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AOF - Adsorbable Organic Fluorine and PFAS

Introduction

The analysis of perfluorinated compounds (PFAS) has become of primary importance due to the environmental and health concerns associated with these contaminants. PFAS are persistent chemicals found in many industrial and consumer products, but their long-term impact on the environment and human health is still being studied.

Over the last few years, numerous studies and academic publications have been carried out aimed at verifying PFAS contamination by checking individual chemical molecules, but a significant change in the knowledge of possible contamination could derive from monitoring the chemical parameter AOF (Adsorbable Organic Fluorine) , which allows to determine the overall presence of fluorinated organic compounds, including numerous chemicals associated with the PFAS family or their precursors.

What are PFAS?

PFAS (Per- and PolyfluoroAlkyl Substances) represent a large family of synthetic chemical compounds containing at least one fully or partially fluorinated carbon atom. The presence of one or more C–F bonds gives these molecules unique properties, such as:

- High chemical resistance (resistant to acids, bases and oxidising agents),
- Water and oil repellency,
- Thermal stability,
- Very low surface tension.

These characteristics have favored their use in various industrial and commercial fields, including:

- Fire Fighting Foam Production (AFFF),
- Water-repellent treatments for fabrics and carpets,
- Non-stick coatings (e.g. Teflon in pans),
- Food packaging (greaseproof paper),
- Electroplating and electronic circuits,
- Cosmetics,
- Personal hygiene products,
- Chemicals (drugs and pesticides).

Within the PFAS we find three large subgroups:

Perfluorinated PFAS (Fully Fluorinated Compounds)

- They are compounds in which all the hydrogen atoms in the carbon chain are replaced by fluorine.
- They are completely fluorinated: no hydrogen remains on the main chain.

Classic examples:

- PFOA (perfluorooctanoic acid)
- PFOS (perfluorooctane sulfonic acid)

Characteristics:

- Extremely stable
- More persistent and bioaccumulative than polyfluorinated chemicals: in December 2023, PFOA was classified as a human carcinogen by the International Agency for Cancer (IARC).

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Polyfluorinated PFAS (Partially Fluorinated Compounds)

- They are compounds in which not all the hydrogen atoms in the carbon chain are replaced by fluorine.
- The chain can contain both fluorine and hydrogen atoms.

Some polyfluorinated chemicals can convert to perfluorinated chemicals in the environment or in the body.

Examples:

- Precursors of perfluorinated
- Some fluorotelomers (FTOH)

Characteristics:

- More reactive than perfluorinated
- Some are less persistent, but many slowly degrade into more stable perfluorinated compounds.

AFFFs - Aqueous Film Forming Foam

- They are fire-fighting foams used mainly to put out fires involving flammable liquids (such as petrol, kerosene, industrial oils).
- AFFFs contain PFAS because these compounds are essential for:
  - Create a thin film over the flammable liquid
  - Smother the fire quickly by preventing contact between the fuel and oxygen

AFFF–PFAS Report

AFFFs have **historically** been formulated with **perfluorinated chemicals** such as **PFOS** or **PFOA** .

Today, many AFFFs still use **new-generation PFAS** (such as fluorotelomers) even as efforts are being made to reduce their use.
Problem :

AFFFs have been a **primary source of PFAS environmental contamination** , especially at military bases, airports, and industrial facilities.
PFAS released by AFFF are **extremely persistent** and **difficult to remove** from water and soil.

TFA (trifluoroacetic acid) is a **chemically stable fluorinated compound** used:

- as a reagent in organic chemistry,
- as a by-product in the degradation of **fluorinated refrigerant gases** and some **PFAS themselves**.

It is very soluble in water and **non-biodegradable**, so it can **accumulate in water bodies and groundwater**. Unlike classic PFAS, **TFA is smaller** but equally worrying for the environment due to its **mobility and persistence**.

Connection between TFA and PFAS

- Some PFAS, such as fluorinated refrigerants, pesticides and drugs can **degrade into TFA** in the environment.
- **TFA is considered an "emerging PFAS"** because it shares with classic PFAS the characteristics of **resistance to degradation and potential ecotoxicological risk.**

AOF – Adsorbable Organic Fluorine

The AOF (Adsorbable Organic Fluorine) is an analytical parameter developed to quantify the total amount of absorbable organic fluoride present in a sample, typically aqueous.

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Unlike traditional target assays that measure single, known PFAS (such as PFOA, PFOS, PFHxS , etc.), AOF also allows for the detection of individually unknown or non-quantifiable compounds, providing a broader view of organofluorine contamination.

The method is based on a sequence of main phases:

1. Adsorption on activated carbon (PAC or GAC).
2. Combustion at high temperatures (> 1000 °C) to destroy fluorinated organic compounds.
3. Capture and quantification of released fluoride by ion chromatography (CIC instrumentation)

The result is expressed in µg /L of total absorbable fluoride. This parameter reflects the sum of fluoride from fluorinated organic compounds adsorbed on activated carbon, including both known PFAS and unidentified precursors.

Importance of the AOF parameter

The AOF (Adsorbable Organic Fluorine) has emerged as a critical parameter for global monitoring of PFAS and other organofluorine substances in the environment. Although it cannot replace specific analyses for individual PFAS, its usefulness lies in its ability to provide a comprehensive view of organic fluoride contamination. In particular, AOF is useful for:

- Assessing global PFAS contamination,
- Detect PFAS precursors, compounds that can transform into more toxic substances over time,
- Perform rapid screening of drinking water, industrial wastewater and surface water,
- Improve water management by monitoring contamination levels in real time.

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This methodology is particularly useful in areas of high contamination intensity, where PFAS are not always identifiable through targeted analytical techniques.

Legislation and regulation

The growing environmental and health impact of PFAS has led to a series of regulatory initiatives at international, European and national levels. The difficulty of managing a large class of chemical compounds, many of which are not yet fully identified, has pushed authorities to develop guidelines and regulations that include not only the known compounds, but also the total load of organic fluorides.

The AOF plays a key role in monitoring PFAS contamination, with particular attention to the protection of water resources.

Study of Italian drinking water

In the period between September and November 2024, Greenpeace Italy has created a sampling plan of over 200 samples of drinking water from numerous Italian municipalities in order to verify possible contamination and have an initial snapshot of the state of health of the Italian water management system in preparation for the implementation of Legislative Decree 18/2023 which will come into force in January 2026.

This regulation imposes a limit threshold of 100 ng/L as the sum of 24 individual PFAS molecules and a limit of 500 ng/L as "total PFAS".

Although AOF is not listed among the techniques available for measuring the "total PFAS" parameter, Test & Innovation Lab has internally carried out a study parallel to the "Acque Senza Veleni" investigation in order to ascertain the technique's identification capacity to detect possible PFAS contamination in drinking water.

The analysis was performed in accordance with the requirements of EPA 1621 - Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC) using a CIC system manufactured by Metrohm.

The quantification limit adopted is equal to 0.5 μg/l of fluoride: the analysis technique does not allow reaching quantification limits comparable to traditional target analysis but is equally usable for intercepting possible sources of PFAS contamination.

Study results

The distribution map of the results is shown in the following graph: only 13% of the examined samples show a presence of AOF higher than the quantification limit used in the study – all data are shown in the following table.

Distribution map of municipalities monitored for the presence of AOF in drinking water.

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City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Bardonecchia	1.79	5.1	<50.0
Ascoli Piceno	1.71	1.1	<50.0
Airola	1.60	<1.0	<50.0
Bergamo	1.50	1.3	53.4
Viterbo	1.39	<1.0	<50.0
Bassano del Grappa	1.31	9.1	105.7
Pesaro	1.29	3.9	<50.0
Siena	1.20	<1.0	<50.0
Ferrara	1.19	43.6	375.5
Altamura	1.07	<1.0	<50.0
Rovigo	1.03	22.4	159.6
Rimini	1.01	4.5	<50.0
Milano	0.97	90.5	87.4
Nuoro	0.90	12.7	197.4
Riva del Garda	0.89	<1.0	89.6
Montoro Superiore	0.81	3.0	<50.0
Bassano del Grappa	0.81	<1.0	55.4
Francavilla Fontana	0.78	<1.0	<50.0
Ceccano	0.75	29.8	<50.0
Conegliano	0.72	<1.0	77.8
Tarquinia	0.71	5.0	<50.0
Chiusi	0.70	7.4	62.9
Montemurlo	0.69	<1.0	55.1
Cantù	0.69	8.1	<50.0
Frosinone	0.68	12.3	59.8
Crotone	0.62	1.5	<50.0
Milano	0.62	58.6	78.4
Imperia	0.61	25.6	<50.0
Vercelli	0.60	1.9	<50.0
Cava de' Tirreni	0.60	<1.0	<50.0
Pontedera	0.60	9.3	<50.0
Palmi	0.57	<1.0	158.1
Africo	0.54	2.1	<50.0
Aprilia	0.54	<1.0	<50.0
Roseto degli Abruzzi	0.52	1.5	58.2
Sant'Ambrogio di Torino	0.50	6.7	93.8
Roma	<0.50	2.0	<50.0
Napoli	<0.50	2.1	<50.0
Padova	<0.50	34.8	<50.0

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City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Rosignano Marittimo	<0.50	6.4	<50.0
Trebisacce	<0.50	2.2	<50.0
Potenza	<0.50	15.0	<50.0
Termoli	<0.50	<1.0	<50.0
Parma	<0.50	<1.0	52.4
Fossano	<0.50	16.3	<50.0
Tortona	<0.50	39.8	88.3
Piacenza	<0.50	2.4	<50.0
Latina	<0.50	<1.0	<50.0
Mestre	<0.50	13.9	157.3
Aversa	<0.50	2.4	<50.0
Policoro	<0.50	2.7	56.0
Montecchio Maggiore	<0.50	<1.0	<50.0
Rieti	<0.50	2.1	<50.0
Chieti	<0.50	<1.0	<50.0
Acireale	<0.50	15.2	<50.0
Bologna	<0.50	1.6	87.5
Torino	<0.50	18.6	138.2
Chioggia	<0.50	27.9	66.9
Orbetello	<0.50	1.1	<50.0
Biella	<0.50	1.8	<50.0
Napoli	<0.50	6.3	<50.0
Comiso	<0.50	<1.0	<50.0
Olbia	<0.50	48.0	105.4
Palazzolo sull'Oglio	<0.50	25.1	63.3
Brugherio	<0.50	25.0	110.4
Livorno	<0.50	<1.0	<50.0
Palermo	<0.50	12.6	77.4
Torino	<0.50	21.1	96.5
Empoli	<0.50	9.5	<50.0
Grosseto	<0.50	<1.0	<50.0
Pescara	<0.50	<1.0	256.4
Faenza	<0.50	9.8	159.1
Trapani	<0.50	<1.0	<50.0
Caserta	<0.50	<1.0	56.2
Verona	<0.50	12.0	<50.0
Falconara Marittima	<0.50	<1.0	<50.0
Ragusa	<0.50	1.6	<50.0
Ancona	<0.50	8.3	<50.0

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City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Nizza Monferrato	<0.50	<1.0	<50.0
Jesolo	<0.50	11.7	<50.0
Cuneo	<0.50	11.7	242.1
Massa Marittima	<0.50	11.1	<50.0
Firenze	<0.50	1.8	127.2
Arzignano	<0.50	56.2	58.4
Agrigento	<0.50	8.2	<50.0
Salerno	<0.50	<1.0	<50.0
Augusta	<0.50	10.0	<50.0
Colorno	<0.50	<1.0	<50.0
Montevarchi	<0.50	8.0	<50.0
Agliana	<0.50	7.4	<50.0
Campobasso	<0.50	3.9	<50.0
Alessandria	<0.50	12.0	68.9
Reggio Calabria	<0.50	<1.0	71.6
Cefalù	<0.50	<1.0	<50.0
Gravere	<0.50	<1.0	60.3
Catania	<0.50	<1.0	<50.0
Follonica	<0.50	6.6	<50.0
Nicotera	<0.50	8.5	<50.0
Montale	<0.50	18.8	<50.0
Quartu Sant'Elena	<0.50	1.8	157.1
Guidonia Montecelio	<0.50	<1.0	<50.0
Pozzilli	<0.50	2.4	<50.0
Alghero	<0.50	<1.0	<50.0
Figline Valdarno	<0.50	9.6	115.6
Lecce	<0.50	2.9	<50.0
Forlì	<0.50	2.2	<50.0
Isola di Capo Rizzuto	<0.50	9.3	<50.0
Marsala	<0.50	10.4	<50.0
Varese	<0.50	12.2	56.9
Manzano	<0.50	5.3	81.1
Cremona	<0.50	1.0	<50.0
Asti	<0.50	<1.0	<50.0
Civitanova Marche	<0.50	15.2	<50.0
Cossato	<0.50	3.4	56.1
Viareggio	<0.50	13.5	<50.0
Cerveteri	<0.50	18.9	<50.0
Livorno	<0.50	6.5	<50.0
Asciano	<0.50	10.8	<50.0

City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Pisa	<0.50	1.6	<50.0
Massa Marittima	<0.50	10.0	52.2
Savona	<0.50	9.0	76.9
Aulla	<0.50	<1.0	<50.0
Carrara	<0.50	10.7	<50.0
Albenga	<0.50	26.6	<50.0
La Spezia	<0.50	4.7	115.9
Sarzana	<0.50	26.4	<50.0
Genoa	<0.50	9.7	114.4
Genoa	<0.50	14.7	126.4
Rapallo	<0.50	28.9	104.4
Bussoleno	<0.50	35.9	69.7
Torino	<0.50	16.7	208.6
Torino	<0.50	<1.0	94.9
Châtillon	<0.50	3.2	70.9
Aosta	<0.50	15.0	<50.0
Novara	<0.50	<1.0	372.6
Galliate	<0.50	2.0	54.3
Casale Monferrato	<0.50	<1.0	206.5
Acqui Terme	<0.50	<1.0	147.6
Ovada	<0.50	2.9	110.9
Morbello	<0.50	<1.0	<50.0
Valenza	<0.50	1.7	148.9
Spinetta Marengo	<0.50	7.3	69.6
Castellazzo Bormida	<0.50	12.4	539.4
Voghera	<0.50	3.7	180.5
Crema	<0.50	12.2	129.6
Fiorenzuola d'Arda	<0.50	10.4	194.9
Pavia	<0.50	<1.0	<50.0
Cinisello Balsamo	<0.50	9.8	<50.0
Crespiatica	<0.50	1.3	<50.0
Lodi	<0.50	12.8	<50.0
Busto Arsizio	<0.50	<1.0	<50.0
Laives	<0.50	1.4	137.7
Mandello del Lario	<0.50	<1.0	<50.0
Lecco	<0.50	<1.0	72.1
Desenzano del Garda	<0.50	<1.0	<50.0
Como	<0.50	<1.0	<50.0
Trecate	<0.50	4.6	<50.0
Bolzano	<0.50	5.9	<50.0

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City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Sondrio	<0.50	<1.0	<50.0
Brescia	<0.50	9.4	<50.0
Milan	<0.50	20.2	<50.0
Treviglio	<0.50	17.5	112.9
Monza	<0.50	31.0	<50.0
Trento	<0.50	1.4	111.8
Modena	<0.50	25.1	<50.0
Poggio a Caiano	<0.50	<1.0	<50.0
Vicenza	<0.50	42.3	<50.0
San Giovanni Lupatoto	<0.50	8.7	<50.0
Lonigo	<0.50	25.2	135.5
San Bonifacio	<0.50	30.3	<50.0
Prato	<0.50	16.6	77.4
Chiomonte	<0.50	<1.0	<50.0
Pistoia	<0.50	7.4	<50.0
Sant'Ambrogio di Torino	<0.50	<1.0	<50.0
Suzzara	<0.50	11.7	<50.0
Mantova	<0.50	<1.0	<50.0
Guastalla	<0.50	<1.0	<50.0
Arezzo	<0.50	104.3	53.4
Verbania	<0.50	21.3	71.4
Carpi	<0.50	5.2	<50.0
Reggio Emilia	<0.50	44.7	<50.0
Scarlino	<0.50	2.7	<50.0
Belluno	<0.50	<1.0	68.2
Narni	<0.50	1,2	<50.0
Duino	<0.50	<1.0	<50.0
Trieste	<0.50	<1.0	<50.0
Piazza Armerina	<0.50	<1.0	<50.0
Udine	<0.50	3.6	58.4
Venezia	<0.50	2.5	85.1
Trieste	<0.50	5.3	57.6
Feltre	<0.50	4.8	109.1
Porcia	<0.50	19.0	<50.0
Monfalcone	<0.50	12.6	54.4
Lucca	<0.50	23.3	70.0
Abano Terme	<0.50	3.1	<50.0
Lamezia Terme	<0.50	12.0	61.5
Enna	<0.50	13.4	<50.0

City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Perugia	<0.50	57.0	58.3
Gorizia	<0.50	20.0	55.6
Terni	<0.50	<1.0	<50.0
Cosenza	<0.50	<1.0	<50.0
Vibo Valentia	<0.50	8.2	60.3
Iglesias	<0.50	6.0	<50.0
Porto Torres	<0.50	<1.0	<50.0
Pordenone	<0.50	<1.0	<50.0
Sassari	<0.50	6.0	215.0
Isernia	<0.50	<1.0	64.3
Siniscola	<0.50	16.3	165.9
Palermo	<0.50	<1.0	<50.0
Gela	<0.50	<1.0	<50.0
Terralba	<0.50	<1.0	<50.0
Giugliano in Campania	<0.50	1.3	<50.0
L'Aquila	<0.50	<1.0	<50.0
Fermo	<0.50	14.3	<50.0
Macerata	<0.50	<1.0	65.8
Bari	<0.50	<1.0	<50.0
Matera	<0.50	<1.0	56.5
Bari	<0.50	<1.0	57.9
Messina	<0.50	<1.0	57.6
Carbonia	<0.50	3.4	167.6
Cagliari	<0.50	<1.0	208.2
Oristano	<0.50	2.9	58.4
L'Aquila	<0.50	<1.0	<50.0
Campobasso	<0.50	3.0	<50.0
Cagliari	<0.50	21.0	100.4
Roma	<0.50	<1.0	<50.0
Foligno	<0.50	1.6	<50.0
Siracusa	<0.50	<1.0	<50.0
Benevento	<0.50	<1.0	<50.0
Avellino	<0.50	<1.0	<50.0
Catanzaro	<0.50	<1.0	55.7
Andria	<0.50	17.4	<50.0
Foggia	<0.50	5.4	67.9
Melfi	<0.50	<1.0	<50.0
Barletta	<0.50	1.3	70.6
Fabriano	<0.50	2.8	75.4
Siderno	<0.50	1.8	60.1

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City	AOF (µg/L)	PFAS sum (24 molecules Legislative Decree 18/2023) (ng/L)	Trifluoroacetic acid - TFA (ng/L)
Bari	<0.50	8.2	<50.0
Fermo	<0.50	<1.0	<50.0
Firenze	<0.50	<1.0	<50.0
Ancona	<0.50	3.4	<50.0
Brindisi	<0.50	<1.0	<50.0
Andria	<0.50	1.6	<50.0
Fano	<0.50	7.2	71.3
Capannori	<0.50	3.1	59.6
Grottammare	<0.50	2.3	<50.0
Riccione	<0.50	10.6	<50.0
Reggio Calabria	<0.50	11.4	72.6
Cesena	<0.50	2.9	59.1
Nardò	<0.50	3.4	<50.0
Ravenna	<0.50	25.4	61.4
Potenza	<0.50	6.3	<50.0
Montesilvano	<0.50	4.5	<50.0
Vasto	<0.50	<1.0	<50.0
Imola	<0.50	4.4	<50.0
Milazzo	<0.50	<1.0	<50.0
Taranto	<0.50	<1.0	<50.0
Grottaglie	<0.50	<1.0	<50.0
Teramo	<0.50	7.8	<50.0
Comacchio	<0.50	49.5	109.6
Dozza	<0.50	4.6	<50.0

Conclusions

The study carried out is to be considered only as a snapshot and not to be considered exhaustive and representative of the situation of drinking water distributed in the Italian territory.

The AOF verification does not represent an alternative investigation technique to the current PFAS verification techniques adopted by Italian laboratories but can be used as a valid complementary resource to intercept possible sources of PFAS pollution in the materials examined: if the analysis provides a positive response, it is appropriate to activate all available resources to ascertain possible sources of pollution of the analyzed water bodies.

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