PFAS groundwater pollution in Veneto Region (Northern Italy):

regulatory implications on environmental harm and judgment case

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I. Background, characterization and implementation of risk mitigation measures: the PFAS contamination in Veneto

II. Legal and regulatory implications

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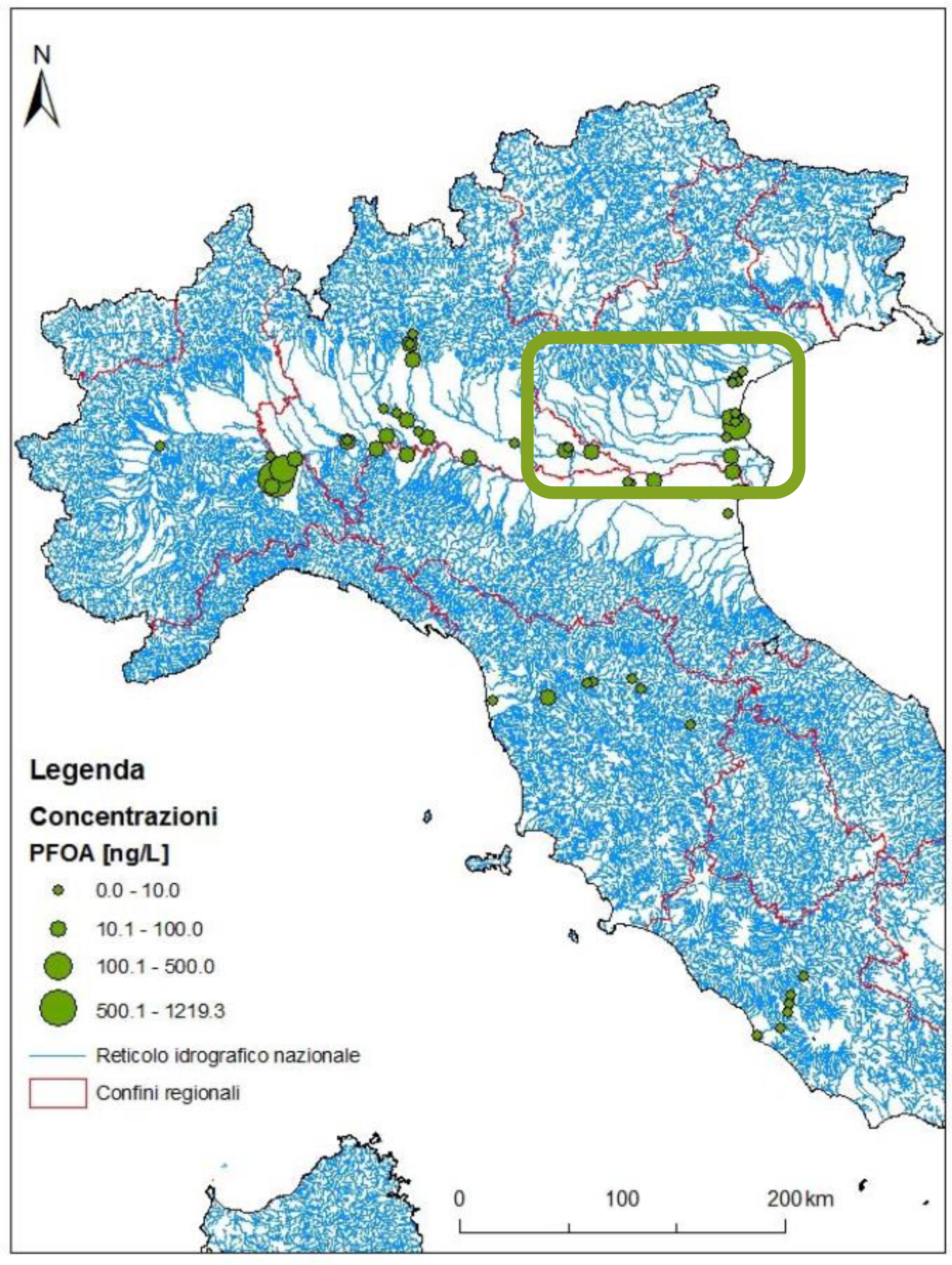
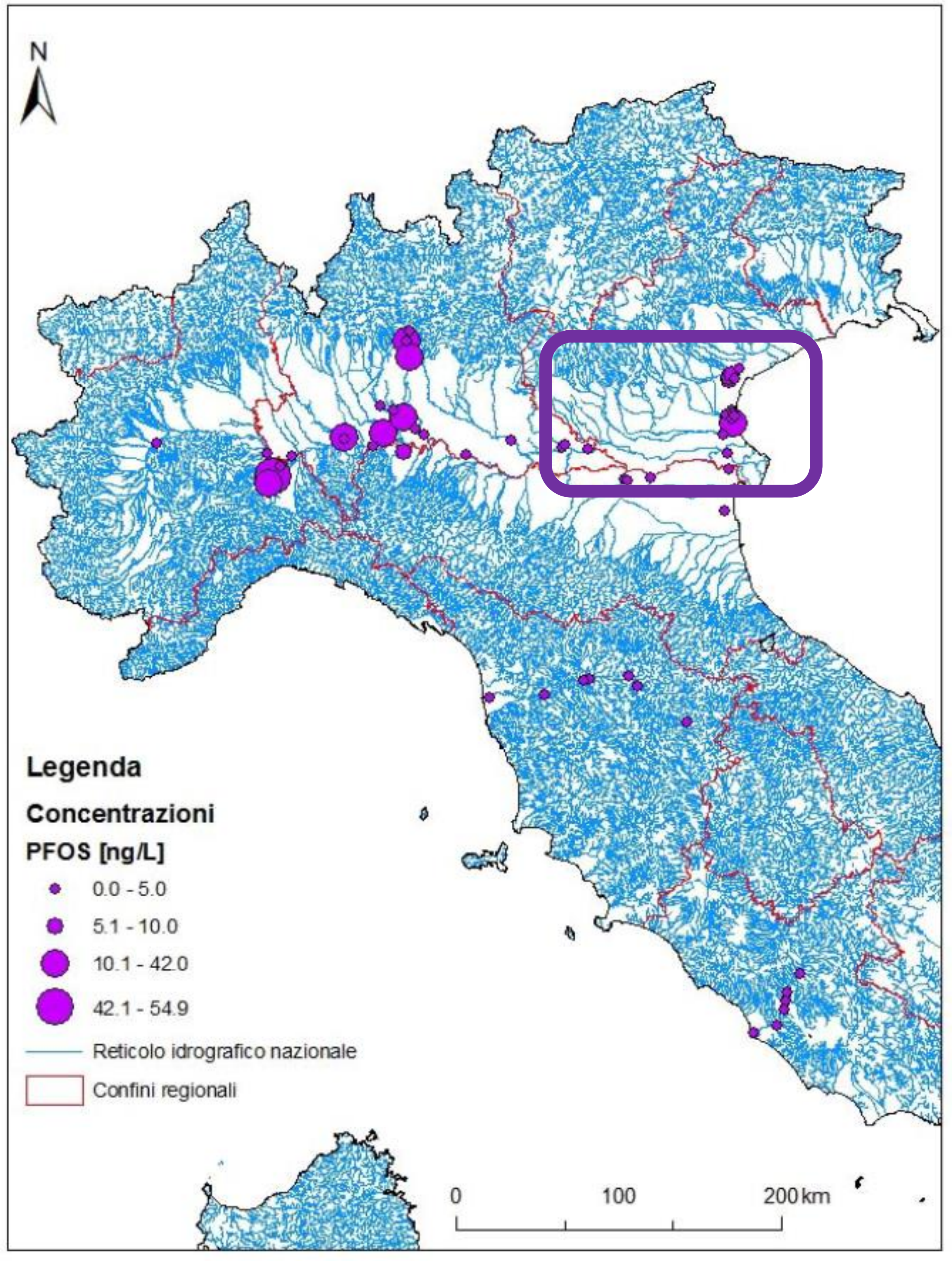
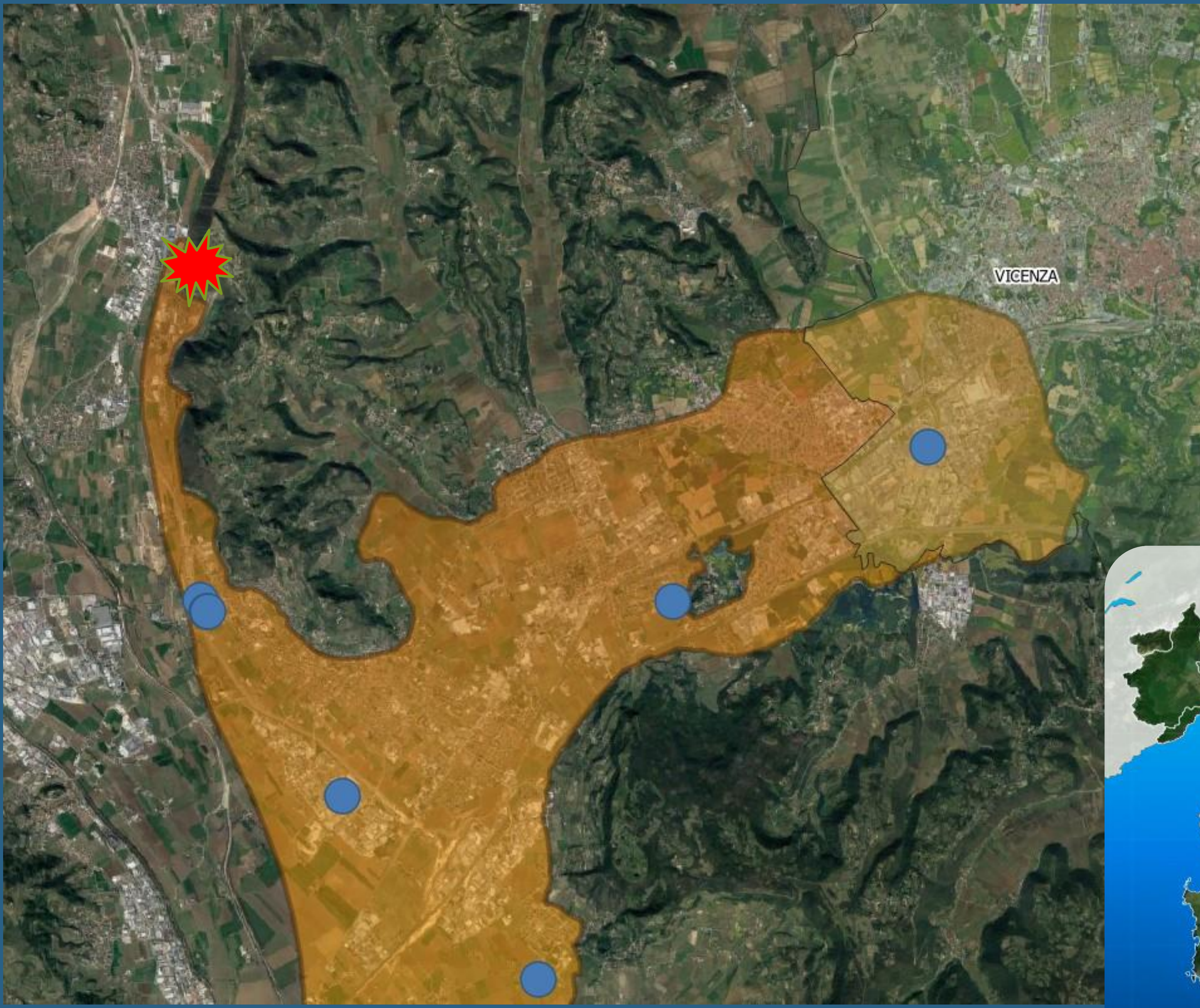
BACKGROUND: setting the scene

2011-2013: the EU PERFORCE project by the Ministry of the Environment and CNR-IRSA to assess the occurrence and emissions of PFAS in the main Italian river basins





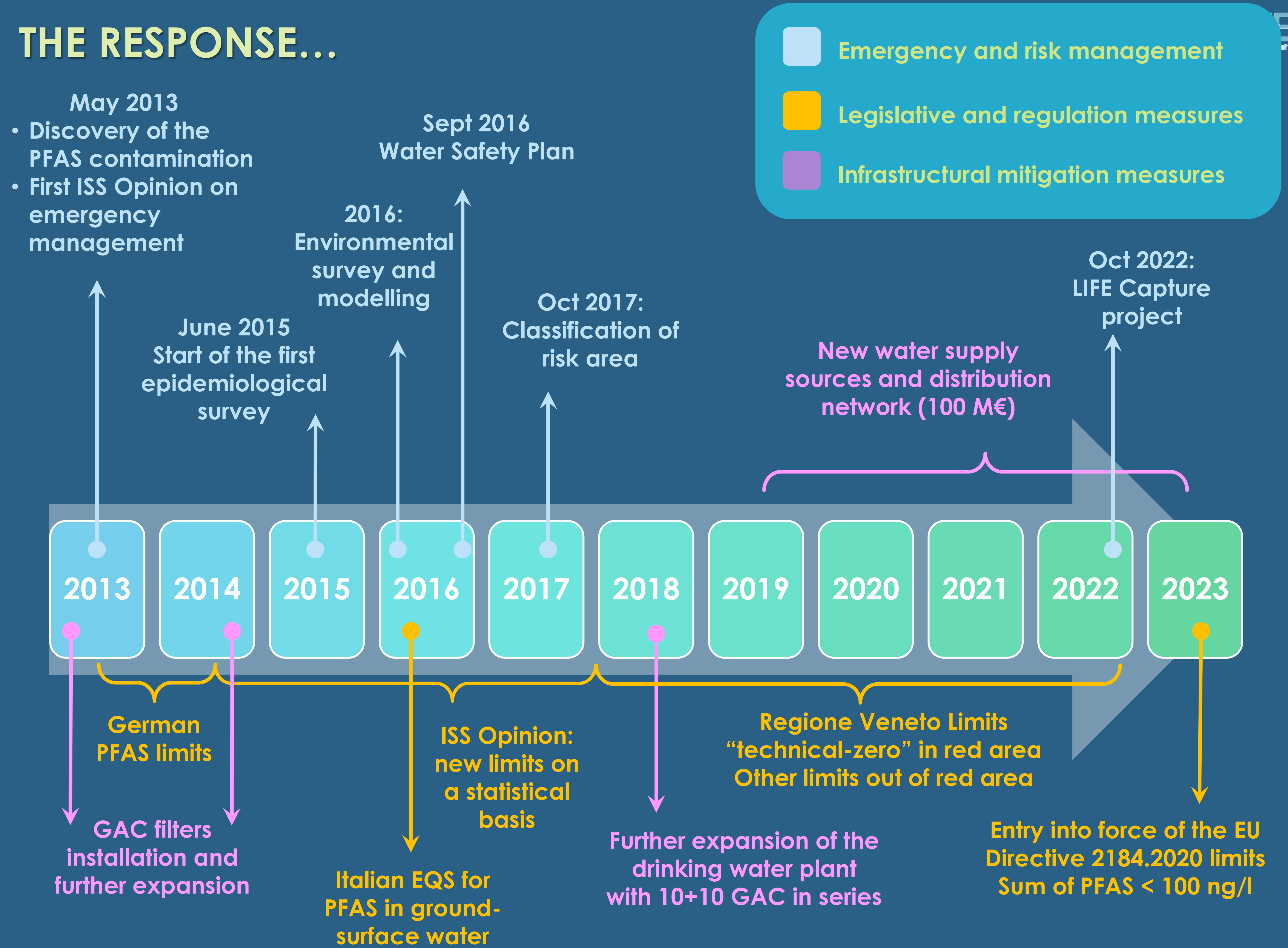
BACKGROUND: setting the scene



- the largest Italian PFAS manufacturing plant (tannery district)
- Producing since the '60s
- From long-chain to "new generation" PFAS (e.g. GenX)

Public water supply

THE RESPONSE...



THE REGULATORY RESPONSE:
European, Central and Regional levels

National Health Institute – ISS

07/06/2013 (Ref. N° 0022264) ISS opinion:

- urgent adoption of alternative supplies to reduce PFAS exposure of the affected population;
- adoption of removal treatments from raw waters;
- implementation of a WSP;
- identification and removal of polluting sources

16/01/2014 (Ref. N° 0001584) ISS opinion

- short-medium and long-term actions pursuing the virtual absence of PFAS at the tap;
- provisional limits were recommended to be applied to drinking water supply:

  PFOS < 30 ng/l

  PFOA < 500 ng/l

  sum of other PFAS (#8) < 500 ng/l
- monitoring study of the PFAS contamination in the environment and in the food chain;
- a biomonitoring study of internal exposure markers

Legislative dec. 13/10/2015 n.172 and Ministerial Dec. 06/07/2016-11/09/2017 (Ref. N° 0026)

- Introduction into national legislation of environmental quality standards (EQS) for PFAS;
- adoption of PFOA and PFOS performance limit values of one order of magnitude lower than the previous ones

EUROPE

Directive EU 2184.2020 :

Sum of PFAS	**≤ 100 ng/L**
PFAS Total	**≤ 500 ng/L**

VENETO REGION

DGR 1590/2017
Performance limits for drinking water supplies :

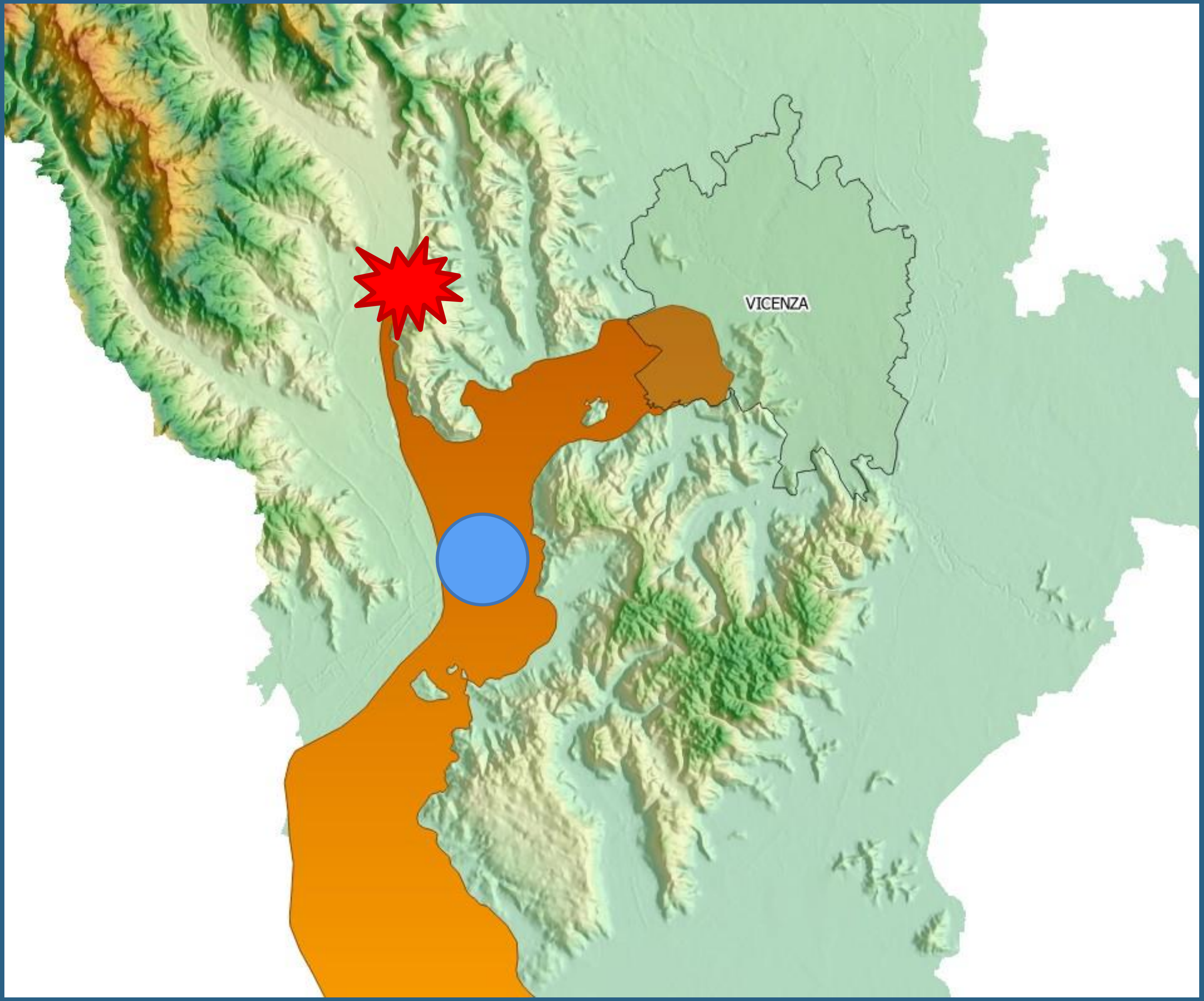
PFOS	**≤ 30 ng/L**
PFOA + PFOS	**≤ 90 ng/L**
Sum of PFAS	**≤ 300 ng/L**

RISK MITIGATION MEASURES

short- and long- term

At the source of contamination site

- **Plug-in of the Pump&Treat system**
- Removal of contaminated industrial waste at the river's banks (2016)



Drinking water supplies

- Closure of contaminated boreholes
- Set up of new GAC filtration units
- **Interconnections with alternative sources**

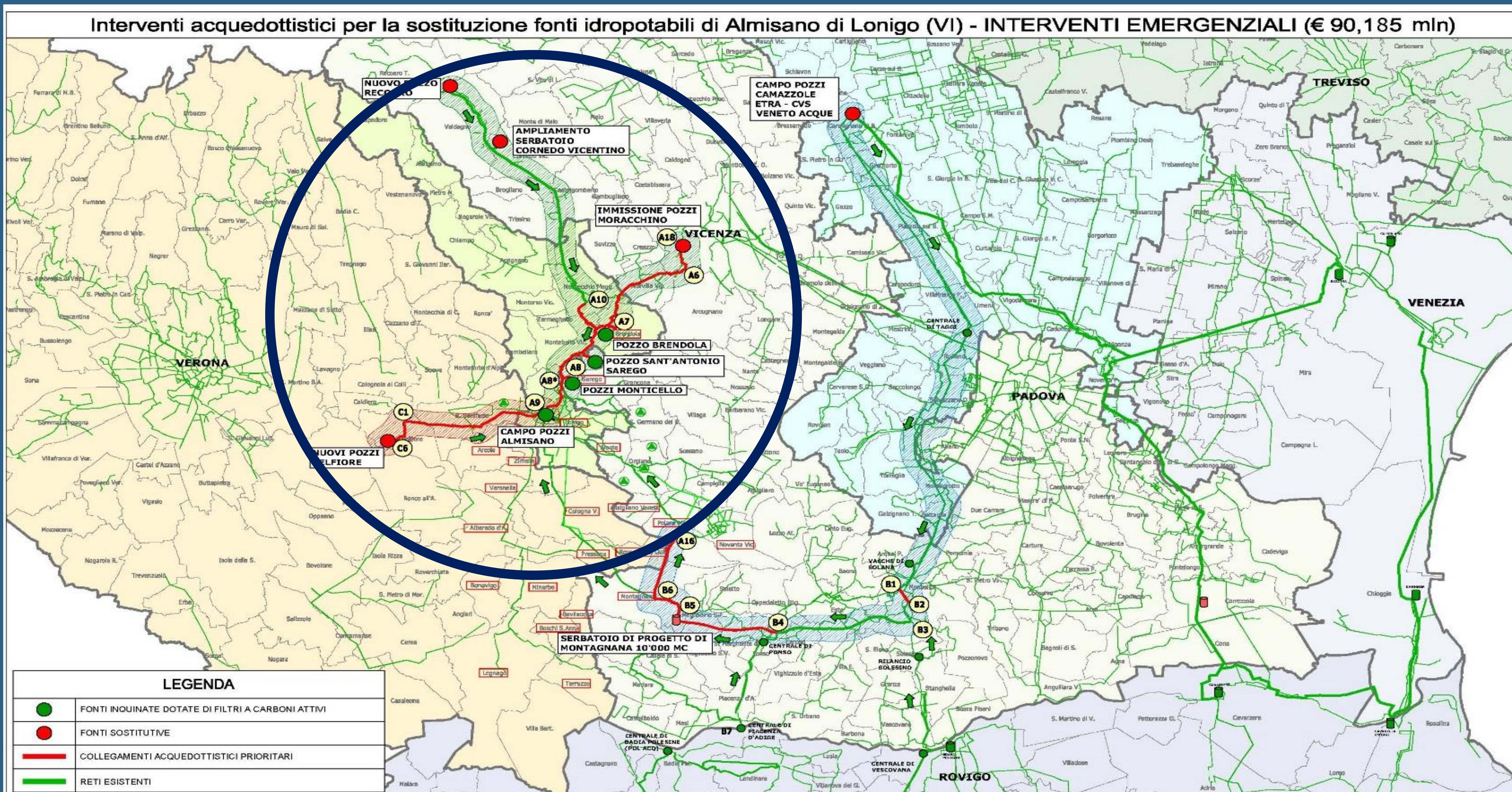
RISK MITIGATION MEASURES
short- and long- term

Installation of CA filters at one large pumping site

- 4 water supply networks served (1.350 km)
- 140.000 population served
- 11.000.000 m^3 of water produced per year
- 1.000.000 Euro/year for GAC replacement (very site specific)

RISK MITIGATION MEASURES

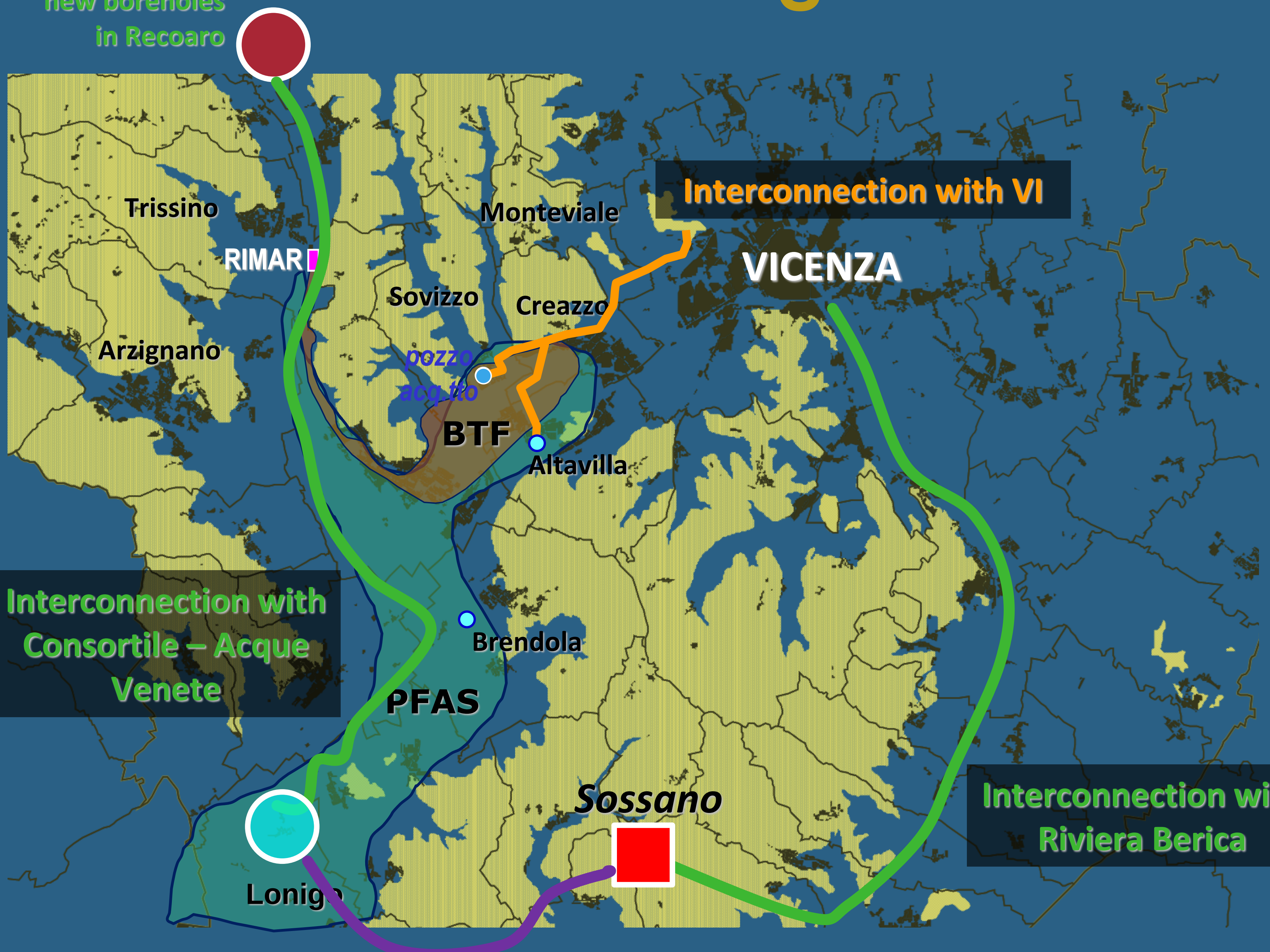
short- and long- term



Drinking water supplies (total cost: 103 M €)

- Interconnections with other distribution networks
- Implementation of new water production sites(boreholes) and storage

RISK MITIGATION MEASURES
short- and long- term



1977
Contamination by benzotrifluoride (BFT)

2013-21
Contamination by PFAS

Drinking water supplies (total cost: 103 M €)

- Interconnections with other distribution networks
- Implementation of new water production sites(boreholes) and storage

The LIFE CAPTURE Project

CAPTURE

General Objective:

- Combining novel analytical protocols for PFAS contamination with technologies for sustainable remediation.

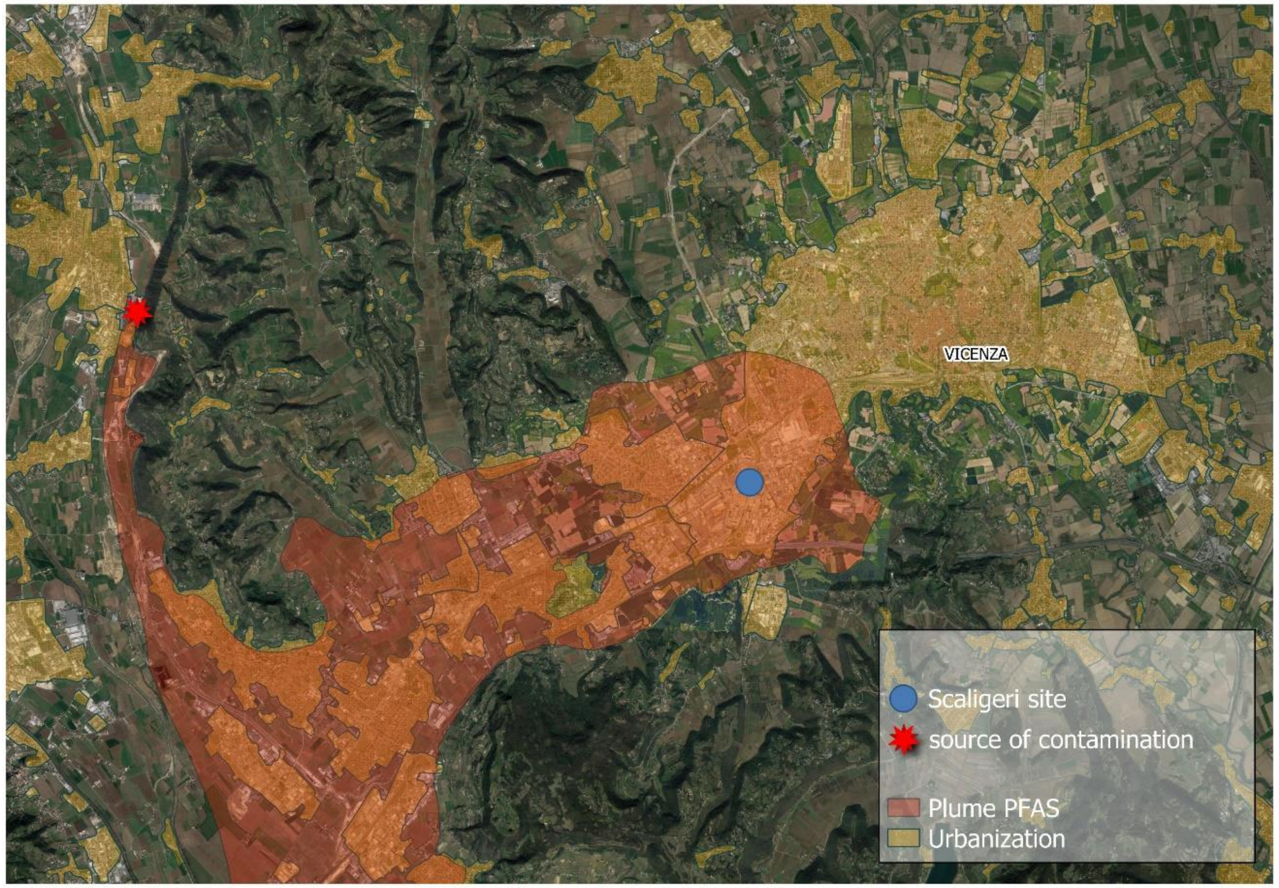
Specific Objectives:

1. Development of robust protocol for the analysis of PFAS. The intention is to enlarge the spectrum of the PFAS family that can be identified and analysed;
2. Development of methods to monitor the transport of PFAS from soil, through groundwater, to receptors
3. Identification, testing and validation in real conditions of remediation technologies
   - **AOP for VIACQUA in Veneto (one drinking water borehole contaminated by PFAS)**
4. Development of risk assessment methods for mixtures of different known or unknown PFAS and methods for assessing risk reductions achieved by remediation

Duration: 2022 – 2027 (5 years)

Partners:

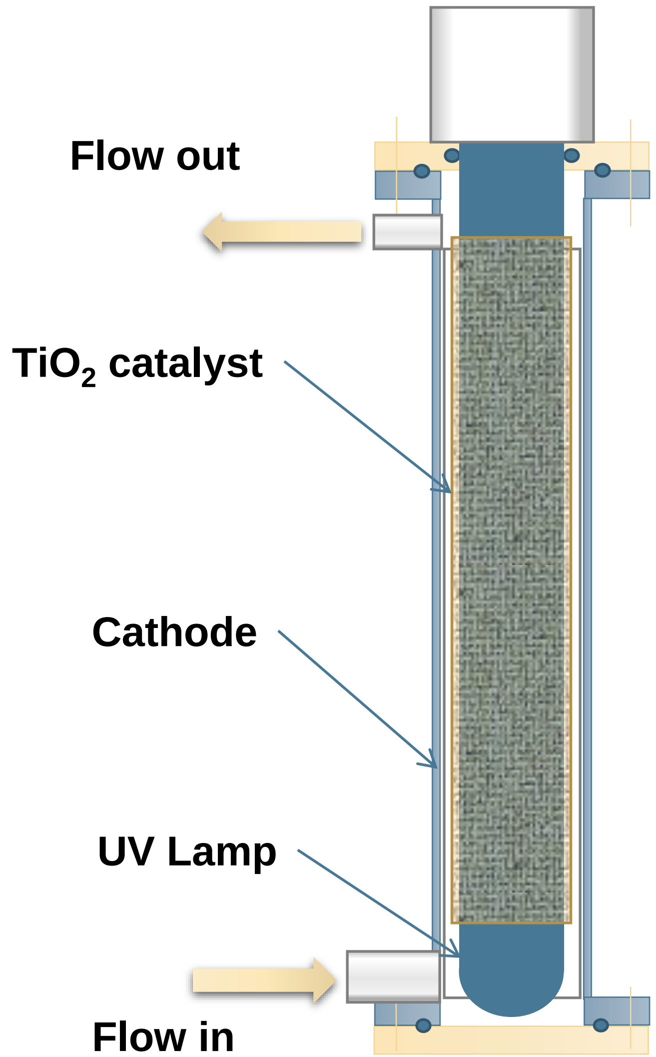
1. ABO NV, Belgium
2. GreenSoil International B.V., Netherlands
3. Politecnico di Milano, Italy
4. Universita' degli Studi di Milano-Bicocca, Ita
5. iFLUX BVBA, Belgium
6. VIACQUA spa, Italy
7. SVERIGES LANTBRUKSUNIVERSITET, Sweden
8. SGS Belgium nv, Belgium



The LIFE CAPTURE Project

CAPTURE

PFAS degradation by PEC: experimental set-up



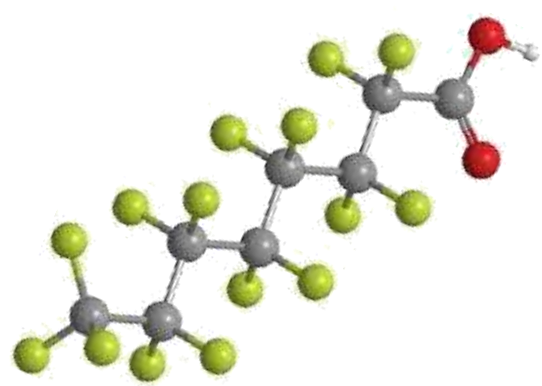
PL = photolysis

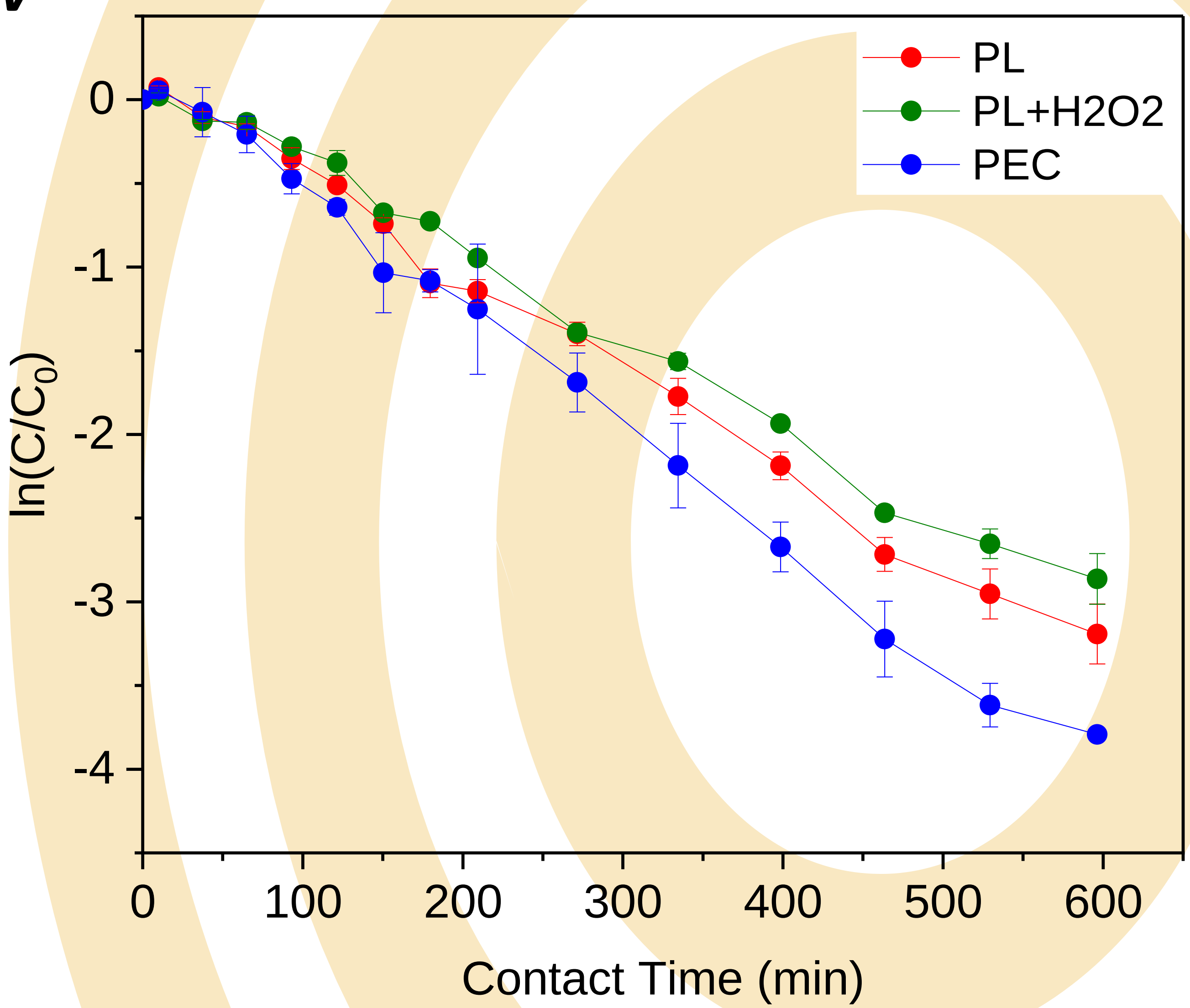
PL+H_2O_2 = H_2O_2 assisted photolysis

PEC = photoelectrocatalysis

- ***Applied bias: 4V***
- ***No additive***

PFOA





THE ALLEGED CRIMES

Merlin & Tonellotto
avvocati penalisti per l'impresa

1. POISONING GROUNDWATER

(Article 439 of the Italian Criminal Code) intended for human consumption, <u>for having committed multiple omissions with respect to the current environmental regulations, allowing the dispersion of various contaminants</u>, including PFAS-PFOA, which "are dangerous to public health as they bioaccumulate within the body, increasing the incidence of unwanted health effects such as an increase in cholesterol levels in human serum"

2. ENVIRONMENTAL DISASTER

(Article 434 of the Italian Criminal Code) <u>for creating a macro-event of damage to both surface and underground waters</u> in three Venetian provinces: Vicenza, Verona and Padua.

CRIMINAL LIABILITY

3. ENVIRONMENTAL POLLUTION

(Article 452-bis of the Italian Criminal Code) <u>for causing a significant and measurable deterioration of groundwater</u> through the introduction of HFPO-DA and C6O4 substances used in the company's production cycle.

THE ALLEGED CRIMES

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JUDGE MUST VERIFIES that the water intended for human consumption contains quantities of contaminating substances that scientifically establish a danger of toxic and harmful effects on health, **INDEPENDENTLY** of any threshold limits established by regulations for water protection *(which, did not exist in the Italian legal system at the time of the alleged offenses for PFAS-PFOA).*

THE ALLEGED CRIMES

Merlin & Tonellotto
avvocati penalisti per l'impresa

2. ENVIRONMENTAL DISASTER

(Article 434 of the Italian Criminal Code) for creating a macro-event of damage to both surface and underground waters in three Venetian provinces: Vicenza, Verona and Padua.

JUDGE MUST VERIFIES the presence of serious and irreparable damage to the involved environmental matrices (surface water and groundwater), which exposed an indeterminate number of people to a serious health hazard.

THE ALLEGED CRIMES

Merlin & Tonellotto
avvocati penalisti per l'impresa

3. ENVIRONMENTAL POLLUTION (since 2015)

(Article 452-bis of the Italian Criminal Code) for causing a significant and measurable deterioration of groundwater through the introduction of HFPO-DA and C6O4 substances used in the company's production cycle.

JUDGE MUST VERIFIES a SIGNIFICANT and MEASURABLE alteration of the original composition of the environmental matrix involved (groundwater). This offense can also be committed in the absence of explicit references to threshold limits imposed by specific regulatory provisions *(which were absent in the Italian legal system)* if there is a situation of macroscopically evident and concretely ascertainable environmental compromise

BETWEEN CRIMINAL REPRESSION AND PRECAUTIONARY AND PREVENTIVE ACTIONS

1. **LACK OF THRESHOLD VALUES** in both Italian legislation and authorizations held by the production plant (related to PFAS) allowed the damage caused to the groundwater matrix to spread over time in a very extensive area of the upper Po Valley.

2. protection provided by Italian criminal law (for non regulated substances) begins when they have already concretely endangered not only the environment but also public safety: **EX-POST PROTECTION**.

3. only **PREVENTIVE PROTECTION** comes from Directive 2004/35/EC on environmental liability where the suspicion of danger (based on scientific data and evaluation) must activate a mechanism for generating (and sharing) information between the latter and the control authorities.

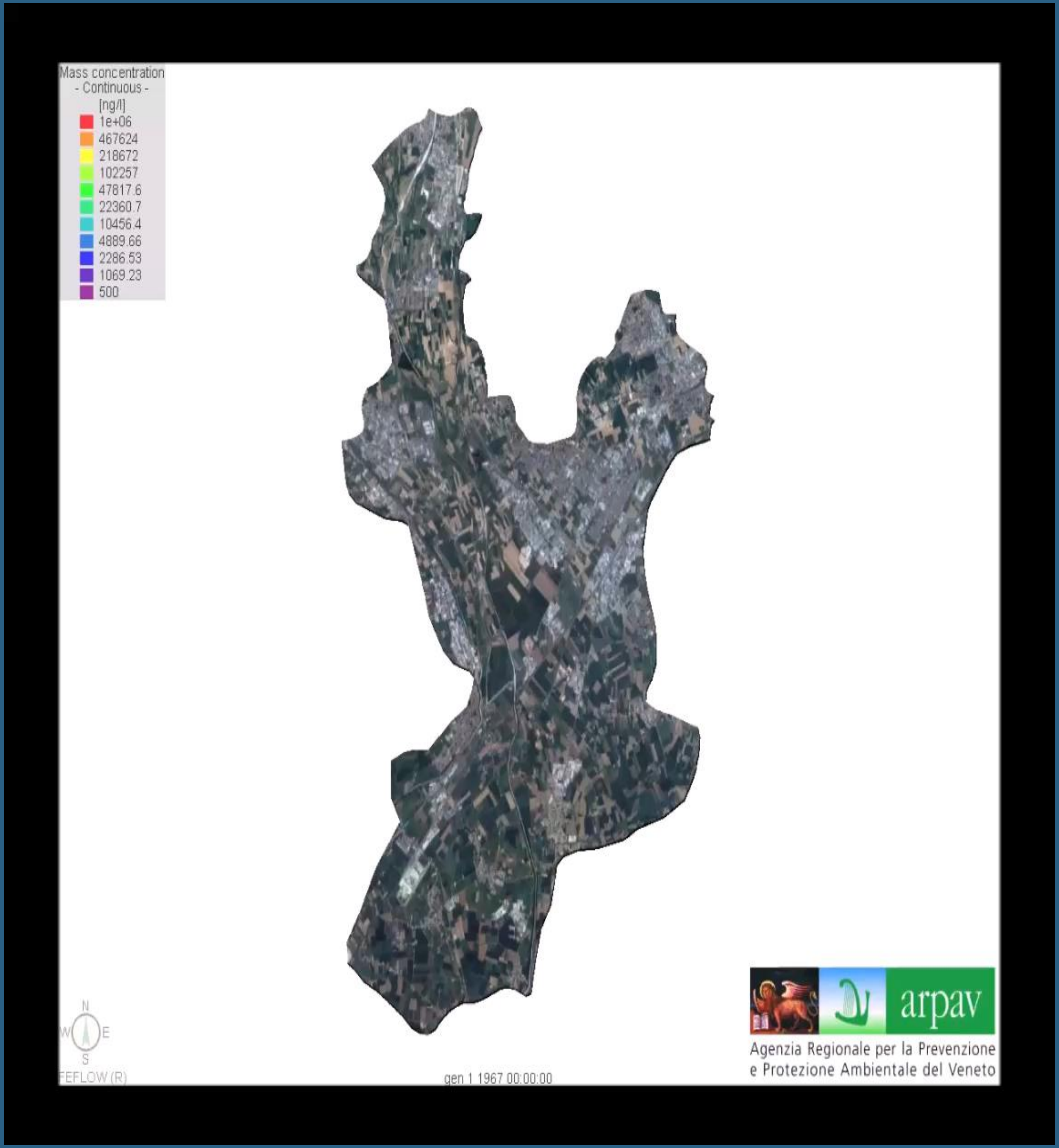
HERE: the company that managed the production plant never took the precautionary actions indicated by this specific regulation, despite being aware of the significant presence of PFAS (PFOA and PFOS) in the groundwater surrounding the company's site (since ‘90ies).

SIGNIFICANCE of the environmental harm from the aquifer point of view

1. The existence of environmental damage must **not** be attributed to the exceeding of a threshold concentration value.

2. The comparison between the ex-ante situation (baseline) and the ex-post one highlights a significant **worsening** of the original conditions under multiple perspectives of analysis:

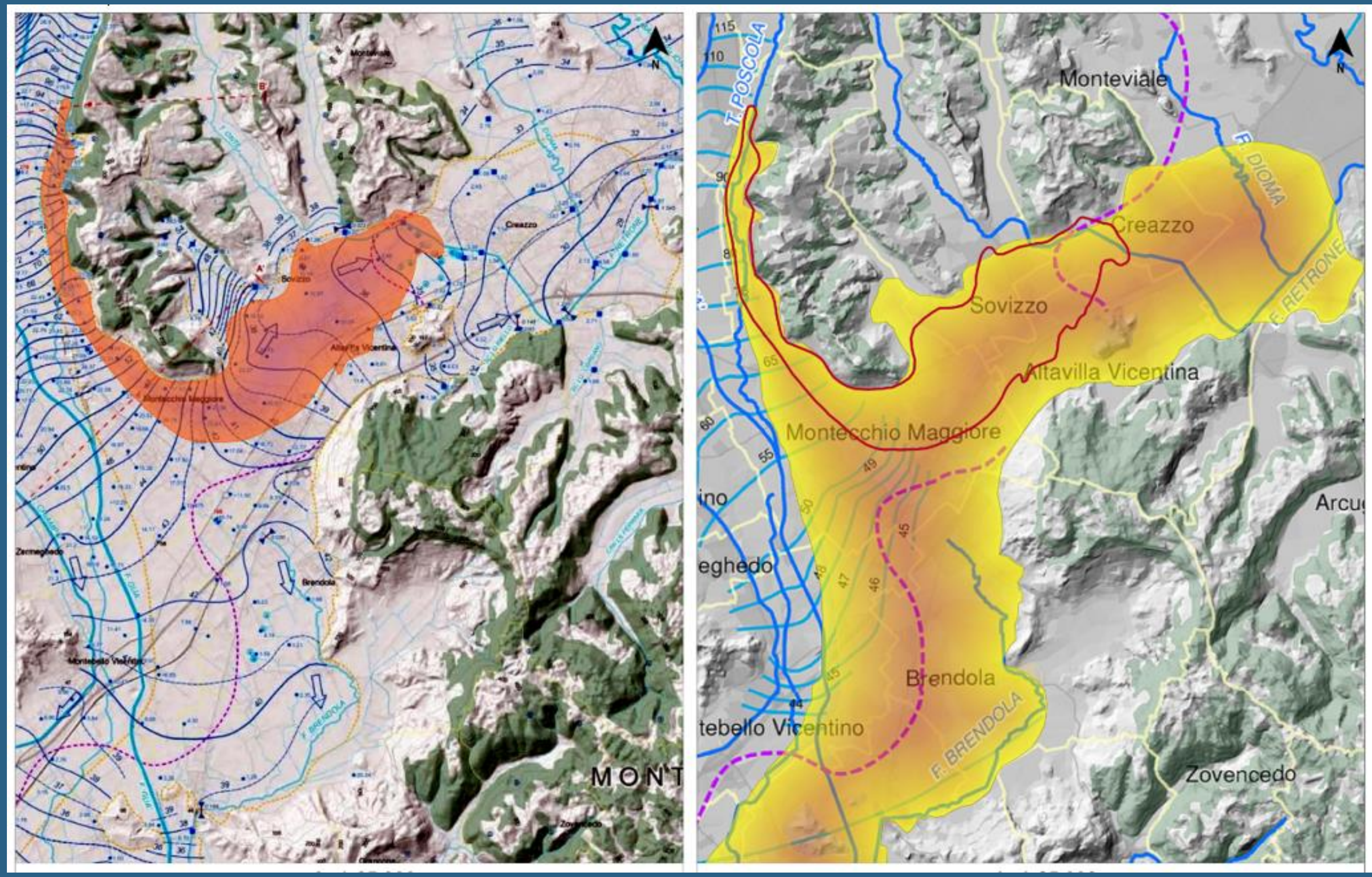
    - DPSIR approach and
    - more than 100.000 analysis in 10 years
    - open data at: *https://www.arpa.veneto.it/dati-ambientali/open-data/idrosfera/concentrazione-di-sostanze-perfluoroalchiliche-pfas-nelle-acque-prelevate-da-arpav*



Conceptual SIGNIFICANCE

Beyond the findings of ubiquity of the compounds (Cousins et al., 2022), connected with multiple uses-releases and despite the vastness of the geographical domain involved, several evidences contribute to support a robust causal relationship between the industrial site and the PFAS occurrences in groundwater:

- ✓ the geographical position of the site
- ✓ the geological, morphological and hydrological characteristics of the area are adequate to justify the emission mechanisms from both primary sources and secondary ones
- ✓ the amount of emissions is certainly much higher than any other
- ✓ the availability of previous data, referring to previous industrial accidents (BTF) that occurred between the 70s and 80s
- ✓ the history of production on the site (1967-2013), and, above all, the volumes of raw material, finished product and waste produced
- ✓ the recent environmental characterization investigations within the factory

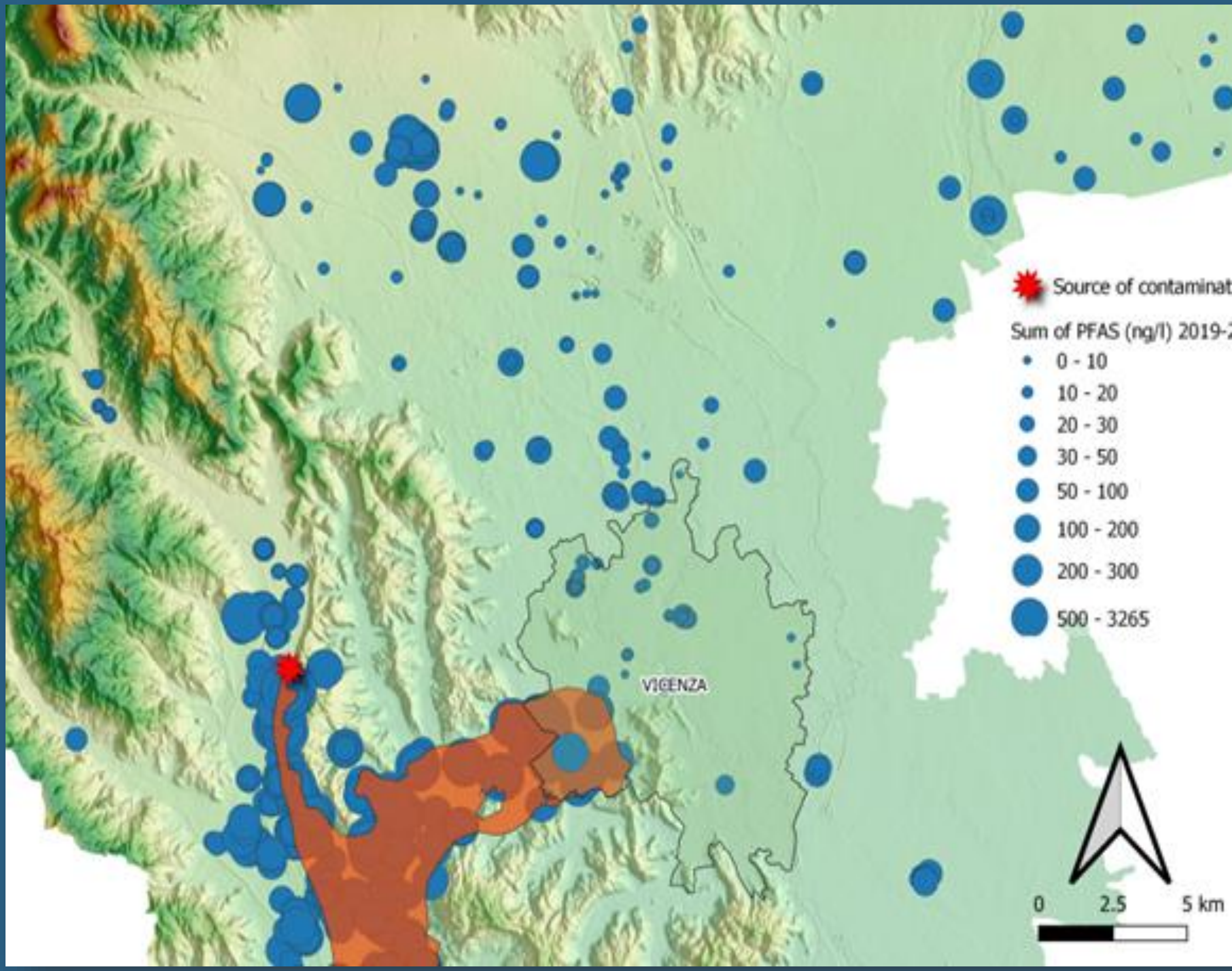


BTFs plume (IRSEV, 1979) **PFAs vs. BTFs plume (2018)**

Statistical SIGNIFICANCE

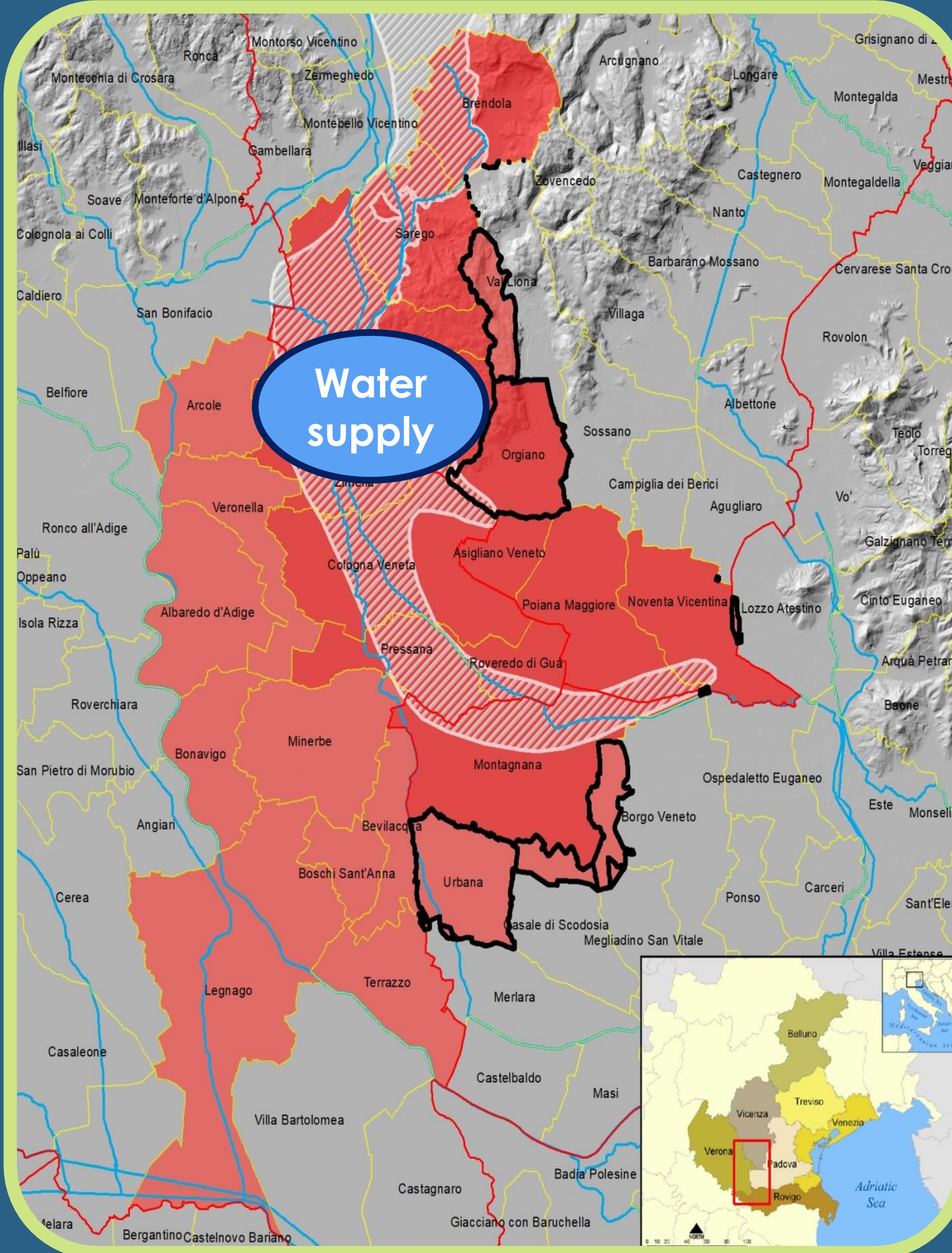
is the accepted benchmark for judging the strength of an observed association, and thus its potential causality:

1. PFAS have a proven anthropogenic origin
2. number of PFAS production sites is absolutely small
3. analysis considered pertain to a single certified laboratory
4. consistency of the data population is scientifically robust as well as adequately geographically distributed
5. Hydro-geo-chemical framework allows the implementation of modeling scenarios of transport consistent with the state of knowledge
6. extent of the PFAS plume and the amount of contaminant mass discharge become also primary indicators of a geographic significance



Statistical SIGNIFICANCE

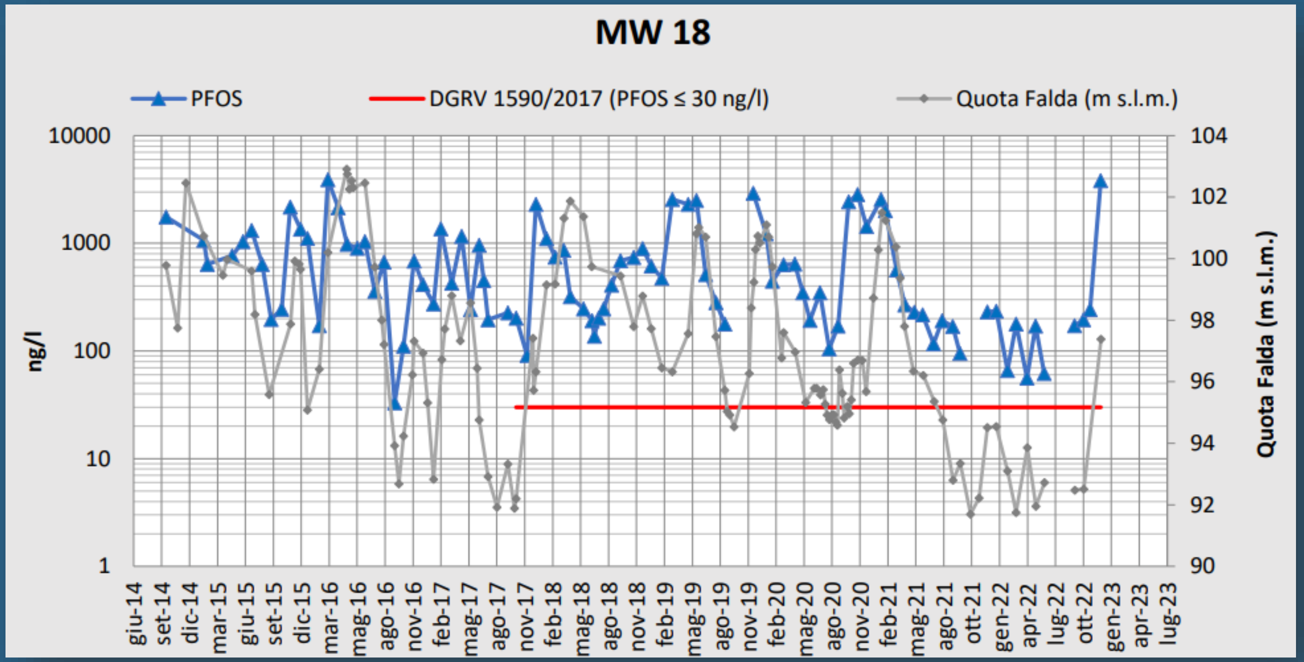
- ✓ **source max conc Sum PFAS**: 250-750 µg/l
- ✓ **plume longitudinal length**: > 40 km
- ✓ **plume transversal width**: 4-5 km
- ✓ **plume vertical depth**: > 100 m
- ✓ **plume area (Sum PFAS> 0,5 ppb):** 150 km^2
- ✓ **static water volume polluted** : > 100 M m^3
- ✓ **drinking water demand** : 30-40 M m^3/y
- ✓ **plume age**: > 50 y
- ✓ **observation period**: 10 y (2013→ 2023)
- ✓ **number of lab analysis**: > 100.000
- ✓ **exposed population (red zone**): 140.000
- ✓ **economic cost for corrective** >> 100 M EUR
- ✓ **time for remediation of the source site**: > 10 y
- ✓ **time for reasonable natural attenuation**: > 50 y
- ✓ **time for complete recovery from pollution**: n.a

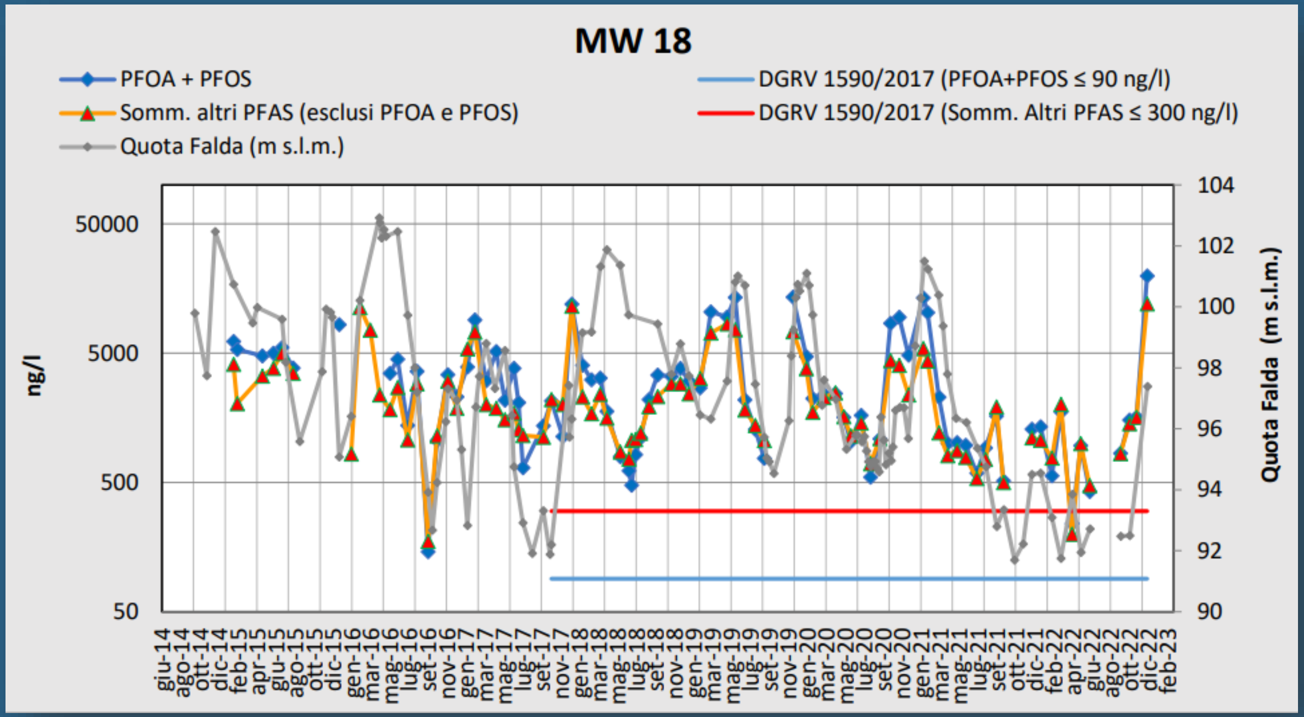


Sinergeo
SINERGIE GEOLOGICHE PER L'AMBIENTE

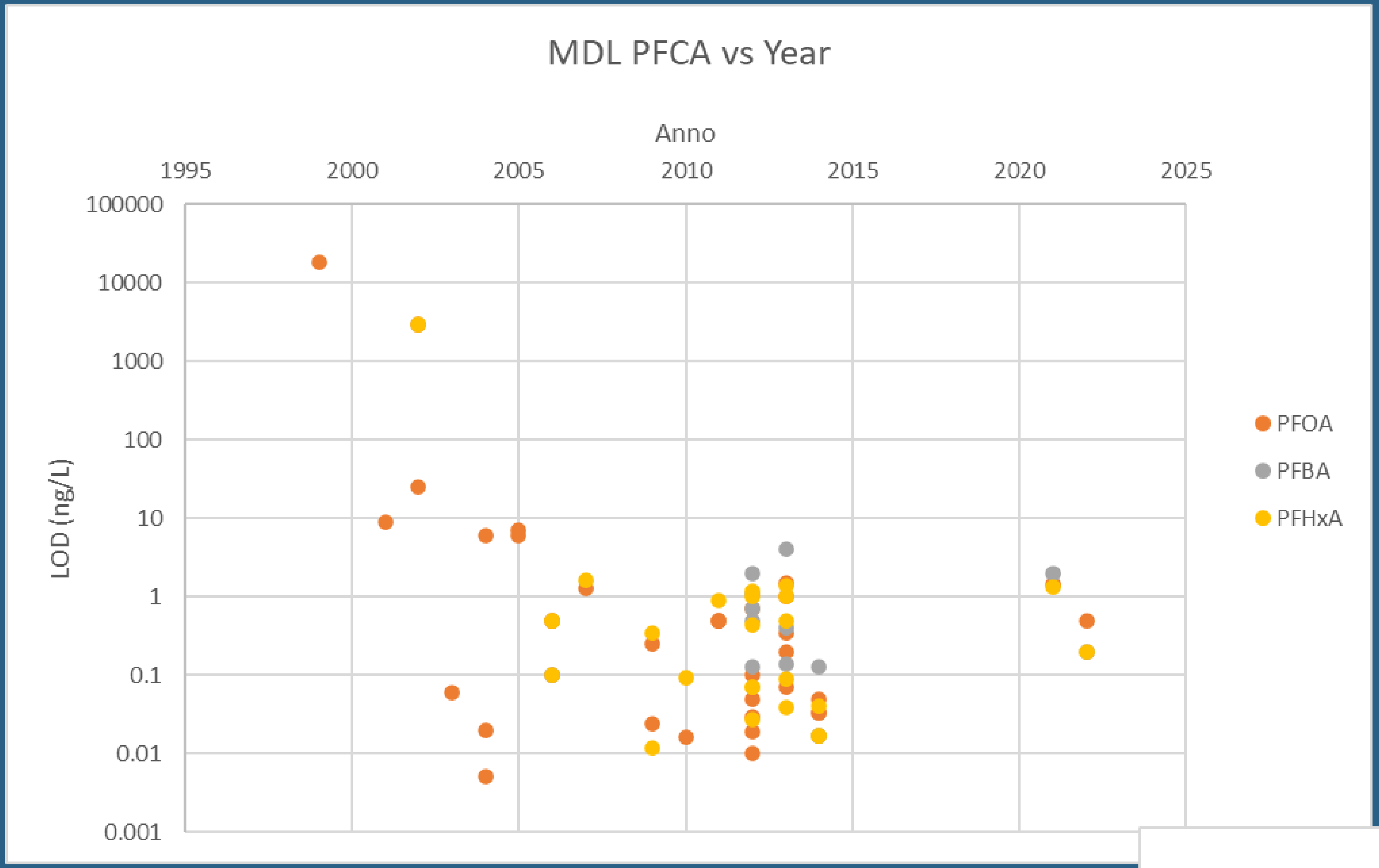
Chronological SIGNIFICANCE

- **TEMPORALITY** of the emissive behaviors is consistent with the transport mechanisms of pollutants and coherent with the long-term diffusion scenarios.
- **PERSISTENCE** of pollutant source, active for several decades with stable emission pattern due to specificity of local industrial production, is confirmed by chemical data (source: ARPAV, update: dec 2022) in correspondence with the POC for groundwater
- **POLLUTION is far from being finished**. The safety systems (P&T) do not yet ensure hydraulic belting.
- The **PFAS MIGRATION** is in progress: currently the mass flow that crosses the site limit is still active, extremely significant and measurable: this evidence concerns both the historical molecules (PFOS, PFOA) and the more recent compounds (cC6O4).



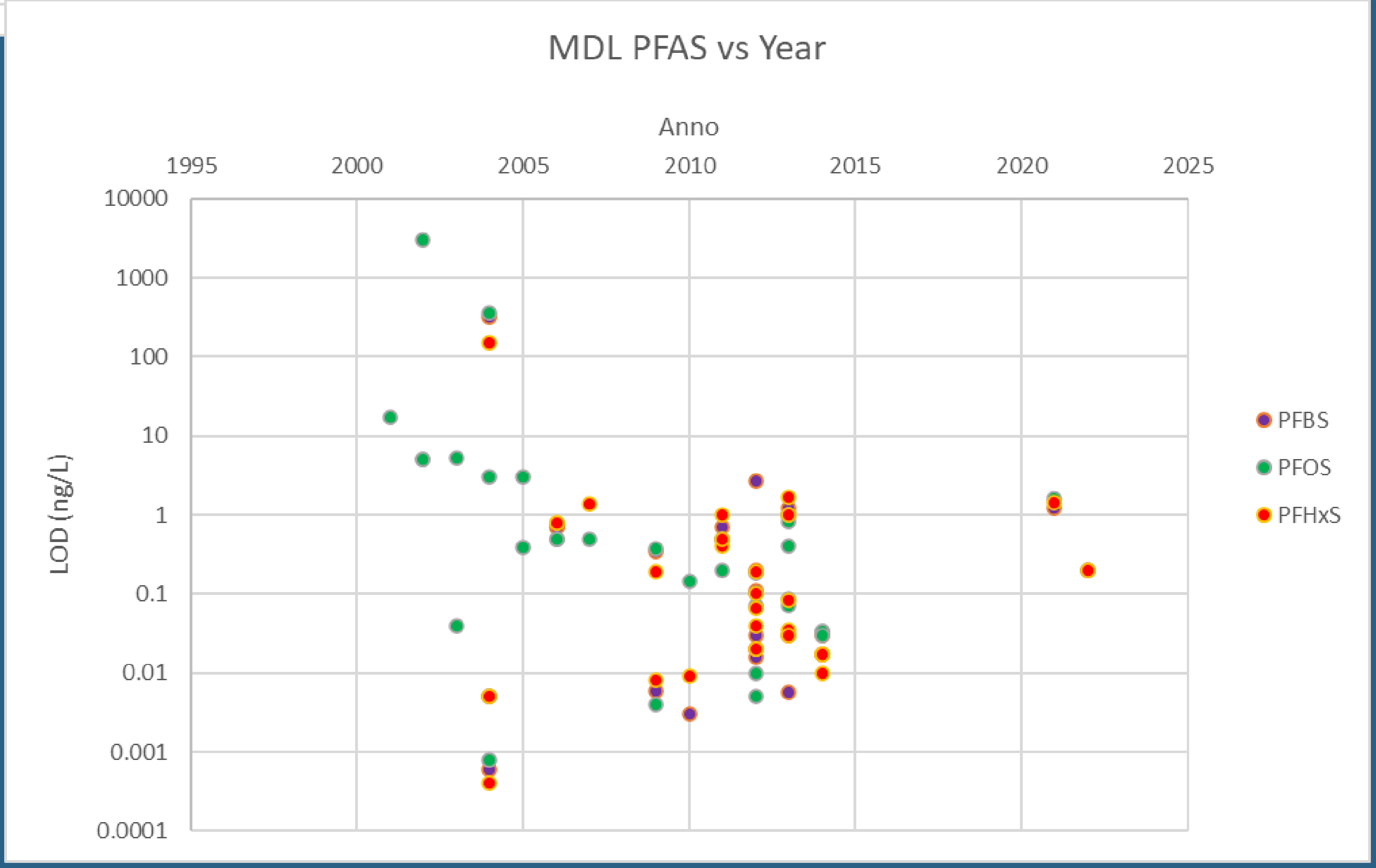


MEASURABILITY



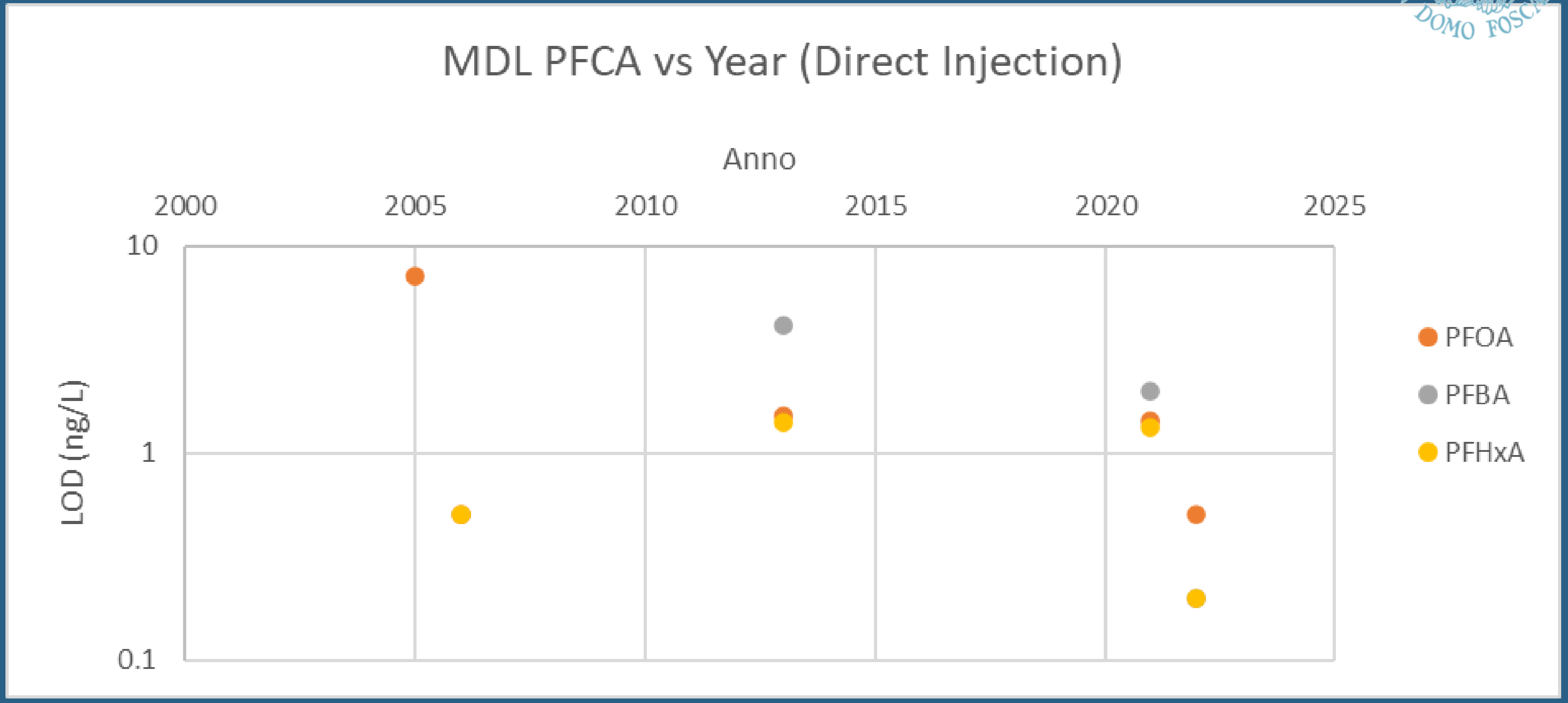
- Field et al., 1999: first scientific publication on analytical measurability of PFAS in environmental matrices
- Method included an enrichment through SPE (solid-phase extraction, SPE) and subsequent derivatization to allow the determination by GC-MS of only PFOA (i.e. PFCA)
- limit of detection (LOD) of 18000 ng/L and limit of quantification (LOQ) of 36000 ng/l, respectively.
- MDL: Method Detection Limit.

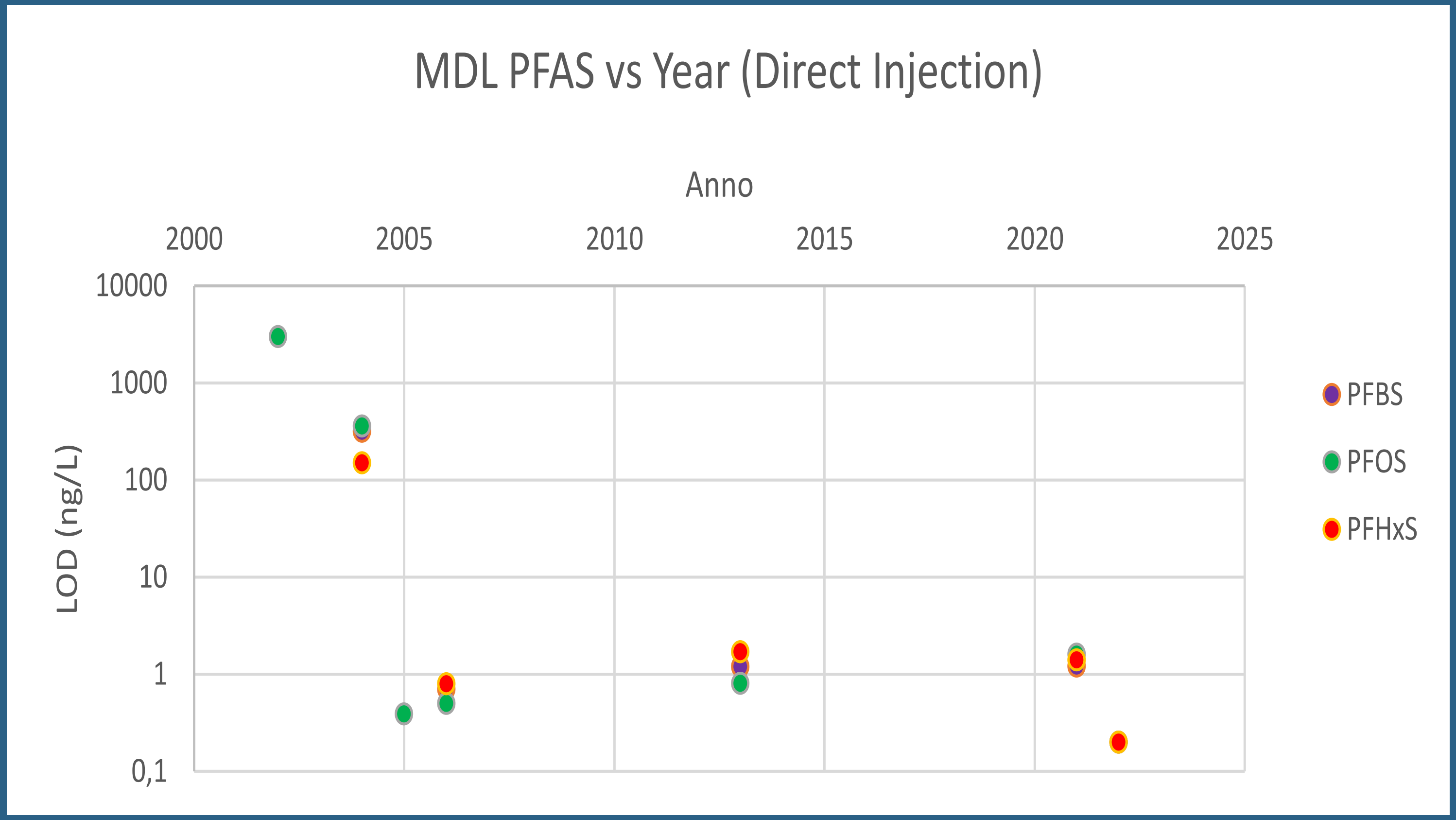
- short-chain PFCAs (i.e. PFBA)
- since half of the 2010s by new chromatographic columns with much higher performance than the previous ones.
- MDL: Method Detection Limit.



MEASURABILITY

- 2001 it was possible to quantify (LOQ) 9 ng/L and 17 ng/L of PFOA and PFOS using a triple quadrupole mass spectrometer.
- best results were achieved with the new generation of mass spectrometer that leads to quantify fraction of nanograms by direct analysis.

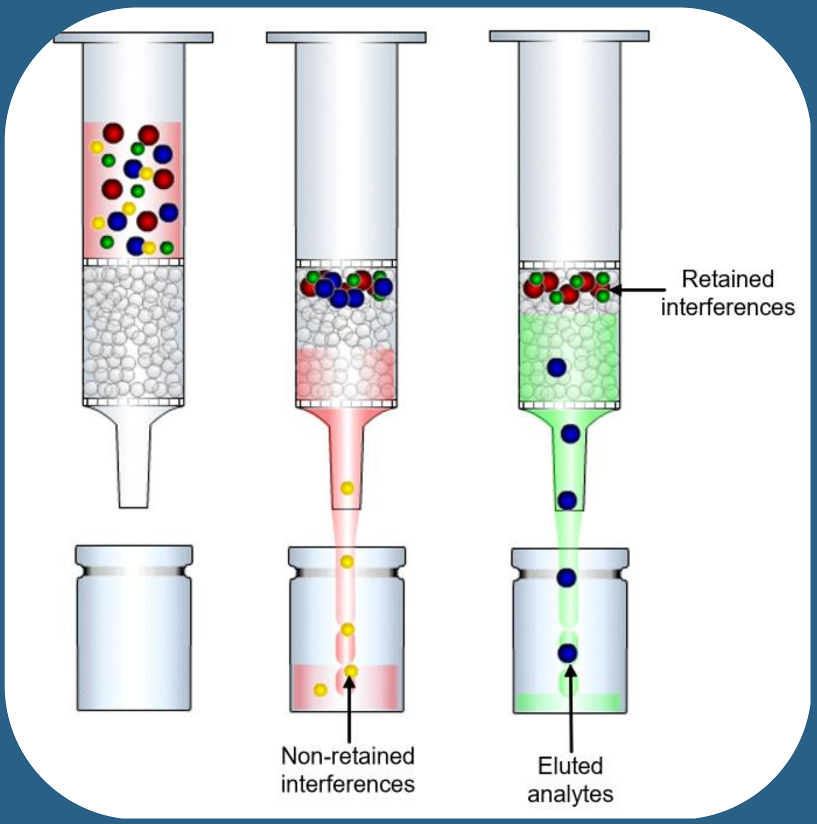




- the standard procedure for PFAS analysis since then has been preconcentration by SPE and subsequent determination by LC-MS triple quadrupole.
- best results were obtained with instruments equipped with Qtrap technology, i.e. triple quadrupoles with a linear trap for ion enrichment, which provided pg/l LOD in 2004.
- first half of the 2000s several studies reported that even with a simple single quadrupole mass spectrometer, it was possible to analyse tens ng/L in relatively clean matrices such as groundwater.

MEASURABILITY: Solid Phase Exctraction (SPE)

2009: EPA published the first version of the standardized method 537 for the analysis of 14 PFAS in drinking water by preconcentration and LC-MS/MS analysis. The scientific publications between 2010 and 2020 reported further analytical improvements expanding the application of the methodology to wastewater, sludge and landfill leachates.



Condition
- Condition WAX SPE by washing with 5 mL of 5 % NH_4OH in 60/40 ACN/MeOH
- Wash with 5 mL of reagent water
- Wash with 5 mL of 1 % acetic acid

Load sample
- Adjust the pH of the water sample (250 mL) to pH 1−2 with 2.5 glacial acetic acid
- Load 1 mL of 1 % acetic acid onto the cartridge
- Load the samples into reservoirs (if using) passing them through the cartridge at a flow rate of ~10 mL/min

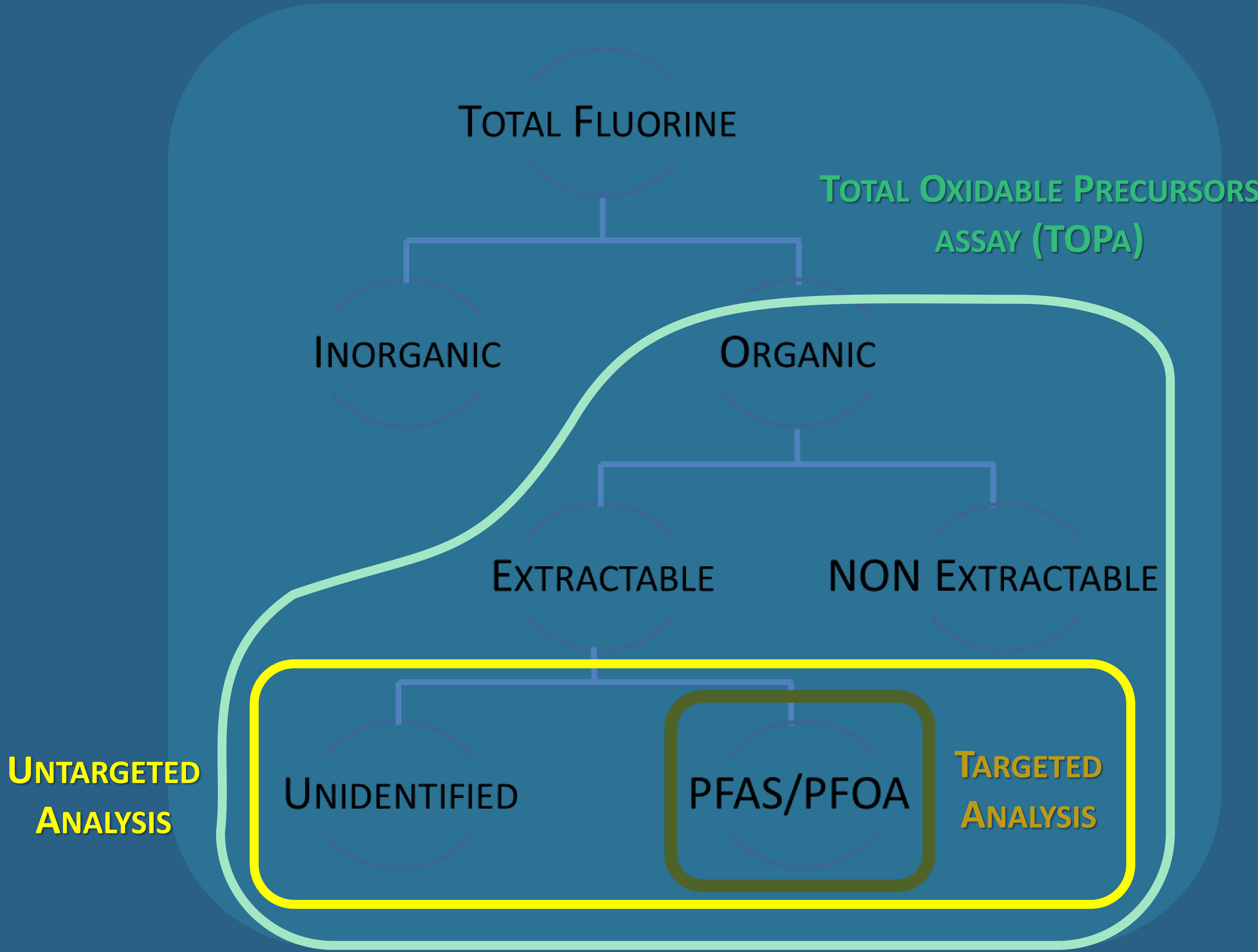
Rinse
- Rinse sample bottles and reservoirs with twice with 7.5 mL of reagent water
- Dry under high vacuum (10−15 mm Hg) for five minutes.

Elute
- Remove reservoirs from the cartridges, and rinse them into sample bottles with 4 mL of 5 % NH_4OH in 60/40 ACN/MeOH.
- Pour the rinse from the bottle onto the cartridge, apply just enough vacuum to soak the sorbent bed with MeOH, then turn off the vacuum and allow to soak for five minutes.
- Meanwhile, rinse the reservoirs into the bottles with another 4 mL of 5 % NH_4OH in 60/40 ACN/MeOH, and add that to the cartridge.
- Elute the cartridge into 15-mL poly centrifuge tubes.

Dry
- Evaporate at 55 °C under a flow of N_2 until the volume is ~500 µL.

Reconstitute
- Adjust to 1 mL with 96 % MeOH.
- Spike with ISTD spiking solution.

MEASURABILITY



Conclusions

- PFAS Contamination in Veneto Region is an extensive and massive event, with lots of consequences for the environment, the public health, the socio-economy, and the regulation

- It evidences the importance of foreseeing a preventive duty of sharing knowledge by companies, both the knowledge they possess and the knowledge they can acquire, along with a stronger commitment to research the effects of their productions

- The capacity of the aquifer to sustain competitive uses (drinking, agriculture, livestock, industry), has been significantly undermined by PFAS pollution and, therefore, an alternative strategy of use and water balance must be archieved soon, given that no recovery or repair option is feasible in acceptable times and at sustainable costs.

- In this sense, water supply risk assessment (WSP) and implementation of mitigation actions proved to be effective and essential, but the way forward must address the cost-effectiveness of water filtration and filters life cycle.

- Overall, while the technical-regulatory management of the contamination has been archieved trough an integrated and inter-institutional approach, more has to be done to COMMUNICATE and ENGAGE with the local communities (the risk dissemination culture)

THANKS FOR THE ATTENTION

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