



**Because you care  
about CONSUMERS' HEALTH**



## **PFASs IN AIR: CHALLENGING CONTAMINANTS TO CONTROL AND TO MEASURE**

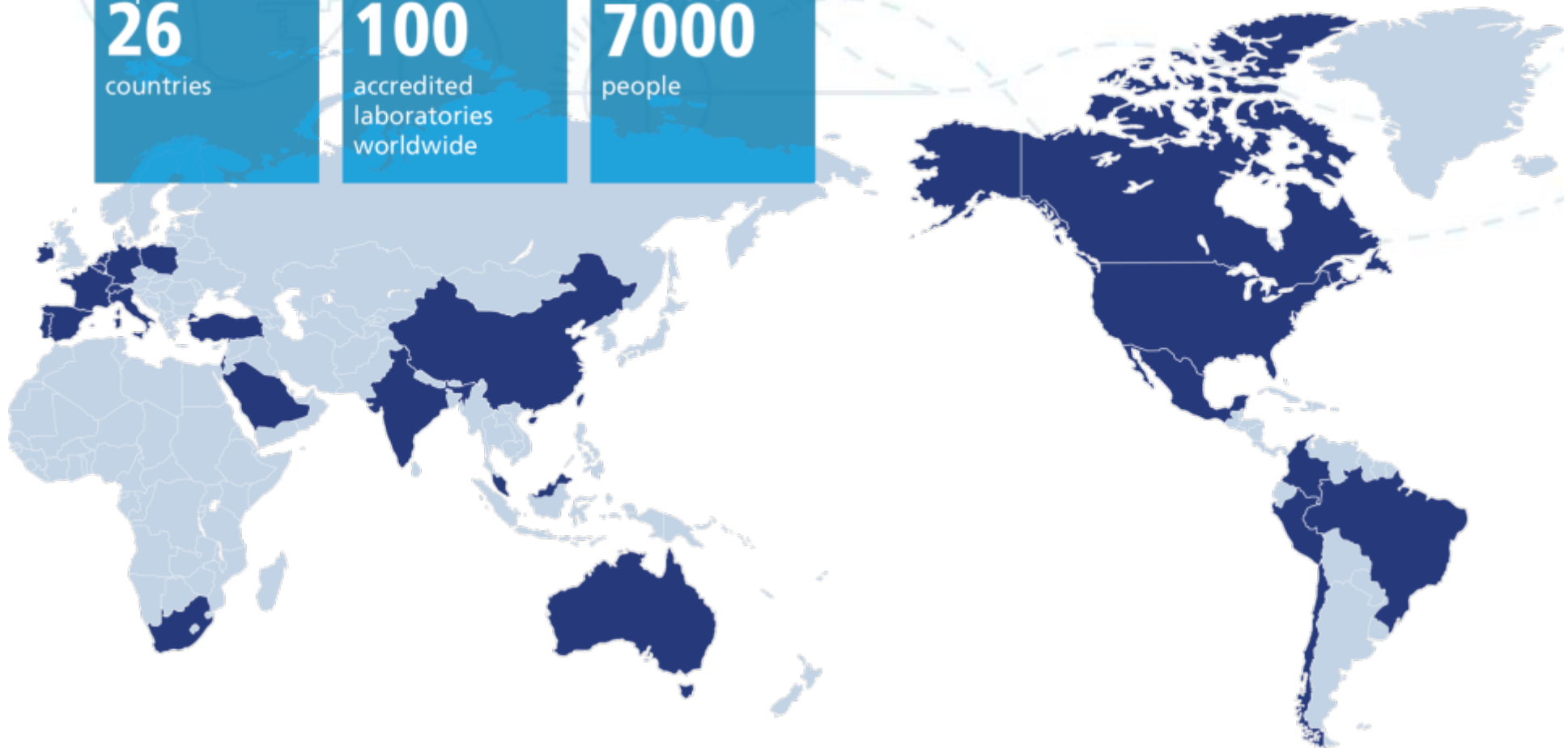
# The power of a global network



A presence in  
**26**  
countries

More than  
**100**  
accredited  
laboratories  
worldwide

More than  
**7000**  
people



# The Mérieux Legacy



- Mérieux NutriSciences was born from Institut Mérieux, an independent **family-owned French group established in 1897 following in the footsteps of Louis Pasteur.**
- From **Lyon**, a multinational corporation Company, a **global network for Life Sciences** analyses and services



# MXNS environmental services



**Water**

**Soil**  
rocks and sediments

**Waste**

**Environmental**  
investigations

**Stack**  
emissions

**Mobile**  
labs

## **Air monitoring**

- Sampling (Tedlar bags, canister)
- Analysis of indoor air and stack emissions
- Verification of air monitoring systems
- Industrial hygiene, environmental monitoring

## **Asbestos**

- Monitoring and analysis

## **Persistent Pollutants**

- PCDD/PCDF
- PCB
- PFASs
- Micro and macro pollutants

## **Water analysis**

- Groundwater
- Waste water
- Drinking and surface water

## **Soil and sediments analysis**

## **Radioactivity measurements**

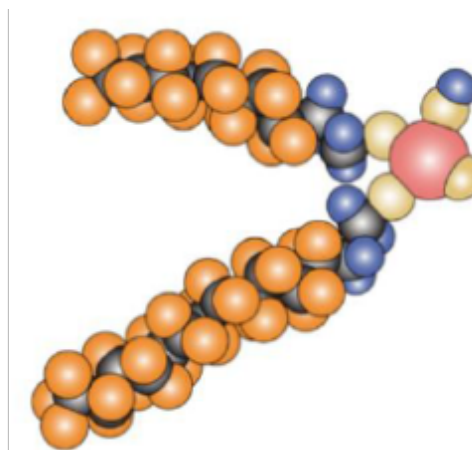
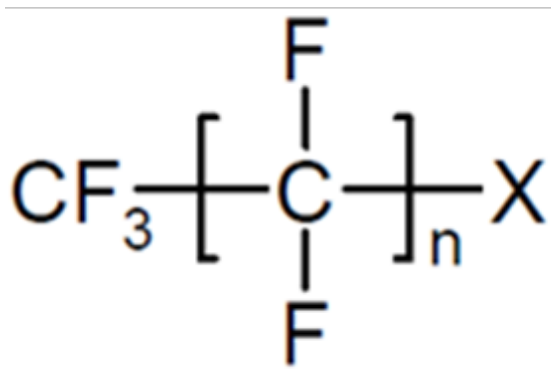
## **Waste characterization and classification**

# Emerging contaminants: PFASs



**Contaminants of emerging concern** are one of the main environmental problems of these years. Emerging pollutants include substances which are confirmed as **hazardous, but which are not specifically regulated by legislation**.

Among them, in particular, **Per- and PolyFluoroAlkyl Substances (PFASs)** for which there is a lack of regulatory harmonization at European level.



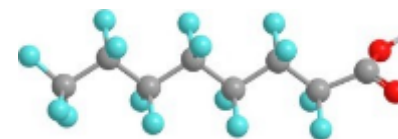
# PFASs, PFOS, PFOA



The most known PFASs are **Perfluorooctanesulfonic acid (PFOS)** and **Perfluorooctanoic acid (PFOA)** belonging to (per) fluorinated organic surfactants.

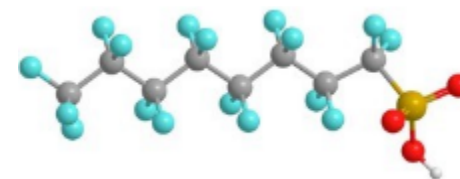
## PFOA:

- completely fluorinated organic acid
- used primarily as emulsifier in industrial applications
- linear 8 carbons- chain structure



## PFOS:

- completely fluorinated compound containing 8 carbon atoms and a sulphonate group
- wide variety of applications due to its surface- active properties



# Risks linked to PFASs



PFASs are **highly persistent chemicals (very slow clearing)** able to **bioaccumulate**

- in the Environment
- in living organisms: toxicological studies ongoing

Suspected **carcinogenic, immunotoxic and endocrine disruptors**

- PFOS and PFOA showed several adverse health effects in experimental animals

**PFASs in polymers** can break down to **PFOS** and **PFOA**

- Very important to better study those compounds



# PFASs are widely used by industries



PFOS, PFOA and other PFASs were and in some cases are still used **in industrial and domestic applications:**

- **stain- and water-resistant coatings** for fabrics and carpets
- **oil-resistant coatings for paper products approved for food contact** (cookie sheets, food paper, fast food packaging, popcorn bags etc.)
- **fire-fighting foams, mining and oil well surfactants, floor polishes and insecticide formulations**





# PFASs in the environment

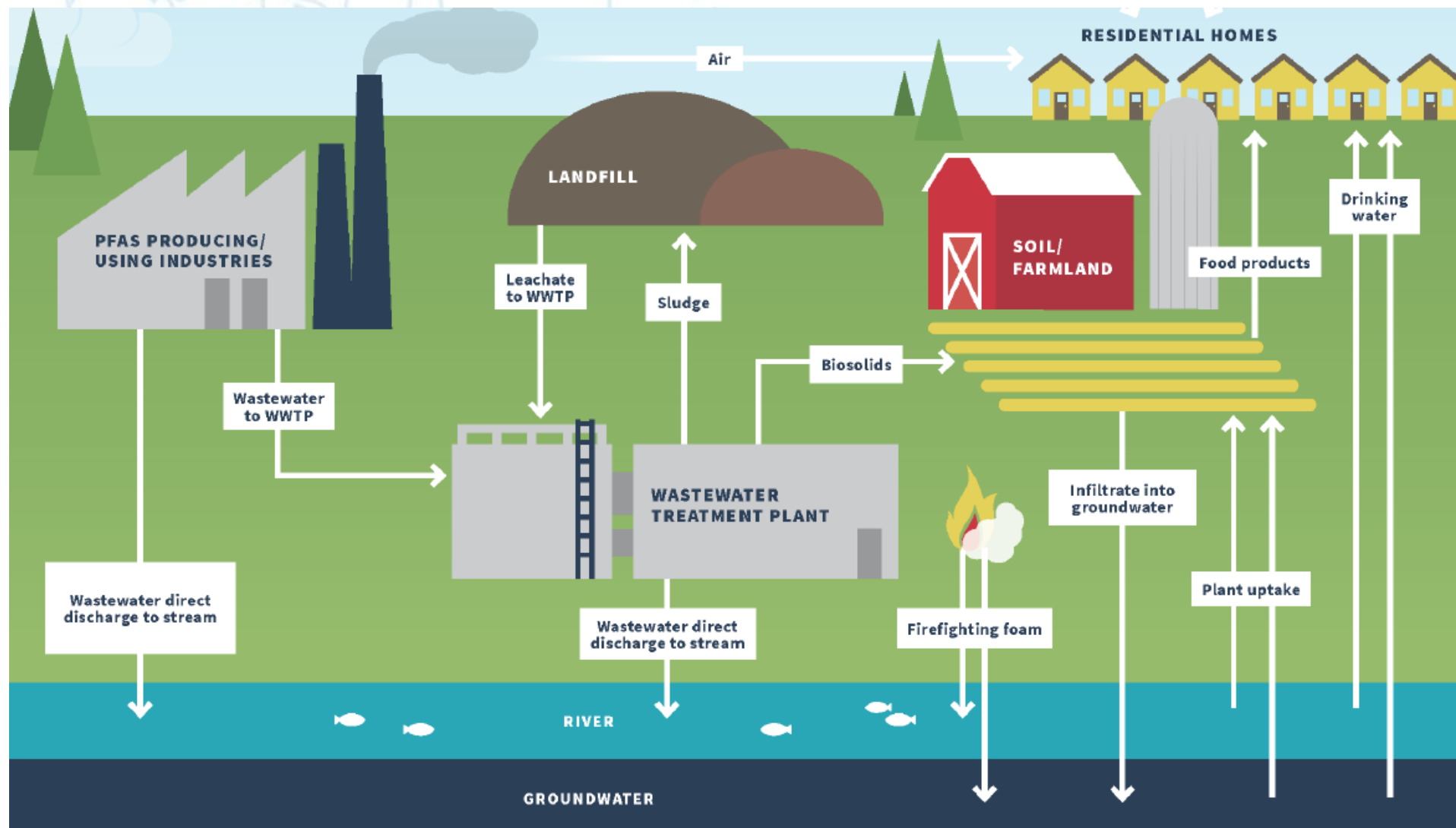


So far the **water environment** is the most contaminated by PFASs, all coming from anthropic sources:

- municipal and industrial **wastewater treatment plants**
- **direct discharges**
- **landfill leachates**
- **fluoropolymer production plants**
- PFASs derived from **atmospheric degradation** of precursor compounds



# PFASs in the environment



# Where are they analysed?



One of the main challenges in managing analyses is the **wide variety** of matrices in which PFAS can be found:

- Water
- Food
- Food contact materials
- Soil
- Waste
- Air



# PFASs awareness



## ENVIRONMENT:

### Stockholm convention (2009 and amendments 2011, 2013, 2019)

- PFOS is included among Persistent Organic Pollutants (POPs), Annex B:  
**restricted in its use**
- PFOA in Annex A, with some exceptions

### Directive 2013/39/EU – Priority Substances – waters

PFOS is included in the list of priority substances in the field of water policy

## WASTE:

### EU Regulation 2019/1021, 20 June 2019

- Concern about the protection of human health and the environment. Prohibition and phase-out of the manufacture, placing on the market and use of substances subject to the Stockholm Convention.
- Establishment about waste consisting of, containing or contaminated by such substances
- **Limit concentration for total PFOS: 50 mg/Kg**

# PFASs awareness in Europe



## **ACTION PLAN to eliminate non essential use of PFASs**

From many Member States:

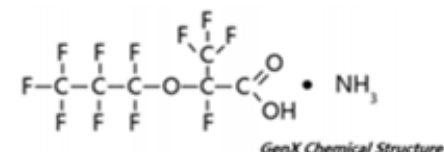
- Request to include it in the EU Green New Deal: present in the chapter *A zero pollution ambition for a toxic-free environment*
- Request to restrict other non essential PFASs

## **FOR WATER: Commission proposal for a LIMIT for all PFASs**

As at the moment there is not an analytical method for all PFAS (family approach), it has been proposed to decide a limit on 20 PFAS until we have a good analytical method.

**Groundwater is monitored in all Countries**, PFASs are probably going to be included in the next Directive on groundwater.

## So Many PFAS Compounds!





# PFAS issue in Italy



In Italy we start speaking about PFAS pollution from 2013.

The contamination started years before: it is considered the most serious water pollution in Italian history and we are still dealing with consequences.

- **Deep study** of the topic
- Involvement of **Environmental Protection Agencies**
- National guidelines
- **Local and national limits in water**
- 2019: local **test method and limits guidelines**



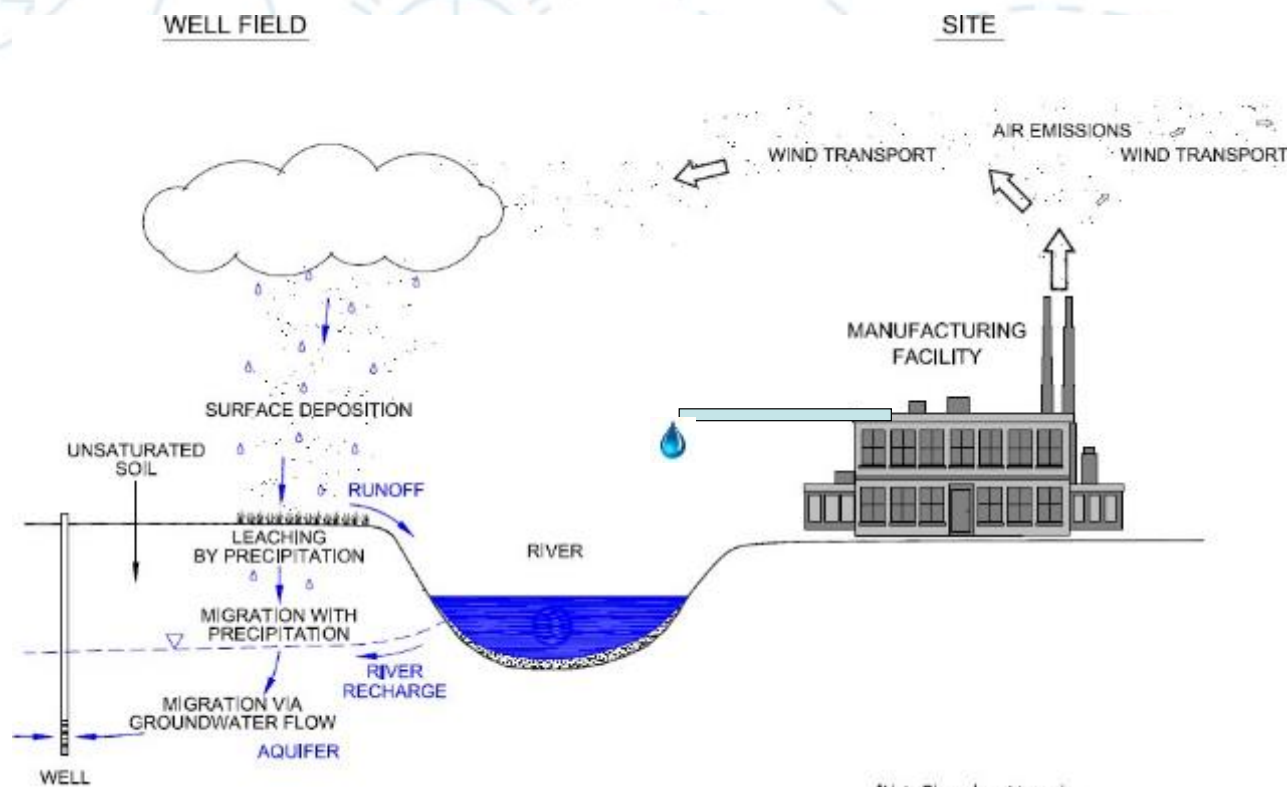
# In Italy

The Regional Protection Agency of Veneto in 2019 issued a communication **to monitor PFASs in landfill sites**.

- Strict limits
- Precise methods
- Need of cutting edge technologies

Matrix	Method	LOQ	Notes
groundwater	ISO 25101:2009	5 ng/L	LOQ for PFOS, PFBS, PFHXS and other linear PFAS C4-C12
leachates	ASTM D7979-17	100-1000 ng/L	LOQ for PFOS, PFBS, PFHXS and other linear PFAS C4-C12
waste entering the plant	ASTM D7968-17a	50µg/Kg	LOQ based on results obtained on soils

# PFASs in air: a significant source



Davis et al. Chemosphere 67 (2007) 2011–2019

# PFASs in air



## Thousands of **products** that become air sources

Emitted into the air during chemical production and product manufacturing, and present everywhere in our homes, schools, workplaces, hospitals .....

<b>Clothing</b>	<b>Building Materials</b>	<b>Food Related</b>	<b>Consumer Products</b>
Outdoor Gear	Teflon	Popcorn Bags	Cosmetics
Lab Coats	Carpets	Cookware	Dental Floss
Aprons	Paints	Cutting Boards	Boat Sails
Shirts	Window Coverings	Grille Mats	Umbrellas
Pants	Wall Coverings	Food Wraps	Dryer Sheets
Shoes	Pipe Sealants	Pizza Boxes	Whiteboards
Swimwear	Furniture	...	Car Wax
Beekeeper Suits	Stadium Roofs		Pool Tables
...	Airport Roofs		...
	Awnings		
	...		

Source: US EPA



# PFASs in air: a US case study



**NORTH CAROLINA** Areas around industrial production, manufacturing and application sites have been found to be particularly contaminated by PFAS

- The presence of significant levels of PFOA (>100 ng/L) in surface water more than 15 miles upstream from the facility and quantifiable levels (>10 ng/L) more than 25 miles away **suggests contamination pathway via air deposition**
- The discovery of GenX at many of the collection sites suggests the replacement PFAS is contaminating the local environment via air deposition as well

## PFAS (GenX) in Rainwater

DAQ Rainwater Collection and Analysis  
Concentrations in part per trillion (ppt)  
January 28-29, & February 4-5, 2018 Rain Events



# Issues in monitoring PFAS in air



- **No legislative references with limits**
- **No standard «attention level» for air quality**
- **No official stack testing and sampling methodology**
- Current emissions tests often target only a small number of PFAS compounds for analysis (usually derived from what is usually done in water) while **significantly more may be present**





# Air and emissions in the atmosphere



## Three decisive phases

01

Sampling (time, flow absorption substrate)

02

Make analytes available (e.g. desorption)

03

Laboratory analysis

# Italian environmental agency - indoor air



ARPAV laboratories (Environmental Protection Agency of Veneto) in 2017, based on previous studies reported in the literature:

- **carried out sampling** using high volume samplers on PUF (polyurethane foams) with glass filter added marked standards (C13)
- **used as extraction method** an ASE (Accelerated solvent extraction) with methanol at a pressure of 1500 psi e a temperature of 100 °C; this involved an initial phase of 5 min heating and three successive "static" cycles
- a portion of the extract (1 mL) was dried and taken up with 1 mL of 10% water methanol
- **analyzed** the extract in **LC MS / MS referring**, for the instrumental part, **to the method ISO 25101: 2009 "Water quality- Determination of "PFOS and PFOA"**

# Italian environmental agency - emissions



ARPAV laboratories in 2017, based on previous studies reported in the literature:

- performed the **sampling** on a filter with added marked standards ( $C^{13}$ )
- **extraction** was made with 3 ultrasonic extraction cycles with 5 mL of MeOH; after that, a purification step with passage on SPE WAX.
- **analysis of extract was carried out in LC MS / MS referring, for the instrumental part, to the method ISO 25101: 2009 "Water quality- Determination of PFOS and PFOA"**

# List of compounds



Perfluorohexane sulfonate (L-PFHxS)

n-Perfluorooctanoic acid (PFOA)

N- Perfluoroesanoic acid (PFHxA)

Perfluorooctanoic acid (PFHpA)

n-Perfluorobutanoic acid (PFBA)

n-Perfluorobutan sulfonate (L-PFBS)

n-Perfluorodecanoic acid (PFDA)

Perfluorooctan sulfonate (L-PFOS)

n-Perfluoropentanoic acid (PFPeA)

Perfluorononanoic acid (PFNA)

n- Perfluoroundecanoic acid (PFUnA)

n-Perfluorododecanoic acid ( PFDoA)

# Our case study



**CONTEXT:** Company that thermally treats **PTFE**, used to produce balls, valves, rings, o-rings.

**REQUESTED SERVICE:** Carry out surveys on PTFE in order **to understand if the thermal treatment could generate PFASs** and if they are detected in the stack emissions.





# Our case study: PTFE, polytetrafluoroethylene

Synthetic fluoropolymer, high molecular weight compound consisting of carbon and fluorine

- **hydrophobic**: neither water nor water-containing substances wet PTFE, as fluorocarbons demonstrate mitigated dispersion forces due to the high electronegativity of fluorine
- used also as a **non-stick coating for pans and other cookware**; where used as a **lubricant**, PTFE reduces friction, wear, and energy consumption of machinery
- commonly used also as a graft material in **surgical interventions and as coating on catheters**; this interferes with the ability of bacteria and other infectious agents to adhere

The well-known **brand name of PTFE-based formulas is Teflon** by Chemours (spin-off from DuPont), which originally discovered the compound in 1938. Another popular brand name of PTFE is Syncolon by Synco Chemical Corporation.





# Our case study: sampling



Sampling was carried out in the **furnace suction chimney**

- Two vials to make the front and the back at a flow of 0.5 L / min for 60 minutes simultaneously with an evaluation of the fluorides with the ISO 15713 method
- Sorbent Tube, Tenax TA OVS (Glass Fiber Filter), 13→8 x 75-mm size, 2 sections, 70/140 mg sorbent, 20/35 mesh, with GO ends and FFGT separators, fits Type V tube cover, pk/10



# Our case study: sample preparation



- Analysis is **performed on both resins** in order to evaluate any saturation effects of the front part. To determine if there has been a saturation of the resin, **laboratory must indicate a percentage of contaminants that may be present with respect to the front part (usually not more than 20%)**.
- **The resins (front and back) are placed in two test tubes.** Marked references relating PFAS ( $C^{13}$  or  $O^{18}$ ) are added.
- After an adsorption time, methanol is added and extracted by ultrasound.
- Solution can be injected directly into a system consisting of an HPLC coupled to HR mass analyzer.

# Equipment and analytical techniques

Equipment: **HIGH RESOLUTION LC/MS**

The election technique in all the official reference methods for PFAS is LC-MS/MS.

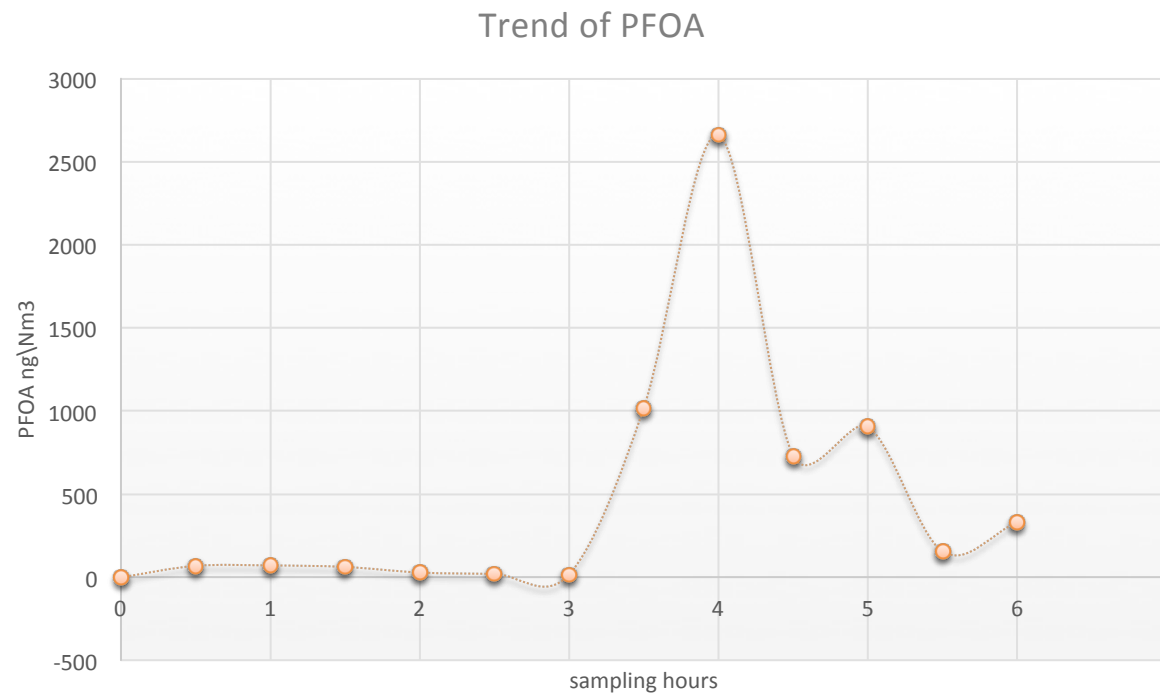
Preparative changes depending from matrix (liquid-solid extraction, dilution, direct injection, concentration) and equipment (standard LC-MS/MS or high resolution).



# Our case study: results



hour	PFOA ng\Nm <sup>3</sup>
0	0
0,5	67,68
1	70,25
1,5	61,4
2	27,63
2,5	19,65
3	15,89
3,5	1018
4	2660
4,5	731
5	906
5,5	155
6	330



PFBA and PFNA and others have the same trend

# Conclusions



## In the absence of an official method for emissions:

- **sampling:** capturing substrate worked well
- maybe, before carrying out the real measurement, it may be necessary to **have an idea of the theoretical concentration** during a process to avoid oversaturation of capturing matrix ( or reducing the sampling time)
- it would be interesting to consider **the fallout on the ground** and try to analyze the top soil of the surrounding soil

## The role of the lab:

- to be updated on the evolution of methods and legislation
- to talk with the contractor to plan the analysis in the specific environmental framework and to give a correct interpretation of the results

# Contacts



Thank you for your kind attention!  
Merci pour votre attention!  
Grazie per l'attenzione!

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