ 2023
PFHpA	NC	oral	Hepatic	25 ng/kg/d	Rate	DJT	Extrapolation of DJT of Health Canada	ANSES 2017
PFOA	NC	oral	Hematologic	0,86 ng/kg/d	Rate	TDI	BMDL 5	UBA 2020 BFR & EFSA 2018
			Hepatic, Mammar, Hematologic	12 ng/kg/d	Mice	RFD	LOAEL (81*100)	TCEQ 2016
		inhalation	Hepatic	4,1 ng/m³	Rate	RFC	NOAEL / (81*3000)	TCEQ 2016
	C	oral	Testicular tumors	2,52 (mg/kg/d)⁻¹	Epidemio	SF	-	New Jersey 2017
PFNA	NC	oral	Hematologic	2,5 ng/kg/d	Mouse	RFD	NOAEL / 300	EPA IRIS 2019New Hampsire DES 2019
		inhalation	Lung, respiratory system	28 ng/m³	Rate	RFC	NOAEL / (81*30 000)	EPA IRIS 2019 TCEQ 2023
PFDA	NC	oral	Hematologic	15 ng/kg/d	Rate	RFD	NOAEL / (81*1000)	TCEQ 2016
		inhalation		53 ng/m³	Rate	RFC	From oral value	TCEQ 2016
PFBS	NC	oral	Hematologic and renal	1,4 µg/kg/d	Rate	RFD	NOAEL / (142*300)	TCEQ 2016
		inhalation		4,9 µg/m³	Rate	RFC	From oral value	TCEQ 2016
PFHxS	NC	oral	Hematologic and thyroïdale	3,8 µg/kg/d	Rate	RFD	LOAEL / (263*300)	TCEQ 2016
		inhalation	3,8 µg/kg/d	13 ng/m³	Rate	RFC	From oral value	TCEQ 2016
PFHpS	NC	oral	Hepatic	0,43 ng/kg/d	Rate	TDI	Potency Factor : 0,6-2	UBA 2020, EFSA 2018, BFR 2018
PFOS	NC	oral	Thyroïdale, neurological and fœtal development	1,86 ng/kg/d	Monkey	TDI	NOAEL	UBA 2020, EFSA 2018, BFR 2018
		inhalation		81 ng/m³	Rate	RFC	From oral value (23 ng/kg/d)	TCEQ 2016
PFOSA	NC	oral	Mammary glands	12 ng/kg/d	Mice	RFD	Same than PFOA NOAEL/(81*300)	TCEQ 2016
		inhalation		4,1 ng/m³	Rate	RFC	Same than PFOA NOAEL(81*300)	TCEQ 2016

Fig. 8: Choice of certain TRVs according to the criteria in Fig. 7 (F. KARG 2022) :

ANSES:	Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail (2017)
ATSDR:	Agency for Toxic Substances and Disease Registry
EFSA:	European Food and Safety Authority
IRIS :	Integrated Risk Information of Substances (U.S. - EPA)
UBA :	Umweltbundesamt (Germany)
BfR:	Bundesinstitut für Risikobewertung (Germany)
OEHHA :	Office of Environmental Health Hazard Assessment
WHO:	World Health Organization
RIVM :	Netherlands Environmental & Health Institute
MDHHS:	Michigan Department of Health and Human Services, Division of Environmental Health
TCEQ:	Texas Commission on Environmental Quality

NJ-DWQIHES: New Jersey Drinking Water Quality Institute Health Effects Subcommittee
Bil et al. 2020 : Toxicological Equivalence Factors on PFOA RfD

The VTRs presented in figure 7 are taken from reports written by national and international institutions. In the scientific literature there are Points of Departure (PoD) and more recent or more specific TRVs.

A complementary stage in the TERQ - HRA is the definition of health compliance control values, in the form of MACs (Maximum Acceptable Concentrations), incorporating an additivity of the risks of pollutants concerning the same targets and toxicological effects, for maximally acceptable Excess Individual Risks (of cancer): ERI < 10E-5 or a Systemic Risk Quotient of QR < 1 (= EDI / TDI: Daily Exposure Dose over Tolerable Daily Dose). MACs are commonly used in the form of Health Monitoring Values, in order to verify or co-elaborate the objectives of corrective measures, or even depollution objectives. Management measures, such as pollution clean-up, are based in France on a Management Plan, a definition of the Source Zones of concentrated pollution and then a Cost-Benefit Assessment of the different management and treatment methods and technologies. The **MAC Values** could be used also as **SS-RG: Site Specific Remediation Goals** for **Remediation Planning and Remediation Cost Estimates.**

A pragmatic description of Health Risk Assessments (HRA) is given in the SFSE's Guide Gestion des PFAS : Société Francophone de Santé et Environnement, Chapter - Fiche 10 (174: Karg, F., Heilier, J.-F., Ronga-Pezeret, S., Rousselle, C., Bouhoulle, E.: 2023).

The following steps should be followed when assessing daily exposure doses and the associated risks:

A. Identify applicable scenarios and exposure pathways

The following exposure pathways may exist on a site:

Inhalation :

· pollutants in gaseous form,
· dust on which the pollutant is adsorbed,
· contaminated water vapour when taking a shower or bath.

Ingestion :

· soil (land outside a building) and dust (land inside a building).
· self-produced foods (fruit, vegetables, etc.),
· contaminated drinking water,
· water when taking a shower or bath (including surface water).

Skin absorption:

· soil and dust,
of pollutant through contaminated water when showering or bathing,
· when bathing in surface water (pond, river, pumped groundwater, sea water, etc.).

In principle, the exposure scenarios and associated exposure routes should be identified using a conceptual diagram (see Fig. 10a & b), showing the sources of pollution, the pollutant transfer routes and the targets concerned (adults, children, etc.).

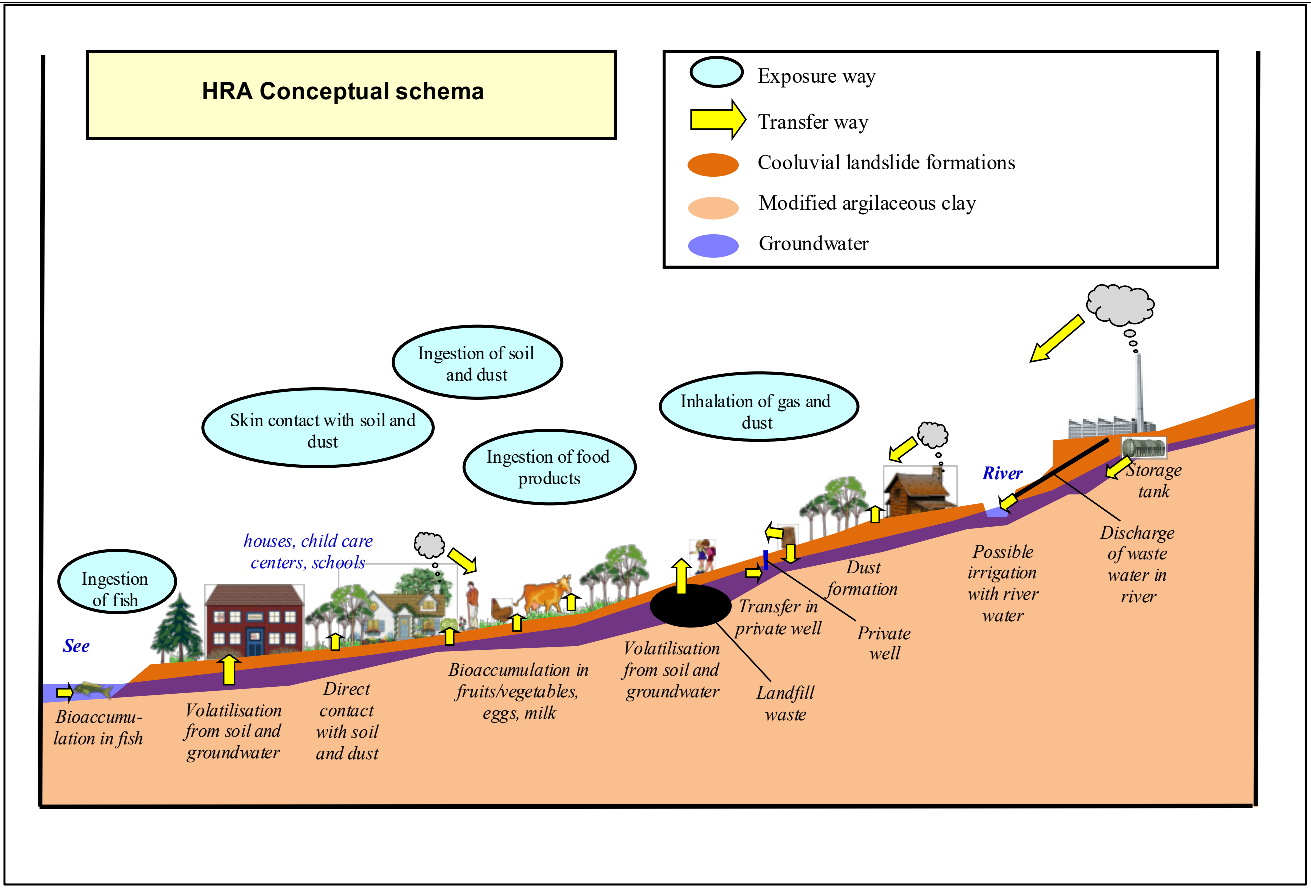


Fig. 10a: Example of a global conceptual scheme, to clearly visualize the applicable exposure routes per exposure scenario (F. Karg & L. Robin-Vigneron 2023a).

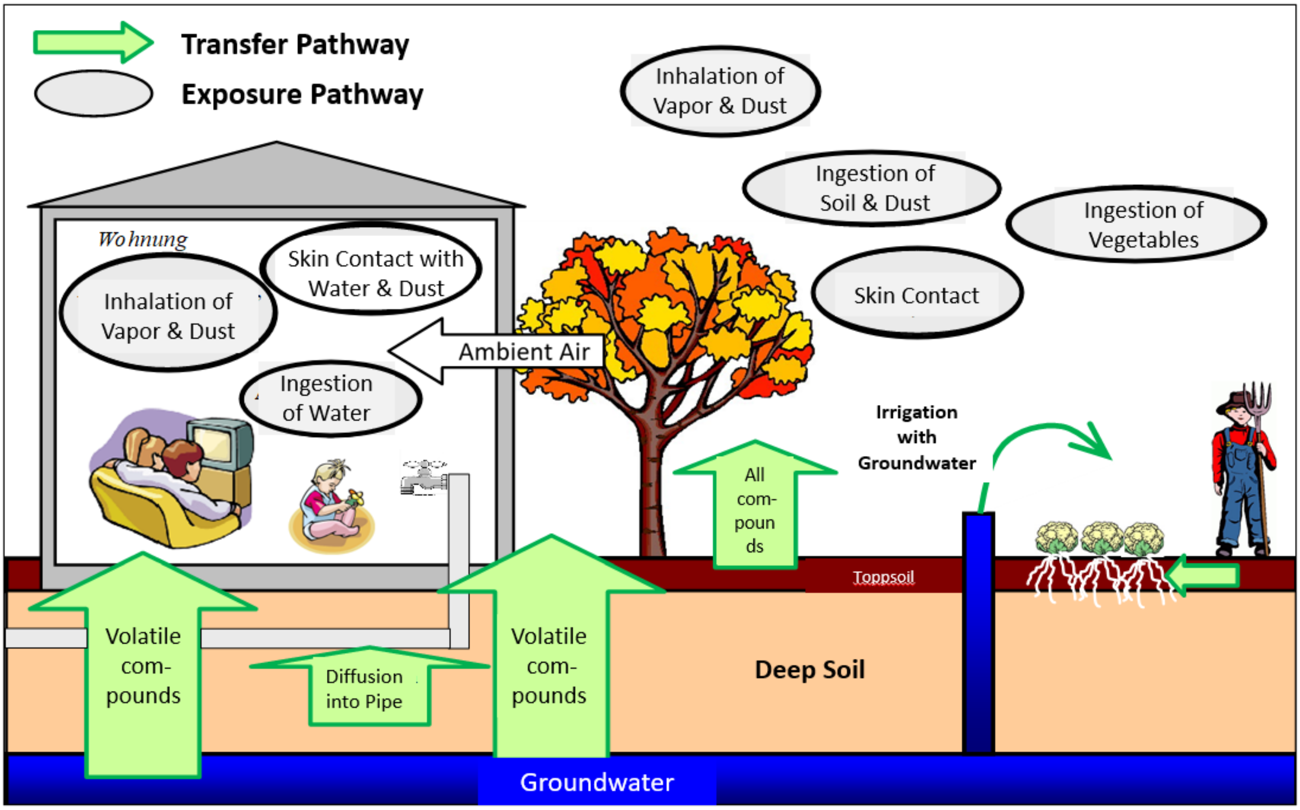


Fig. 10b: Example of a detailed conceptual scheme, to clearly visualize the applicable exposure routes per exposure scenario (F. Karg & L. Robin-Vigneron 2023a).

Particular attention should be paid to volatile PFAS, e.g. Fluorotelomer alcohols (FTOH), especially in case of 6:2-FTOH and 8:2-FTOH inhalation. The Table 1 shows the exposure pathways by site use and exposure scenario.

Table 1: Exposure scenarios and associated exposure pathways

Table 1: Exposure scenarios and associated exposure pathways/ Sources of exposure		Industry and Com-merce	Parks & Hobby / Activities sports	Kinder-gartens	Collective residential and nursery & Schools	Agriculture and food production	Residential with individual gardens
Inhala-tion	Breathing vapors or gases: Ground gases→ Ambient air (indoors & outdoors)	Yes	Yes	Yes	Yes	Yes	Yes
	Dust breathing	Yes	Yes	Yes	Yes	Yes	Yes
	Breathing in contaminated steam during a shower or hot bath	(Yes)	(Yes)	No	Yes	No	Yes
Oral	Passive (children & adults) or active (children) ingestion of contaminated soil	Yes	Yes	Yes	Yes	Yes	Yes
	Self-produced foods	No	No	No	No	Yes	Yes
	Ingestion of contaminated water	(Yes)	(Yes)	No	Yes	Yes	Yes

Table 1: Exposure scenarios and associated exposure pathways							
Table 1: Exposure scenarios and associated exposure pathways/ Sources of exposure		Industry and Com-merce	Parks & Hobby / Activities sports	Kinder-gartens	Collective residential and nursery & Schools	Agriculture and food production	Residential with individual gardens
Skin	Direct contact with polluted soil	Yes	Yes	Yes	Yes	Yes	Yes
	Skin contact: shower or bath	(Yes)	(Yes)	No	(J)	No	Yes
	Skin contact: bathing in contaminated surface water, sea water or pumped groundwater	No	Yes	No	(No)	(No)	(Yes)

(*) : for example in the case of drinking water pipes buried in contaminated subsoil

<u>Quantifying Daily Exposure Doses (DJE)</u>

Daily exposure doses - **DED_{ing}** (by mouth), **DED_{inh}** (respiratory), **DED_{cut}** (dermal) are all expressed in mg of pollutant / kg of body weight / day [mg ● kg^{-1} ● day^{1}] and depend:

- **<u>pollutant concentrations in exposure media</u>** (e.g. in mg/kg or µg/l in food or drinking water or in mg/kg or µg/l in dust or water likely to cause skin contact or in µg/m3 for ambient air),
  Cm = Pollutant concentration in the exposure medium: Csoil [mg/kg], Cwater [mg/l], Cfood [mg/kg]
  Ca = Pollutant concentration in air [mg/m^3] indoor and/or outdoor.
  Cs = Pollutant concentration in soil [mg/kg] or in water (mg/l)

Two main approaches can be applied to determine pollutant concentrations in exposure media: direct measurements (sampling and analysis) and modelling by simulating pollutant transfers to exposure media.

Modelling of pollutant transfers between media (e.g. from groundwater or soil or to soil gas &ambient air or to feed & food) is possible and can be calibrated using analyses of real samples (recommended, if possible).

By taking into account the concentrations of pollutants in soils, soil gas (vapor), ambient air, groundwater and surface water, it is possible to apply, for chronic exposure (longer than 6 months) only, average concentrations taking into account the measured natural attenuation.

This natural attenuation of PFAS degradation concerns only the biotransformation of poly-fluorinated PFAS, but not per-fluorinated PFAS (see e.g. Fig. 2 - 4).

- **<u>space-time budgets</u>** (presence of people exposed in the polluted environment, taking into account the number of hours per day, the number of days per year and the number of years),
  Ex = Total exposure per adult or child [a]
  Ve = Lifetime years per adult or child [a]. In the case of exposure to substances with a limit value : Ve = Ex [a]
  Fexa = Annual exposure frequency [year/365 days]
  Fexj = Daily exposure frequency [hrs/24 hrs]

- **quantity** of food or drinking water ingested (in kg/d) and/or the volume of air inhaled per day (in m^3/d) and/or the quantity of soil or water in contact with the skin (e.g. in g/cm2 of skin surface),

Q_{ing} = Quantity ingested of soil and/or food [kg/d] and/or water [l/d], distinct between adults ($Q_{inh}a$) and children ($Q_{inh}e$)
Q_{inh} = Quantity of air inhaled [m^3/d], distinct between adults ($Q_{inh}a$) and children ($Q_{inh}e$)
Fa = Absorption factor (by bioresorption) of the pollutant (failing which: 100 % = [1])
Facut = Absorption factor for a pollutant (failing this: 100% = [1]) or absorption rate [m/h] for the cutaneous pathway. m/h] for the cutaneous pathway
Fsp = Fraction of soil in dust (if failing: 100 % = [1])
Spex = Surface area of exposed skin, distinct between adults and children [m²]
Qsp = Amount of soil (or dust) on the skin [kg/m²]

- **body weight.**

P(a) = Adult body weight [70 kg]
P(e) = A child's body weight [15 kg]

the formulae for quantifying daily exposure doses are as follows :

Oral exposure by ingestion :

$DJE_{ing} = Cm \bullet Q_{ing} \bullet P^{-1} \bullet Fa \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$

Inhalation exposure * :

$DJE_{inh} = Ca \bullet Q_{inh} \bullet P^{-1} \bullet Fa \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$

* Exposure via outdoor ambient air can be assessed separately from exposure via indoor ambient air.

Exposure through skin contact (soil, dust, water) :

$DJE_{cut} = Cs \bullet Fsp \bullet Q_{ing} \bullet P^{-1} \bullet Fa_{cut} \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$

The applicable parameters should be justified. Default values from 'Black-Box' type risk assessment software should be avoid, unless they can be transparently justified for the exposure scenario in question.

B. Once the appropriate TRVs have been selected, quantitative risk assessments must be carried out for :

I : Effects without a dose threshold:

- In general, these are genotoxic effects (carcinogenic, mutagenic and teratogenic), with the exception of epigenetic cancer effects.
- In this case, the Daily Exposure Doses (DED) are multiplied by the TRV, in the form of Unit Cancer Risk (UCR) or Slope Factor (SF) or Unit Risk (UR), expressed for example in [$(mg/kg/j)^{-1}$], :

UCR [$(mg/kg/j)^{-1}$]● DED (mg/kg/j) = ICR (-) : **Individual Cancer Risk**

- **The ICR must be less than « 10^{-5} », if not, the risk is considered unacceptable.**

II : Effects with a dose threshold:

- These are systemic toxicological effects (neurotoxicity, hepatotoxicity, nephrotoxicity, etc.).
- In this case, the Daily Exposure Doses (DED) are divided by the TRV, in the form of a TDI (Tolerable Daily Intake), expressed e.g. in [mg/kg/d], i.e.:

DED (mg/kg/j) / TDI (mg/kg/j) = RQ (Risk Quotient)

- **The RQ must remain less than '1', otherwise the risk is considered unacceptable.**

Combination effects:

In general, the effects of mixing pollutants (or 'Combined Exposure to multiple Chemicals') have been considered since 2009 by the IPCS & WHO etc. via an additivity of exposure doses if the toxicological effects are similar or the same. The exceptions are:

- synergies (interaction) that show greater toxicological effects than the additivity of doses, or,
- antagonisms (interaction) which cause less toxicological effects than the additivity of doses.

According to the IPCS & WHO 2009 etc., a distinction must be made between :

A. **Aggregate exposure** to individual pollutants via all exposure pathways,
B. **Cumulative Exposure,** which assesses the combined risk of several pollutants**.**

When assessing cumulative exposure, pollutants with the same toxicological mechanisms (or target organs) need to be identified. These groups of pollutants are known as 'MOAs': Common Toxic Mode of Action.

The addition of exposure doses is taken into account for each MOA group showing the same toxicological mechanisms (or target organs), e.g. via the following application:

- **Risk Quotient: RQ = Exposition 1/TDI+ Exposition 2/TDI + ….**
- **Individual Cancer Risk: ICR = Exposition 1 ● ICR + Exposition 2 ● ICR+ ….**

This application is simplified, as in the case of the Toxicity Equivalence Factors for Dioxins (PCDD/F) and Dioxin-like PCBs, PAHs and also by 'Potency-Corrections' for PFAS, e.g. via RPF: Relative Potency Factors.

The toxic equivalence approach applies to mixtures whose effects are additive. In particular, it is described to interpret the effect of mixing certain organochlorines (chlorodibenzo-p-dioxins, chloro-dibenzofurans and polychlorobiphenyls) that share a common mode of action mediated by binding to a specific receptor, the AhR receptor (Guyton et al. 2018).
As each congener does not have the same efficacy, they are classified using **Relative Potency Factors (RPF)** compared with a reference congener. This congener is called an index compound. It is, for example, the most toxic or the one whose action is best documented. For dioxins and furans, the Seveso dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin) is used as a reference with a factor of 1, and the toxicity factor is called the Toxic Equivalency Factor (TEF).
However, the use of RPF is subject to strict conditions:

1. In accordance with the definition given above, the compounds must share the same mode of action ;

2. The critical effect identified for the reference compound must also be identified for the other compounds. In other words, an index compound exhibiting a critical neurotoxic effect cannot be used as a reference for another compound whose toxicity is mainly expressed at renal level, for example;

3. Ideally, compounds should have dose-response characteristics of the same efficacy, but obviously differ in potency. In addition, the dose-effect curves should be congruent, i.e. they should not cross. These conditions are necessary for the comparison of Benchmark doses (BMD) for the same level of response. (*Benchmark Response* : BMR).

RIVM researchers (Bil, 2021; Zeilmaker, 2018) propose an RPF approach applied to the oral toxicity of 14 PFAS and two precursors (6:2 FTOH and 8:2 FTOH). They select PFOA (perfluoro-octanoic acid [335-67-1]) as the index compound. Along with PFOS (perfluoro octane sulphonic acid [1763-23-1]), PFOA is one of the most widely studied PFASs. Among the toxic effects attributed to PFOA (but also to PFOS), they identified hepatic hypertrophy as the critical effect.

The RPF is established on the basis of the ratio between the BMD (Benchmark Dosis) of PFOA and the BMD of the congener of interest (equation 1).

Equation 1:

$$RPF_i = \frac{BMD_{PFOA}}{BMD_i}$$

BMD corresponds to a BMR equivalent to a 5% increase in liver weight (absolute and relative) based on continuous data, or to a 10% excess risk of hepatic hypertrophy. The latter expression of risk is based on dichotomized data. The excess risk is adjusted for incidence rates for the same effect. The approach of Zeilmaker and Bil (Bil, 2021; Zeilmaker, 2018) leads to the RPF proposal summarized in Table 2.

Table 2: RPF according to Bil et al, 2021.

Congener	CAS number	RPF
Sulphonic acids		
PFBS	375-73-5	0,001
PFPeS	2706-91-4	0,001 ≤ RPF ≤ 0,6
PFHxS	355-46-4	0,6
PFHpS	375-92-8	0,6 ≤ RPF ≤ 2
PFOS	1763-23-1	2
PFDS	335-77-3	2
Carboxylic acids		
PFBA	375-22-4	0,05
PFPeA	2706-90-3	0,01 ≤ RPF ≤ 0,05
PFHxA	307-24-4	0,01
PFHpA	375-85-9	0,01 ≤ RPF ≤ 1
PFOA	335-67-1	1
PFNA	375-95-1	10
PFDA	335-76-2	4 ≤ RPF ≤ 10
PFUnDA	2058-94-8	4
Sulphonic acids		
PFTrDA	72629-94-8	3
PFDoDA	307-55-1	0,3 ≤ RPF ≤ 3
PFTeDA	376-06-7	0,3
PFHxDA	67905-19-5	0,02
PFODA	16517-11-6	0,02
Carboxylic acid ethers		
HFPO-DA	13252-13-6	0,06
ADONA	919005-14-4	0,03
Telomeric alcohols		
6:2 FTOH	647-42-7	0,02
8:2 FTOH	678-39-7	0,04

The application of RPFs by Zeilmaker (2018) and Bil (2021) in risk assessment is clearly contested by Rietjens et al. (2022). They support the use of RPFs in QSRAs but question the robustness of those calculated by Bil (2021).

Rietjens et al and Bil disagree about the selection of data and the impact of the mode of exposure of PFAS in the rodent population. Bil et al (2022) reject these criticisms, pointing out that numerically the values do not differ significantly by modifying the dataset according to Rietjens' recommendations.

Goodrum et al. (2021) also criticise Bil and Zeilmaker's approach, pointing out the differences in the mode of action of short-chain PFASs compared with those with long chains (C>8). Long-chain PFASs are able to bind to a greater number of nuclear receptors (between 6 and 16) than short-chain PFASs, which are limited to two receptors. For this reason, Goodrum et al. dispute the existence of similar dose-response relationships.

Consequently, the application of RPFs is not recommended (in 2024).

The greatest unknown in the effects of mixtures with PFAS concerns the large proportion of poly-fluorinated PFAS. It is recommended that PFAS analyses (28 - 70 molecules, see also the French Ministerial Order of 20/06/2023) be carried out before and after the ‘Top Assay’.

The ‘Top Assay’ (Total Oxidizable Precursor) transforms poly-fluorinated PFASs into perfluorinated PFASs (Fig. 11a & b). In the environment, all poly-fluorinated PFAS (Precursors) are bio-transformed to stable per-fluorinated PFAS.

Using the ‘Top Assay’, it is possible to include in the TERQ - Health Risk Assessment immediately the per-fluorinated PFASs, which are also the products of bio-transformation in an exposure scenario. However, it is not sufficient to carry out the health risk assessment solely on per-fluorinated PFAS after the ‘Top Assay’, as the dose-threshold effects of certain more stable poly-fluorinated PFAS may be significant in sub-chronic and chronic exposures, e.g. in the case of volatile PFAS (FTOH: fluorotelomer alcohols, etc.) or 6:2-FTAB etc. (Karg 2023c).

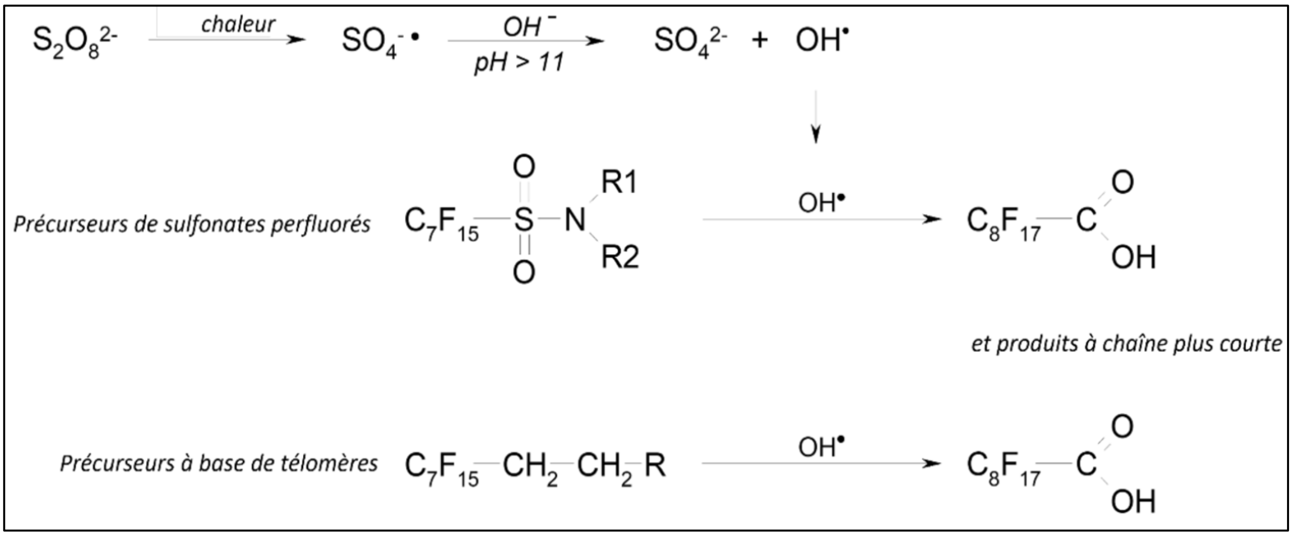


Fig. 11a : Top Assay (Total Oxidizable Precursor) analysis of the total quantity of precursors (poly-fluorinated PFAS) oxidizable via persulphate (Houtz and Sedlak: 2012, Glöckner et al.: 2021)

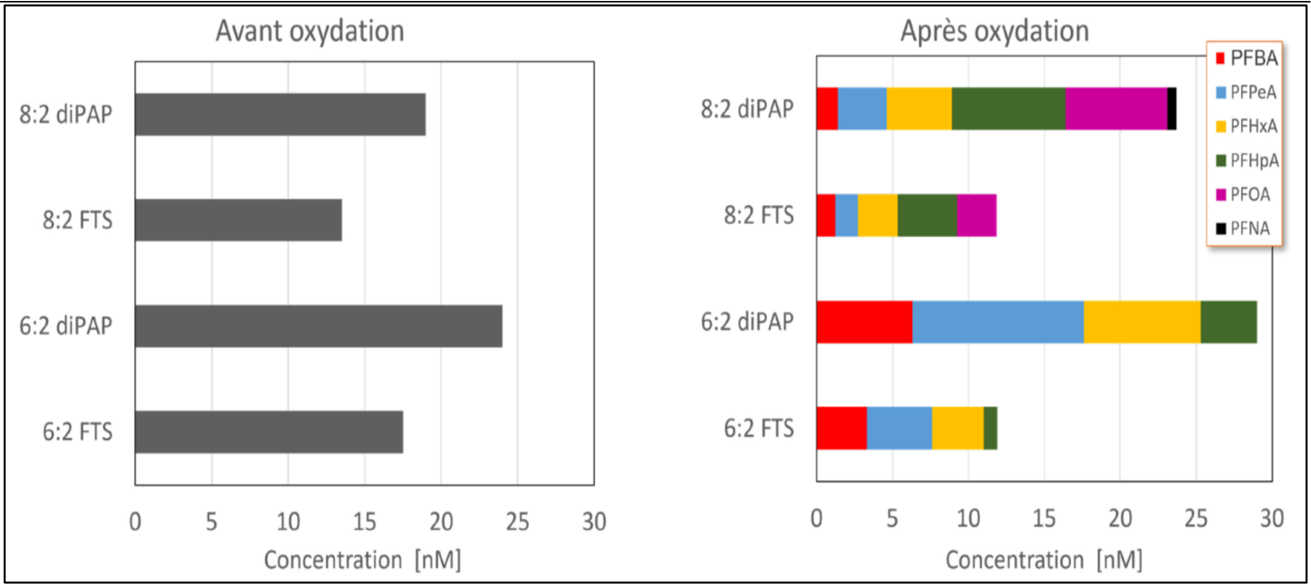


Fig. 11b: Top Assay: Example of quantification of poly-fluorinated PFAS via their corresponding final perfluorinated carboxylic acids after degradation (Houtz and Sedlak: 2012, Glöckner et al.: 2021), to be taken into account in an HRA.

5. Conclusion

The Challenge of PFAS Health Risk Assessments and Assessment of Toxicological Risks (HRA & TERQ) is to ensure the right choice of updated TRVs (Toxicological Dose-Effect Relationship Reference Values) and to manage the large number of poly-fluorinated PFAS. The fact that they are biotransformed (but also by photolysis) into per-fluorinated PFAS allows to group them via the Top Assay directly into the TERQ-HRA (Toxicological Exposure Risk Quantification – Health Risk Assessment). However, it is also necessary to integrate also certain individual and relatively stable poly-fluorinated PFAS directly into the TERQ-HRA (e.g. 6:2-FTAB, 4:2- & 6:2-FTS, FTOHs, etc.).

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Evaluation des risques toxicologiques (EQRS & ARR) des PFAS par le bon choix des VTR et via l'application du Top Assay, en d'autre par l'application du Guide de Gestion des PFAS de la SFSE (F.10)

Human Health Risk Assessment via Toxicological Exposure Risk Quantification (HRA & TERQ) of PFAS by the correct choice of TRVs and via the application of the Top Assay; according the SFSE PFAS Management Guideline (F.10)

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1. Introduction

Les PFAS : Per- & Polyfluoro-Alkyl Substances sont devenues progressivement depuis des années 1960 une préoccupation environnementale majeure, mais également pour la Santé Publique, en raison de leur application multiple et vaste (historique et toujours actuelle). Cette menace environnementale et pour la Santé Publique commence à être prise en compte petit à petit depuis les années 2010 et plus fortement en 2022 - 2024. Par conséquent, les PFAS se retrouvent aujourd'hui dans les sols, les eaux souterraines, les aliments et l'eau potable ainsi que dans les gaz du sol et l'air ambiant pour les familles de PFAS volatils, par ex. les FTOH : Fluorotélomère-Alcools. Entre 9 000 à 12 000 polluants synthétiques de PFAS ont été produits.

Les PFAS polymères du type « Teflon » (ou PFTE) etc. ne disposent pas d'une bonne biodisponibilité et sont par conséquent beaucoup moins toxiques que les PFAS monomères. Ces PFAS monomères font l'objet des travaux présentés ci-joint. Les PFAS sont connus notamment pour leurs effets toxicologiques de perturbateurs endocriniens, d'hépatotoxicité, d'immunotoxicité, leurs effets sur le développement des fœtus et pour certains, de cancérogénicité (par ex. le PFOA) [1 – 84, 184, 185].

Une caractéristique importante des PFAS est leur comportement dans la Chimie Environnementale, car seuls les PFAS polyfluorés sont modifiés par bio-transformation microbiologique en PFAS perfluorés, qui demeurent totalement stables et non-dégradables, voire même bioaccumulables.

Les sources de Pollutions par PFAS sont multiples et notamment présentes sur les sites industriels, qui ont utilisé ces produits, les sites d'anciens incendies ou d'entrainement anti-incendie, où des mousses anti-incendie **(AFFF : Aqueous Film Forming Foam ou Anti Fire Fighting Foams, par ex. sur des aéroports)** ont été utilisées. Les terrains agricoles sont aussi des sources de pollution par des PFAS, en raison de l'apport de boues de STEP (Stations d'Epuration) qui comportent des PFAS accumulés.

Les activités (historiques) suivantes peuvent être à l'origine de pollutions par des PFAS :

- Entrainements anti-incendie,
- Aéroport ou base aérienne de site militaire,
- Site d'incendie et d'utilisation des AFFF,
- Galvanisation électrochimique,
- Production de papiers ou cartons « cirés »,
- Production de Textiles imperméables,
- Sprays, peintures, laques d'imperméabilisation,
- Production et application de Téflons (PTFE, etc.),
- Sites pétroliers et de l'industrie chimique et/ou production et application de peintures, de

teintures, d'encres, de pigments, de cires chimiques et de produits de polissage,

- Applications de solvants (garages, pressings, blanchisseries, etc.,)
- Décharges et anciennes décharges municipales, etc. (ISDD, ISDND, ISDD, etc.),
- Teintureries & Tanneries,
- Moquettes, tapis, tissus et plastiques avec des retardateurs de flammes,
- Production d'objets et meubles (application sur les surfaces),
- Production de produits de nettoyage,
- Chimie photographique (laboratoires, et production des papiers et films, etc.),
- Production d'éléments électroniques,
- Production et applications de pesticides et biocides,
- Production de produits cosmétiques,
- Sites ayant reçus des Boues de STEP.

2. Chimie environnementale

La Chimie environnementale des PFAS est particulièrement importante et compliquée. Il n'existe aucun groupe de polluants montrant une chimie environnementale plus complexe que les PFAS. En particulier, il faut constater qu'il existe **plus que 9 000 substances PFAS**, divisées en **33 catégories de substances**. Les plus connues sont les Acides perfluoroalkane-sulfoniques (PFASs), les Acides perfluoroalkyliques-carboxyliques (PFCA), les Perfluoroalkyliques-phosphates & leurs esters, les Fluorotélomére-alcooles (**FTOH**), etc. (dont plus de **32 autres groupes**…). Certains d'entre eux, comme par ex. le **PFOA :** Acide perfluoro-octanoïque et le **PFOS** : Perfluoro-octane-sulfonate (cf. Fig. 1) sont bannis (et **interdit en CE et USA & Canada**) par la **Convention de Stockholm** dans la catégorie des **POPs** : Persistent Organic Pollutants. Le PFOA est cancérigène. Les **produits commerciaux** contiennent principalement des **mélanges**.

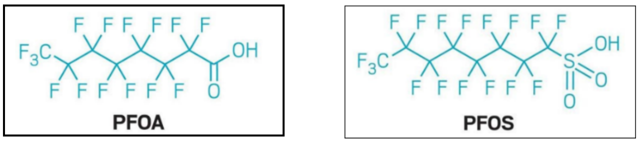


Fig. 1 : Formules structurelles des PFOA & PFOS

La raison de la forte solubilité dans l'eau associée à une lipophilie est basée sur le fait qu'il existe des **PFAS** :

- **Anioniques** (par ex. les sulfonates, les sulfates, les carboxylates et les phosphates),
- **Cationiques** (par ex. ammonium quaternaire),
- **Amphotères** (par ex. betaines et sulfo-betaines) : base + acide
- **Non ioniques** (par ex. polyéthylène glycols, oligomères d'acrylamide).

Il est très important de souligner, que les PFAS poly-fluorés non entièrement fluorés (« Précurseurs ») peuvent être convertis par bio-transformation en produits chimiques persistants et entièrement fluorés, les PFAS per-fluorés [87 – 94, 161, 168]**. La dégradation complète microbiologique des PFAS n'a pas encore été démontrée.**

Les schémas suivants (2 - 4) montrent des exemples de biotransformation des 6 :2 FTAB, 6 :2- & 8 :2 FTS et alkylphosphates polyfluorés (PAP) dans les sols et eaux souterraines vers les Fluorotélomère alcools (FTOH) volatils qui migrent par la suite dans les gaz du sol et vers l'air ambiant. Par la suite, les FTOH sont transformés microbiologiquement en PFAS per-fluorés stables. Par exemple ; le 6:2-FTOH est bio-transformé en PFHxA, PFPeA & PFBA et le 8:2-FTOH en PFOA, PFHpA, PFHxA, PFPeA et PFBA (cf. les Fig. suivantes).

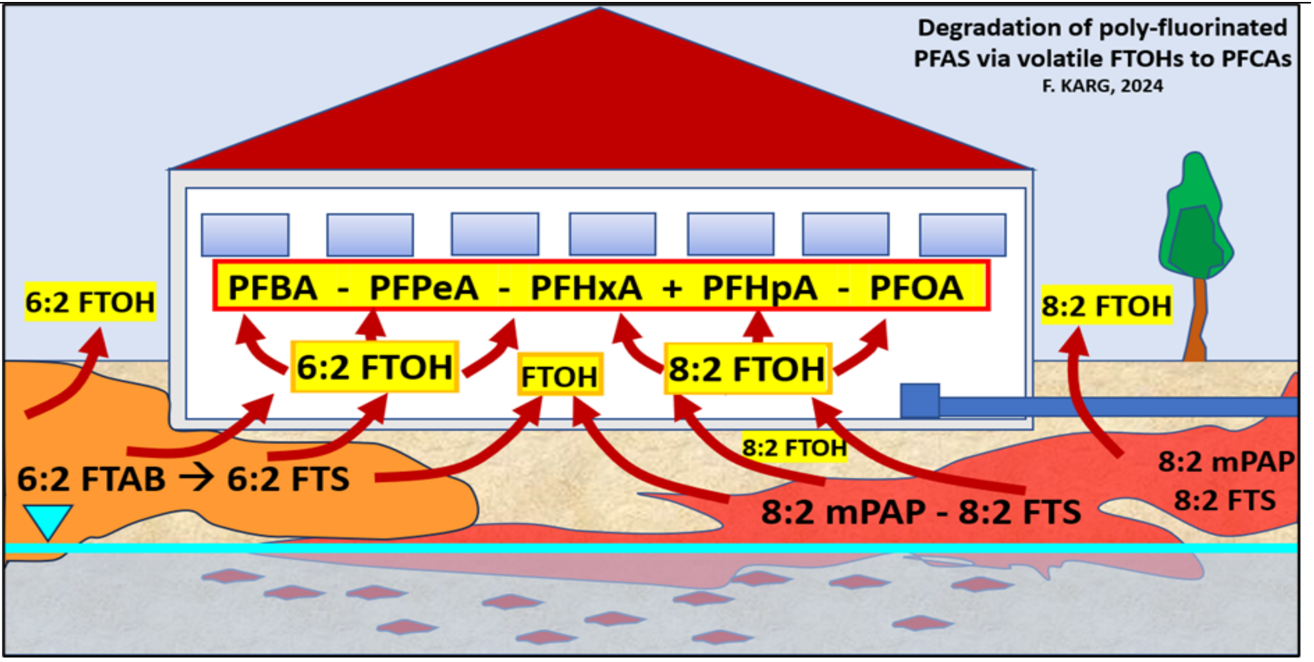


Fig. 2: Exemple de biotransformation des 6 :2 FTAB, 6 :2 FTS, 8 :2 FTS et les alkyl phosphates polyfluorés (PAP), dans les sols et eaux vers Fluorotelomer alcools (FTOH) et des PFAS per-fluorés, par ex. vers le PFOA, PFHpA, PFHxA, PFPeA et PFBA (L. KOPF / HPC, 2017 et F. KARG, 2022 & 2024)

Le Schéma suivant montre un exemple de la biotransformation du 8:2-FTOH ($F(CF_2)_8CH_2CH_2OH$) via des produits intermédiaires vers des PFAS perfluorés stables, comme par exemple le PFPeA (Acide perfluoro-pentanonic), le PFHxA (Acide perfluoro-hexanonic), le PFHpA (Acide perfluoro-heptanonic), le 2H-PFOA, l'Acide 7:3 et le PFOA (Acide perfluoro-octanonic) cancérigène.

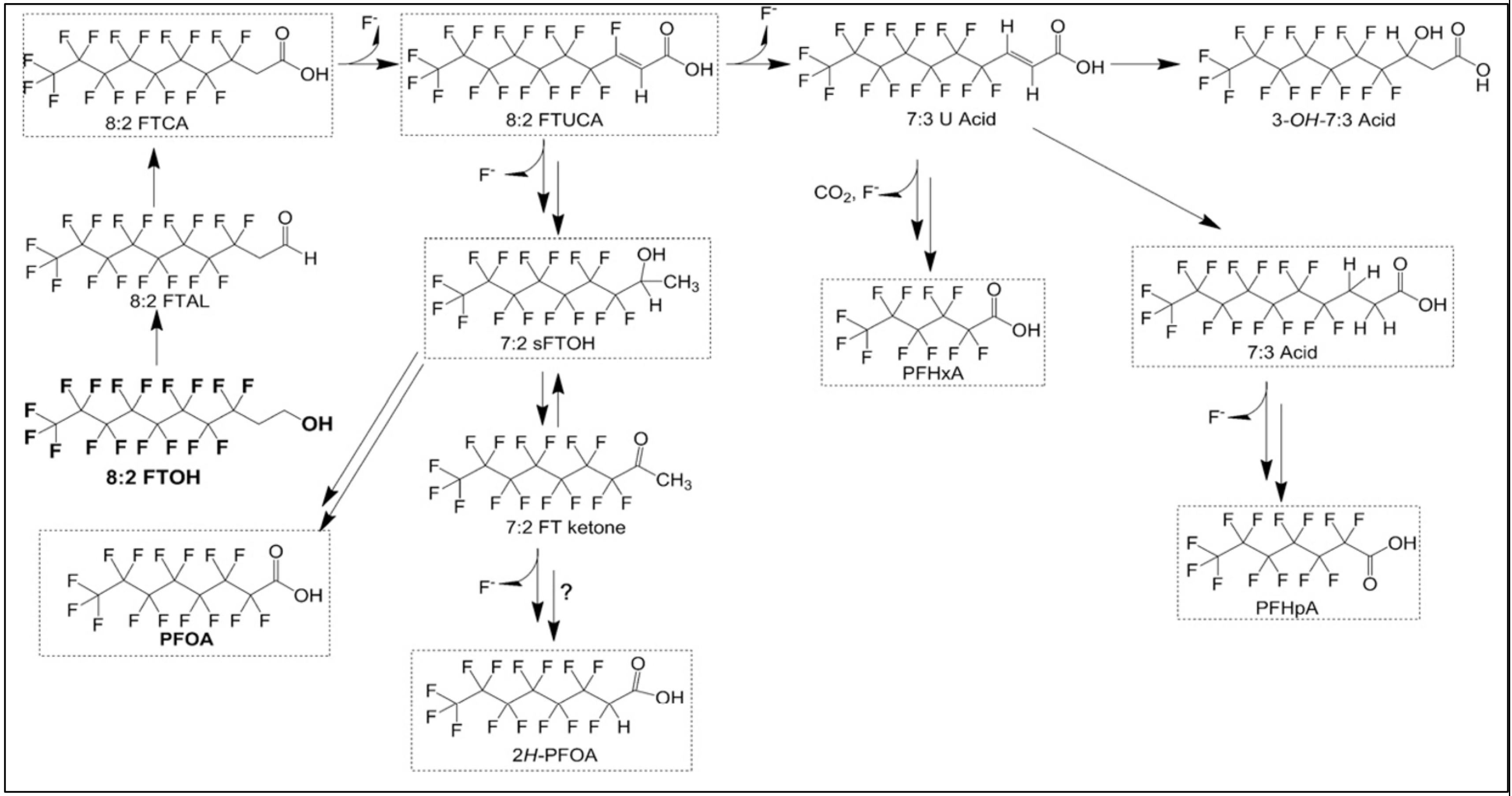


Fig. 3 : Exemple de biotransformation aérobique du 8:2 FTOH ($F(CF_2)_8CH_2CH_2OH$) dans les sols. Des flèches doubles indiquent la formation des substances perfluorés stables (Wang et al. 2009, modifié).

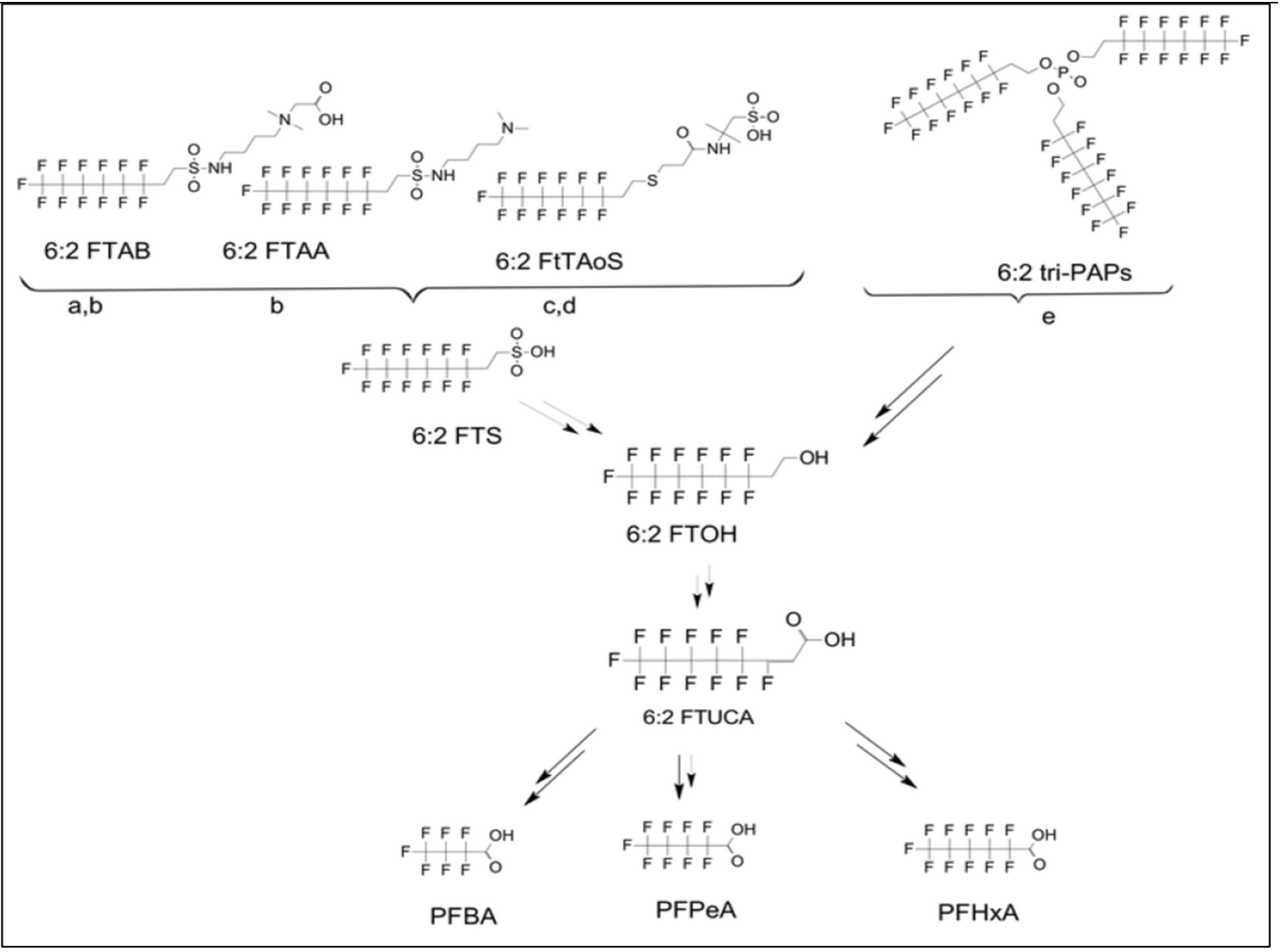
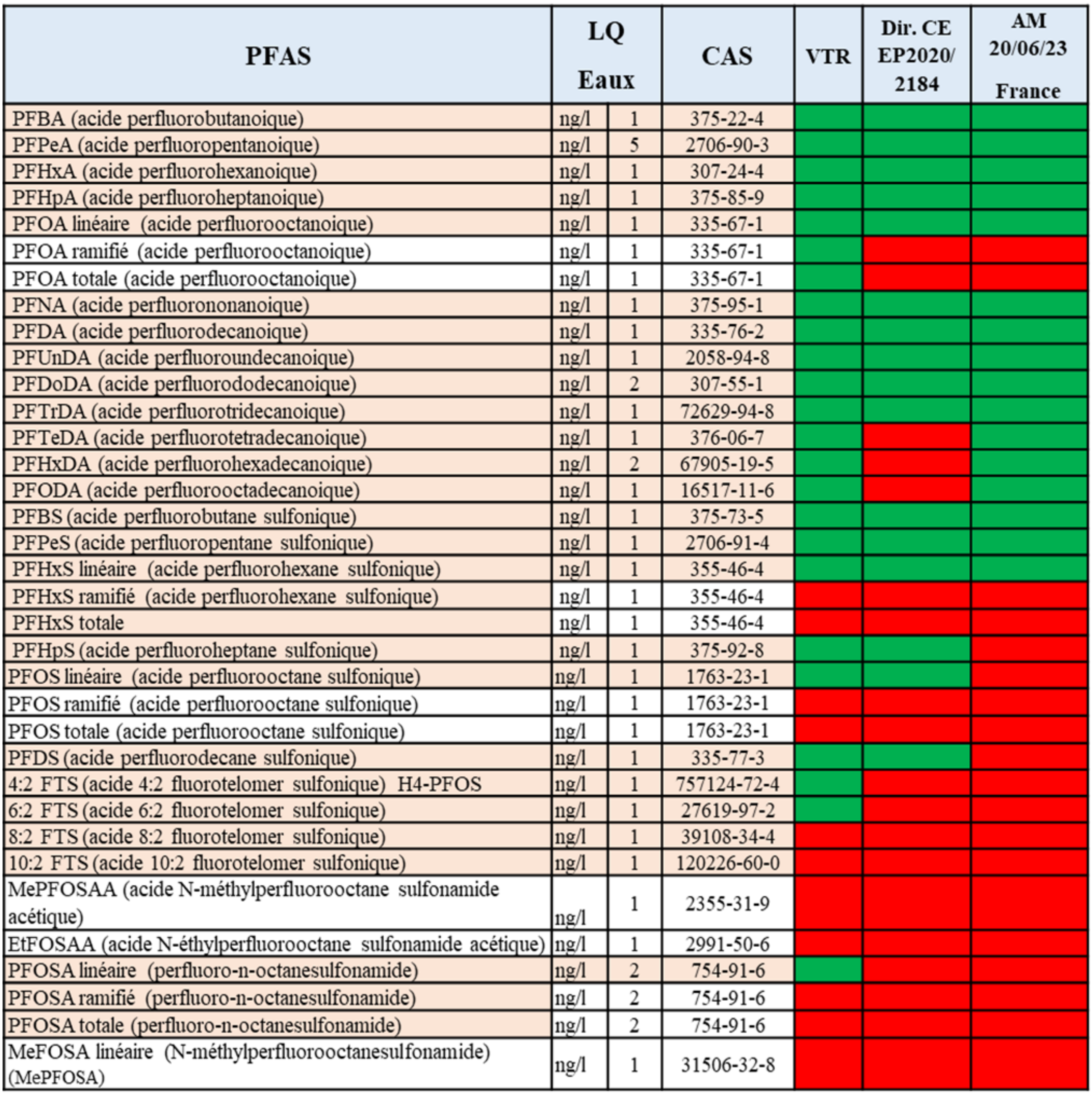


Fig. 4 : Schéma de biotransformation des PFAS polyfluorés (Précurseurs) : Exemple : 6 :2 FTAB et sa dégradation via le 6 :2 FTS et le 6 :2 FTOH vers les PFAS per-fluorés PFBA, PFPeA et PFHxA (LaFond et al. 2024, D.M.J. Shaw et al. 2019 ,Ying Shi, 2018 et V. Mendeza et. al. 2022)

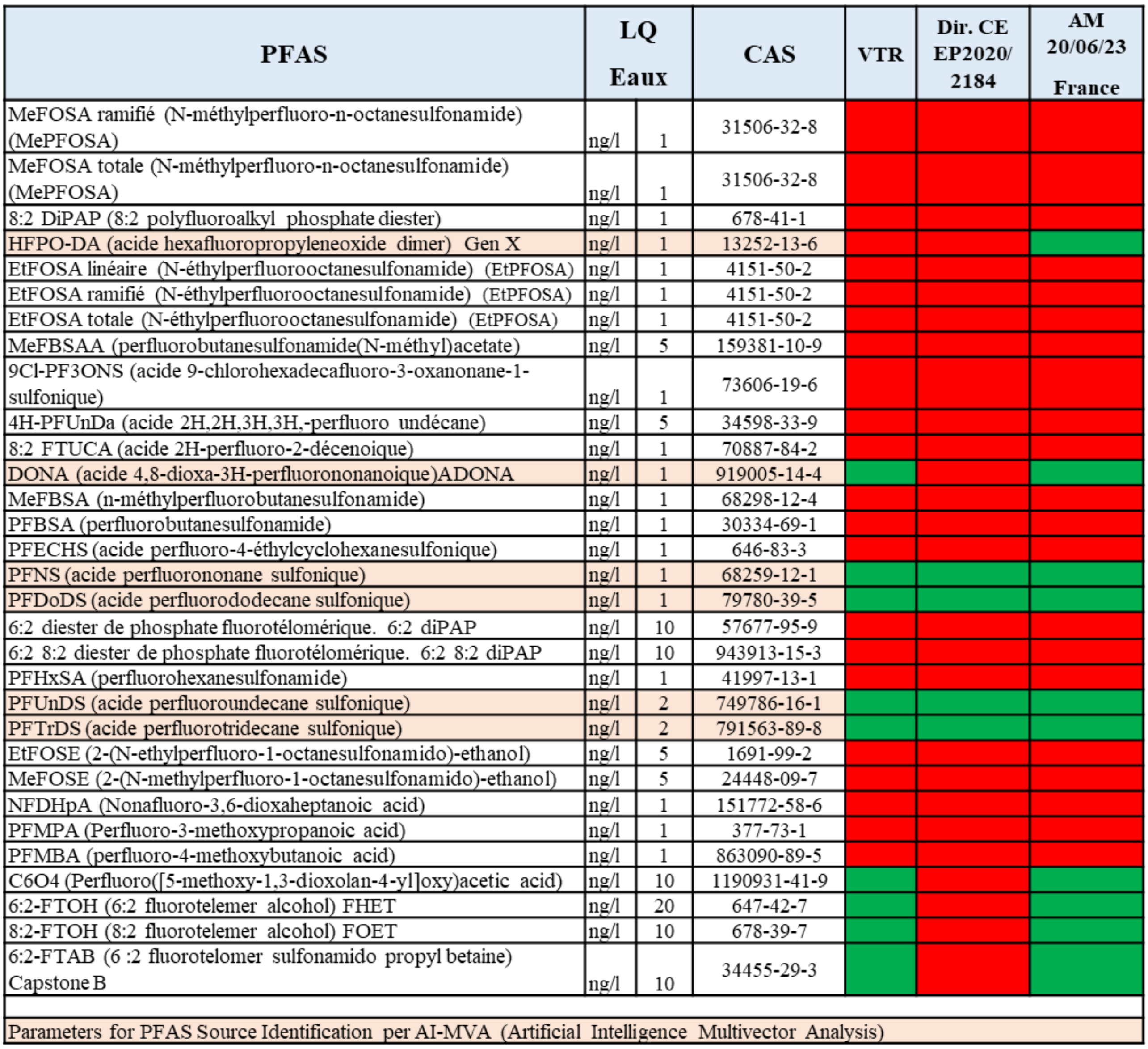
3. Evaluation des risques toxicologiques (EQRS & ARR)

De manière générale préalable, il est recommandé d'intégrer dans les diagnostics de contaminations par les PFAS au minimum les polluants, listés dans les tableaux suivants :



PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
PFBA (acide perfluorobutanoique)	ng/l	1	375-22-4	🟩	🟩	🟩
PFPeA (acide perfluoropentanoique)	ng/l	5	2706-90-3	🟩	🟩	🟩
PFHxA (acide perfluorohexanoique)	ng/l	1	307-24-4	🟩	🟩	🟩
PFHpA (acide perfluoroheptanoique)	ng/l	1	375-85-9	🟩	🟩	🟩
PFOA linéaire (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟩	🟩
PFOA ramifié (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFOA totale (acide perfluorooctanoique)	ng/l	1	335-67-1	🟩	🟥	🟥
PFNA (acide perfluorononanoique)	ng/l	1	375-95-1	🟩	🟩	🟩
PFDA (acide perfluorodecanoique)	ng/l	1	335-76-2	🟩	🟩	🟩
PFUnDA (acide perfluoroundecanoique)	ng/l	1	2058-94-8	🟩	🟩	🟩
PFDoDA (acide perfluorododecanoique)	ng/l	2	307-55-1	🟩	🟩	🟩
PFTrDA (acide perfluorotridecanoique)	ng/l	1	72629-94-8	🟩	🟩	🟩
PFTeDA (acide perfluorotetradecanoique)	ng/l	1	376-06-7	🟩	🟥	🟩
PFHxDA (acide perfluorohexadecanoique)	ng/l	2	67905-19-5	🟩	🟥	🟩
PFODA (acide perfluorooctadecanoique)	ng/l	1	16517-11-6	🟩	🟥	🟩
PFBS (acide perfluorobutane sulfonique)	ng/l	1	375-73-5	🟩	🟩	🟩
PFPeS (acide perfluoropentane sulfonique)	ng/l	1	2706-91-4	🟩	🟩	🟩
PFHxS linéaire (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟩	🟩	🟩
PFHxS ramifié (acide perfluorohexane sulfonique)	ng/l	1	355-46-4	🟥	🟥	🟥
PFHxS totale	ng/l	1	355-46-4	🟥	🟥	🟥
PFHpS (acide perfluoroheptane sulfonique)	ng/l	1	375-92-8	🟩	🟩	🟥
PFOS linéaire (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟩	🟩	🟥
PFOS ramifié (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFOS totale (acide perfluorooctane sulfonique)	ng/l	1	1763-23-1	🟥	🟥	🟥
PFDS (acide perfluorodecane sulfonique)	ng/l	1	335-77-3	🟩	🟩	🟥
4:2 FTS (acide 4:2 fluorotelomer sulfonique) H4-PFOS	ng/l	1	757124-72-4	🟩	🟥	🟥
6:2 FTS (acide 6:2 fluorotelomer sulfonique)	ng/l	1	27619-97-2	🟩	🟥	🟥
8:2 FTS (acide 8:2 fluorotelomer sulfonique)	ng/l	1	39108-34-4	🟥	🟥	🟥
10:2 FTS (acide 10:2 fluorotelomer sulfonique)	ng/l	1	120226-60-0	🟥	🟥	🟥
MePFOSAA (acide N-méthylperfluorooctane sulfonamide acétique)	ng/l	1	2355-31-9	🟥	🟥	🟥
EtFOSAA (acide N-éthylperfluorooctane sulfonamide acétique)	ng/l	1	2991-50-6	🟥	🟥	🟥
PFOSA linéaire (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟩	🟥	🟥
PFOSA ramifié (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
PFOSA totale (perfluoro-n-octanesulfonamide)	ng/l	2	754-91-6	🟥	🟥	🟥
MeFOSA linéaire (N-méthylperfluorooctanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥

Fig. 5a : Paramètres d'analyses PFAS recommandés à minima



PFAS	LQ Eaux		CAS	VTR	Dir. CE EP2020/ 2184	AM 20/06/23 France
MeFOSA ramifié (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
MeFOSA totale (N-méthylperfluoro-n-octanesulfonamide) (MePFOSA)	ng/l	1	31506-32-8	🟥	🟥	🟥
8:2 DiPAP (8:2 polyfluoroalkyl phosphate diester)	ng/l	1	678-41-1	🟥	🟥	🟥
HFPO-DA (acide hexafluoropropyleneoxide dimer) Gen X	ng/l	1	13252-13-6	🟥	🟥	🟩
EtFOSA linéaire (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA ramifié (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
EtFOSA totale (N-éthylperfluorooctanesulfonamide) (EtPFOSA)	ng/l	1	4151-50-2	🟥	🟥	🟥
MeFBSAA (perfluorobutanesulfonamide(N-méthyl)acetate)	ng/l	5	159381-10-9	🟥	🟥	🟥
9Cl-PF3ONS (acide 9-chlorohexadecafluoro-3-oxanonane-1-sulfonique)	ng/l	1	73606-19-6	🟥	🟥	🟥
4H-PFUnDa (acide 2H,2H,3H,3H,-perfluoro undécane)	ng/l	5	34598-33-9	🟥	🟥	🟥
8:2 FTUCA (acide 2H-perfluoro-2-décenoique)	ng/l	1	70887-84-2	🟥	🟥	🟥
DONA (acide 4,8-dioxa-3H-perfluorononanoique)ADONA	ng/l	1	919005-14-4	🟩	🟥	🟩
MeFBSA (n-méthylperfluorobutanesulfonamide)	ng/l	1	68298-12-4	🟥	🟥	🟥
PFBSA (perfluorobutanesulfonamide)	ng/l	1	30334-69-1	🟥	🟥	🟥
PFECHS (acide perfluoro-4-éthylcyclohexanesulfonique)	ng/l	1	646-83-3	🟥	🟥	🟥
PFNS (acide perfluorononane sulfonique)	ng/l	1	68259-12-1	🟩	🟩	🟩
PFDoDS (acide perfluorododecane sulfonique)	ng/l	1	79780-39-5	🟩	🟩	🟩
6:2 diester de phosphate fluorotélomérique. 6:2 diPAP	ng/l	10	57677-95-9	🟥	🟥	🟥
6:2 8:2 diester de phosphate fluorotélomérique. 6:2 8:2 diPAP	ng/l	10	943913-15-3	🟥	🟥	🟥
PFHxSA (perfluorohexanesulfonamide)	ng/l	1	41997-13-1	🟥	🟥	🟥
PFUnDS (acide perfluoroundecane sulfonique)	ng/l	2	749786-16-1	🟩	🟩	🟩
PFTrDS (acide perfluorotridecane sulfonique)	ng/l	2	791563-89-8	🟩	🟩	🟩
EtFOSE (2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	1691-99-2	🟥	🟥	🟥
MeFOSE (2-(N-methylperfluoro-1-octanesulfonamido)-ethanol)	ng/l	5	24448-09-7	🟥	🟥	🟥
NFDHpA (Nonafluoro-3,6-dioxaheptanoic acid)	ng/l	1	151772-58-6	🟥	🟥	🟥
PFMPA (Perfluoro-3-methoxypropanoic acid)	ng/l	1	377-73-1	🟥	🟥	🟥
PFMBA (perfluoro-4-methoxybutanoic acid)	ng/l	1	863090-89-5	🟥	🟥	🟥
C6O4 (Perfluoro([5-methoxy-1,3-dioxolan-4-yl]oxy)acetic acid)	ng/l	10	1190931-41-9	🟩	🟥	🟩
6:2-FTOH (6:2 fluorotelemer alcohol) FHET	ng/l	20	647-42-7	🟩	🟥	🟩
8:2-FTOH (8:2 fluorotelemer alcohol) FOET	ng/l	10	678-39-7	🟩	🟥	🟩
6:2-FTAB (6 :2 fluorotelomer sulfonamido propyl betaine) Capstone B	ng/l	10	34455-29-3	🟩	🟥	🟩
Parameters for PFAS Source Identification per AI-MVA (Artificial Intelligence Multivector Analysis)						

Fig. 5b : Paramètres d'analyses PFAS recommandés à minima

A ce jour, l'analyse des 20 PFAS individuels de la Directive Européenne 2020/2184 est une première approche, mais elle n'est pas suffisante dans tous les cas.

4. Evaluation des Risques Toxicologiques

Pour l'évaluation des risques sanitaires, les données toxicologiques (VTR : Valeurs Toxicologiques de Référence) sont à rechercher et à actualiser au niveau international quasiment de façon hebdomadaire. Les VTR les plus récentes sont disponibles surtout aux USA (US-EPA…), l'ATSDR et l'EFSA. L'ANSES avait publié aussi en 2017 des VTR des PFAS, mais au vu de l'avancement rapide des études toxicologiques, ces VTR sont pour une grande partie déjà dépassées.

Dans le cas des FTOH présents dans les sols, eaux souterraines et gaz du sol, il faudra impérativement réaliser aussi des investigations de FTOH dans l'air ambiant intérieur des bâtiments, surtout dans le cas d' usage sensible (ERP : Ecoles, Crèches, etc.) ou résidentiel, sur la base de seuils de quantification (ou au moins pour les seuils de détection), de l'ordre de 4 – 8 ng/m^3, afin de posséder une bonne base exploitable pour les EQRS : Evaluation Quantitative des Risques Sanitaires.

Une première approche d'évaluation des risques simplifiée est possible via des valeurs limites existantes, comme par ex. en Allemagne, ou publiées par la Communauté Européenne. En Allemagne il existe des Valeurs limites pour l'eau potable, pour les sols et pour les eaux souterraines.

L'US-EPA considère que la plus grande partie des expositions provient aujourd'hui de l'eau potable, en dehors des sites pollués, du fait de l'absence de surveillance et de traitement des PFAS.

Selon la Directive (UE) 2013/39/UE « Cadre sur l'eau » européenne (DCE), concernant le PFOS & dérivés (et d'autres substances prioritaires) une Norme de Qualité Environnementale (NQE-MA) de 0,65 ng/l pour les Eaux superficielles et de 0,13 ng/l pour les Eaux du milieu marin (et des NQE-CMA : Concentrations Maximales Admissibles) a été fixée.

Il est important de noter qu'une simple application des Valeurs limites, génériques et individuelles, dans le cadre d'une évaluation simplifiée des risques, ne prend pas en compte les scénarios d'expositions spécifiques et les expositions aux mélanges (« Cocktails ») de polluants avec, au minimum, une prise en compte de l'additivité des risques des polluants ayant les mêmes cibles et effets toxicologiques. Par conséquence, il est préférable de réaliser des EQRS (ou ARR, HRA, TERQ), ce qui correspond bien à la Méthodologie Française de Gestion des Sites Pollués, selon la note du Ministère en charge de l'Environnement, du 19/04/2017.

Un autre aspect important est que seule une EQRS (ou ARR, TERQ, HRA) permettra de définir des Valeurs de Contrôle de conformité sanitaire, sous forme de CMA (Concentration Maximale Admissible), qui permettent d'assurer des Excès de Risques Individuels (de cancer) acceptables : ERI < 10^{-5} ou des Quotients de Risque systémique acceptable : QR < 1 (= DJE / DJT : Dose Journalière d'Exposition sur la Dose Journalière Tolérable).

Concernant les EQRS (Evaluations Quantitatives des Risques Sanitaires), la base est soit la mesure des concentrations dans les milieux d'exposition, soit la modélisation du transfert des polluants d'un compartiment à un autre (par ex. des polluants dans les eaux souterraines ou les sol vers les gaz du sol et l'air ambiant).

Une étape importante de l'EQRS est le choix pertinent des VTR (Valeurs Toxicologiques de Référence), car leur évolution est rapide. Une Dose Hebdomadaire Tolérable (DHT) de 4,4 ng/kg/Semaine (ou la Dose Journalier Tolérable (DJT) de 0,63 ng/kg/j pour des PFAS : PFOA, PFOS, PFNA & PFHxS) a été publiée par l'EFSA, le 17/09/2020. En 2020 des facteurs d'équivalence de toxicité par rapport au PFOA ont été aussi publiés par W. Bil et al. sous la forme de RPF : Relative Potency Factors.

Le choix des VTR constitue une étape importante de l'EQRS car leur évolution est rapide en ce qui concerne les PFAS. Par exemple, l'ANSES a publié en 2017 un rapport sur les PFAS comportant certaines VTR (ANSES, 2017). Ces valeurs sont déjà partiellement dépassées. Aujourd'hui, les VTR publiées sont devenues beaucoup plus contraignantes, comme le montre l'évolution des VTRs publiées par l'EFSA depuis 2015, cf. la Fig. 6.

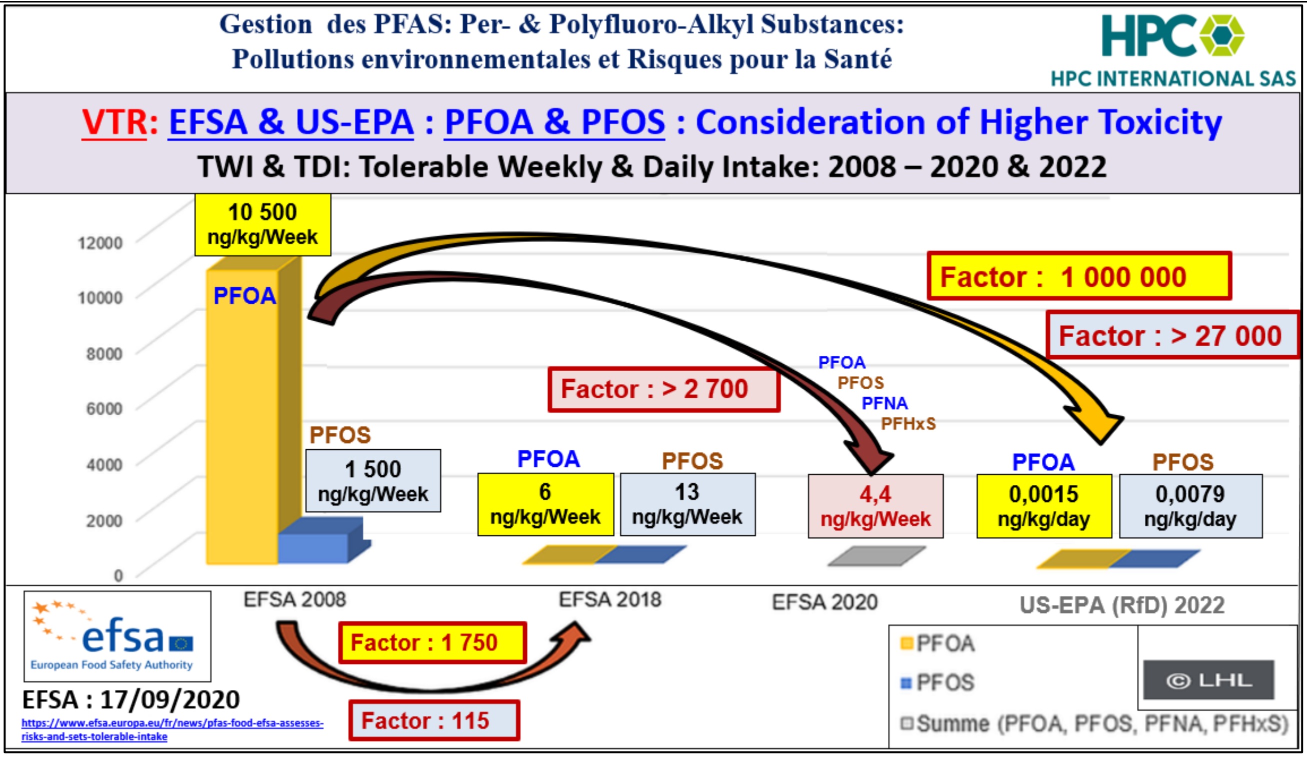
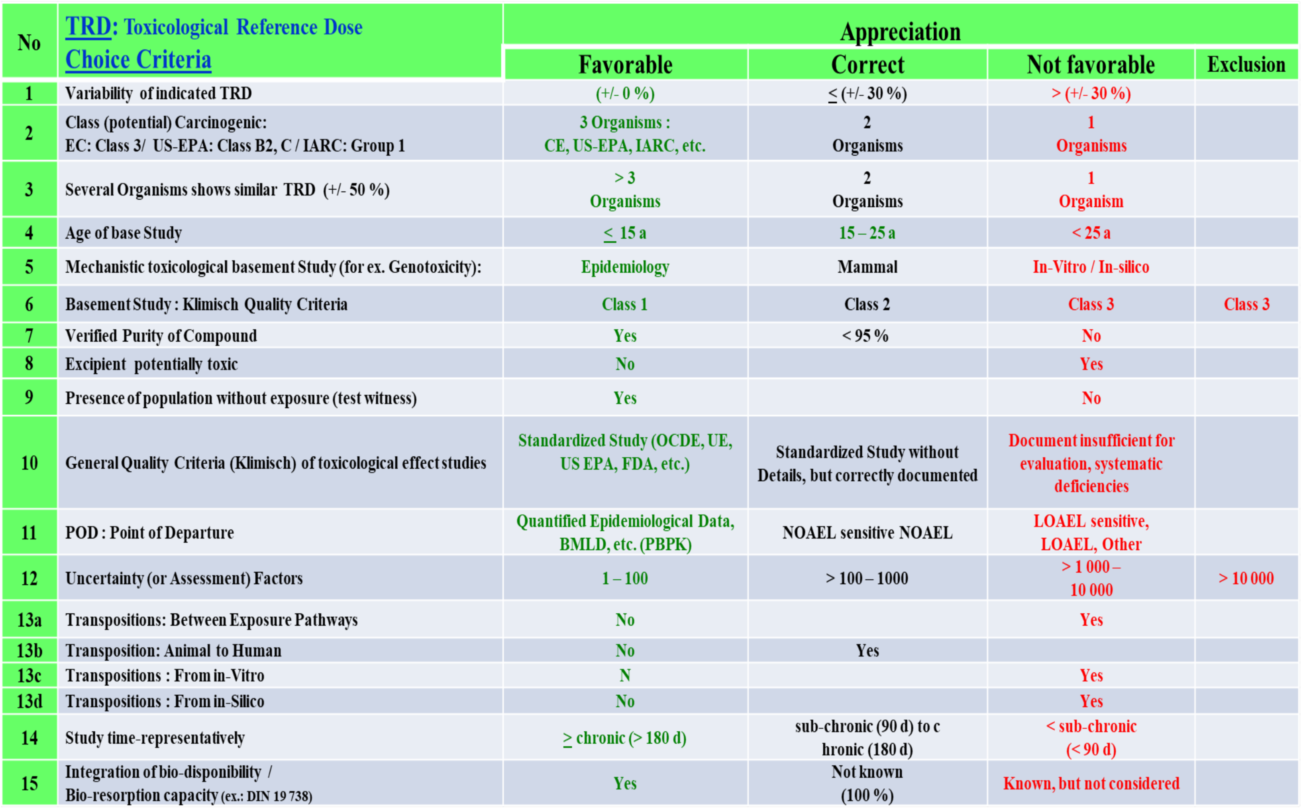


Fig. 6 : Evolution des VTR concernant le PFOA & PFOS et PFNA & PFHxA, sur la base des TWI & TDI de l’EFSA (2020) et RfD de l’ US-EPA (2022), (F. KARG 2023a & b)

Afin d’assurer le bon choix des VTR des PFAS, il est recommandé d’appliquer des critères de choix scientifiques et non des critères nationaux. La figure suivante montre les critères de choix des VTR applicables, afin de prendre en compte les meilleures connaissances toxicologiques concernant les relations de dose à effet des PFAS.



No	TRD: Toxicological Reference Dose Choice Criteria	Appreciation			
		Favorable	Correct	Not favorable	Exclusion
1	Variability of indicated TRD	(+/- 0 %)	≤ (+/- 30 %)	> (+/- 30 %)	
2	Class (potential) Carcinogenic: EC: Class 3/ US-EPA: Class B2, C / IARC: Group 1	3 Organisms : CE, US-EPA, IARC, etc.	2 Organisms	1 Organisms	
3	Several Organisms shows similar TRD (+/- 50 %)	> 3 Organisms	2 Organisms	1 Organism	
4	Age of base Study	≤ 15 a	15 – 25 a	< 25 a	
5	Mechanistic toxicological basement Study (for ex. Genotoxicity):	Epidemiology	Mammal	In-Vitro / In-silico	
6	Basement Study : Klimisch Quality Criteria	Class 1	Class 2	Class 3	Class 3
7	Verified Purity of Compound	Yes	< 95 %	No	
8	Excipient potentially toxic	No		Yes	
9	Presence of population without exposure (test witness)	Yes		No	
10	General Quality Criteria (Klimisch) of toxicological effect studies	Standardized Study (OCDE, UE, US EPA, FDA, etc.)	Standardized Study without Details, but correctly documented	Document insufficient for evaluation, systematic deficiencies	
11	POD : Point of Departure	Quantified Epidemiological Data, BMLD, etc. (PBPK)	NOAEL sensitive NOAEL	LOAEL sensitive, LOAEL, Other	
12	Uncertainty (or Assessment) Factors	1 – 100	> 100 – 1000	> 1 000 – 10 000	> 10 000
13a	Transpositions: Between Exposure Pathways	No		Yes	
13b	Transposition: Animal to Human	No	Yes		
13c	Transpositions : From in-Vitro	N		Yes	
13d	Transpositions : From in-Silico	No		Yes	
14	Study time-representatively	≥ chronic (> 180 d)	sub-chronic (90 d) to c hronic (180 d)	< sub-chronic (< 90 d)	
15	Integration of bio-disponibility / Bio-resorption capacity (ex.: DIN 19 738)	Yes	Not known (100 %)	Known, but not considered	

Fig. 7: Critères de choix des VTR (F. KARG 2022)

En se basant sur ces critères de choix, il est possible de définir par ex. les VTR indiquées en figure suivante. Il est important de prendre en compte, que les Administrations de certains états US-américains sont très avancées dans la recherche toxicologique et la publication des VTR concernant des PFAS, du fait de la forte présence d’industries chimiques et pétrolières (avec des utilisations historiques importantes des AFFF) ou de la forte présence de grandes décharges industrielles (et les pollutions environnementales associées). Il s’agit notamment des états du Texas, du Michigan et de New Jersey. Ces VTR sont souvent à la base des publications des VTR des PFAS de la US-EPA fédérale.

Substance	Cancerogene / not cancerogene	Chronic toxicological value			Species	Sigle	Security Factor	Organization
		Exposure path	Target organ	Value				
PFBA	NC	oral	Hepatic	1 µg/kg/d	Rate	RFD	NOAEL / 2400	TCEQ 2023
		inhalation	Hepatic	3,5 µg/m^3	Rate	RFC	From oral value	TCEQ 2023
PFPeA	NC	oral	Hepatic	0,5 µg/kg/d	Rate	RFD	Same than PFHxS LOAEL/(263*300)	TCEQ 2023
PFHxA	NC	oral	Hepatic	0,5 µg/kg/d	Rate	RFD	Same than PFHxS LOAEL/(263*300)	TCEQ 2023
PFHpA	NC	oral	Hepatic	25 ng/kg/d	Rate	DJT	Extrapolation of DJT of Health Canada	ANSES 2017
PFOA	NC	oral	Hematologic	0,86 ng/kg/d	Rate	TDI	BMDL 5	UBA 2020 BFR & EFSA 2018
			Hepatic, Mammar, Hematologic	12 ng/kg/d	Mice	RFD	LOAEL (81*100)	TCEQ 2016
		inhalation	Hepatic	4,1 ng/m^3	Rate	RFC	NOAEL / (81*3000)	TCEQ 2016
	C	oral	Testicular tumors	2,52 (mg/kg/d)$^{-1}$	Epidemio	SF	-	New Jersey 2017
PFNA	NC	oral	Hematologic	2,5 ng/kg/d	Mouse	RFD	NOAEL / 300	EPA IRIS 2019New Hampsire DES 2019
		inhalation	Lung, respiratory system	28 ng/m^3	Rate	RFC	NOAEL / (81*30 000)	EPA IRIS 2019 TCEQ 2023
PFDA	NC	oral	Hematologic	15 ng/kg/d	Rate	RFD	NOAEL / (81*1000)	TCEQ 2016
		inhalation		53 ng/m^3	Rate	RFC	From oral value	TCEQ 2016
PFBS	NC	oral	Hematologic and renal	1,4 µg/kg/d	Rate	RFD	NOAEL / (142*300)	TCEQ 2016
		inhalation		4,9 µg/m^3	Rate	RFC	From oral value	TCEQ 2016
PFHxS	NC	oral	Hematologic and thyroïdale	3,8 µg/kg/d	Rate	RFD	LOAEL / (263*300)	TCEQ 2016
		inhalation	3,8 µg/kg/d	13 ng/m^3	Rate	RFC	From oral value	TCEQ 2016
PFHpS	NC	oral	Hepatic	0,43 ng/kg/d	Rate	TDI	Potency Factor : 0,6-2	UBA 2020, EFSA 2018, BFR 2018
PFOS	NC	oral	Thyroïdale, neurological and fœtal development	1,86 ng/kg/d	Monkey	TDI	NOAEL	UBA 2020, EFSA 2018, BFR 2018
		inhalation		81 ng/m^3	Rate	RFC	From oral value (23 ng/kg/d)	TCEQ 2016
PFOSA	NC	oral	Mammary glands	12 ng/kg/d	Mice	RFD	Same than PFOA NOAEL/(81*300)	TCEQ 2016
		inhalation		4,1 ng/m^3	Rate	RFC	Same than PFOA NOAEL(81*300)	TCEQ 2016

Fig. 8 : Choix de certains VTR selon les critères en Fig. 7 (F. KARG 2022) :

ANSES: Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail (2017)
ATSDR: Agency for Toxic Substances and Disease Registry
EFSA: European Food and Safety Authority
IRIS : Integrated Risk Information of Substances (U.S. - EPA)
UBA : Umweltbundesamt (Germany)
BfR: Bundesinstitut für Risikobewertung (Germany)
OEHHA : Office of Environmental Health Hazard Assessment
WHO: World Health Organization
RIVM : Netherlands Environmental & Health Institute
MDHHS: Michigan Department of Health and Human Services, Division of Environmental Health
TCEQ: Texas Commission on Environmental Quality

NJ-DWQIHES: New Jersey Drinking Water Quality Institute Health Effects Subcommittee
Bil et al. 2020 : Toxicological Equivalence Factors on PFOA RfD

Les VTR présentées en figure 8 sont issues des rapports rédigés par des institutions nationales et internationales. Dans la littérature scientifique il existe des *Points of Departure* (PoD ou Doses d'exposition de départ des effets toxiques) et des VTR plus récentes ou plus spécifiques.

Une étape complémentaire de l'EQRS (ou ARR, TERQ, HRA) est la définition des Valeurs de contrôle de conformité sanitaire, sous forme de CMA (Concentrations Maximales Admissibles) tenant compte d'une additivité des risques des polluants agissant sur les mêmes cibles et ayant les mêmes effets toxicologiques, pour des Excès de Risques Individuels (de cancer) acceptables : ERI < 10E-5 ou des Quotients de Risque systémique acceptables : QR < 1 (= DJE / DJT : Dose Journalière d'Exposition sur Dose Journalière Tolérable). Les CMA sont couramment utilisées sous forme de Valeurs de contrôle sanitaire, afin de vérifier ou de co-élaborer les objectifs des mesures correctives, voire des objectifs de dépollution. Les mesures de Gestion, comme par ex. la dépollution sont basées en France sur un Plan de Gestion, une définition des Zones Sources de pollutions concentrées puis un Bilan Coût-Avantages des modalités et technologies différentes de gestion et des traitements. Ces mesures font l'objet d'une validation sanitaire via une ARR.

Une description pragmatique des Evaluations des Risques Sanitaires (EQRS) est donnée par le Guide Gestion des PFAS de la SFSE : Société Francophone de Santé et Environnement, Chapitre – Fiche 10 (174 : Karg, F., Heilier, J.-F., Ronga-Pezeret, S., Rousselle, C., Bouhoulle, E. : 2023).

Concernant les évaluations des doses journalières d'exposition et des risques associés, il faudra appliquer les étapes suivantes :

A. Identifier les scénarios et les voies d'exposition applicables

Les voies d'exposition suivantes peuvent exister sur un site :

Inhalation :

- des polluants sous forme gazeuse,
- des poussières sur lesquelles est adsorbé le polluant,
- de vapeur d'eau de distribution contaminée lors de la prise d'une douche ou d'un bain.

Ingestion :

- directe de sol (terres à l'extérieur d'un bâtiment) et de poussières (terres à l'intérieur d'un bâtiment),
- d'aliments auto-produits (fruits, légumes, produits animaux), ou issus d'activités de loisirs (pêche…)
- d'eau de distribution contaminée (y compris lors d'une douche ou d'un bain),
- d'eau superficielle ou de mer en cas de baignade par exemple.

Absorption cutanée :

- de sol et de poussières,
- de polluant par l'eau de distribution contaminée lors de la prise d'une douche ou d'un bain,
- lors de la prise d'un bain dans des eaux superficielles (étang, rivière, eau souterraine pompée, etc.) ou dans la mer.

En principe les scénarios d'exposition et les voies d'exposition associées sont à identifier via un Schéma conceptuel (cf. Fig. 10a & b), montrant les sources de pollution, les voies de transfert des polluants et les cibles concernées (adultes, enfants…).

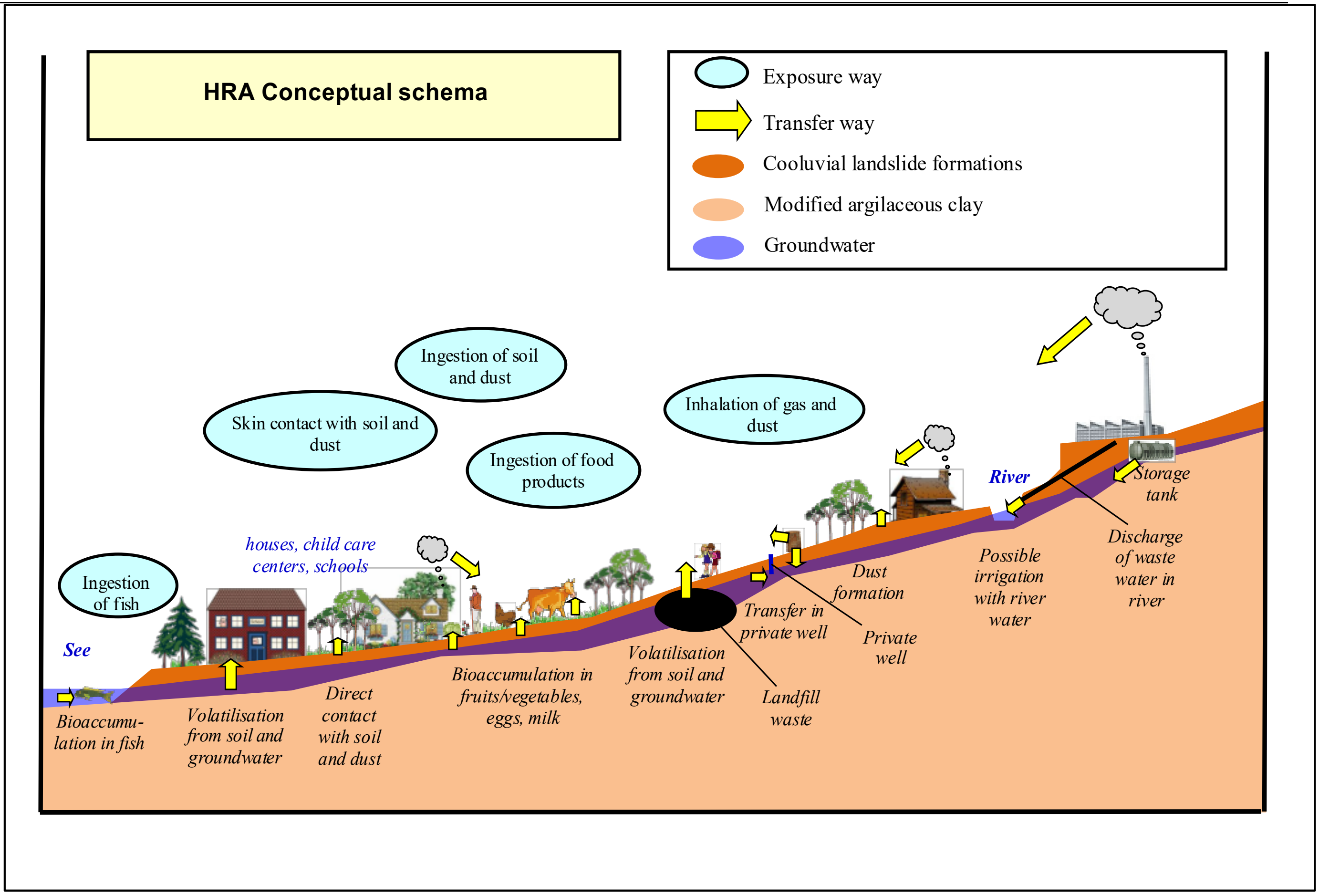


Fig. 10a : Exemple d’un schéma conceptuel global, afin de bien visualiser les voies d’expositions applicables par scénario d’exposition (F. Karg & L. Robin-Vigneron 2023a).

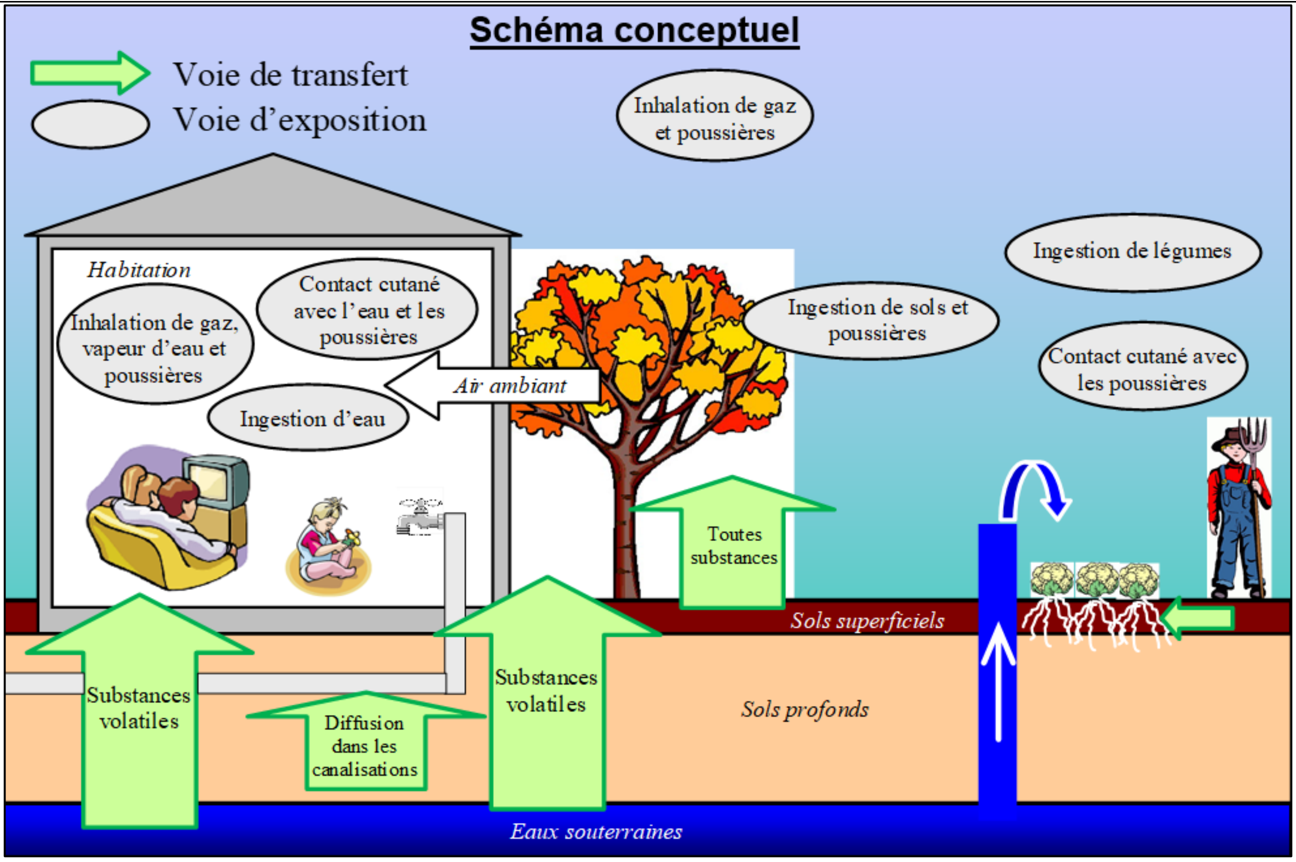


Fig. 10b : Exemple d'un schéma conceptuel détaillé, afin de bien visualiser les voies d'expositions applicables par scénario d'exposition (F. Karg & L. Robin-Vigneron 2023a).

Une attention particulière doit être apportée aux PFAS volatils, comme par ex. les Fluorotélomère-alcools (FTOH), en particulier 6 :2-FTOH et 8 :2-FTOH concernant l'inhalation. Le tableau 1 montre les voies d'exposition par scénario d'usage ou d'exposition sur un site.

Tableau 1 : Scénarios d'expositions et voies d'expositions associées

Scénario d'exposition sur site / Voies d'exposition		Industrie et Com-merce	Parcs & Loisirs / Activités sportives	Jardins d'enfants	Résidentiel collectif et Crèches & Ecoles	Agricole et produc-tion d'aliments	Résidentiel avec jardins individuels
Inhala-tion	Respiration des Vapeurs ou gaz : Gaz du sol → Air Ambient (Intérieur & Extérieur)	Oui	Oui	Oui	Oui	Oui	Oui
	Respiration de poussières	Oui	Oui	Oui	Oui	Oui	Oui
	Respiration de vapeur contaminée pendant la prise d'une douche ou d'un bain (*)	(Oui)	(Oui)	Non	Oui	Non	Oui

Scénario d'exposition sur site / Voies d'exposition		Industrie et Com-merce	Parcs & Loisirs / Activités sportives	Jardins d'enfants	Résidentiel collectif et Crèches & Ecoles	Agricole et produc-tion d'aliments	Résidentiel avec jardins individuels
Oral	Ingestion passive (Enfants & Adultes) ou active (Enfants) du sol contaminé	Oui	Oui	Oui	Oui	Oui	Oui
	Aliments autoproduits	Non	Non	Non	Non	Oui	Oui
	Ingestion d'eau contaminée (*)	(Oui)	(Oui)	Non	Oui	Oui	Oui
	Ingestion d'eau lors d'une baignade (**)						
Cutané	Contact direct avec du sol pollué	Oui	Oui	Oui	Oui	Oui	Oui
	Contact cutané: douche ou bain	(Oui)	(Oui)	Non	(J)	Non	Oui
	Contact cutané lors d'une baignade (**)	Non	Oui	Non	(Non)	(Non)	(Oui)

(*) : par exemple dans le cas de conduites d'eau potable enterrées en sous-sol contaminé
(**) : dans les eaux superficielles ou eaux souterraines pompées contaminées ou eau de mer

Quantifier les Doses Journalières d'Exposition (DJE)

Les doses journalières d'exposition - **DJE$_{ing}$** (voie orale), **DJE$_{inh}$** (voie respiratoire), **DJE$_{cut}$** (voie cutanée) sont toutes exprimées en en mg de polluant / kg de poids corporel / jour [mg ● kg^{-1} ● j^{-1}] et dépendent :

- <u>des concentrations en polluants dans les médias d'exposition</u> (par ex. en mg/kg ou µg/l dans les aliments ou l'eau potable ou en mg/kg ou µg/l dans les poussières ou eaux susceptibles de provoquer un contact cutané ou en µg/m^3 pour l'air ambiant),

Cm = Concentration en polluant dans le milieu d'exposition : Csol [mg/kg], Ceau [µg/l], Caliment [mg/kg]
Ca = Concentration en polluant dans l'air [µg/m^3] intérieur et/ou extérieur.
Cs = Concentration en polluant dans le sol [mg/kg] ou dans les eaux (µg/l)

Deux grandes démarches sont applicables pour **déterminer les concentrations** en polluants dans les **médias d'exposition** : les **mesures directes** (prélèvements et analyses) et les **modélisations par simulation des transferts de polluants** vers les médias d'exposition.

Les modélisations des transferts de polluants entre des médias (par ex. des eaux souterraines ou des sols vers les gaz du sol et l'air ambiant ou vers les aliments) sont possibles et pourront être calibrées via des analyses d'échantillons réels (recommandé, si possible).

Concernant la prise en compte des concentrations des polluants dans les sols, les gaz du sol, l'air ambiant, les eaux souterraines et les eaux superficielles, il est possible d'appliquer, pour les expositions chroniques (supérieures à 6 mois) uniquement, des concentrations moyennes prenant en compte l'atténuation naturelle mesurée. Cette atténuation naturelle de dégradation des PFAS concerne uniquement la biotransformation des PFAS poly-fluorés mais pas les PFAS per-fluorés (cf. par ex. la Fig. 2 - 4).

- **des budgets espace-temps** (présence des personnes exposées dans le milieu pollué en tenant compte du nombre d'heures par jour, nombre de jours par an et nombre d'années),

  Ex = Exposition totale par adulte ou enfant [a]
  Ve = Années de la vie entière par adulte ou enfant [a]. En cas d'exposition aux substances avec seuil : Ve = Ex [a]
  Fexa = Fréquence d'exposition annuelle [j/365 j]
  Fexj = Fréquence d'exposition journalière [hrs/24 hrs]

- **des quantités** d'aliments ou d'eau potable ingérés (en kg/j) et/ou du volume de l'air inhalé par jour (en m^3/j) et/ou de la quantité de sol ou de l'eau en contact avec la peau (par ex. en g/cm^2 de surface cutanée),

  Q_{ing} = Quantité ingérée de sol et/ou aliment [kg/j] et/ou d'eau [l/j], distincte entre les adultes ($Q_{ing}a$) et les enfants ($Q_{ing}e$)
  Q_{inh} = Quantité inhalée d'air [m^3/j], distincte entre adultes ($Q_{inh}a$) et enfants ($Q_{inh}e$)
  Fa = Facteur d'absorption (par biorésorption) du polluant (à défaut : 100 % = [1])
  Facut = Facteur d'absorption d'un polluant (à défaut : 100 % = [1]) ou vitesse d'absorption [m/h] pour la voie cutanée
  Fsp = Fraction de sol dans la poussière (à défaut : 100 % = [1])
  Spex = Surface de peau exposée, distincte entre les adultes et des enfants [m^2]
  Qsp = Quantité du sol (ou poussières) sur la peau [kg/m^2]

- **du poids corporel.**

  P(a) = Poids corporel d'un adulte [70 kg]
  P(e) = Poids corporel d'un enfant [15 kg]

Les formules de la quantification des doses journalières d'exposition sont les suivantes :

Exposition orale par ingestion :

$$DJE_{ing} = Cm \bullet Q_{ing} \bullet P^{-1} \bullet Fa \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$$

Exposition par inhalation * :

$$DJE_{inh} = Ca \bullet Q_{inh} \bullet P^{-1} \bullet Fa \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$$

* Il est possible d'évaluer l'exposition via l'air ambiant extérieur séparément de l'exposition via l'air ambient d'intérieur.

Exposition par contact cutané (sol, poussières, eaux) :

$$DJE_{cut} = Cs \bullet Fsp \bullet Spex \bullet Q_{sp} \bullet P^{-1} \bullet Fa_{cut} \bullet Ex \bullet Ve^{-1} \bullet Fexa \bullet Fexj$$

Les paramètres applicables sont à justifier. Une application des valeurs par défaut des logiciels d'évaluation des risques de type « Black-Box » est à prescrire, à défaut d'être justifiée de façon transparente pour le scénario d'exposition concerné.

B. A la suite de la sélection des VTR adaptées, il faudra réaliser les évaluations des risques quantitatives pour :

I : Les **Effets sans seuil** de dose :

- En général, il s'agit des effets génotoxiques (cancérigènes, mutagènes et tératogènes) à l'exception des effets épigénétiques cancrigènes.

- Dans ce cas, les Doses Journalières d'Exposition (DJE) sont multipliées par la VTR, sous forme d'Excès de Risque Unitaire (ERU) ou *Slope Factor* (SF) ou *Unit Risk* (UR), exprimés par ex. en [(mg/kg/j)$^{-1}$], soit :

ERU [(mg/kg/j)$^{-1}$]● DJE (mg/kg/j) = ERI (-) : **Excès de Risque Individuel**

- **L'ERI doit rester inférieur à « 10^{-5} », sinon le risque est considéré comme non-acceptable.**

II : <u>Les Effets avec seuil</u> <u>de dose</u> :

- Il s'agit des effets toxicologiques systémiques (neurotoxicité, hépatotoxicité, néphrotoxicité, etc.).
- Dans ce cas, les Doses Journalières d'Exposition (DJE) sont divisées par la VTR, sous forme de DJT (Dose journalière Tolérable), exprimée par ex. en [mg/kg/j], soit :

DJE (mg/kg/j) / DJT (mg/kg/j) = QR (Quotient de Risque) **ou QD** (Quotient de Danger)

- **Le QR (ou QD) doit rester inférieur à « 1 », sinon le risque est considéré comme non-acceptable.**

Effets de mélange :

En général, les effets de mélange des polluants (ou « *Combined Exposure to multiple Chemicals*") sont considérés depuis 2009 par l'IPCS & OMS (WHO) etc. via une additivité des doses d'exposition, si les effets toxicologiques sont similaires ou identiques. Les exceptions sont :

- les synergies (interaction) qui montrent des effets toxicologiques plus importants que l'additivité des doses ou,
- les antagonismes (interaction) qui provoquent des effets toxicologiques moins importants que l'additivité des doses.

Selon l'IPCS & OMS (WHO) 2009 etc., une différence doit être faite entre :

A. **l'exposition agrégée (« *Aggregate Exposure* »)** aux polluants individuels par l'ensemble des voies d'exposition,

B. **l'exposition cumulée (« *Cumulative Exposure* »)** évaluant un risque combiné par plusieurs polluants.'

Dans le cas de l'évaluation d'une exposition cumulée, il faudra identifier les polluants montrant les mêmes mécanismes toxicologiques (ou organes cibles). Ces groupes de polluants sont appelés les « *MOA : Common Toxic Mode of Action* ».

L'addition des doses est prise en compte pour chaque groupe MOA montrant les mêmes mécanismes toxicologiques (ou organes cibles), par ex. via l'application suivante :

- **Quotient de Risque : QR = Exposition 1/DJT+ Exposition 2/DJT + ….**
- **Excès de Risque Individuel : ERI = Exposition 1 ● ERU + Exposition 2 ● ERU + ….**

Cette application est simplifiée, comme par ex. dans le cas des Facteurs d'équivalence de toxicité pour les Dioxines (PCDD/F) et les « Dioxine-like PCB », les HAP et aussi par des « *Potency-Corrections* » pour les **PFAS**, par ex. via les RPF : *Relative Potency Factors*.

L'approche d'équivalence toxique s'applique à des mélanges dont les effets sont additifs. Elle est notamment décrite pour interpréter l'effet du mélange de certains organochlorés (chlorodibenzo-*p*-dioxines, chloro-dibenzofuranes et polychlor-obiphényls) qui partagent un mode d'action commun médié par la fixation à un récepteur spécifique, le récepteur AhR (Guyton et al. 2018).

Chaque congénère ne possédant pas la même efficacité, ils sont classés à l'aide de facteurs de toxicité relative (**Relative Potency Factors**, **RPF**) comparativement à un congénère de référence. Ce congénère est appelé composé index (*index compound*). Il est, par exemple, le plus toxique ou celui dont l'action est la mieux

documentée. Pour les dioxines et furanes, la dioxine de Seveso (2,3,7,8-tétrachlorodibenzo-p-dioxine) est utilisée comme référence avec un facteur de 1 et le facteur de toxicité est dénommé Toxic Equivalency Factor (TEF).
L'usage de RPF reste toutefois soumis au respect de conditions strictes :

1. en application de la définition présentée ci-avant, les composés doivent partager un même mode d'action ;

2. l'effet critique identifié pour le composé de référence doit l'être également pour les autres composés. Autrement dit, un composé index présentant un effet critique neurotoxique ne peut servir de référence pour un autre composé dont la toxicité s'exprimerait principalement au niveau rénal, par exemple ;

3. idéalement, les composés devraient posséder des courbes de relation dose-réponse de même efficacité tout en se différenciant, bien évidemment, par des puissances différentes. En outre, les courbes devraient être congruentes, c'est-à-dire qu'elles ne se croisent pas. Ces conditions sont nécessaires à la comparaison des Benchmark doses (BMD) pour un même niveau de réponse (*Benchmark Response* : BMR).

Les chercheurs du RIVM (Bil, 2021; Zeilmaker, 2018) proposent une approche RPF appliquée à la toxicité orale de 14 PFAS et de deux précurseurs (6:2 FTOH et 8:2 FTOH). Ils sélectionnent le PFOA (acide perfluoro-octanoïque [335-67-1]) comme composé index. Le PFOA est avec le PFOS (acide perfluoro-octanesulfonique [1763-23-1]), l'un des PFAS les plus étudiés. Parmi les effets toxiques attribués au PFOA (mais également au PFOS), ils identifient l'hypertrophie hépatique comme effet critique.

Le RPF est établi sur la base du rapport entre la BMD du PFOA et la BMD du congénère d'intérêt (équation 1).

Equation 1:

$$\boldsymbol{RPF_i = \frac{BMD_{PFOA}}{BMD_i}}$$

La BMD correspond à un BMR équivalent à 5% d'augmentation du poids du foie (absolu et relatif) établi sur des données continues ou à un excès de risque de 10% d'hypertrophie hépatique. Cette dernière expression du risque est établie sur base de données dichotomisées. L'excès de risque est ajusté pour les taux d'incidence pour un même effet. L'approche de Zeilmaker et Bil (Bil, 2021; Zeilmaker, 2018) débouche sur la proposition de RPF résumée dans le Tableau 2.

Tableau 2 : RPF selon Bil et al, 2021.

Congénères	Numéro CAS	RPF
Acides sulfoniques		
PFBS	375-73-5	0,001
PFPeS	2706-91-4	0,001 ≤ RPF ≤ 0,6
PFHxS	355-46-4	0,6
PFHpS	375-92-8	0,6 ≤ RPF ≤ 2
PFOS	1763-23-1	2
PFDS	335-77-3	2
Acides carboxyliques		
PFBA	375-22-4	0,05
PFPeA	2706-90-3	0,01 ≤ RPF ≤ 0,05
PFHxA	307-24-4	0,01
PFHpA	375-85-9	0,01 ≤ RPF ≤ 1
PFOA	335-67-1	1
PFNA	375-95-1	10
PFDA	335-76-2	4 ≤ RPF ≤ 10
PFUnDA	2058-94-8	4
PFTrDA	72629-94-8	3
PFDoDA	307-55-1	0,3 ≤ RPF ≤ 3
PFTeDA	376-06-7	0,3
PFHxDA	67905-19-5	0,02
PFODA	16517-11-6	0,02
Ethers des acides carboxyliques		
HFPO-DA	13252-13-6	0,06
ADONA	919005-14-4	0,03
Alcools télomériques		
6:2 FTOH	647-42-7	0,02
8:2 FTOH	678-39-7	0,04

L'application des RPF de Zeilmaker (2018) et Bil (2021) dans le cadre de l'évaluation des risques est clairement contestée par Rietjens et al. (2022). Ils soutiennent l'usage de RPF dans les EQRS mais contestent la robustesse de ceux calculés par Bil (2021). Rietjens et al et Bil s'opposent sur la sélection des données et sur l'impact du mode d'exposition des PFAS chez les rongeurs. Bil et al. (2022) rejettent ces critiques signalant que numériquement les valeurs ne diffèrent pas significativement en modifiant le jeu de données selon les recommandations de Rietjens.

Également Goodrum et al. (2021) critiquent l'approche de Bil et Zeilmaker en indiquant les différences dans le mode d'action des PFAS à chaînes courtes par rapport à ceux à chaînes longues (C>8). Les PFAS à chaines longues ont la capacité de se fixer à un nombre plus important de récepteurs nucléaires (entre 6 et 16) que ceux à chaînes courtes qui seraient limités à deux récepteurs. Pour cette raison Goodrum et al. Contestent l'existence d'une similarité dans les relations dose-réponse.

Par conséquent, l’application des RPF n’est pas recommandée (en 2024).

La plus grande inconnue dans les effets des mélanges par des PFAS concerne la grande partie des PFAS poly-fluorés. Il est recommandé d’appliquer les analyses des PFAS (28 – 70 molécules, cf. aussi l’Arrêté Ministériel en France du 20/06/2023) avant et après le « Top Assay ».

Le « Top Assay » (Total Oxidizable Precursor) transforme les PFAS poly-fluorés vers les PFAS perfluorés (Fig. 11a & b). Dans l’environnement, l’ensemble des PFAS poly-fluorés (Precurseurs) sont bio-transformés vers les PFAS per-fluorés stables. Via le « Top Assay » il est possible d’intégrer dans l’évaluation des risques sanitaires immédiatement les PFAS per-fluorés, produits des bio-transformations dans un scénario d’exposition. Cependant, il ne faut pas se contenter de réaliser l’évaluation des risques sanitaires uniquement sur les PFAS per-fluorés après le « Top Assay », car les effets avec-seuil de dose de certains PFAS poly-fluorés plus stables peuvent être importants dans les expositions sub-chroniques et chroniques, comme par ex. concernant les PFAS volatils (FTOH : fluorotéloméré-alcools) ou 6 :2-FTAB etc. (Karg 2023c).

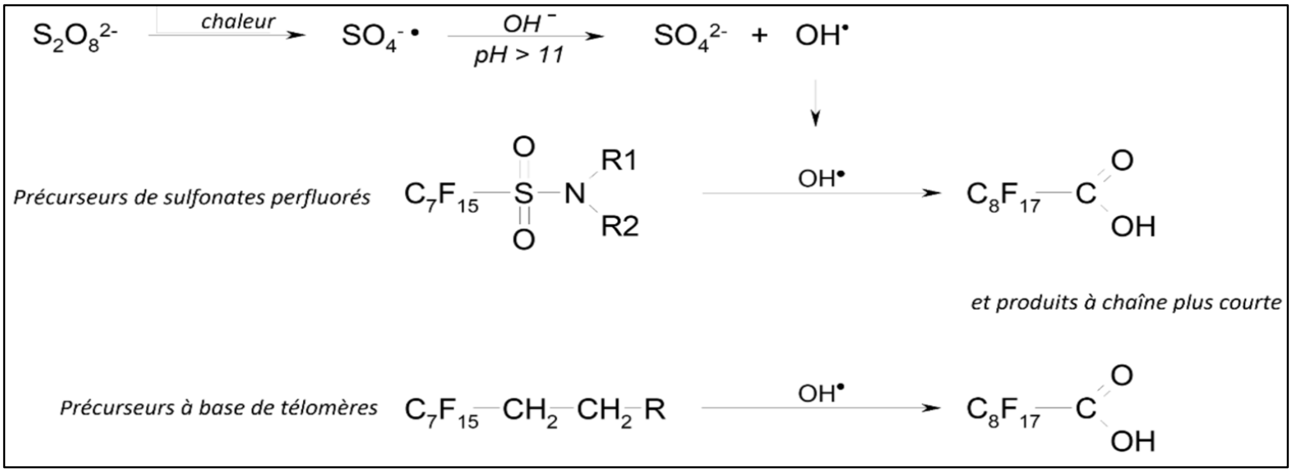


Fig. 11a : Top Assay (Total Oxidizable Precursor) analyse de la quantité totale de précurseurs (PFAS poly-fluorés) oxydables via persulfate (Houtz et Sedlak : 2012, Glöckner et al. : 2021)

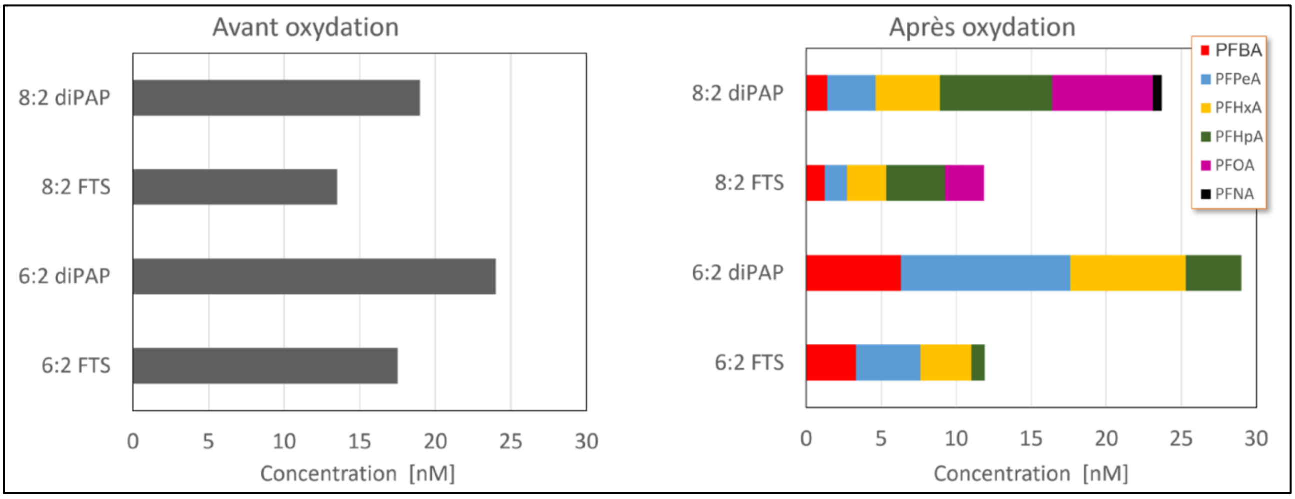


Fig. 11b : Top Assay : Example de quantification des PFAS poly-fluorés via leurs acides carboxyliques perfluorés finaux correspondants après dégradation (Houtz et Sedlak : 2012, Glöckner et al. : 2021), à prendre en compte dans une EQRS

5. Conclusion

Le défis de l'évaluation des risques sanitaires et toxicologiques (EQRS & TERQ) des PFAS est d'assurer le bon choix des VTR actualisées et de gérer le grand nombre des PFAS poly-fluorés. Le fait qu'ils sont biotransformés (mais aussi par photolyse) vers des PFAS per-fluorés permet de les regrouper via le Top Assay directement dans les EQRS. Néanmoins, il faut aussi intégrer certains PFAS poly-fluorés relativement stables directement dans l'évaluation des risques sanitaires et toxicologiques (par ex. le 6 :2-FTAB, les 4 :2- & 6 :2-FTS, les FTOH, etc.).

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Determination of sustainable health risk based soils standards for PFOA and PFOS with a combination of epidemiological data and a multimedia, one-compartment toxicokinetic and probabilistic model

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KEYWORDS: PFOA, PFOS, toxicokinetic model, sustainable soil standards.

ABSTRACT:

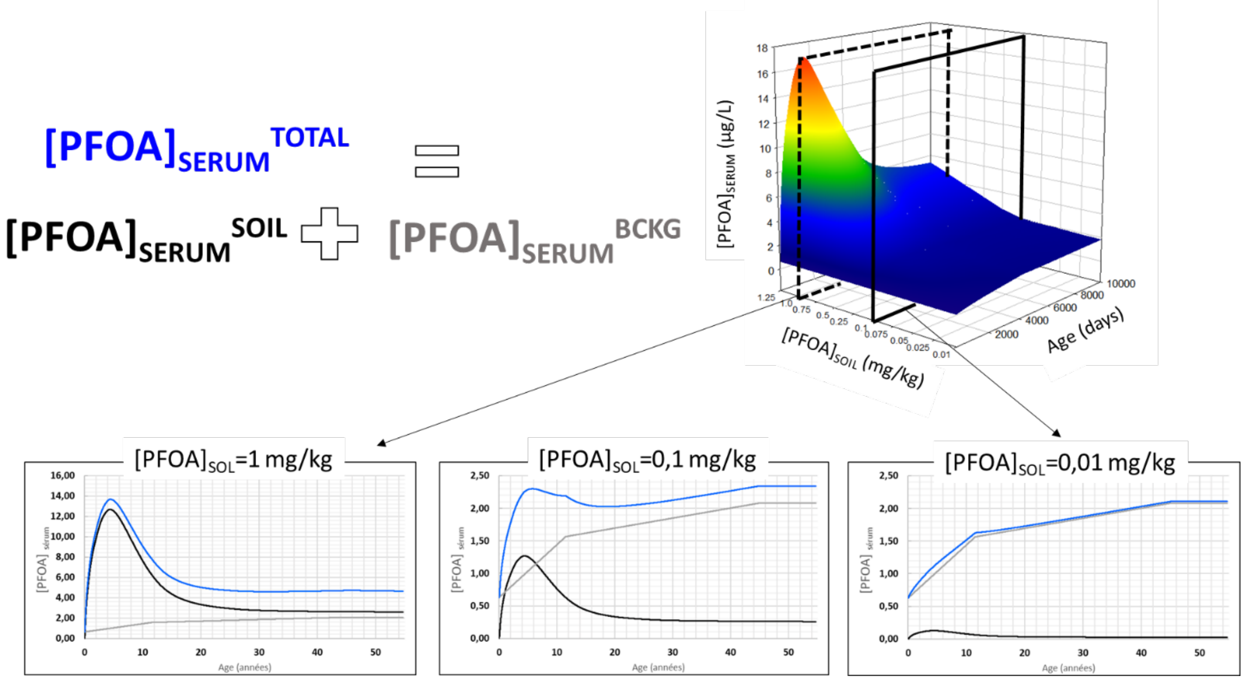
PFOA and PFOS are the two most known PFAS that pose serious health risks for humans. When it comes to human health risk assessment (HHRA) related to PFAS contaminated soils, the dose-to-reference dose approach using deterministic multimedia models give rise to unsustainable soil standards with respect to the recent toxicity assessment by EFSA (2020) [1]. They are often lower than typical background concentrations or instrumental quantification limits (in the range of 1-2 µg/kg). As a consequence, higher "arbitrary" values (i.e. not risk-based) are chosen for management purpose, therefore leaving in place contaminated soils that are deemed unacceptable with respect to public health and HHRA methodologies. Moreover, current HHRA models mostly focus on direct and indirect transfer from soil to humans but often omit the major PFAS sources (total dietary intake) as well as close contact ones (intake from the use of textiles, cosmetics, food packaging, cooking pans, etc.), which is not a safe approach to the PFAS public health problem. In fact, recent epidemiological surveys (i.e. ESTEBAN study [2], for the French population) shows that a large part of children and adults already have serum PFAS concentrations above HBM I values (i.e. 50% of adults for PFOA), thus are already at potential risks.

In this context, we propose an alternative approach to HHRA for PFAS due to contaminated soils. A model is built on the current biological exposure of the general population (epidemiological data from ESTEBAN PFOA and PFOS distributions) and uses a one compartment toxicokinetic component including a first order elimination kinetic (i.e. Lynch et al. 2023 [3], Goeden et al. 2019 [4]). The model calculates daily intakes of PFAS from soil, converted as daily PFAS serum concentration increments and further added to the median value of the PFAS levels serum distribution measured in the general population, for children and adults (FIGURE 1).

Risk is evaluated against a 5% probability to have a PFAS serum concentration above the upper confidence interval of the 95th percentile of the distribution in the general population. This mathematical formalism allows performing a risk evaluation on biomarker data, therefore intrinsically integrating all PFAS sources of exposure, as well as physiological differences and exposure history at the population scale.

Backward calculation provides soil standards values of 50 and 29 µg/kg for PFOA and PFOS, respectively, i.e. one order of magnitude above those determined with the classical reference dose approach. Despite higher values, the approach stays safe since it accounts for all possible exposure sources and population variability.

Further developments will focus on expanding the range of exposure scenarii and improve multimedia components (soil-plant transfer, soil-dust transfer, etc).



$$[PFOA]_{SERUM}^{TOTAL} = [PFOA]_{SERUM}^{SOIL} + [PFOA]_{SERUM}^{BCKG}$$

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Study of the endocrine activity of per- and polyfluorinated compounds (PFAS) and development of an integrative methodology aimed at evaluating the residual toxicity of treated matrices

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Per and polyfluoroalkyls substances (PFAS) belong to a large family of environmental pollutants that appeared in the 1950s. These compounds are used in many home and industrial applications that lead to global contamination of soil and water. This contamination may lead to the exposure of human populations and thus to adverse effects that should be limited by environmental remediation measures.

Hazards class of some PFAS have been established by CLP Regulation (EC) n°1272/2008. Indeed, PFOS and PFOA are harmful if swallowed or inhaled, cause damage to organs through prolonged or repeated exposure (liver), may cause harm to breast-fed children, may damage the unborn child, are suspected of causing cancer and PFOA causes serious eye damage (ECHA, PFOS: ATP01; ECHA PFOA: ATP05). Moreover, in the literature, PFAS and especially PFOS and PFOA are suspected to be endocrine disruptors (ED).

WHO defines an endocrine disruptor as an exogenous substance or mixture that alters the function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations. These adverse effects could be cancer, reproductive, metabolic, or immune system disorders. Recent evolutions of the CLP Regulation introduced new hazard classes for ED for human and environment. To assess the ED properties of PFOS and PFOA on thyroid and androgenic axis, SPUMA collaborated with WATCHFROG and tested PFOS and PFOA on OECD n°248 (XETA test) and OECD n°251(RADAR test) guidelines. These level 3 (OECD 150) alternatives assays use genetically modified tadpoles (*Xenopus Eleutheroembryonic*) and fish (*Oryzias latipes*) that fluoresce during a thyroid and androgenic endocrine response.

In our study, genetically modified organisms have been exposed to increasing concentrations of PFOS and PFOA during 72 hours in single exposure, in non-stimulated and stimulated condition with thyroid hormone (3.25 µg/L of T3) for XETA test and a reference substance (3 µg/L of 17MT) for RADAR test. XETA test highlighted a decrease of the thyroid response after 72h exposure to PFOA (100 mg/L) and PFOS (5, 16, 50 mg/L) in stimulated conditions with T3, which could correspond to an antithyroid effect. RADAR test highlighted an increase of the androgenic response after 72h exposure to PFOS (5 mg/L) in stimulated condition with 17MT. These tests would have demonstrated the potential of PFAS to affect endocrine regulation, both at the thyroid and androgenic level and could lead to classify PFOS and PFOA as endocrine disruptor substances in a weight of evidence approach.

The absence of an international consensus on the threshold values for PFAS in water, guaranteeing the absence of risks for humans and ecosystems, is an issue for the treatment of water containing PFAS.

SPUMA developed a bio-foam fractionation (BFF) method that extracts PFAS from water under the different international threshold values. A method of demonstrating the effectiveness of SPUMA water treatment, or more generally of treating water containing PFAS, could be to monitor and test the toxicity of the residual quantity of PFAS in water after treatment. The residual quantities of PFAS present in treated water could be monitored by using contamination bioindicators, allowing PFAS to be detected where they are not usually detected in water. Moreover, toxicity assessment of aquatic matrices could be assured by testing waters with OCDE guidelines. Since we demonstrated that PFOS and PFOA seem to be ED, using WATCHFROG bioassays to assess the endocrine disrupting potential of waters contaminated by PFAS seems pertinent. Those tests have the advantage of using entire aquatic organisms with a functional endocrine system similar to that of humans and to test ED on the entire hormonal axis, not just at receptor level. Those assays could be used for the assessment of water quality/toxicity like surface and groundwater, wastewater treatment plants (WWTP), industrial effluent contaminated by PFAS. They could also be used to assess the residual toxicity of a treated water (before/after treatment) or to monitor treatment efficacity by setting an alert threshold (fluorescence of organism) signaling a drop in treatment efficacity.

However, these tests would not differentiate the endocrine disrupting effects of PFAS from those of other substances, such as micropollutants which could be present in water at very low concentrations. Therefore, the *in vivo* fluorescence measurement of endocrine disrupting effects could be considered to assess the quality of PFAS- treated water downstream of WWTPs before and after the application of SPUMA treatment.

Human biomonitoring around the metal shredders targeted on metals and others hazardous chemicals in Wallonia (Belgium)

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Environmental monitoring has assessed the contamination by toxics elements, such as persistent organic pollutants (POPs) or metallic elements, in the vicinity of shredding plants. These facilities actors of the circular economy, are 7 in Wallonia (southern part of Belgium). The objectives of this study are to assess the exposure of residents near metal shredders to hazardous chemicals, to compare it with the general Walloon population (reference population, recruited between Nov.2019 and June 2020) and to assess the risk to human health. Around each shredder plant, an area was determined based on several criteria related to the plant (stack height, gas temperature and velocity), topography and meteorological conditions (wind speed and direction frequencies). This study focused on adolescents because they are considered sentinels of their local living environment and they are representative of recent exposure during youth. Another part of this study concerned indoor dust. Almost fifty substances of interest (PCBs, ETM…), per- and polyfluoroalkyl substances (PFAS) were analysed, in both biological and environmental samples.

Only 121 teenagers living close to a metal shredder participated in this human biomonitoring by the collection of blood and urine (Sept-Oct 2022). So, this research cannot draw specific conclusions by shredders's location. The results show that several pollutants are found in the bodies of adolescents living near metal shredders. Although some biomarkers have not been quantified or only to a very limited extent, living around a shredding plant seems to have an impact on the exposure of local population. Compared with Walloon adolescents, concentrations in biological matrices are significantly higher among adolescents living near a site containing a metal shredder for arsenic, lead in urine and PCB-138 and PFOS in blood (fig 1) (also PFHxS in blood for one shredder location). Given the small size of the study group (for all 7 shredders), differences and similarities between the 'Shredders' group and the reference population should be treated as trends and with caution.

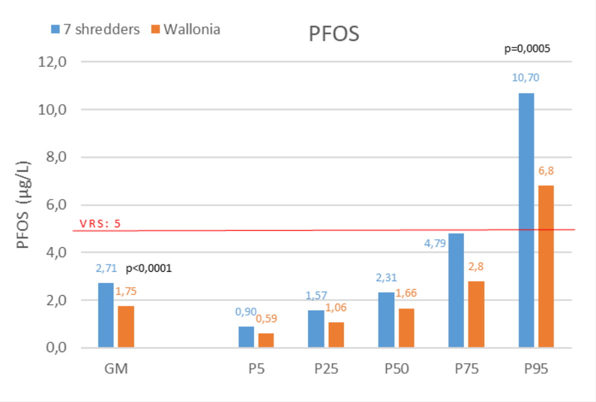

Figure 1: Comparison between PFOS concentrations measured in blood of adolescents in Wallonia and around the shredders.

Exceedances of the health guide value were observed for urinary arsenic (Toxic Relevant Arsenic), for urinary cadmium, for blood lead, for PFOA and for PFOS in blood.

A sample of indoor dust was taken by each participant with their vacuum cleaner in almost 200 houses. The results showed the following trend: “closer the shredders, greater is concentrations pollutants in house dust”. The ingestion of indoor dust contributes to the overall exposure and impregnation of resident adolescents, but dust is not the only source of exposure. Food remains preponderant, particularly depending on the individuals and pollutants considered.

Comparing the sustainability of active and passive groundwater containment systems for the treatment of PFAS plumes

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Kris Maerten (REGENESIS) and Jarno Laitinen (Ramboll Oy, Finland)

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The chemical-physical properties of PFAS limit current remediation techniques for groundwater to securing the contamination, usually using pump-and-treat (Pump&Treat) systems. Colloidal activated carbon (CAC) has been available on the market for some years as an alternative: CAC is injected into the subsurface to coat the solid matrix with a thin layer of activated carbon and allow PFAS to be adsorbed. Thanks to this action of immobilising PFAS within an injectable, permeable and reactive barrier, concentrations in the plume downgradient can be reduced to a level that minimises further intervention.

Ramboll analysed in an independent study the sustainability of the technique with CAC in comparison with the classical Pump & Treat approach, using two alternative filtration technologies. The CAC product compared was PlumeStop® from Regenesis.

Ramboll carried out a life cycle analysis (LCA) regarding the production of climate-damaging gases (carbon footprint) and remediation costs, in accordance with the relevant ISO standards. In addition, a sustainability assessment was carried out for the three different techniques using Ramboll's SURE (SUstainable REmediation) model, which considers 15 different sustainability indicators. This method is made available to the public to compare the sustainability of different remediation approaches.

The presentation will briefly review the three remediation methods and then describe the complete sustainability analysis using the different methods. Some general indications for sustainable PFAS remediation will be drawn from the comparative study.

PFAS destruction via nonthermal plasma in (waste)water

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Tectero is a privately owned SME established in 2013 and based in Ghent (Belgium). Tectero BV is ISO 9001 certified since 2021. The main goal and activities of Tectero BV are the development of nonthemal plasma technology for the conversion of liquids and gases and carrying out contract research and development for third parties in the field of green chemistry, renewable energy and environment.

PFAS substances are synthetic compounds with unique properties including high chemical and thermal stability which are very persistent in the environment. Since the 1940s PFAS have been used in numerous consumer products and industrial applications. PFAS are and have been used in firefighting foams, paints, coatings, textiles, paper, pesticides, pharmaceuticals, etc. PFAS is an omnipresent collection of over 12 000 compounds. The main problem for the environment is attributed to the fact that the carbon-fluorine bond in PFAS is thermodynamically very robust and provides persistence, inertness and stability to PFAS substances.

By applying a nonthermal plasma Tectero BV is able to destroy the carbon-fluorine bond in PFAS. Tectero's nonthermal plasma technology focusses on a continuous flow process and a full destruction and mineralisation of PFAS present in (waste)water. Tectero's process is able to degrade PFAS in many different types of water such as drinking and groundwater with a relative low PFAS load (hundreds of ng/L to tens of µg/L), process water with medium PFAS load (hundred µg/L to mg/L) and leachate water with a combined high PFAS load (mg/l to 5 mg/L) and high salt content. Also emergency response water (for example from fire fighting incidents) can be treated in a similar way. No pre-treatment is required except sand filtration. The process can be integrated as a first bulk remover, a final polishing or stand-alone wastewater treatment step.

The process main driver is powered by electricity. When the electricity used is sourced from alternative energy production facilities the complete process if fully sustainable.

In this presentation Tectero BV will provide insight in the application results of nonthermal plasma destruction of PFAS in various types of (waste)water.

Efficient removal of per- and polyfluorinated alkyl substances from potable- and waste water with selective Lewatit® resins

Dr. Dirk Steinhilber, Lanxess Deutschland GmbH

PFAS is a family of highly efficient surface-active agents used in various applications such as firefighting foams, water repellent textiles, galvanics, and lithium ion batteries. However, when they are not handled and disposed of thoroughly they can leach into the ground- and surface water where they persist as a result of their high chemical stability. Due to their hazardous potential, drinking water limits have been set strictly. Standard technologies such as activated carbon usually cannot comply with the low effluent limits, especially for short-chain PFAS, that represent an important challenge in remediation. On the other hand, reverse osmosis, an alternative technology for PFAS removal, generates large amounts of aqueous concentrates that have to be handled. Therefore, LANXESS has developed new types of selective ion exchange resins (IER) that reduces PFAS reliably below the drinking water limits and which can safely be disposed after use.

In this paper we will present the performance of our PFAS selective Lewatit® TP 108 DW resin that is particularly applicable for the removal of short- and long-chain PFAS to very low levels. For applications in which the regeneration of PFAS is preferred, we additionally offer our regenerable resins Lewatit® MP 62 WS and Lewatit® MonoPlus TP 109.

This presentation will highlight the excellent performance of PFAS selective Lewatit® ion exchange resins, which leads to benefits, including substantial cost savings. Ion exchange resins (IER) can be operated about 5 times longer than granular activated carbon (GAC). As a result, customers need to replace the Lewatit® ion exchange resin less frequently and achieve savings in investment costs. Remarkably, the much shorter EBCT of IER enables a smaller footprint while treating a larger volume of waste stream. A cost calculation will be presented for a plant with five years' operation which indicates that Lewatit® TP 108 DW costs 58% less than GAC, and 29% less than a competitive resin.

Contact details of speaker

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INTERNAL

Process Development for Removal of Ultra-Short Chain PFAS using Regenerable Ion Exchange Resin

Francis Boodoo, Global Director of Innovation – Purolite, an Ecolab Company

email: francis.boodoo@purolite.com

This presentation will explore the development of a treatment process for removal of short and ultra-short chain PFAS from water using regenerable ion exchange resin. Apart from long chain PFAS, there is a growing need to remove short chain PFAS in especially Europe and elsewhere. Focus is also now turning to the removal of ultrashort chain PFAS like trifluoroacetic acid (TFA) due to its growing widespread occurrence in rainfall.

It is known that highly PFAS-selective anion exchange resins, like Purolite PFA694E and PSR2+, show much lower capacities for short chain PFAS like PFBA vs long chain PFAS like PFOA. For instance, when treating drinking water with a moderate mineral background, operating capacities for PFAS-selective resin may generally range from 100,000 to 300,000 bed volumes. At such capacities it is economically justifiable to use the resin once and then dispose of it. This results in a very simple operator-friendly process. But for short chain PFAS, resin capacities are much lower. Capacities for PFBA can generally range from 5,000 to about 20,000 bed volumes. At these low capacities, a single use of the resin is generally difficult to justify economically. Instead, a regenerable resin process using resins with moderate to low PFAS selectivity may be needed.

A regenerable resin process would also make sense for removal of ultrashort chain PFAS, like TFA. TFA removal is becoming important as recent studies show increasing concentrations in rainfall globally. For example, a recent report on rainfall in Germany showed TFA levels at about 5 µg/L, and scientists, according to the report, were expecting a tenfold increase by 2050.(Trifluoroacetic acid from fluorinated refrigerants contaminates rainwater | Umweltbundesamt). Similar increases having been observed in the USA and China. The main driver seems to be the oxidative breakdown in the atmosphere of the newer fluorinated refrigerant F1234yf (known as F-gas) used for the last couple of decades to replace older R-134a chlorinated hydrocarbon type refrigerants.

In the USA, similar compounds, like trihaloacetic acids (THAs), a group of six chemicals, are regulated at a combined total of 60 µg/L. With fluoride being a halogen, similar controls are expected for TFA. In Germany, the proposed reduction level for TFA is already at 10 ug/L. Thus, developing a regenerable resin process for removal of short and ultrashort chain PFAS seems to be needed.

Piloting studies in progress in Europe and USA are helping to develop and commercialize a two-step resin process for removal of short, ultrashort, and long chain PFAS. The first step uses a regenerable weak base anion (WBA) exchange resin for removal primarily of short and ultrashort chain PFAS. Some long chain PFAS are also expected to bind to the WBA resin, but eventually spill-over or leakage of long chain PFAS would be removed by the resin in the second step. This will usually be a PFAS-selective strong base anion exchange resin (SBA).

The WBA process step may require pre-adjustment of the feedwater pH if the alkalinity is too high; CO2 dosing is a good option for this. It is proposed to limit the operating capacity of the WBA resin to about 1000 to 3000 bed volumes in between regenerations. During regeneration, a very dilute caustic solution (e.g. 0.5 to 1.0%) is proposed for regeneration. But, unlike the usual once through passage of the regenerant, the process calls for recirculating the caustic solution through the resin multiple times. The recirculation method for regeneration is not widely practiced but is shown in a current patent by the author on oxyanion removal using weak base resin. After the regenerant phase is completed, the regenerant is stored for later reuse. Rinsing of excess caustic from the resin is also done with recirculated rinse water while dosing CO2 into the rinse water to neutralize the caustic. The rinse is stopped when the pH is close to neutral to mildly-acidic, and the rinse water is also stored for later use.

Both the spent regenerant and rinse water are reused multiple times to minimize chemicals, water usage, and wastewater volumes to be disposed of. When it is time to reduce PFAS in the spent regenerant, the alkaline solution is then passed through multiple smaller ion exchange resin vessels with a scavenger resin (e.g. PFA694) for removal of PFAS. Multiple vessels in series are used to maximize the loading on the resin before it is disposed of. Once the PFAS-depleted caustic solution is ready to be disposed of, CO2 is dosed into the solution to convert caustic to a dilute sodium bicarbonate solution. This can then be more easily disposed of, for example, at a local wastewater treatment plant where bicarbonate can be helpful to the biological process.

An additional benefit of the two-step ion exchange process is use it for joint reduction of TOC and PFAS, if both are present. This may be particularly useful for surface water plants where TOC can be present at 2 to 15 mg/L. Under those conditions, TOC reduction may be needed to avoid formation of disinfection byproducts on subsequent chlorination of the water. The single-use selective strong base anion (SBA) resin used downstream of the WBA resin would also benefit as prior reduction of TOC by the WBA can drastically improve its capacity for PFAS removal; losses in SBA capacity of as much as seventy-five percent or more would be avoided. Operator attention would also be minimized as the use of only liquid chemicals and this would facilitate the automation of the process. Since the wastewater produced is a dilute alkali and it would likely be disposable at an onsite WWTP, the process would also be suitable for replacing strong base anion resin processes that are currently using brine for regeneration of TOC, and paying very high cost to haul away and dispose of spent sodium chloride brine.

Overall, the process would fill a niche need in the overall PFAS removal market that can allow water treatment plants to more efficiently deal with the global PFAS issues.

Jeudi 6 juin 2024

09h00
Accueil des participants

Présidents :
- *Philippe Rolland, ARET & Expert IMDS & Substances - Renault Group, France*
- *Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne*

Technologies de traitement pour l'eau, les sols, les sédiments, l'air & les émissions

09h30
Importance des Polymères fluorés non-toxiques dans la vie quotidienne des transports, notamment dans les pièces automobiles.
Quels sont les enjeux, comment Renault Group s'organise-t-il, quelles attentes ? : cas d'école de bonne / mauvaise substitution
Philippe Rolland, Expert IMDS & Substances - Renault Group, France

10h00
Traitement des PFAS des eaux usées industrielles par procédé de réduction avancée
Baptiste Mathon, Ingénieur R&D - Treewater, France

10h30
Pause café & thé

11h00
Nouveaux développements et progrès dans le traitement des sols et de l'eau contaminés par des PFAS
Nicolas Etard, Ingénieur projets - Züblin Umwelttechnik GmbH, France

11h30
Système de traitement des PFAS construit par ECT2 à l'aéroport de Swedavia Arlanda
Jeffrey Lewis, Directeur général - ECT2, Montrose Environmental Group, Suède

12h00
Les traitements in-situ des PFAS dans les eaux souterraines, les sols & gaz du sol (FTOH) et l’application des Bio-Polymères protéiniques : Bilans Coûts-Avantages
Dr. Frank Karg, SFSE & ARET, Expert judiciaire, Directeur scientifique - HPC International, France & Allemagne

12h30
Déjeuner

13h45
Comparaison multicritère de trois technologies de traitement des 42 PFAS dans l'eau potable par une approche expérimentale globale
Delphine Steinmann, Ingénieur Recherche et Développement - Suez, France

14h15
Réhabilitation catalytique des eaux souterraines contaminées par les PFAS
Dr. Silvan Staufert, Directeur de la technologie et co-Fondateur - Oxyle, Suisse

14h45
Remédiation à base de biopolymères des sols contaminés par des PFAS - Traitement sur site dans des piles de lixiviation
Anja Wilken, Responsable de la gestion de projet - Sensatec GmbH, Allemagne

15h15
Pause café & thé

15h45
Procédés d'oxydation avancés photoélectrocatalytiques pour la dégradation des polluants organiques fluorés dans les eaux contaminées par les afffs
et les eaux souterraines

- *Silvia Franz, Professeur associé - École Polytechnique de Milan, Italie*
- *Paolo Ronco, Responsable Recherche & Innovation - Viacqua, Italie*

Recherche et développement

16h15
Zéolites naturelles modifiées pour le traitement des eaux contaminées par les PFAS
Cosimo Masini, Président-directeur général - DND Biotech, Italie

16h45
Collecte de PFAS en phase gazeuse à l'aide de résine styrène-divinylbenzène
Jason Hoisington, Scientifique - Restek Corporation, Etats-Unis

17h15
Performance de l'osmose inverse pour le traitement des déchets liquides dangereux contenant des PFAS en concentration et composition différentes
Manon Granger-Delacroix, Ingénieur Expert Process - SARPI Veolia, France

17h45
Assainissement intégré des sols contaminés par les PFAS d'une installation française de lutte contre l'incendie
Muhammad Usman, Chercheur - Ecole Nationale Supérieure de Chimie de Rennes (ENSCR), France

18h15
Discussion & Conclusions

18h30
Fin du congrès

Thursday, June 6, 2024

09h00
Welcoming participants

Presidents:
- *Philippe Rolland, ARET & IMDS and Substances Expert - Renault Group, France*
- *Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany*

Treatment Technologies for Water, Soils, Sediments, Air & Emissions

09h30
Importance of non-toxic fluorinated polymers in everyday transport, particularly in automotive parts. What are the stakes, how is Renault Group organizing, what are the expectations?: Two textbook cases of good / and of bad substitution
Philippe Rolland, IMDS & Substances expert - Renault Group, France

10h00
Treatment of PFAS from industrial wastewater by advanced reduction process
Baptiste Mathon, R&D engineer - Treewater, France

10h30
Coffee & Tea break

11h00
New developments and advances in treating PFAS-contaminated soil and water
Nicolas Etard, Project Engineer - Züblin Umwelttechnik GmbH, France

11h30
PFAS treatment system built by ECT2 at Swedavia Arlanda Airport
Jeffrey Lewis, Managing Director - ECT2, Montrose Environmental Group, Sweden

12h00
In-situ treatments of PFAS in groundwater, soils and soil vapor (FTOH) and the application of protein Bio-Polymers: Advantages & Inconvenients
Dr. Frank Karg, SFSE & ARET, Court Expert, Scientific Director - HPC International, France & Germany

12h30
Lunch

13h45
Multicriteria comparison of three technologies for the treatment of 42 PFAS in drinking water using a comprehensive experimental approach
Delphine Steinmann, Research and Development Engineer - Suez, France

14h15
Catalytic remediation of PFAS contaminated groundwater
Dr. Silvan Staufert, Chief Technology Officer and Co-Founder - Oxyle, Swiss

14h45
Biopolymer based remediation of PFAS contaminated soils - On Site Treatment in leaching piles
Anja Wilken, Head of Project Management - Sensatec GmbH, Germany

15h15
Coffee & Tea break

15h45
Photoelectrocatalytic advanced oxidation processes for the degradation of fluorinated organic pollutants in afff-contaminated water and groundwater
• Silvia Franz, Associate Professor - Polytechnic of Milan, Italy• Paolo Ronco, Research & Innovation Manager - Viacqua, Italy

Research & Development

16h15
Modified Natural Zeolites for the Treatment of PFAS Contaminated water
Cosimo Masini, CEO - DND Biotech, Italy

16h45
Collection of gas-phase PFAS Using Styrene-Divinylbenzene Resin
Jason Hoisington, Scientist - Restek Corporation, USA

17h15
Performance of reverse osmosis for the treatment of hazardous wastewater containing various concentrations and types of PFAS
Elisabeth Geldof, Cold Sector Expert-Laboratory Manager - SARPI Veolia, France

17h45
Integrated remediation of PFAS-Contaminated Soil from a french firefighting facility
Muhammad Usman, Researcher - National School of Chemistry of Rennes (ENSCR), France

18h15
Discussion & Conclusions

18h30
End of the Congress

Advanced reduction process for treatment of PFAS in industrial wastewater

Baptiste Mathon, R&D engineer – Treewater, France; Email: bmathon@treewater.fr

Baptiste MATHON[1], Yara ARBID[2], Thibault PAULET[1], Claire-Lise FRANQUART[1], Khalil HANNA[2], Bruno CEDAT[1]

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Keywords: PFAS, Advanced Reduction, UV/sulfites, Industrial Effluent, Pilot

I. CONTEXT

The perfluoroalkyl and polyfluoroalkyl substances (PFAS), widely used in various consumer products and industrial processes due to their unique properties, pose a growing challenge in both urban and industrial wastewater. However, their presence in wastewater is a major concern due to their toxicity and persistence in the environment (Evich et al., 2022). Most conventional treatment systems based on biodegradation are not designed to effectively remove PFAS, resulting in their persistent presence in treated effluents. A recent study revealed that 70% of wastewater treatment plants worldwide studied had PFAS concentrations ranging from 15 to 1500 ng/L (Lenka et al., 2021). The PFAS Action Plan 2023-2027, initiated by the Ministry of Ecological Transition and Territorial Cohesion, aims to mitigate risks at the source, continue monitoring environmental conditions, accelerate scientific knowledge production, and improve public access to information regarding these pollutants.

II. OBJECTIVES

The PREFAS project (Processes for Remediation of PFAS) aims to develop a treatment solution for per- and polyfluoroalkyl substances (PFAS) in complex industrial effluents through advanced reduction. The main objective is to develop a pilot reaching a Technology Readiness Level (TRL) of 5 by the end of the project.

III. EXPERIMENTAL PROTOCOL

Treatment by advanced reduction UV/sulfites and UV/sulfites/iodides.

Advanced reduction experiments were conducted on a two-liter laboratory pilot consisting of a 24W low-pressure UVc lamp (Figure 1). The effluent was continuously recirculated via a pump at a flow rate of 5 L/min to accumulate a UV dose of up to approximately 16000 mJ/cm². Series of experiments were carried out to evaluate the effectiveness of PFOA treatment in ultrapure water, wastewater treatment plant (WWTP) effluent, and in a real matrix of industrial effluent (paper mill water). PFOA was initially spiked at 1 mg/L, and sulfite injection was performed to obtain a concentration of 20 mM (UV/sulfites) and 10 mM sulfites combined with 10 mM iodides (UV/sulfites/I). Control experiments were conducted in the absence of UV alone and in the absence of sulfites alone to assess possible degradation by UVc radiation.

IV. EXPERIMENTAL RESULTS

The results of the experiments are presented in Figure 1. Degradation experiments in the absence or presence of UVc alone for PFOA did not show significant degradation regardless of the matrix (between 5 and 15%). The removal performance of PFOA in ultrapure water with UV/sulfite treatment was excellent, achieving 99% removal to reach a residual concentration of 2 µg/L. Sulfites react under UVc radiation to form e-(aq), which generates reduction mechanisms for PFOA (transformation of a functional group -CF2- into -CH2- or elimination of a -CF2- group). Maintaining the same operating conditions, removal performance in real paper mill effluent matrix decreased to 65% with a residual concentration of 353 µg/L. A similar trend was observed with the sewage treatment plant (STEP) effluent, where removal performance decreased to

40% with a residual concentration of 610 µg/L. Advanced reduction experiments using UV/sulfites/iodides achieved nearly 100% degradation in ultrapure water and STEP water. However, a decrease in performance to 60% was observed in industrial effluent. The complex matrix of real effluents contains species that can trap e-(aq). Dissolved oxygen is a significant consumer of e-(aq). Furthermore, dissolved organic matter is an important consumer of e-(aq) as it contains numerous oxygenated functional groups (aldehyde, ketone, quinone, etc.).

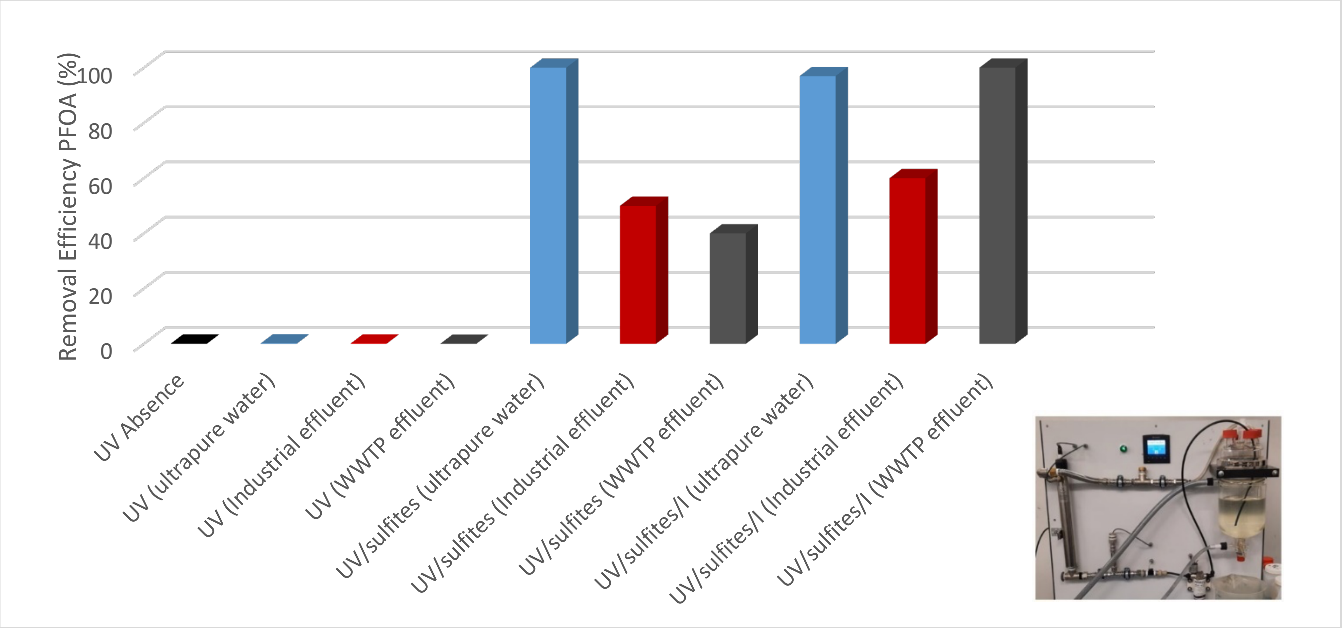

Figure 1 : Evolution of the concentration of initially spiked 1 mg/L PFOA in ultrapure water, STEP effluent, and industrial effluent during treatment by advanced reduction; [Sulfites]=0, 10, or 20 mM and [Iodides]=10 mM.

V. CONCLUSIONS AND FUTURE DIRECTIONS

These initial experiments mark the starting point of the PREFAS project and highlight the possibility of achieving destructive treatment of PFAS in simple matrices. Adaptation of operational conditions is necessary to obtain similar results in complex matrices. Further experiments are underway by combining advanced oxidation processes such as UV/H_2O_2 or electro-oxidation with advanced reduction. The aim is to degrade organic pollution to mitigate matrix effects while initiating degradation mechanisms of the C-C bonds of PFAS. Monitoring of fluoride ion concentration will be conducted in combination with measurement of the AOF parameter (Adsorbable Organic Fluorine) to estimate the complete degradation of PFAS degradation products. Once the optimal conditions are selected, a pilot-scale system will be installed at an industrial site to evaluate continuous treatment of real effluent contaminated with PFAS.

New developments and advances in treating PFAS-contaminated soil and water

Nicolas Etard (Project manager), Michael Linke (Project development),
Hans-Georg Edel (Manager R&D)

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Introduction

PFAS contamination in soils and aqueous media differs in terms of the composition and concentration of the individual compounds, depending on the cause of the damage. In order to ensure efficient and cost-effective, but also sustainable removal of PFAS, specific processes or combinations of processes must therefore be selected for each individual case and appropriate systems designed. In particular, the different types of soil and the varying qualities of groundwater, leachate, process water or fire extinguishing water must be considered.

Since 2009, Züblin Umwelttechnik GmbH has designed and built around 60 customised PFAS treatment plants for soils and aqueous media for various sites in Germany, Switzerland, France, and Italy [1, 2, 3]. New developments and progress in the cleaning of soils and water with PFAS contamination are the subject of the presentation.

Fig. 1*: Soil washing plant for* PFAS-contaminated *soils in Northern Germany, throughput approx. 2,000 tonnes of soil/d, integrated process/sludge water treatment*

PFAS soil washing

Soil washing is currently the only economically viable process for cleaning PFAS-containing soils on a large scale [1, 2]. Due to technical progress, we can now also wash soils with an increased fines content (<0.63 µm) and thus save disposal costs. The lecture will present results from the operation of a large-scale PFAS soil washing plant (***Fig. 1***). Since February 2023, 220,000 tonnes of soil have already been washed and reinstalled at the site as of May 2024. Based on tests carried out with different soil types from several European PFAS sites, both on a laboratory and technical scale (***Fig. 2***), the current possibilities, but also the limits of PFAS soil washing will be demonstrated.

PFAS water treatment

For aqueous media, adsorption on special activated carbons is in the majority of cases the most efficient and economical solution for removing PFAS [3]. This applies in particular to low-polluted groundwater with concentrations of Σ PFAS of approx. 0.1 - 20 µg/L. If necessary, the activated carbon stage can be supplemented with an ion exchanger to remove short-chain PFAS even more efficiently. Very high levels of Σ PFAS of 100 - 1,000 µg/L and more are sometimes present in leachate and fire extinguishing water, making adsorption uneconomical due to the increased activated carbon consumption. In this case, it makes sense to first reduce the high PFAS content by foam fractionation [4] and then use preferably an activated carbon filter to reliably meet the low PFAS purification targets [5]. Initial practical applications with leachate and fire extinguishing water are presented (***Fig. 3***). The results show that the process combination of foam fractionation and activated carbon adsorption can significantly improve the treatment performance and economic efficiency.

Fig. 2: *PFAS soil washing pilot plant (left), washing fractions (right)*

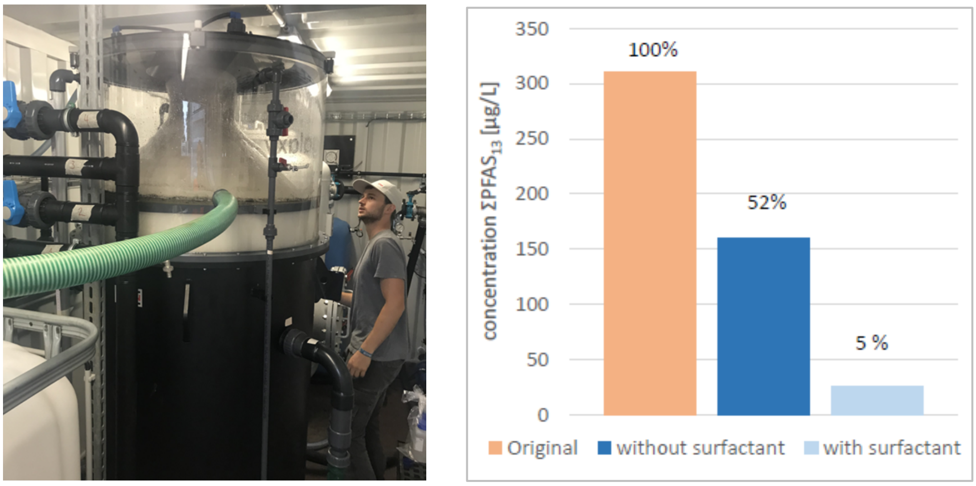

Fig. 3: *PFAS foam fractionation, leachate treatment Bavaria (left), residual contents* $\Sigma PFAS_{13}$ *after foam fractionation without/with addition of surfactant (right)*

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PFAS treatment system built by ECT2 at Swedavia Arlanda Airport

Jeffrey Lewis, Ph.D.

General Manager, ECT2

Technical Summary

The PFAS treatment system built by ECT2 at Swedavia Arlanda Airport is to our knowledge one of the largest in Sweden.

The system is based on SORBIX™ PURE ion exchange resin. The water is pumped from sumps in a train tunnel located 30 m below ground level, and these pumps are stand-alone, meaning that our system had no control over the incoming flow. We needed to design a robust, automated system that could handle flow rates varying from 4 m3/hr to 17 m3/hr. Break tanks were instrumented to monitor water levels and in so doing control the speed of the treatment system's internal pumps. Pretreatment was accomplished using GAC vessels in parallel while the SORBIX™ vessels were placed in a lead/lag configuration.

Because the system was located in a remote corner of the airport where no drinking water supply was available, treated water was saved in tanks and used for backwashing the GAC pretreatment vessels as required. The residue from the backwash water is collected in a filter tank and the remaining water is led back into the inlet water for another round of treatment.

The system was designed and built in less than six months. It was started up in August 2023 and to date has treated over 45 million liters of water.

Les traitements in-situ des PFAS dans les eaux souterraines, les sols & gaz du sol (FTOH) et l'application des Bio-Polymères protéiniques : Bilans Coûts-Avantages

In-situ treatments of PFAS in groundwater, soils and soil vapor (FTOH) and the application of protein Bio-Polymers: Advantages & Inconvenients

Frank KARG[1], Philippe GIRARD[2], Ulrike HINTZEN[3], Lucie ROBIN-VIGNERON[4]

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Abstract

Because of PFAS' high solubility, chemical stability, mobility in the environment and bioaccumulation, poly- and perfluorinated alkylated substances (PFAS) represent a significative concern regarding their potential Environmental & Health Impact. Across Europe (Belgium, France, Germany, Italy and other countries, numerous sites with PFAS contamination in soil, groundwater, surface waters, etc. are identified, some of which cover extensive areas, such as the contamination of agriculture topsoil on more than 800 hundred hectares in the Rastatt area (Baden-Württemberg, GER), where PFAS containing paper composting and WWTP sludge was used as fertilizer.

At present, no in-situ remediation technology for PFAS-contaminations in the saturated and non-saturated zone was applicable. Realized remediation strategies applied mostly very expensive methods like excavation of polluted soil (& dumping, off-site washing and thermal treatment) or very costly P&T (pump-and-treat) as a hydraulic groundwater remediation technology.

The objective of the R&D project in cooperation with Sensatec and the French University of Rouen is the development and implementation of an alternative in-situ and on-site remediation treatments of PFAS from the saturated and non-saturated zone and off excavated soil, using a washing process with biodegradable proteinic Bio-polymer compounds and beta-Cyclo- dextrines (cf. Fig. 1). The Specially developed tension-active biopolymer ingredients are used to separate correctly the PFAS from the soil.

The washing leachate is also positively active in the groundwater and subsequently pumped from the aquifer by means of a hydraulic washing system (cf. Fig. 1).

This technology enables in-situ-/ and on-site extraction and subsequent elimination of monomer PFAS from top- and deep soil without destructive methods as excavation. This approach don't needs the separation of the soil's different grain size fractions.

During extensive process development, the effectiveness of this technical remediation approach is proven first in a laboratory scale feasibility study and after in an on-site field test. Starting with small scale soil column tests is the first step and then in soil lysimeters and after some weeks (3 – 4) pilot application in the field.

With the column - lysimeter tests and also by the pilot-scale on-site test a larger PFAS parameter list as also TOF and the Top Assay for covering a maximum of into perfluorinated PFAS transformable poly-fluorinated PFAS to quantify the effectiveness of the remediation technology are used.

The short-chain perfluorinated carboxylic acids (as PFBA, PFPeA, etc.) can be leached from the topsoil simply by using water as washing ingrediant. Longer carboxylic acids with a chain length > C8 (PFOA, PFNA, PFDA, PFUnDA, etc.) and sulfonic acids (PFOS, PFNS, etc.) are less mobile. The washing technology with proteinic bio-polymers are providing clear evidence that these compounds can be mobilized by means of the specially developed biotensids. Lysimeter tests showed that a 95%-reduction of the PFAS concentration of the soil was achieved by applying the newly developed technology. Via field test the PFAS concentrations were reduced by > 80% within a 3-week duration.

In comparison of Cost – Advantage analysis, the in-situ Washing Treatments are about 30 times cheaper than Excavations or P&T: Pump and Treat. The technology is also applicable for volatile PFAS, like FTOH (Fluorotelomer alcohols, etc.).

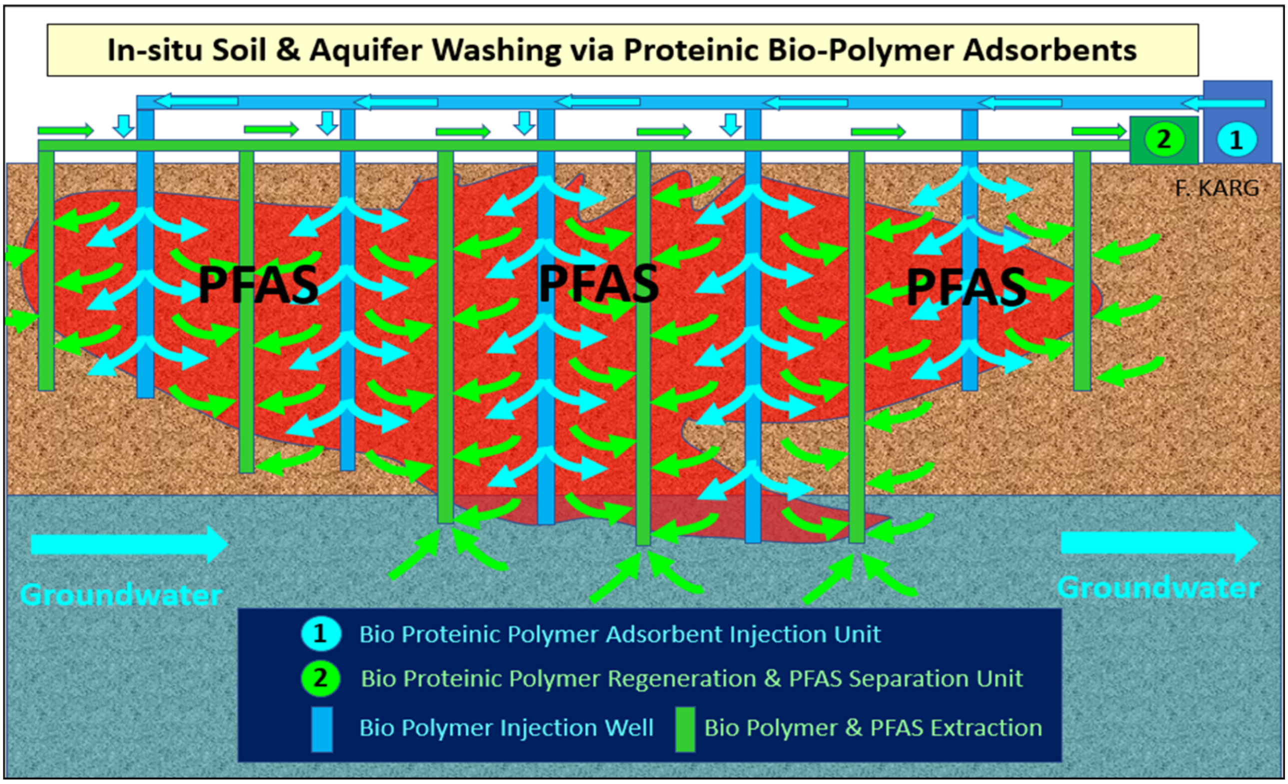


Fig. 1: In-situ soil washing for PFAS decontamination with proteinic Bio-polymers or beta-Cyclodextrins.

The developed process offers the possibility to treat PFAS-containing soils in-situ within the saturated and non-saturated zone by mobilizing PFAS and subsequently treating the groundwater using a state-of-the-art technology. A further possible application of the developed method that is currently applied in the field is the ex-situ treatment of excavated PFAS-containing soils on-site & off-site) by using the proteinic biopolymers via washing in cyclic technology.

In the next steps, the application of beta-Cyclodextrins coating on nano-Magnetites with additional magnetic activation and deactivation is planned in cooperation with the CNRS Rouen (cf. Fig. 2a &b).

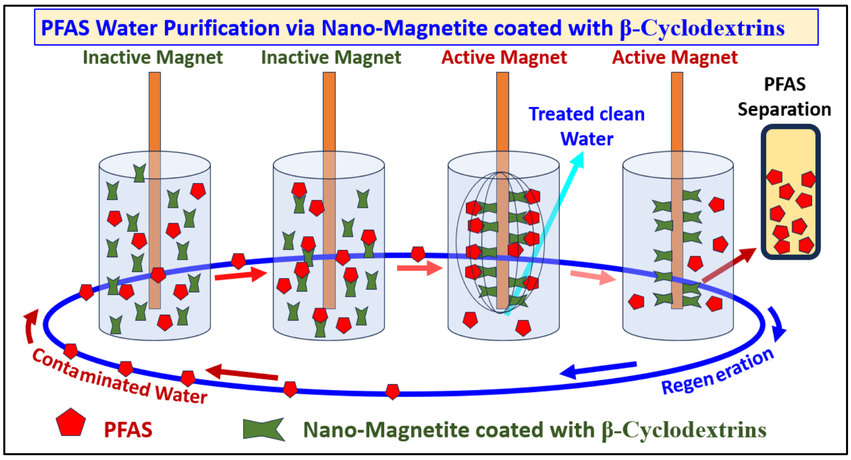
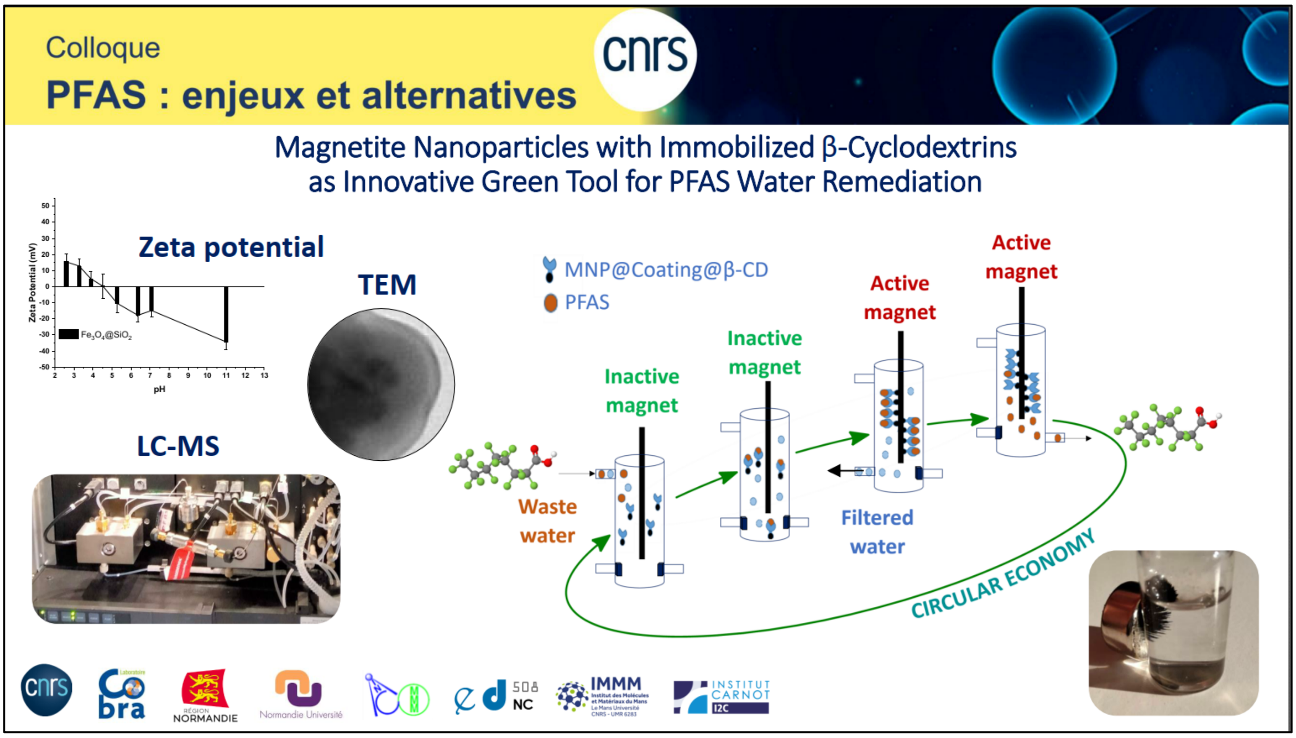


Fig. 2a: PFAS Water Purification via Nano-Magnetite coated with β-Cyclodextrins


Colloque

PFAS : enjeux et alternatives

Magnetite Nanoparticles with Immobilized β-Cyclodextrins as Innovative Green Tool for PFAS Water Remediation

Fig. 2: Application of beta-Cyclodextrine Coating on nano-Magnetites with additional magnetic activation and deactivation (Gouriou, L. & Gouhier, G.: 2024)

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Les traitements in-situ des PFAS dans les eaux souterraines, les sols & gaz du sol (FTOH) et l'application des Bio-Polymères protéiniques : Bilans Coûts-Avantages

In-situ treatments of PFAS in groundwater, soils and soil vapor (FTOH) and the application of protein Bio-Polymers: Advantages & Inconvenients

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Résumé

En raison de leur grande solubilité, de leur stabilité chimique, de leur mobilité dans l'environnement et de leur bioaccumulation, les substances alkylées poly- et perfluorées (PFAS) représentent une préoccupation importante en ce qui concerne leur impact potentiel sur l'environnement et la santé. Dans toute l'Europe (Belgique, France, Allemagne, Italie et autres pays), de nombreux sites contaminés par des PFAS dans le sol, les eaux souterraines, les eaux de surface, etc. ont été identifiés, dont certains couvrent de vastes zones, comme la contamination de la couche arable de plus de 800 hectares dans la région de Rastatt (Baden-Württemberg, GER), où des boues de compostage de papier et de stations d'épuration contenant des PFAS ont été utilisées comme fertilisants.

À l'heure actuelle, aucune technologie de dépollution in-situ n'est applicable aux contaminations par les PFAS dans les zones saturées et non saturées. Les stratégies de dépollution mises en œuvre appliquent principalement des méthodes très coûteuses telles que l'excavation des sols pollués (& mise en décharge, lavage hors site et traitement thermique) ou le P&T (pump-and-treat) très coûteux en tant que technologie de dépollution hydraulique des eaux souterraines.

L'objectif du projet de R&D en coopération d'HPC INTERNATIONAL avec Sensatec et l'Université française de Rouen est le développement et la mise en œuvre d'un traitement alternatif de réhabilitation in-situ et sur site des PFAS des zones saturées et non saturées et des sols excavés, en utilisant un processus de lavage avec des composés de bio-polymères protéiniques biodégradables et des bêta-cyclodextrines (cf. Fig. 1). Les

ingrédients biopolymères tensioactifs spécialement développés sont utilisés pour séparer correctement les PFAS du sol.

Le lixiviat de lavage a également une action positive sur les eaux souterraines et est ensuite pompé de l'aquifère au moyen d'un système de lavage hydraulique (cf. Fig. 1).

Cette technologie permet l'extraction in-situ et/ou sur place et l'élimination ultérieure des PFAS monomères dans les sols superficiels et profonds sans recourir à des méthodes destructrices telles que l'excavation. Cette approche ne nécessite pas la séparation des différentes fractions granulométriques du sol.

Au cours de la mise au point du processus, l'efficacité de cette approche technique de dépollution est d'abord testée par une étude de faisabilité en laboratoire, puis par une application pilote sur le terrain. La première étape consiste à effectuer des essais à petite échelle sur des colonnes de percolation de sol, puis dans des lysimètres de sol et, après quelques semaines (3 à 4), dans le cadre d'une application pilote sur le terrain.

Les essais en colonne et en lysimètres ainsi que l'essai pilote sur site ont permis d'établir une liste plus large de paramètres relatifs aux PFAS, ainsi que le TOF et le Top Assay pour couvrir un maximum de PFAS perfluorés transformables en PFAS polyfluorés, afin de quantifier l'efficacité de la technologie d'assainissement.

Les acides carboxyliques perfluorés à chaîne courte (comme le PFBA, le PFPeA, etc.) peuvent être lessivés de des sols en utilisant simplement de l'eau comme ingrédient de lavage. Les acides carboxyliques à chaîne plus longue > C8 (PFOA, PFNA, PFDA, PFUnDA, etc.) et les acides sulfoniques (PFOS, PFNS, etc.) sont moins mobiles. La technologie de lavage avec des bio-polymères protéiniques prouve clairement que ces composés peuvent être mobilisés au moyen des biotensides spécialement développés. Des tests lysimétriques ont montré qu'une réduction de 95 % de la concentration en PFAS dans le sol est obtenue en appliquant la nouvelle technologie développée. Des essais sur le terrain ont permis de réduire les concentrations de PFAS de plus de 80 % en l'espace de trois semaines.

En comparaison avec l'analyse coût-avantage, les traitements de lavage in situ sont environ 30 fois moins chers que les excavations ou le P&T : Pump and Treat. La technologie est également applicable aux PFAS volatiles, comme les FTOH (alcools fluorotélomères, etc.).

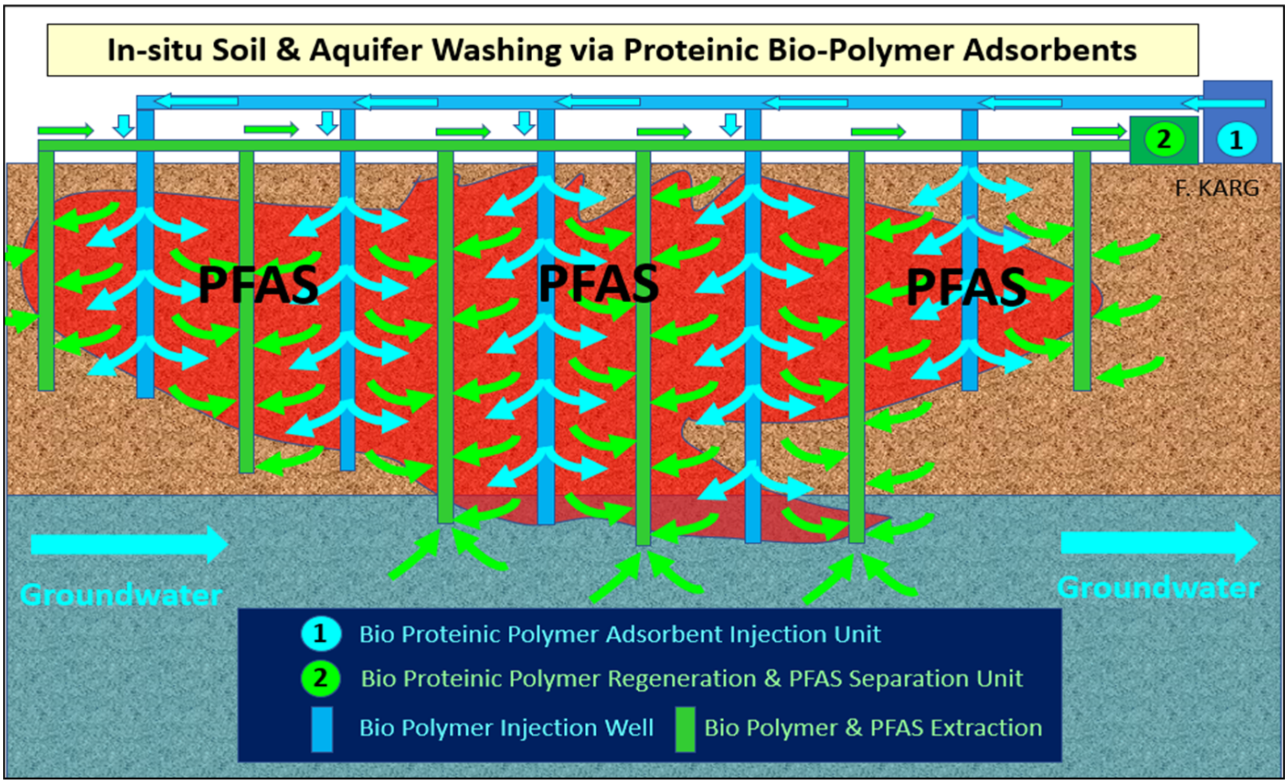


Fig. 1 : Lavage du sol in situ pour la décontamination des PFAS avec des bio-polymères protéiques ou des bêta-cyclodextrines.

Le processus développé offre la possibilité de traiter les sols contenant des PFAS in situ dans la zone saturée et non saturée en mobilisant les PFAS et en traitant ensuite les eaux souterraines à l'aide d'une technologie de pointe. Une autre application possible de la méthode développée qui est actuellement appliquée sur le terrain est le traitement ex-situ des sols excavés contenant des PFAS (sur site et hors site) en utilisant les biopolymères protéiniques par lavage dans une technologie cyclique.

Dans les prochaines étapes, l'application d'un *coating* par les bêta-cyclodextrines sur des nano-magnétites avec activation et désactivation magnétiques supplémentaires est prévue en coopération avec le CNRS de Rouen (cf. Fig. 2a &b).

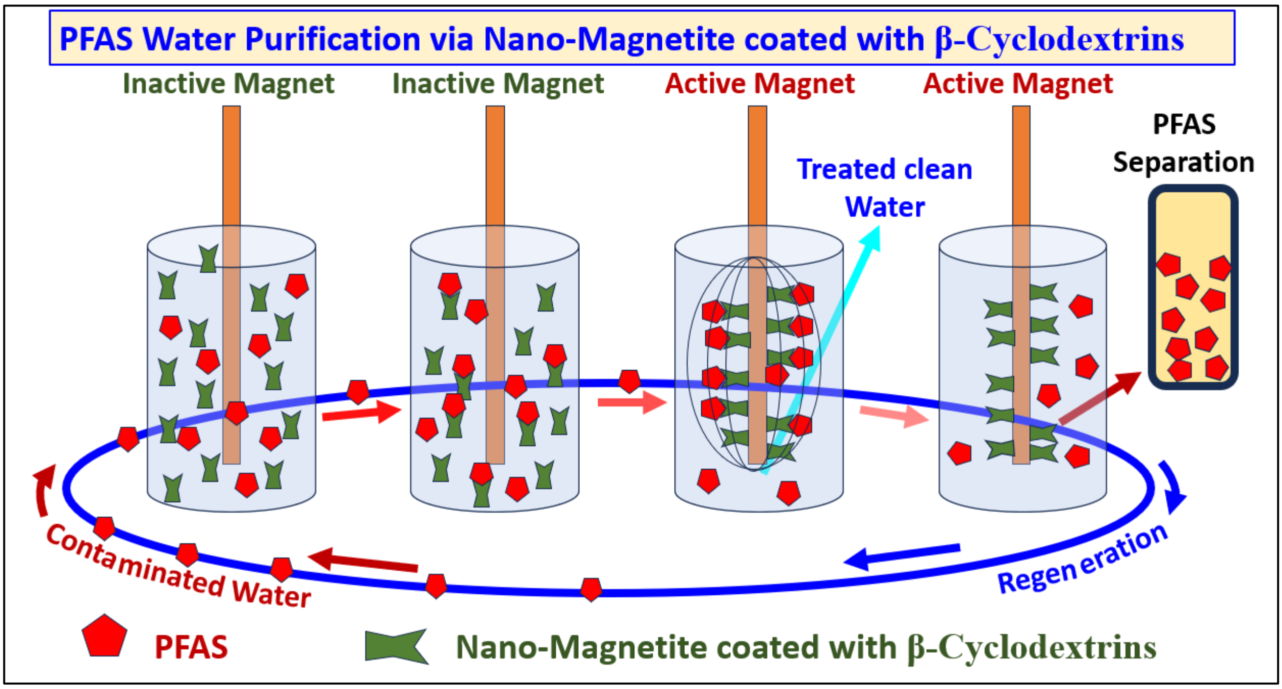
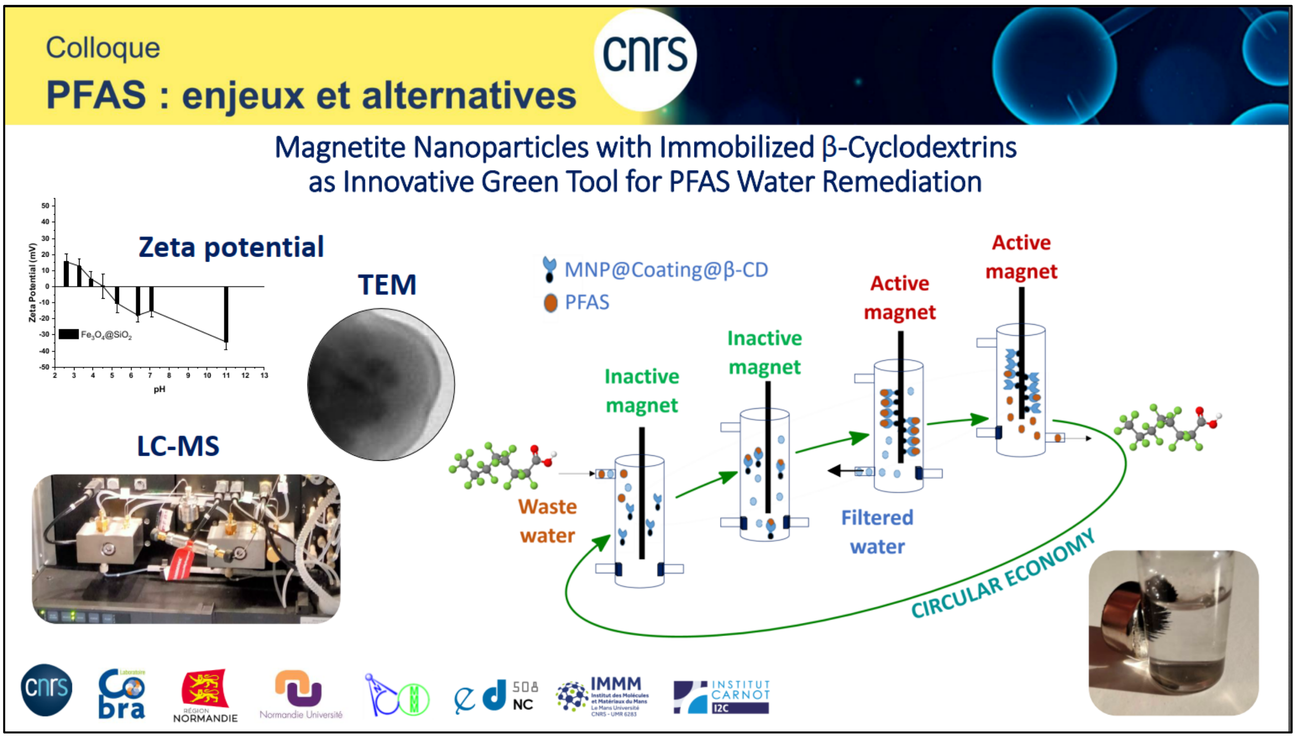


Fig. 2a : Purification de l'eau par les PFAS grâce à la nano-magnétite recouverte de β-cyclodextrines


Colloque

PFAS : enjeux et alternatives

Magnetite Nanoparticles with Immobilized β-Cyclodextrins as Innovative Green Tool for PFAS Water Remediation

Fig. 2 : Application d'un revêtement de bêta-cyclodextrine sur des nano-magnétites avec activation et désactivation magnétiques supplémentaires (Gouriou, L. & Gouhier, G. : 2024)

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Multicriteria comparison of three technologies for the treatment of 42 PFAS in drinking water using a comprehensive experimental approach

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Keywords: Activated Carbon, Drinking Water, Low Pressure Reverse Osmosis, Nanofiltration, PFAS, Resin.

1. Context and objectives

Perfluorinated substances (PFAS) contamination is broad and worldwide: it includes thousands of compounds and is found in all environmental compartments. Regulation is enforced in many countries, with a large variety of compounds and concentrations of targeted PFAS. Existing treatment processes for drinking water production use adsorbent medias, ion exchange resins, reverse osmosis or nanofiltration membranes.

The first objective of this project is to improve scientific knowledge about the individual performance of the 3 key treatment solutions for 42 PFAS for drinking water production to provide design rules and operational recommendations. The second objective is to define the best treatment solution for each site, using a multi-criteria approach including technical, economic, and environmental aspects.

2. Method

42 compounds are selected as representative of the contamination issue and the treatment challenge. PFAS are analyzed by direct injection on high-performance liquid chromatography and mass spectrometer through a protocol adapted from the standard project (prEN 17892:2022). Limits of quantification are in the range of 1 - 10 ng/L.

Trials were conducted at lab and pilot scales to evaluate performances of 4 membranes (2 LPRO -Low Pressure Reverse Osmosis, 2 nanofiltration), 5 activated carbon (2 granular, 3 powdered) and 3 PFAS specific resins (non-regenerable).

The performance results obtained by unitary processes were used to simulate several full treatment lines for typical water resources which will be compared in a real case study.

3. Results

Individual process performances

Results are summarized in Table 1.

Results on activated carbon (AC) show a wide elimination range depending mainly on carbon chain length (high MW >> low MW), functional group of PFAS (sulfonic acid > carboxylic acid, and Neutral >

anionic > cationic), organic matter (OM) content of raw water, AC type (higher for agglomerated media, high surface specific, high Iodin index) and contact time but is not impacted by pH conditions.

LPRO show excellent levels of rejection (> 90 %), from the smallest compound tested (TFMS, C1 - XS) to the largest (PFTeDA, C14 - L). Nanofiltration is less efficient for very small and small PFAS but still allows more than 50 % of removal.

Results on resins are promising and better than AC. They show no significant difference between the 3 tested resins, no impact of OM level and no significant impact of PFAS compounds size. Pilot trials are still on-going.

*Table 1 : Performances of each treatment (*Groundwater DOC 1 mg/L)*

PFAS size	**PFAS examples in the 20 of European Directive**	**Examples of other PFAS**	**% removal for PAC @ 50 ppm - CT = 30'**	**GAC breakthrough* @ 10 % - CT = 12'**	**Nanofiltration**	**LPRO**
XSmall PFAS (MW < 300 g/mol)	PFBA, PFPeA	PFPrA, TFMS, PFEtS, PFMPA, PFMBA, 3:3 FTCA, FBSA	15 - 70 %	< 3 500 VV	50 – 80 %	> 90 %
Small PFAS (MW : 300-400)	PFHxA, PFHpA **PFBS**, PFPeS	**GenX,** ADONA, 5:3 FTCA, 4:2 FTS, 6:2 FTS FBSE, N-Me-FBSE	60 - 95 %	< 10 000 VV	80 – 90 %	> 90 %
Medium PFAS (MW : 400-550)	**PFOA , PFNA** → PFDA **PFHxS** → **PFOS**	FOSA, N-Me-FOSE, 9Cl-PF3ONS	80 - 99 %	< 20 000 VV	> 90 %	> 90 %
Large PFAS (MW > 550 g/mol)	PFUnDA → PFTrDA PFNS → PFTrDS	PFTeDA PFHxDS	90 - 99 %	> 20 000 VV	> 90 %	> 90 %

Multicriteria comparison

The main treatments available for eliminating PFAS therefore have varying individual performances, depending mainly on the molar mass of the molecules. However, these technical elements are not sufficient to define the most suitable solution for a given site. There are other factors to consider: carbon footprint, capital costs (CAPEX), operating costs (OPEX), use of chemicals, speed of implementation, ease of operation, water losses, waste management, footprint, resilience.

This multi-criteria approach was applied to define the most suitable solution for the rehabilitation of an 11,000m^3/d drinking water production plant in France historically equipped with GAC filters. The groundwater is polluted with PFAS (∑20 PFAS 0.14 to 0.31 µg/l for a target in treated water of 0.1 µg/l), with 9 perfluorinated compounds detected, including mainly the degradation by-products of 6:2 FTSA: PFBA (C4-XS), PFPeA (C5-XS), PFHxA (C6-S) but also other less stringent molecules such as PFOS (C8-M).

3 treatment lines were proposed and compared: 1/ Increase the regeneration frequency of existing GACs 2/ Retrofit existing filters with continuous renewal reactors (Carbazur Simplex SUEZ) 3/ Supplement existing filters with LPRO membranes. The result is that option 2, rehabilitating existing filters, is the most adapted to the local context, as it has a low CAPEX, optimizes existing structures, is available in the short/medium term, and does not produce liquid waste containing PFAS (Figure 1).

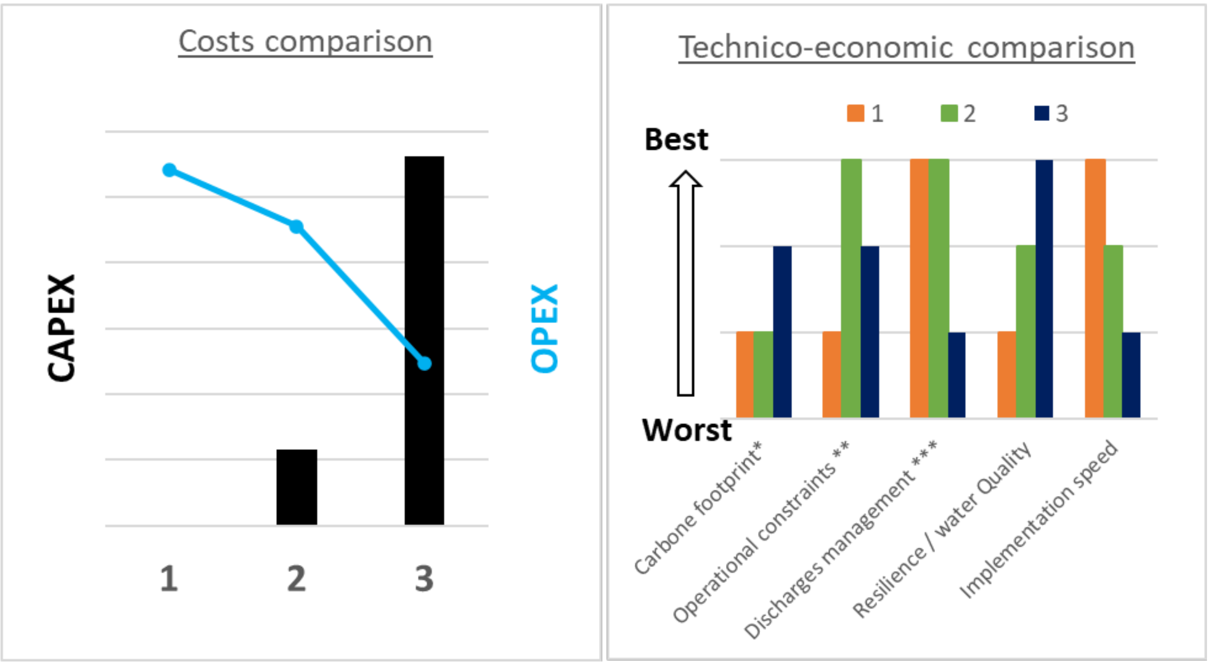


Figure 1 : Multicriteria comparison for PFAS treatment option selection (GAC regenerated, energy for mb only, excl CIP and antiscalant - ** GAC charge regeneration, chemical, membrane washing - *** quantity, pollutant loads, diversity of discharges)*

4. Conclusions and perspectives

There are several treatments already available and efficient for drinking water production from resources containing perfluorinated compounds. However, there are still some technical bottlenecks to overcome, essentially for PFAS destruction to really reach the environment depollution. Moreover, process optimization and innovation for alternative treatments are key to making PFAS treatment economically viable.

Catalytic remediation of PFAS contaminated groundwater
Réhabilitation catalytique des eaux souterraines contaminées par les PFAS

Dr. Silvan Staufert our Co-Founder and Chief Technology Officer - Oxyle

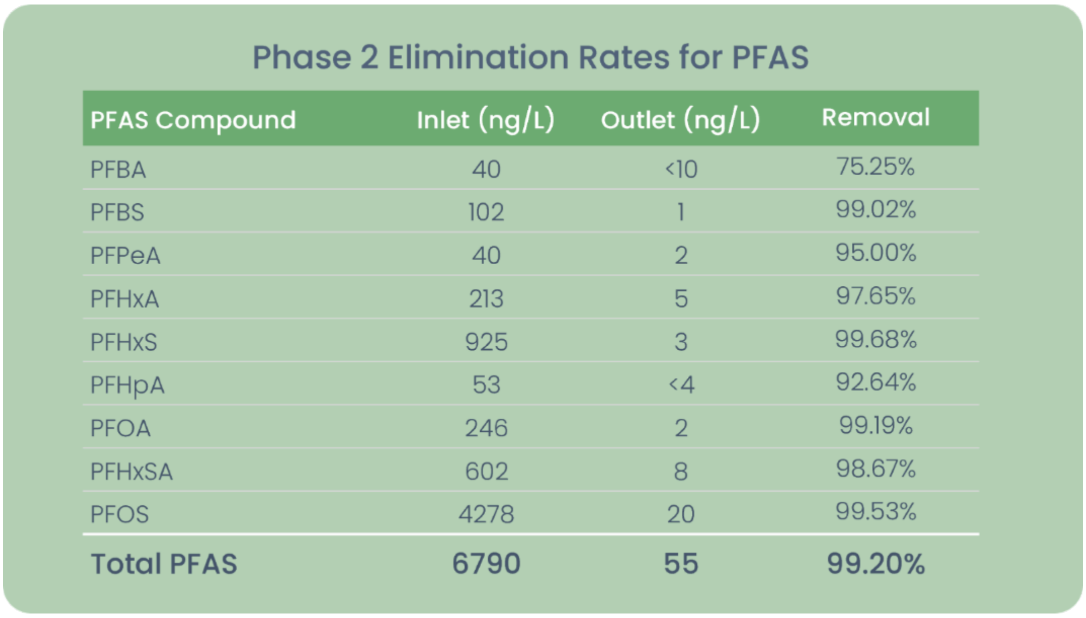
Summary:

Groundwater, hidden beneath the Earth's surface, acts as a vital lifeline for billions globally: drinking water for communities, sustenance for agriculture, a life source for diverse ecosystems. However, a widespread contamination crisis is currently impacting these critical groundwater resources. Thousands of micropollutants, namely PFAS (per- and polyfluoroalkyl substances), have infiltrated our groundwater posing a critical threat to both the environment and public health.

Tackling PFAS contamination within groundwater remediation efforts is an arduous task. Existing methods for PFAS extraction are often inefficient, costly, and generate secondary waste, leading to increased operational and financial challenges. These factors deter municipal and industrial entities from undertaking such environmental clean-up initiatives.

The described catalytic process marks a substantial breakthrough in PFAS elimination, offering an effective, cost-efficient and waste-free solution. Characterized by its leading energy efficiency, this technology significantly reduces the costs associated with remediating PFAS-contaminated groundwater. With extremely high elimination efficacy (99%+), this makes treatment of PFAS from contaminated groundwater achievable.

This technology was successfully applied to contaminated groundwater in a recent 6-month on-site pilot with CIMO, a Swiss Wastewater Management Company. The pilot was conducted in two phases. In Phase 1, contaminated groundwater was collected through a pumping system and then directed into the Oxyle batch reactor. In Phase 2, the water was filtered via nanofiltration, increasing the concentration of PFAS by 3-4x. 10m^3 of this up-concentrated water was channeled into Oxyle's reactor daily. Once activated via aeration, the catalysts generated an abundance of reactive radicals, effectively breaking down the PFAS into safe-to-discharge inorganic compounds like calcium fluoride. The technology demonstrated removal rates exceeding 94% in Phase 1 and 99% in Phase 2 (from 6790 ng/L to 55 ng/L), targeting both long-chain and short-chain PFAS variants. The performance remained consistent even in the face of substantial fluctuations in inlet concentrations, ranging from 3000 ng/L to 7000 ng/L, and 180 days of continuous use. Throughout the pilot, the technology exhibited exceptionally low energy consumption, at 2.6 kWh/m^3 in Phase 1 and 4.5 kWh/m^3 in Phase 2. This efficiency offered a more cost-effective alternative compared to traditional treatment.



Phase 2 Elimination Rates for PFAS

PFAS Compound	Inlet (ng/L)	Outlet (ng/L)	Removal
PFBA	40	<10	75.25%
PFBS	102	1	99.02%
PFPeA	40	2	95.00%
PFHxA	213	5	97.65%
PFHxS	925	3	99.68%
PFHpA	53	<4	92.64%
PFOA	246	2	99.19%
PFHxSA	602	8	98.67%
PFOS	4278	20	99.53%
Total PFAS	**6790**	**55**	**99.20%**

Biopolymer based remediation of PFAS contaminated soils- On Site Treatment in leaching piles

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Summary:

The biopolymer-based remediation technology developed in the FABEKO research project has successfully been implemented in an on-site leaching pile. Using the specially developed surface-active biopolymer compounds an improved PFAS Elution from the soil compared to water has been possible. The results of the first on-site pilot test (paper sludge contaminated site) show up to 82% PFAS removal within 8 weeks of treatment based on the 2:1 eluate in the mixed soil sample. The leachate analysis showing high concentrations of PFOA, PFNA, PFDA and PFOS confirms that not only short chain PFAS can be detected in the eluate but also long chain PFAS with a chain length > C8 can be easily eluted using the tailored biopolymers. Furthermore, an optimization of the PFAS elution system has been possible by reducing the necessary biopolymer amount and recycling the process water.

In this pilot test the process water has been treated with two varying treatment systems: 1) flotation and 2) electrostimulated activated carbon adsorption/ desorption modules. The flotation system has already been established in the previous research project and has shown removal rates of up to 95% under optimal conditions (50% to 75% removal in the field). The electrostimulated activated carbon was newly developed in the FABEKO project and shows promising removal rates especially for short chain PFAS.

An important aspect in the development of the biopolymer based PFAS elution was to ensure that the important soil functions are not negatively affected by the treatment. Parameters such as nutrient availability for plants show no adverse effects, that the soil can continue to be used for e.g. agricultural purposes after treatment.

PHOTOELECTROCATALYTIC ADVANCED OXIDATION PROCESSES FOR THE DEGRADATION OF FLUORINATED ORGANIC POLLUTANTS IN AFFF-CONTAMINATED WATER AND GROUNDWATER

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Per- and polyfluoroalkyl substances (PFASs) are a family of man-made chemicals that have been widely used since the 1950s in a range of applications from anti-stick coating on cookware, over waterproof clothing, to firefighting foams. They form a group of more than 6000 fluorinated organic compounds which are very persistent and have different behavior/mobility in the environment. Recently it has been recognized that PFASs pose severe risks to human health and to the environment, and initiatives are being activated not only towards regulation but also on remediation. In this context, in 2022, CAPTURE has been selected by the EU among the projects aimed to manage PFAS contamination. The objective of LIFE CAPTURE is to develop sustainable management methods for dealing with PFASs in soil and groundwater. In this work, focus has been paid on the developing of a new remediation technique based on photoelectrocatalysis (PEC). PEC is an advanced oxidation process that exploits supported photocatalysts electrically polarized during operation. This allows to synergistically combine electrochemical phenomena and heterogeneous photocatalysis (PC) to minimize electron-hole recombination, which usually hampers conventional photocatalysis.

In this study, PEC has been employed to remediate both water contaminated by aqueous fire-fighting foams (AFFF) and groundwater from the Veneto region, where a well-known PFAS contamination is still present. The total concentration of the C4-C10 organic fluorinated acids and sulphonates was about 723 ng/L in groundwater and about 47286 ng/L in AFFF-contaminated water. Degradation tests were carried out in a 1-L lab-scale reactor equipped with a UV-C lamp working at different powers, and an electrical bias of 4 V was applied [1]. Photolysis tests were also performed for comparison.

AFFF-contaminated water mainly contained 6:2 FTS (44500 ng/L). PEC tests lead a 6:2 FTS removal of about 92% after 6 h, with the transient formation of other PFASs mostly consisting in shorter C chains. The unexpected transient formation of 6:2 FTS suggested the presence of undetected PFASs and remarked the need of a comprehensive analytical approach to evaluate PFAS contamination, which is one of the specific goals of the CAPTURE project.

As shown in **Figure *1*** a, PEC tests of PFAS-contaminated groundwater lead to a total PFAS removal of about 50% (from 580 ng/l to 290 ng/l) in 3 h, complying with the current EU regulation limits (500 ng/L) [2]. Groundwater mostly contained PFOA, whose concentration reduced from 290 ng/l to 100 ng/l within 2.5 h. Shorter-chain carboxylic acids transiently formed, suggesting a reaction mechanism including decarboxylation and the release of a CF_2 unit at a time.

Both in AFFF-contaminated waters and in PFAS-contaminated groundwater, it was demonstrated that the UV lamp power plays a pivotal role on the degradation kinetics.

Electrical energy for order (E_{EO}), defined as the electrical energy required to remove 90% of a target contaminant, was used as figure of merit to preliminarily and comparatively evaluate PEC in the context of available literature on laboratory-scale advanced processes. Based on the E_{EO} values on PFOA degradation reported in **Figure *1*** b, PEC is more efficient than electrochemical oxidation, sonolysis and photochemical oxidation, and shows a comparable performance to the less energy-consuming techniques known in literature, i.e. Plasma treatment and advanced reduction processes [3].

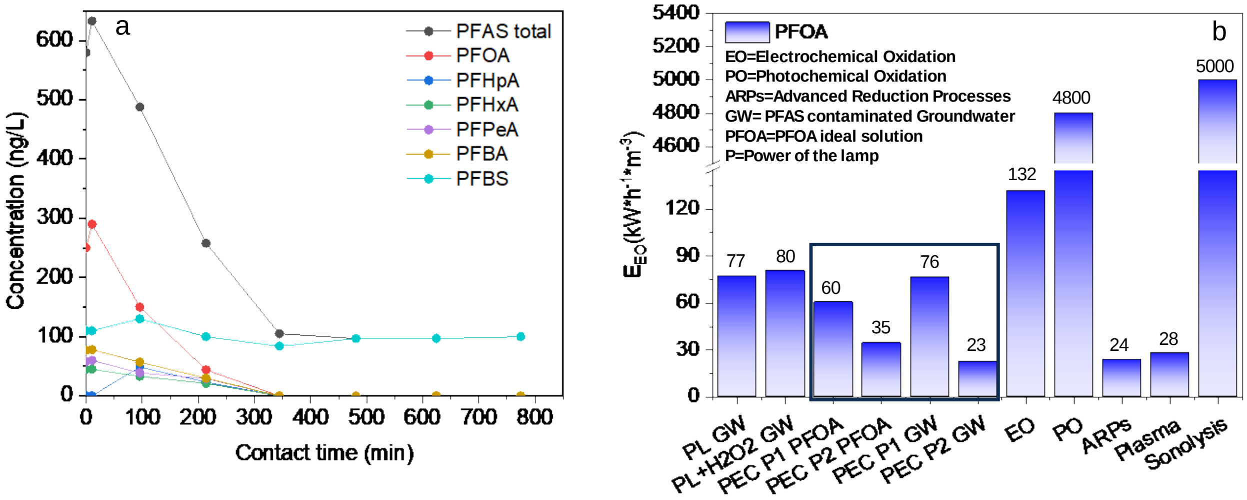

Figure 1. (a) Concentration profile vs time of individual PFASs and total PFAS during PEC treatment of groundwater; (b) E_{EO} values for PFOA degradation by PEC (P1=2*P2) and other advanced oxidation process reported in literature.

The investigation demonstrated that PEC can be a viable technology for the remediation of PFAS in both process water and groundwater. Further efforts are needed in order to deepen the knowledge on reaction mechanisms, to minimize processing costs and times and to scale-up the process to the pilot scale.

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Modified Natural Zeolites for the Treatment of PFAS Contaminated Water

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Background

The increasing industrial activity generates large amounts of wastewater containing different chemicals, such as nitrogenous compounds, heavy metals, surfactants, and emerging contaminants like per- and polyfluoroalkyl substances (PFAS). If improperly disposed of, these species may have negative effects on the environment and on human health. Removal of contaminants from wastewater requires cost effective technologies and, among these, adsorption is one of the most promising and investigated techniques.

Zeolites are low-cost, environmentally friendly natural minerals with excellent adsorption capacity. These crystalline aluminosilicate minerals have a crystalline symmetrical structure which forms a porous, open three-dimensional framework. For water treatment, zeolite acts through three main mechanisms:

- Physical barrier: it acts as a molecular sieve, trapping molecules and particles with diameters larger than the size of the zeolite channels.
- Cation exchange: it releases sodium, calcium, magnesium, and potassium ions and captures cations present in water.
- Chemical adsorption: contaminants are retained on the mineral surface by weak chemical bonds.

Thanks to their cation-exchange ability and to their molecular sieve properties, natural zeolites are already largely used as adsorbents in separation and purification processes, especially for the removal of cations such as ammonium and heavy metals.

Aim

The present study is focused on the development of new zeolite-based adsorbent media to effectively remove PFAS from water. Functionalization of natural zeolites was aimed at increasing the number of hydrophobic and electrostatic sites, that are highly specific for PFAS molecules. Modification of natural zeolites was performed through several methods such as thermal treatment, acid activation, organic or metal modification, to improve selectivity towards PFAS species. Modified zeolites were prepared starting from a natural zeolite obtained from Slovakia, composed of 85% clinoplilotite, 8% cristobalite, 4% illite and 3–4% plagioclast, with a Si/Al ratio of 4.8–5.5.

Conclusions

Several natural and modified zeolites were tested with batch tests, using a groundwater sample with a PFAS concentration of 1600 ng/L. While natural zeolite can only remove PFAS by physical adsorption, its chemical modification allows the level of retention to be greatly increased through electrostatic and hydrophobic interaction mechanisms. Among all formulations, the modified zeolite ZNAVS showed excellent adsorption performances, lowering the total PFAS concentration to < 5 ng/l, with high efficiency even to short-chain PFAS molecules (85% PFBA removal).

Collection of gas-phase PFAS Using Styrene-Divinylbenzene Resin

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PFAS compounds have become a topic of great concern in recent years, due to their ubiquity and health effects, such as cancer, thyroid disease, and pregnancy issues. While numerous methods exist for the analysis of PFAS in water matrices, the analysis of PFAS in air is relatively underdeveloped. In 2021 the EPA released draft method OTM-45, providing a method for stack gas sampling, but official methods for ambient and indoor air sampling are still needed. The use of various sampling techniques including thermal desorption, canisters, polyurethane foam, and styrene-divinylbenzene (SDVB) resins have been found in literature.

This presentation will outline a method using accelerated solvent extraction (ASE) for the extraction of PFAS collected on SDVB resin and show how it compares to the extraction outlined in OTM-45. Ambient and indoor air monitoring of PFAS using small-volume samplers with SDVB resin will also be explored. Breakthrough volumes and recoveries for commonly tested PFAS compounds will be evaluated.

Performance of Reverse Osmosis for the treatment of hazardous wastewater containing various concentrations and types of PFAS

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INTRODUCTION

Conventional water treatment technologies are insufficient in effectively treating short-chain PFAS, especially carboxylic acids with less than 6 carbons (scPFCAs). The accumulation and spread of these pollutants in water bodies highlight the urgent need to redefine technologies for retaining PFAS from wastewaters before their discharge into the aqueous environment.

As a leading company in hazardous waste treatment in Europe, SARPI-Veolia is greatly concerned with constantly achieving the most relevant processes for retaining pollutants. Reverse osmosis (RO) has already proven its high efficiency in retaining various pollutants, including PFAS, from surface and groundwater. However, the high organic and inorganic load in hazardous wastewater presents challenges for RO processes.

This work investigates the potential of RO run with a high recovery rate for removing PFAS from pretreated hazardous wastewater, considering the varying ratios of organic/inorganic loads.

MATERIAL & METHODS

Industrial-scale RO experiments were run using a mobile processing unit designed by SEMEO and equipped with polymeric spiral-wound membranes. The RO system operated in feed-and-bleed mode to treat up to 240 m^3 of pre-treated waste daily in two or three stages at ambient temperature and constant permeation flow rate.

The RO system was fed with pretreated hazardous wastewater containing an inorganic load of 10.2 $mS \cdot cm^{-1}$ and either a low organic load of 280 $mg \cdot L^{-1}$ or a high organic load of 1157 $mg \cdot L^{-1}$. The pretreatment step aimed to reduce suspended matter into hazardous wastewater in order to protect RO membranes.

SARPI aims to improve the carbon footprint of its processes while ensuring the best quality of discharged effluent. Reducing energy consumption and minimising the volume of retentate (the concentrated waste stream) are two potential solutions.

Therefore, in this study, maximising the recovery rate during RO, defined as the ratio between permeate (treated water) and feed flow rates, was crucial. Ensuring the ability of subsequent treatment and further concentration of the generated retentate was also a great concern explored in this study.

Global recovery rate was gradually increased and the process performances were evaluated by monitoring the stability of the transmembrane pressure over the filtration time. The increase in the global recovery rate was halted when the first stage transmembrane pressure response reached 35 bar. Subsequently, the filtration was carried out for 24 h to ensure steady-state conditions before collecting samples of feed solution, retentate and permeate.

PFAS in the feedstocks, permeate, and retentate were determined by LC-MS-MS and GC-MS-MS analysis conducted by an external laboratory. Both low- and high-organic load feed solutions exhibited a total PFAS of approximately 21 $\mu g \cdot L^{-1}$. However, the concentrations of scPFCAs differed slightly, with the low-organic load solution containing 3.6 $\mu g \cdot L^{-1}$ and the high-organic load solution containing 2.5 $\mu g \cdot L^{-1}$. PFAS retention was then calculated as the ratio of the PFAS concentration in the permeate to the concentration in the retentate.

RESULTS

Both low- and high-organic load feedstocks have been successfully treated by RO.
In the first stage, the recovery rate for high-organic load feedstock was lower at 88% compared to 92% for low-organic load feedstock. However, in the second stage, both feedstocks achieved a recovery rate of 96%. As a consequence, for low-organic load feedstock, after three stages of RO treatment, the global recovery rate was 89% while 85% of the high-organic load feedstock were recovered in permeate after two stages of RO treatment. Moreover, the retentates were successfully additionally concentrated.

PFAS were effectively removed by the RO membrane for both the low-organic load and high-organic load feedstocks.
After the first stage of RO treatment for the low-organic load feedstock, the remaining concentration of PFAS in the permeate was 0.8 $\mu g \cdot L^{-1}$, indicating a 99.5% retention. Among the PFAS remaining in the permeate, scPFCAs were present at a concentration of 0.1 $\mu g \cdot L^{-1}$ corresponding to a 98.9% retention. For the high-organic load feedstock, the remaining concentration of PFAS in the permeate after the first stage of RO was 0.2 $\mu g \cdot L^{-1}$, indicating a 99.8% retention. Notably, no scPFCAs were detected in the permeate after the stage of RO treatment for the high-organic load feedstock.
Regardless of the organic load in the feedstock, concentration of total PFAS was below the limit of quantification in the permeate after the second stage. This indicates that the global retention for total PFAS exceeded 99.9%.

RO is a promising solution to prevent water scarcity, as the generated permeate, free of micropollutants, including PFAS, could potentially be employed for REUSE purposes after pH adjustment.

Key words: PFAS, reverse osmosis, micropollutants, hazardous wastewater

Integrated Remediation of PFAS-Contaminated Soil from a French Firefighting Facility

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Abstract

Poly- and perfluoroalkyl substances (PFAS), commonly known as "forever chemicals," represent emerging environmental hazards. The widespread existence of PFAS-contaminated soils on a global scale underscores the soil's crucial role as a significant reservoir of PFAS contamination. Given their notable mobility and stability, PFAS within soils can translocate to diverse environmental compartments, including surface water, groundwater, air, and plants, thereby leading to their contamination and potential human exposure.

In this study, we investigated a multi-stage treatment strategy to remediate PFAS-contaminated soil sampled from a firefighting facility in France. The site, characterized by long-term use of aqueous film forming foams (AFFF), exhibited substantial PFAS levels, reaching more than 400 µg/kg, with 75% of this concentration attributed to the combined presence of PFOS and PFHxS. The treatment involved soil washing utilizing efficient and environmentally friendly extracting agents, implemented under various experimental conditions, including saturated and non-saturated flow-through setups. Subsequent steps consisted of adsorption and/or oxidative degradation processes. Analysis of the treated soil samples, focusing on 24 PFAS compounds, revealed a remarkable soil washing efficiency ranging from 91% to 98%. To further evaluate the washing efficiency, we developed a model for the kinetic release of PFAS. Subsequent application of adsorption using carbonaceous materials and/or degradation techniques resulted in the removal of up to 95% of PFAS in concentrated soil washing effluent. This comprehensive approach demonstrated the effectiveness and cost-efficiency of a multi-stage treatment for remediating soils historically contaminated with PFAS.

RÉSUMÉS SUPPLÉMENTAIRES
ADDITIONAL ABSTRACTS

State of the Art for PFAS-impacted Soils. What are the Available Remediation Technologies?

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Background/Objectives: This presentation delves into the contemporary landscape of remediating soils contaminated with Per- and Polyfluoroalkyl Substances (PFAS). While PFAS contamination in water and waste streams has garnered substantial attention, this discussion centers on the specific challenges posed by PFAS-contaminated soils. The aim is to provide a comprehensive overview of the current status of remediation technologies for PFAS-impacted soils, highlighting the evolution of these methods and their effectiveness. By focusing exclusively on soil-based contamination, this presentation contributes a nuanced perspective, shedding light on the latest advancements, limitations, and promising approaches in addressing this pressing environmental concern.

Approach/Activities: The approach to addressing PFAS-impacted soils begins with a foundation in the known physical and chemical properties of PFAS, while acknowledging the significant gaps in our understanding regarding their complex interactions, degradation chemistry, and long-term behavior in soil. From this starting point, our activities focus on elucidating the feasibility and effectiveness of separating PFAS from the soil matrix and managing the resulting contaminants.

We meticulously evaluate various technologies, including Stabilization, Soil Washing, Thermal Desorption, and Incineration, with the overarching goal of gaining insight into their capacity to tackle PFAS-contaminated soils. These technologies serve as the cornerstones of our comparison, with an emphasis on their capabilities, limitations, and the nuances of their interactions with PFAS compounds present in the soil.

Stabilization, a method aimed at immobilizing contaminants in the soil, offers potential advantages in terms of reducing PFAS mobility. Soil Washing, utilizing a combination of mechanical and chemical means, effectively extracts PFAS from soil, albeit with cost and applicability considerations. Thermal Desorption, relying on heat-induced separation, presents promise for PFAS removal, while also raising questions about energy intensity and suitability for diverse soil types. Incineration, a high-temperature destruction method, provides an option for PFAS disposal but entails its own set of challenges.

It is crucial to underscore that the efficacy of these technologies hinges on several factors, including the specific PFAS compounds involved, soil characteristics, and environmental conditions. Recognizing the interplay between advantages and limitations, and considering the variations observed in different scenarios, is paramount when selecting an appropriate treatment strategy. Our endeavor acknowledges the intricacies of PFAS behavior in soil and strives to provide a comprehensive understanding of the available remediation technologies within this multifaceted context.

Results/Lessons Learned: This study provides a comprehensive overview of diverse technologies deployed to address soil contamination, particularly in the context of Per- and Polyfluoroalkyl Substances (PFAS). These technologies encompass Containment (landfilling or on-site containment), Stabilization (on-site or at landfill sites), Soil Washing, Thermal Desorption, and Incineration. Each of these approaches offers unique advantages and challenges. Containment effectively isolates contaminants but raises concerns about long-term sustainability. Stabilization presents prospects for immobilizing PFAS but requires vigilant oversight. Soil Washing physically extracts contaminants but may be cost-prohibitive in certain scenarios. Thermal Desorption shows promise but necessitates careful energy consumption evaluation, and Incineration offers disposal options but warrants comprehensive scrutiny. Combinations of these remediation technologies can offer flexible solutions for PFAS-impacted soils. While numerous unknowns persist in PFAS science, the lessons learned from these approaches and their combinations play a pivotal role in addressing this pressing environmental concern, guiding practitioners toward more effective and sustainable soil remediation strategies.

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PFAS – a methodology for prioritizing actions over large territories

Per- and polyfluoroalkyl compounds (PFAS) have been measured in the environment since several years. Environmental pollution linked to PFAS and revealed to the general public in Europe has led to awareness of the impact of this pollution on the health of the population.

Today, manufacturers, metropolis and local authorities wish to implement a global strategy to improve knowledge, monitor PFAS pollution and protect the population. As such, they wish to know the sites potentially exposed to PFAS at the scale of their territories which can bring together several dozen municipalities over several hundred square km often with a dense industrial history.

Drawing on its multi-disciplinary expertise, Ginger BURGEAP has developed a tool for mapping and prioritizing actions with regard to the risk of PFAS. The study has been completed on a +500 square km territory in France involving more than 50 cities (Figure 1). Information covered included past and present industrial activities, fire brigade training plot, reported industrial accident, landfills, WWT plant, current land use,… .

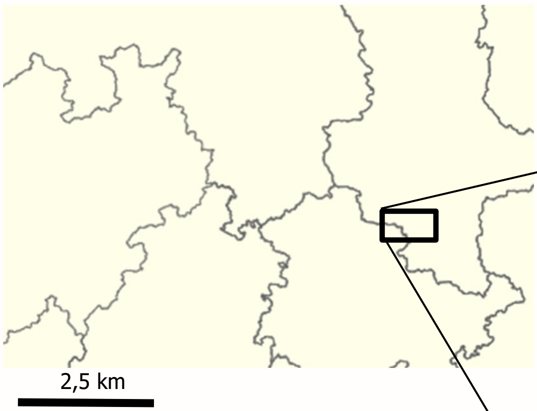

Figure 1 : large territory covered (example)

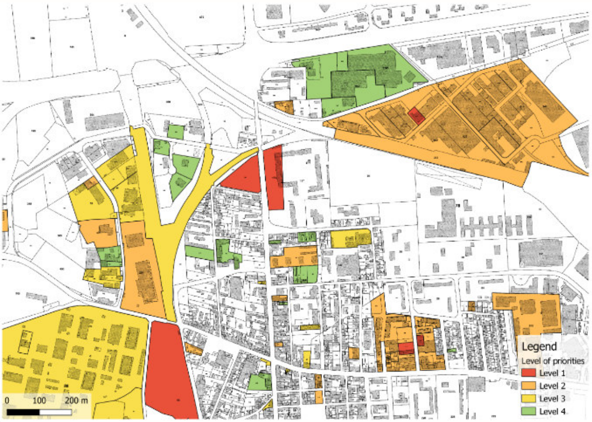

Figure 2 : cadastral parcel scale priorization (example)

This GIS tool integrates the industrial history of a territory, allows the visualization of quantitative data and provides mapping at the scale of the cadastral parcel (Figure 2). It prioritizes actions among the +900 000 parcels of the area according to the policy defended by the communities and allows clear communication with stakeholders.

Oliver CHILCOTT, Amandin HANIN, Andrea ESPEISSE, David PITAVAL – Ginger BURGEAP

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