WHITE PAPER

Adsorbable organic fluorine (AOF) – a sum parameter for non-targeted screening of per- and polyfluorinated alkyl substances (PFASs) in waters

The prevalence of per- and polyfluorinated alkyl substances (PFASs) and other perfluorinated compounds (PFCs) that persist and accumulate in the environment (as well as in our own bodies) is becoming an increasing concern to international health authorities. These chemicals are a class of stable compounds known as «forever chemicals» and are comprised of nearly 10,000 different substances. They are a challenge to monitor individually and quantify in low concentrations, even in drinking water. Expensive analytical instrumentation and experience is required to determine a small selection of individual PFASs, and such analyses can be time-consuming and difficult to validate.

A large fraction of synthetic organofluorine substances is assumed to be covered by the sum of all adsorbable fluorine in waters (AOF). Measuring AOF is simpler and faster than targeted analysis methods, and also more sensitive than total fluorine (TF) determination (comprising all organic and inorganic F). Measurement of AOF in water samples as an initial screening step gives a fast overview of the actual amount of organic fluorinated compounds present. This can be followed by targeted analyses of individual PFASs if indicated by higher AOF concentrations.

PER- AND POLYFLUORINATED ALKYL SUBSTANCES

OVERVIEW

Per- and polyfluorinated alkyl substances (PFASs) are the class of almost 10,000 manmade organofluorine compounds [**1**] more commonly known as «**forever chemicals**» and have been included in Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) since 2009 [**2**]. These fluorinated compounds as well as their decay products are extremely stable [**3**]. For this reason, they tend to persist and accumulate in the environment. Due to their widespread use they are released all across the globe and have become a serious worldwide concern. The majority of these chemicals have little or no data about their usage, nor their properties and effects on organisms. Because certain PFASs and their degradation products bioaccumulate and biomagnify, they are considered a global health issue [**4–6**].

PFASs are made of carbon chains of various lengths that are heavily substituted with fluorine in place of hydrogen. The presence of fluorine is the main difference between per- and polyfluorinated alkyl substances— aside from the functional group(s), **perfluorinated compounds** only contain C–F bonds while **polyfluorinated compounds** still contain some C–H bonds (**Figure 1**). The properties of these compounds are also quite variable depending on the length of the carbon backbone—from completely insoluble to highly volatile. They are resistant to water, oil, and heat, and such properties are sought after highly by several industries for a multitude of purposes.

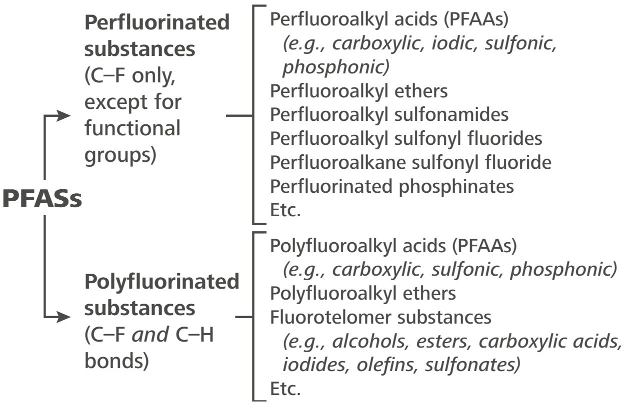
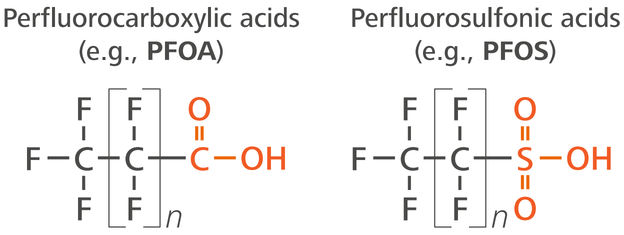


Figure 1. A broad, non-comprehensive overview of some of the subfamilies encompassed by the term «PFASs».

Thousands of chemicals are included under the umbrella of PFASs, including fluoropolymers, poly- / perfluoroalkyl ethers, poly- / perfluoroalkyl acids (PFAAs), PFAA precursors, and more (**Figure 1**).

PFAAs, as a subclass of PFASs, include sulfonic and carboxylic acids that display extreme environmental persistence and exhibit chain-length-dependent bioaccumulation and adverse effects in organisms [**7**]. The studies of four major PFAAs including perfluorooctanoic acid (PFOA, also known as «C8»), perfluorooctane sulfonic acid (PFOS) (**Figure 2**), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS), have contributed the most to our current understanding about the biological impact of PFASs [**5**].


Perfluorocarboxylic acids (e.g., **PFOA**)

Perfluorosulfonic acids (e.g., **PFOS**)

Figure 2. General examples of PFAAs. If the backbone is made of eight carbons, these compounds are perfluorooctanoic acid (PFOA) and perflurooctane sulfonic acid (PFOS), respectively.

HISTORY AND BACKGROUND

Commercial development of PFASs began in the late 1940's at the chemical company DuPont, and was picked up shortly after by 3M [**8,9**]. DuPont began manufacturing products under the Teflon® brand (polytetrafluoroethylene, PTFE) in 1946 [**10**] while 3M launched Scotchgard®, a protective stain-resistant coating used on textiles (e.g., clothing and carpets) in the 1950's [**9**]. Other companies such as GORE-TEX followed suit after seeing the success of these chemicals on the market [**11**]. In more recent years, PFASs have also been used in food packaging coatings because of their oil and water repellant properties.

Beyond fabrics and cookware, PFASs were also used in aqueous film-forming foams (AFFF) developed first by 3M for extinguishing fires, though the company has stopped producing this specific product [**9**]. DuPont has also committed to replace AFFF products containing PFASs with fluorine-free foams by the end of 2021, and has already phased out production of longer-chain organofluorine compounds [**12**]. PFOA and PFOS specifically have been phased out of production by both DuPont and 3M [**8,9,13**]. Still, companies continue to produce these kinds of chemicals for a variety of different uses [**14**] despite the ongoing research into how they affect humans and the environment.

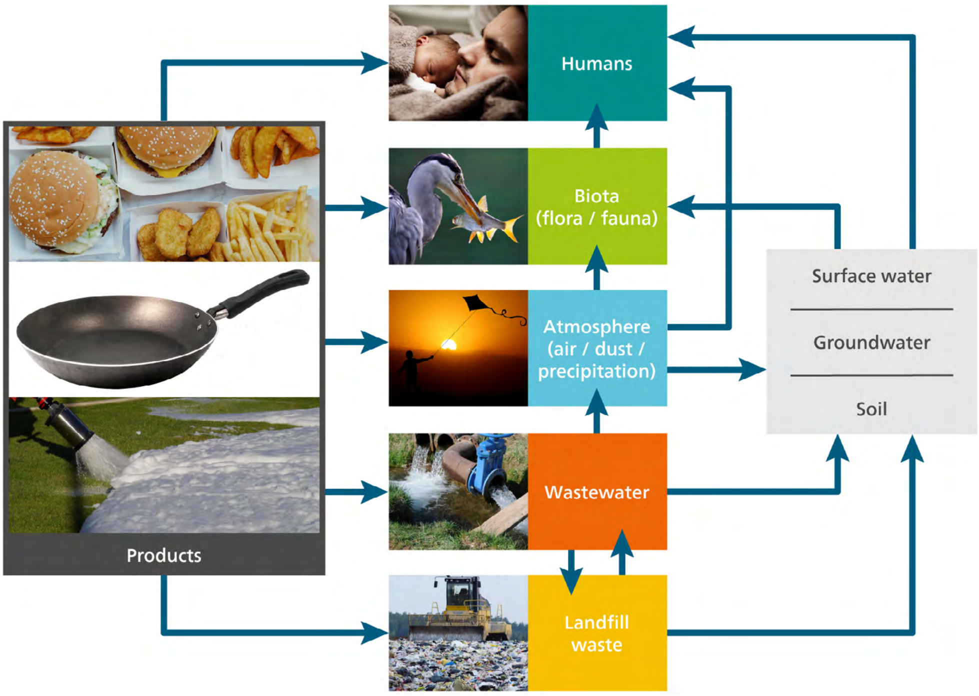


Figure 3. Illustration of the PFASs lifecycle.

Health effects for most of these substances are poorly understood. This is especially true for newer formulations (e.g., GenX, a fluoroether replacement for PFOA from DuPont, now Chemours) as it can take several years to prove a relationship between exposure to a specific chemical and any resulting negative impacts. Exposure to PFASs can occur through the direct use of consumer products, but also through several environmental pathways (**Figure 3**) [**15**]. The stability of PFASs gives them the ability to persist in the environment for many years [**3**]. Uptake of PFASs in our bodies can occur via drinking water, eating contaminated food, or even by simply breathing [**4,16**].

Water sources can become contaminated with PFASs in several ways. One of these is from the use of extremely water soluble firefighting foams, especially around military bases, training facilities for firefighters, and other high-use areas [**4,17**]. These foams penetrate the soil and contaminate the groundwater which then spreads these chemicals even further beyond the source. Ineffective water treatment processes at wastewater treatment plants and municipal water facilities that do not address specific removal of perfluorinated compounds (PFCs) can lead to the widespread distribution of water contaminated with these forever chemicals [**17**].

The air is not safe from per- and polyfluorinated alkyl substances either. Air emissions from the stacks of chemical manufacturers that produce these substances can lead to localized contamination of the surrounding communities. It is believed that high temperature incineration of these substances is insufficient for their complete degradation, which results in more toxic and volatile short-chain PFCs becoming airborne. Additionally, precipitation contaminated by such emissions can leach into the soil, contaminating the groundwater or surface water directly or through runoff. Plants growing on such soils take up the contaminants with them.

These are just some of the many ways we can ingest PFASs without even being fully aware.

– EFFECTS ON HUMAN HEALTH

It has been suggested that most people on the planet have some measurable content of PFASs in their blood, although without comprehensive testing, this is difficult to confirm. Exposure to per- and polyfluorinated alkyl substances through inhalation, oral consumption, and/or dermal contact can lead to severe negative health effects [**4,16**]. As mentioned previously, PFASs (especially long-chain compounds) bioaccumulate and biomagnify in our bodies over time. This is not only due to their stability, but also because of their affinity to bind to proteins (not lipids, unlike other POPs) [**18**]. For long-chain PFASs such as PFOA and PFOS, the half-life in humans is on the order of several years (PFOA: 2.1–10.1 years, PFOS: 3.3–27 years) [**4**].

Most health studies until now have been performed concerning PFOA and PFOS, though these substances have been phased out of production by 3M [**9**] and

Chemours (DuPont) [**8,13**]. Regardless, new PFASs are developed and brought to market each year, many of which have not been thoroughly studied with regards to their effects on human health.

These chemicals are suggested carcinogens, associated with an increased risk of kidney, prostate, and testicular cancers [**4,16,19**]. A decrease in fertility for adults is noted along with associated low birth weights in babies and developmental delays in children after exposure to certain long-chain PFASs [**4,16,19**]. Other negative effects are linked to exposure to these substances including increased cholesterol and risk of obesity, hormonal interferences, increased blood pressure in pregnant women, and reduced immune response [**4,16,19**].

– ADVISORY GUIDELINES AND REGULATIONS

The most strict guidelines regarding PFASs can be found in the United States, however five European countries (the Netherlands, Denmark, Germany, Norway, and Sweden) are working to propose an EU-wide group ban on all non-essential uses of per- and polyfluorinated alkyl substances, which would lead to less risk of exposure [**20**]. The Stockholm Convention on Persistent Organic Pollutants (POPs) which covers the elimination of PFOA and restriction of PFOS in Annexes A and B, respectively, began enforcement in 2004 and has been signed by 152 countries as of 2021 [**2**]. The EU Directive 2020/2184 for drinking water was adopted in late 2020 to establish technical guidelines regarding analysis methods and detection limits for «PFAS Total» (defined as the totality of per- and polyfluoroalkyl substances) and «Sum of PFAS» (defined as a subset of PFAS Total substances that contain a perfluoroalkyl moiety with three or more carbons, or a perfluoroalkylether moiety with two or more carbons) by 2024 [**21**]. The minimum requirement values used to assess the quality of water intended for human consumption according to EU Directive 2020/2184 says «PFAS Total» must not exceed 0.50 µg/L and «Sum of PFAS» must not exceed 0.10 µg/L [**21**]. Regarding PFASs in food sources and their tendency to bioaccumulate, the European Food Safety Authority (EFSA) has established a safety threshold for four substances—PFOA, PFOS, PFNA, and PFHxS—at a tolerable weekly intake (TWI) of 4.4 ng/kg body weight (bw) [**22**].

In the US, the Environmental Protection Agency (EPA) has not set any specific regulations for per- and polyfluorinated alkyl substances in drinking water, but rather a non-enforceable lifetime health advisory (LHA) level of 70 ng/L for the sum of PFOA and PFOS in water [**19**]. There are currently no enforceable maximum contaminant levels (MCLs) given for PFASs by the US EPA National Primary Drinking Water Regulations [**23**]. Some individual states have adopted their own advisory levels that are even more strict, even going so far as to implement MCLs for specific PFASs (including Massachusetts [**24**], Michigan [**25**], New Jersey [**26**], and Vermont [**27**]).

– METHODS OF ANALYSIS

Determination of various per- and polyfluorinated alkyl substances can be a tricky and time-consuming endeavor, especially when laboratories must analyze samples for several compounds of interest. On the other hand, non-targeted analysis gives a broader overview of total sample loads as well as offering the possibility to capture precursor substances which may be too unstable to determine in other assays. **Table 1** lists a selection of analysis methods used for both targeted analysis and non-targeted screening of PFASs. More details are given in the rest of this paper and in the references cited.

Expensive instrumentation and analyst experience are required for accurate quantification of individual PFASs even in simple matrices like drinking water. In addition, the low levels of quantification listed in various regulations can be difficult to measure [**19,21,22,24–27**]. Analytical methods must be sensitive enough to measure single-digit ng/L amounts of a small range of PFASs in some cases, and therefore most of the time liquid chromatographs or gas chromatographs hyphenated to triple quadrupole mass spectrometers are used (LC-MS/MS or GC-MS/MS). These targeted methods separate individual compounds by LC or GC and then use isotopic calibrations to quantify them. US EPA Methods 533 and 537.1 both stipulate the use of LC-MS/MS for analysis of a selection of PFASs in drinking water [**28,29**]. This analysis method is also required for US EPA SW-846 (24 PFASs measured in surface water, groundwater, and wastewater) [**30**] and ASTM D7979 (analysis of six PFASs in water, sludge, influent, effluent, and wastewater) [**31**]. Even the US Food and Drug Administration (US FDA) specifies using LC-MS/MS to determine 16 targeted PFASs in different foods including bread, lettuce, milk, and fish [**32**].

Validation of targeted analysis approaches can be challenging. Since PFASs are found in nearly every-

Table 1. Selection of suitable analysis methods used to determine fluorinated compounds in samples.

Analysis Method	Measurement	Notes
LC-MS/MS or GC-MS/MS	targeted analysis	Separates individual PFASs and uses isotopic calibrations to quantify individual substances. Expensive, time-consuming, and only measures a limited number of PFASs.
Total oxidizable precursor (TOP) assay	non-targeted screening	Not capable of accurately determining total fluoride concentration as the sum of organic and ionic species.
Combustion ion chromatography (CIC)	non-targeted screening	Supports direct measurement of total fluorine (TF) and indirectly total organic fluorine (TOF). Simple to use as a screening tool for PFASs, their precursors, and related fluorinated compounds.

thing nowadays, it can be very difficult to source control samples or find blank materials with little to no background levels. Additionally, standard reference materials are very difficult to procure, and many laboratories must perform this validation work for individual PFASs themselves.

Targeted analysis approaches miss the detection of other potentially important PFASs and therefore do not give a fully representative view of the total environmental impact of these substances. Only dedicated compounds are analyzed—just a fraction of the nearly 10,000 PFASs listed by the EPA [**1**], not including precursors, isomers, metabolites, or other related substances. Currently, non-targeted comprehensive analysis methods are becoming more popular in laboratories to screen samples for PFASs and a full range of other related chemicals. Some laboratories have developed workflows to obtain an overall picture of total PFASs with tentative identification of unknowns by combining non-targeted screening and targeted analysis techniques [**33**].

One of these methods that bridges the targeted analysis and non-targeted screening approaches is the total oxidizable precursor (TOP) assay [**34**]. The TOP assay exposes samples to hydroxyl radicals under basic conditions in order to transform precursors of perfluorinated compounds into measurable PFASs, which are then determined by LC-HRMS (high resolution mass spectrometry) or LC-MS/MS [**34–36**]. However, this method takes a significant amount of time to perform and still does not quantify all fluorochemical species which may be present in a sample.

Rather than determining individual per- and polyfluorinated alkyl substances via complex analytical methods, a simpler screening method of combustion ion chromatography (CIC) can be used. CIC can determine the total fluorine (TF) content in various sample matrices, such as solids, liquids, gels, and foams (**Table 1** and **Figure 4**). Through direct injection into the IC, total inorganic fluorine (i.e., TIF, fluoride, F^-) is determined and subtracted from TF after combustion, resulting in the total organic fluorine (TOF) content. TOF is a general measure of the total impact of organic fluorine to the environment. It encompasses not only PFASs, but other related compounds that may not yet be included in environmental and health guidelines due to the vast amount of these unregulated chemicals.

The full scope of organofluorine compounds that are potentially detrimental to the environment is largely unknown, and therefore TOF is a good indicator for routine monitoring of such substances in surface water and wastewater. However, lower detection limits and higher sensitivity can be achieved by measuring a different parameter: the adsorbable organic fluorine (AOF, **Figure 4**).

ADSORBABLE ORGANIC FLUORINE (AOF) – A SUM PARAMETER

Combustion IC can not only determine TF and TOF (by calculating the difference between TF and TIF), but also AOF and EOF (extractable organic fluorine) in waters and solids, respectively [**37**]. Beside PFASs, AOF and EOF also include non-PFASs that still have similar properties (**Figure 4**), as well as pesticides, pharmaceuticals, and other fluorinated compounds that are not included when using more targeted analysis methods. Measurement of the sum parameter of AOF in water samples as an initial screening step is simpler, faster, and more robust than targeted methods [**37**], giving laboratories an overview of the actual amount of fluorinated compounds present in samples which

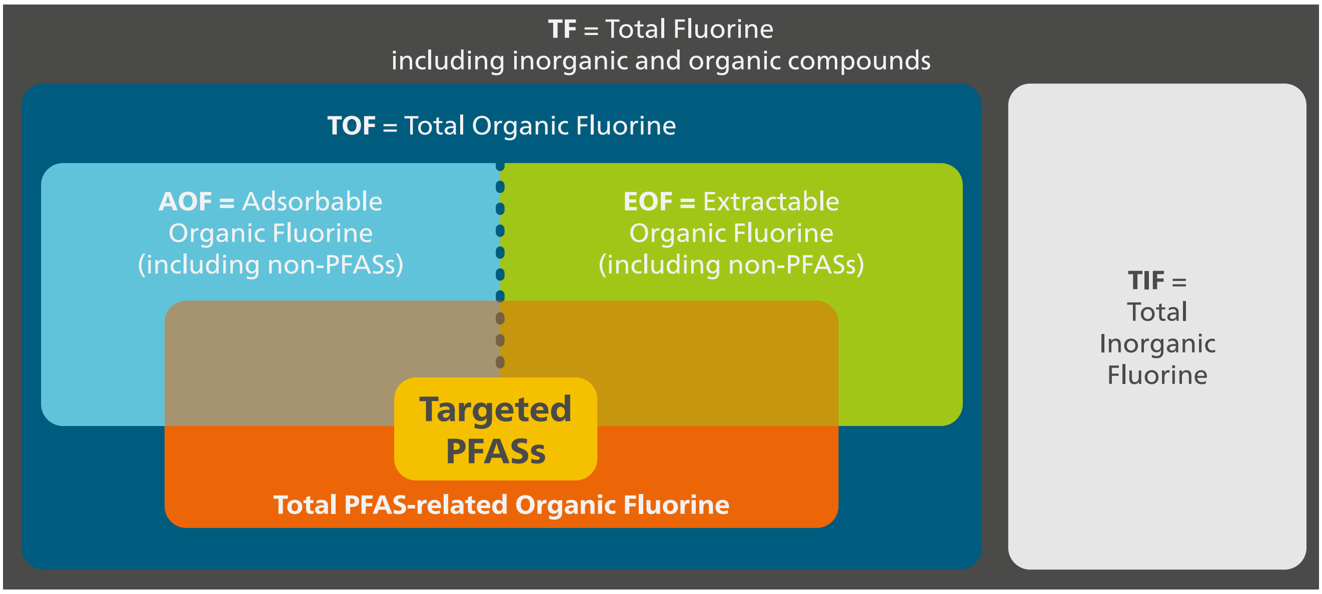


Figure 4. General overview of the relationships and overlaps from total fluorine (measured by CIC) to targeted PFASs (measured by LC-MS/MS or GC-MS/MS).

can be followed by targeted analyses of individual PFASs if indicated by higher concentrations of AOF.

Measuring AOF via CIC follows the sample preparation according to DIN EN ISO 9562 beginning with adsorption of the non-acidified liquid sample on a stationary phase (activated carbon), generally with a packed column or cartridge. To ensure complete adsoption, at least two consecutive packed columns or cartridges are used. The activated carbon becomes enriched with organofluorine compounds after a specified amount of sample is introduced (100 mL) and is then washed with sodium nitrate ($NaNO_3$) to remove the sample matrix and any inorganic fluoride in order to achieve the most accurate results. The rinsed AOF-enriched carbon is transferred to ceramic sample boats and then is inserted into the combustion module at 1050 °C for pyrohydrolytic combustion in an oxygen/

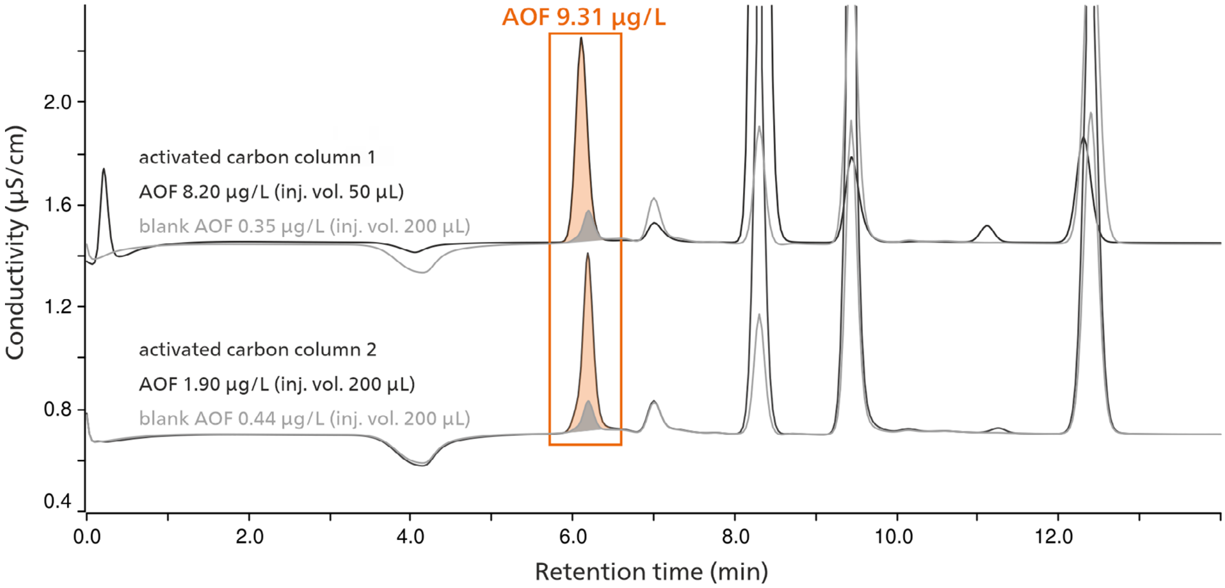


Figure 5. AOF determination in a wastewater sample. A volume of 100 mL sample (not acidified) was adsorbed on two consecutive activated carbon cartridges (disposable tube for AOF determination, APUsim, Analytik Jena, flow rate: 3 mL/min) and treated with a neutral $NaNO_3$ rinsing solution (0.01 mol/L). The rinsed activated carbon enriched with organic fluorine was subsequently combusted and analyzed using Metrohm CIC (Metrosep A Supp 5 - 250/4.0 column, column temperature: 55 °C, eluent: 2.8 mmol/L Na_2CO_3, sequential suppression). The total AOF concentration of the wastewater sample was determined as sum of the individual AOF contents of the two adsorption cartridges (in orange) from which the AOF method blank (in grey) was substracted.

argon gas stream. This stream is passed through an absorption solution which captures the fluorine as fluoride (F^-) and is then transferred, injected, and analyzed with IC using an anion exchange separation column (**Figure 5**). The AOF-CIC method can determine F^- in a range of 1–100 µg/L, with a limit of detection (LOD) of 0.5 µg/L F^- (determined according to DIN 32645).

With such a setup, low levels of organofluorine compounds including PFASs, isomers, precursors, metabolites, pharmaceuticals, pesticides, and other related substances can be quickly measured. Higher values of the sum parameter AOF measured with CIC can be used as a trigger for laboratories to check samples with a more in-depth targeted analysis method for specific PFASs. The complementary approach of measuring AOF as a non-targeted screening method for PFASs alongside targeted methods like LC-MS/MS helps researchers to better monitor the actual amount of fluorinated substances in water, and in the environment in general.

SUMMARY

Measurement of AOF with CIC as a non-targeted screening method for PFASs in waters can be faster and easier, and is a more robust alternative to the determination of individual substances with the more costly, complex TOP assay method or compared to the targeted analysis of individual substances with LC-MS/MS or GC-MS/MS. The advantage of measuring AOF as an estimate for PFASs over the indirect TOF analysis lies in its higher accuracy and sensitivity due to preconcentration and direct determination.

The AOF sum parameter is more comprehensive to estimate the overall impact of organofluorine substances in water samples. It is a good indicator to initiate detailed targeted analyses if values are high. This can be especially helpful to determine whether water treatment processes have been effective enough in municipal water facilities and wastewater treatment plants to sufficiently remove harmful fluorinated substances before they are released to the environment or to the general water supply.

References

[1] U.S. Environmental Protection Agency. PFAS Master List of PFAS Substances (Version 2) **https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster** (accessed 2021-11-05).

[2] Secretariat of the Stockholm Convention (SSC). *Stockholm Convention on Persistent Organic Pollutants (POPs)*; Châtelaine, Switzerland, 2020; p 79.

[3] Buck, R. C.; Franklin, J.; Berger, U.; et al. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integr. Environ. Assess. Manag.* **2011**, *7* (4), 513–541. **DOI:10.1002/ieam.258**

[4] U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Perfluoroalkyls; 2021; pp 993.

[5] Cousins, I. T.; DeWitt, J. C.; Glüge, J.; et al. Strategies for Grouping Per- and Polyfluoroalkyl Substances (PFAS) to Protect Human and Environmental Health. *Environ. Sci. Process. Impacts* **2020**, *22* (7), 1444–1460. **DOI:10.1039/D0EM00147C**

[6] Cousins, I. T.; DeWitt, J. C.; Glüge, J.; et al. The High Persistence of PFAS Is Sufficient for Their Management as a Chemical Class. *Environ. Sci. Process. Impacts* **2020**, *22* (12), 2307–2312. **DOI:10.1039/D0EM00355G**

[7] ASTM International. *ASTM E3302 Standard Guide for PFAS Analytical Methods Selection*; ASTM International, 2021. **DOI: 10.1520/E3302-21**

[8] DuPont. Information on PFAS - Historical Use **https://www.dupont.com/pfas/historical-use.html** (accessed 2021-10-27).

[9] 3M. History of PFAS and 3M
https://www.3m.com/3M/en_US/pfas-stewardship-us/pfas-history/ (accessed 2021-11-03).

[10] The Chemours Company. The History of Teflon™ Fluoropolymers
https://www.teflon.com/en/news-events/history (accessed 2021-11-08).

[11] GORE-TEX. Our History | GORE-TEX Brand
https://www.gore-tex.com/technology/history (accessed 2021-11-03).

[12] DuPont. Information on PFAS - Milestones
https://www.dupont.com/pfas/milestones.html (accessed 2021-11-03).

[13] DuPont. Information on Poly and Per-Fluorinated Alkyl Substances (PFAS)
https://www.dupont.com/pfas.html (accessed 2021-11-03).

[14] Glüge, J.; Scheringer, M.; Cousins, I. T.; et al. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22* (12), 2345–2373. **DOI:10.1039/D0EM00291G**

[15] Trudel, D.; Horowitz, L.; Wormuth, M.; et al. Estimating Consumer Exposure to PFOS and PFOA. *Risk Anal.* **2008**, *28* (2), 251–269. **DOI:10.1111/j.1539-6924.2008.01017.x**

[16] US EPA. Our Current Understanding of the Human Health and Environmental Risks of PFAS
https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas (accessed 2021-11-08).

[17] Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; et al. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* **2016**, *3* (10), 344–350. **DOI:10.1021/acs.estlett.6b00260**

[18] ARCADIS Geraghty & Miller International. *Environmental Fate and Effects of Poly- and Perfluoroalkyl Substances (PFAS)*; Report no. 8/16; Brussels, Belgium, 2016.

[19] US EPA. Drinking Water Health Advisories for PFOA and PFOS
https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos (accessed 2021-11-08).

[20] RIVM (Rijksinstituut voor Volksgezondheid en Milieu / National Institute for Public Health and the Environment). Questions and answers on the proposal for a ban on the use of PFAS (restriction)
https://www.rivm.nl/en/pfas/restriction-proposal-pfas/qas-pfas-restriction-proposal (accessed 2021-11-08).

[21] Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the Quality of Water Intended for Human Consumption, Annex I, Part B. *Off. J. Eur. Union* **2020**, *L 435*, 1–62.

[22] EFSA Panel on Contaminants in the Food Chain (EFSA CONTAM Panel); Schrenk, D.; Bignami, M.; et al. Risk to Human Health Related to the Presence of Perfluoroalkyl Substances in Food. *EFSA J.* **2020**, *18* (9), e06223. **DOI:10.2903/j.efsa.2020.6223**

[23] US EPA. National Primary Drinking Water Regulations
https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations (accessed 2021-11-09).

[24] Massachusetts Department of Environmental Protection. PFAS MCL Revisions to 310 CMR 22.00 - Clean Version 9-16-2020. September 16, 2020.

[25] Department of Environment, Great Lakes, and Energy - Michigan PFAS Action Response Team. PFAS Response - PFAS MCLs and Drinking Water
https://www.michigan.gov/pfasresponse/0,9038,7-365-95571_99970---,00.html (accessed 2021-11-09).

[26] New Jersey Department of Environmental Protection - Division of Water Supply and Geoscience. N.J.A.C. 7:10 - Safe Drinking Water Act Rules. June 1, 2020.

[27] Vermont Department of Health. PFAS in Public Drinking Water. July 2019.

[28] US EPA. Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry **https://www.epa.gov/dwanalyticalmethods/method-533-determination-and-polyfluoroalkyl-substances-drinking-water-isotope** (accessed 2021-11-09).

[29] US EPA. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) **https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL** (accessed 2021-11-09).

[30] US EPA. SW-846 Test Method 8327: Per-and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) **https://www.epa.gov/hw-sw846/sw-846-test-method-8327-and-polyfluoroalkyl-substances-pfas-liquid-chromatographytandem** (accessed 2021-11-09).

[31] ASTM International. *ASTM D7979 Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)*; ASTM International. **DOI:10.1520/D7979-20**.

[32] Genualdi, S.; deJager, L. Determination of 16 Per and Polyfluoroalkyl Substances (PFAS) in Food Using Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) - US FDA Method C-010.01. US Food and Drug Administration November 1, 2019.

[33] Dubocq, F.; Wang, T.; Yeung, L. W. Y.; et al. Characterization of the Chemical Contents of Fluorinated and Fluorine-Free Firefighting Foams Using a Novel Workflow Combining Nontarget Screening and Total Fluorine Analysis. *Environ. Sci. Technol.* **2020**, *54* (1), 245–254. **DOI:10.1021/acs.est.9b05440**

[34] Chandramouli, B. Understanding Precursor Contributions: The Total Oxidizable Precursor Assay. In *Perfluoroalkyl Substances in the Environment*; CRC Press, 2018. **DOI:10.1201/9780429487125-3**

[35] Houtz, E. F.; Sedlak, D. L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environ. Sci. Technol.* **2012**, *46* (17), 9342–9349. **DOI:10.1021/es302274g**

[36] Zhang, C.; Hopkins, Z. R.; McCord, J.; et al. Fate of Per- and Polyfluoroalkyl Ether Acids in the Total Oxidizable Precursor Assay and Implications for the Analysis of Impacted Water. *Environ. Sci. Technol. Lett.* **2019**, *6* (11), 662–668. **DOI:10.1021/acs.estlett.9b00525**

[37] von Abercron, E.; Falk, S.; Stahl, T.; et al. Determination of Adsorbable Organically Bound Fluorine (AOF) and Adsorbable Organically Bound Halogens as Sum Parameters in Aqueous Environmental Samples Using Combustion Ion Chromatography (CIC). *Sci. Total Environ.* **2019**, *673*, 384–391. **DOI:10.1016/j.scitotenv.2019.04.068**

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