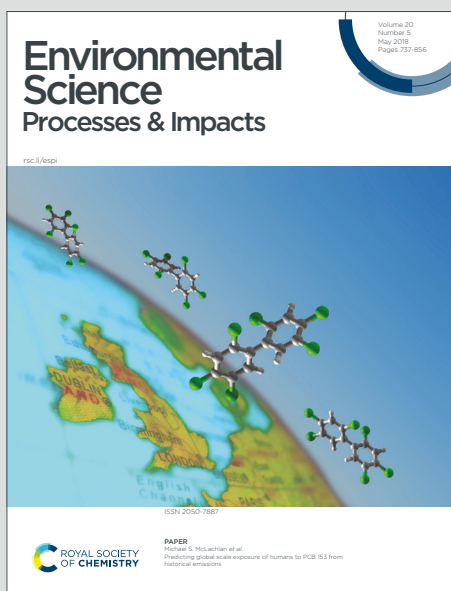


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Environmental Significance

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Sum-parameter approaches such as extractable organofluorine (EOF) analysis are increasingly used to assess PFAS contamination in drinking water, yet their environmental interpretation remains challenging. This study shows how highly mobile fluorinated compounds, including trifluoroacetic acid and inorganic fluorinated species, can bias EOF-based PFAS Total assessments, leading to potential over- or underestimation of contamination. By proposing an improved analytical workflow, the work advances understanding of how fluorinated substances are detected and interpreted in drinking water systems, supporting more meaningful environmental assessment of PFAS occurrence.

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Approaches and Limitations of using Extractable Organofluorine - Combustion Ion Chromatography to Assess PFAS Total in Drinking Water

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are now widely detected in drinking water globally as a result of decades of production and use. Although recent regulations aim to address this issue, including the recast EU Drinking Water Directive (DWD), which introduces a PFAS Total parametric value, no standardized analytical method has yet been established for its determination. Here, extractable organofluorine (EOF) analysis of drinking water using combustion ion chromatography (CIC) was evaluated as a proxy for assessing PFAS Total under the EU DWD. Due to the low recovery of trifluoroacetic acid (TFA) in the EOF extraction, a workflow was presented that separated TFA from the PFAS Total reporting. The impact of different fluorine mass fractions on the conversion factor used to translate EOF concentrations into a PFAS Total parametric value was evaluated. Based on this assessment, PFOA (67% F) was selected as a representative reference compound. Due to the broad, non-specific coverage of the EOF method, contributions from non-PFAS organofluorine compounds or inorganic

fluorinated species may occur, potentially inflating the PFAS Total parametric value. Therefore, a structured follow-up protocol for investigation of PFAS Total parametric value exceedance was presented to support the use of EOF-CIC as a screening and compliance-support tool.

Key words: PFAS Total, drinking water, EOF, CIC, TFA, EU DWD

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a type of organofluorine compounds that have been extensively used globally¹. While the exact definition of PFAS differs between institutions and agencies², the Organization for Economic Co-operation and Development (OECD) defines a PFAS as a compound which contains at least one fully fluorinated methyl or methylene carbon atom³. PFAS has seen extensive use in both industrial and consumer applications such as electronics and printing products, textiles, food contact materials and fire-fighting foams¹. As various health effects have been associated with PFAS⁴⁻⁶, it is important to understand and limit human exposure to this group of contaminants. Drinking water serves an important route for human exposure and drinking water quality is one of the greatest factors which affect human health⁷. Numerous studies have detected PFAS in drinking water globally⁸⁻¹⁰ and standards or guideline values of PFAS in drinking water has been proposed by different authorities¹¹⁻¹⁵.

Most agencies¹¹⁻¹⁵ have aimed regulation at individual PFAS or the sum of selected few PFAS such as perfluoroalkyl carboxylic acids (PFCAs, C4 – C13), perfluoroalkyl sulfonic acids (PFSAs, C4 – C13), 6:2 fluorotelomer sulfonic acid (6:2 FTSA) and hexafluoropropylene oxide dimer acid (HFPO-DA). However, these compounds may only cover a small fraction of the entire group of PFAS. The lack of analytical reference standards also results in narrow coverage. High-resolution mass spectrometry (HRMS) enables the detection of compounds without *a priori* knowledge on their identity via non-target analysis or through suspect screening based on comparison with PFAS databases. While HRMS is used for quantitative analysis in targeted workflows, its application in suspect and non-target screening is typically qualitative or semi-quantitative unless supported by appropriate reference standards¹⁶. Such screening approaches



can subsequently guide fully quantitative analysis through the acquisition of standards. Besides, the monitoring of an expanding list of targeted PFAS is limited by resources¹⁷. There are currently different available techniques to widen the analytical coverage and determine a sum parameter of organofluorine or assess the totality of PFAS¹⁸. Using fluorine analysis as proxy for PFAS Total is used in adsorbable organofluorine analysis (AOF) and extractable organofluorine analysis (EOF) using combustion ion chromatography (CIC), continuum source molecular absorption spectrometry (CS-MAS), and particle induced gamma-ray emission spectroscopy (PIGE)¹⁹⁻²⁴. In AOF, activated carbon is used as the sorbent for the extraction of organofluorine and is combusted after adsorption, while in EOF analysis, organofluorine are eluted following adsorption to a sorbent and the extract is subsequently combusted. Both AOF and EOF measurements using CIC operate under the principle of converting organic and inorganic forms of fluorine into hydrogen fluoride by combustion at around 1000 °C in the presence of water. The formed hydrogen fluoride is dissociated in an aqueous solution and subsequently quantified via an ion conductivity detector.

In 2021, the recast of the Drinking Water Directive (DWD) in the European Union (EU) introduced parameters and parametric values for PFAS; these parametric values were 500 ngL⁻¹ for the “PFAS Total” and 100 ng L⁻¹ for the “Sum of PFAS” parameter. The latter is defined as the sum concentration of a list of 20 PFAS and was recently evaluated²⁵. Member States are required to comply with one of these parameters by 12 January 2026²⁶. The EU defines PFAS Total as “*the totality of per- and polyfluoroalkyl substances*”. Notably, there is no stated definition of what constitutes a PFAS in the DWD. However, the guidance document noted that the broadly agreed definition when the DWD was adopted in 2018, was the technical definition published 2018 by OECD²⁷. That definition was revised in 2021²⁸, which expanded the scope of PFAS leading to the inclusion of ultra-short chain PFAS such as trifluoroacetic acid (TFA) and e.g., certain pesticides and pharmaceuticals that contain a C-CF₃ moiety. Compared to Sum of PFAS, the PFAS Total can more comprehensively cover PFAS in drinking water and obtain information that is overlooked from targeted analysis. Technical guidelines regarding methods of analysis for monitoring of PFAS in water intended for human consumption was published in August 2024²⁹. The guidance document describes the methods of analysis for monitoring the

“Sum of PFAS” and “PFAS Total” including detection limits (limit of quantification), frequency of sampling and uncertainty of measurements. The technical guidance states that available TFA monitoring results from raw water sources across Member States already indicate that TFA concentrations may have led to exceedances of the PFAS Total parametric value³⁰. The guidance document also states no analytical method currently is effective at selectively quantifying all possible structure within the diverse group of PFAS; thus, PFAS Total cannot currently be determined “as is”. However, the outcomes from three methods referred to may serve as proxies for determining PFAS Total. These include the total oxidizable precursor assay (TOP assay), EOF-CIC, and liquid chromatography (LC)- HRMS-based screening methods.

In this investigation, we applied EOF-CIC for determining PFAS Total in drinking water with the objectives to evaluate the suitability when following the instructions in the DWD technical guideline. Consequently, an improved workflow was proposed to refine the proxy assessment of PFAS Total within the current scope of the EOF-CIC method including follow-up investigations in the case of exceedance.

2 Methods

2.1 Chemicals

A list of chemicals used can be found in supporting information (SI).

2.2 Sample information

Tap water samples were collected between 2022 and 2023 in Sweden, Norway, Denmark, Germany and Austria. Detailed sample information can be found in table 1. In addition, samples from Shanghai, China were included for comparative purposes. The results from these has previously been published and information regarding sampling and analysis is referred to Jiao et al., 2023³¹.

Table 1 Sample information of drinking water collected from Sweden (n=26), Norway (n=11), Denmark (n=1), Germany (n=4) and Austria (n=1), between the years 2022-2023, and methods of analysis included volumes extracted.

Sampling location	Year of sampling	Methods of analysis	Extraction volume (mL)
Sweden (n=3, Lidköping, Örebro and Malmö)	2022	TFA _{target} , TFA _{EOF} , EOF-CIC	500
Norway (n=2, Oslo and Bergen)			500
Denmark (n=1, Copenhagen)			1000
Germany (n=4, Frankfurt, Berlin, Hamburg and Munich)	2023	EOF-CIC	100
Austria (n=1, Vienna)			
Sweden (n=23, Lidköping, Malmö, Luleå, Umeå, Sundsvall, Gävle, Uppsala S, Uppsala C, Åkersberga, Stockholm, Linköping, Visby, Oskarshamn, Kalmar, Karlskrona, Landskrona, Halmstad, Jönköping, Göteborg, Mölndal, Helsingborg, Borås and Östersund)	2022-2023	TFA _{direct}	-
Norway (n=9, Oslo, Bergen, Alta, Sorland, Trondheim, Alesund, Klepp, Moss, Kristiansand)			

Note: TFA_{target} is recovery corrected target analysis using isotope dilution; TFA_{EOF} is target analysis on modified EOF extract (after fluoride removal) using labeled injection standard. EOF-CIC is fluoride analysis on modified EOF extract (after fluoride removal); TFA_{direct} represents direct injection without any extraction, analyzed with LC-MS/MS.

2.3 Extraction methods

TFA_{direct}. The direct injection (20 μ L) was performed for tap water samples from Sweden (n=23) and Norway (n=9) by Eurofins Food & Feed Testing Sweden AB. The samples were spiked with $^{13}\text{C}_2$ -TFA in methanol (leading to a 1.02 dilution factor) and injected directly into the instrument, without any prior sample extraction.

TFA_{target}. The samples (500-1000 mL) were spiked with 4 ng of extraction standard ($^{13}\text{C}_2$ -TFA) and were then extracted via a solid-phase extraction method based on previous publications^{31, 32}. In brief, the weak anion exchange cartridges (150 mg, 6 mL, 30 μ m, Oasis WAX cartridges, Waters Corporation) were preconditioned with 4 mL 0.1% ammonium hydroxide in methanol followed by 4 mL each of methanol ultrapure water before loading the samples. The cartridges were then washed by passage of 4 mL of Milli-Q water followed by 4 mL ammonium acetate buffer solution (pH 4) and ultrapure water with 20% methanol. After drying under vacuum for 30 min, the cartridges were eluted with 4 mL 0.1% ammonium hydroxide in methanol and the extracts were evaporated under nitrogen gas. Two ng of the injection standard ($^{13}\text{C}_3$ -PFBA) was spiked in extracts prior to instrumental analysis.

EOF-CIC. Samples were extracted using a similar extraction method as *TFA_{target}*, but without spiking any extraction standards. In addition, 20 mL of 0.01% ammonium hydroxide in ultrapure water, 30 mL of ultrapure water, 4 mL of an ammonium acetate buffer solution (pH=4), and 4 mL of ultrapure water with 20% methanol were used as washing solutions. Details of the method can be found elsewhere³¹.

TFA_{EOF}. One aliquot of the EOF-CIC extracts was further spiked with $^{13}\text{C}_2$ -TFA (injection standard) for the analysis of TFA in the EOF extract, without any extraction recovery correction.

2.4 Instrumentation and quantification

TFA_{direct}. The direct injection was conducted by Eurofins Food & Feed Testing Sweden AB. Analysis of TFA was performed by an in-house method developed at Eurofins SE. The method was based on mixed mode (reversed phase/anion-exchange) separation using a 1290 UHPLC coupled to a 6495 tandem mass spectrometer, both from Agilent Technologies (Santa Clara, CA, USA). For separation, an Atlantis PREMIER BEH C18 AX analytical column (2.1 mm x 100 mm, 1.7 μ m; Waters Corporation Milford, USA), together with the mobile phases 2.5 mM dibutylammonium acetate, 5% acetonitrile and 0.1% acetic acid in water (A) and acetonitrile (B) was used. This anion exchange mechanism enables TFA to have improved retention over conventional C18 columns. The retention time of TFA in this method was 2.6 min. Representative chromatograms are referred to SI figure S2.



TFA_{target} , TFA_{EOF} . TFA, were analyzed via 2 μ l injection onto an SFC-MS/MS (Acquity Ultra Performance Convergence Chromatograph and Xevo TQ-S micro, Waters Corporation, Milford, USA) operated in electrospray ionization negative (ESI-) mode. Simultaneously, tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) were analyzed as potential causes for false positive results. TFA was measured by multiple reaction monitoring, while BF_4^- and PF_6^- was measured via single ion recording of the molecular ion. A Torus DIOL column (3 mm x 150 mm, 1.7 μ m; Waters Corporation Milford, USA) maintained at 40 $^{\circ}$ C was used for chromatographic separation. CO_2 (A) and 0.1% ammonium hydroxide in methanol (B) were used as mobile phase and gradient eluting was slightly modified based on previously published method³³. Further information can be found in SI table S2 and S3 and elsewhere³³.

TFA_{direct} , TFA_{target} , TFA_{EOF} . As TFA was quantified using three separate approaches in this manuscript, it is important to consider the differences between TFA_{direct} , TFA_{target} and TFA_{EOF} and how it impacts interpretation of the results. For both TFA_{direct} and TFA_{target} , internal standard ($^{13}C_2$ -TFA) is added directly to samples, which results in an accurate representation of TFA concentration in the samples. Conversely, for TFA_{EOF} , the internal standard is added after extraction, which results in measurement of TFA concentration that does not account for losses during extraction. Thus, TFA_{EOF} concentration only represents concentration of TFA in extracts but not samples.

EOF-CIC. EOF was measured by combustion ion chromatograph (CIC, Metrohm, Herisau, Switzerland) where 100 μ l of sample extract was injected. After the combustion, an ion exchange column (Metrosep A Supp5, 4 mm x 150 mm), together with a mobile phase consisting of a carbonate buffer (3.2 mM sodium carbonate and 1 mM sodium bicarbonate) was used for separation. An ion conductivity detector was used for measurement of fluoride. Detailed information is described elsewhere³⁴.

2.5 QA/QC

For analysis of TFA_{target} , two procedure blanks and one recovery sample (ultrapure water spiked with 4 ng of TFA) were extracted together with tap water samples. TFA was quantified based on an internal calibration method and the lowest point of the calibration curve (2.5 ng mL⁻¹) was used as the method quantification limit (MQL) as no TFA was detected in procedural blanks above this level. The spiked recovery of TFA in the recovery samples was 121%. In contrast, the recoveries of $^{13}C_2$ -TFA in tap water samples ranged from 20% to 90%. These values reflect the recovery of TFA during SPE extraction and indicate matrix-dependent variability in extraction efficiency for TFA in environmental samples.

For EOF analysis, two procedure blanks were analyzed and an external calibration curve of PFOA (ranging from 50-1000 ng mL⁻¹ F) was used for quantification. The blanks showed no detectable levels of EOF; therefore, the lowest point of calibration curve was used as method detection limit (MDL), which was calculated on either 500 mL sample volume (MDL 50 ng L⁻¹ F) and 100 mL (MDL 250 ng L⁻¹ F). The quantifications of BF₄⁻ and PF₆⁻ were based on an external calibration curve.

2.6 Conversion of fluorine equivalent concentration to mass concentration

In EOF-CIC, sample extracts are combusted at around 1000 °C to convert organically bound fluorine into hydrogen fluoride, which is subsequently adsorbed in water and disassociated, before an aliquot is injected on an ion chromatograph for fluoride determination. As a result, EOF concentration obtained is mass concentration of fluoride (ng L⁻¹ F). To align this concentration to the DWD parametric value (i.e., ng L⁻¹), a conversion based on the fluorine mass fraction of a PFAS is needed. This was done with the following equation:

$$C_F = \frac{n_F A W_F}{M W_{PFAS}} * C_{PFAS}$$

For example, 10 ng L⁻¹ of PFOA can be converted accounting for the molecular weight of PFOA (MW_{PFAS}; 413 g/mol) and atomic weight of fluorine (AW_F; 19 g/mol), together with the number of fluorine atoms (n_F; 15). Thereby, 10 ng L⁻¹ PFOA is equivalent to 6.9 ng L⁻¹ F.

3 Results and discussion

3.1 Concentrations of TFA and EOF in drinking water

TFA_{direct} was detected in all the samples with concentrations ranging from 92 ng L⁻¹ to 720 ng L⁻¹ in samples from Sweden and from 70 ng L⁻¹ to 330 ng L⁻¹ in samples from Norway. Lower values were found in West and North Norway. The relatively higher concentrations were measured along the South-Eastern Swedish coast and the island of Gotland (Visby). As TFA_{direct} involves direct injection without extraction, it provides a measurement of TFA that is not influenced by extraction-related losses and can therefore be considered representative of the actual TFA concentrations in the samples. Detailed results are provided in SI table S4.

TFA_{target} and EOF were detected at a 100% detection frequency in tap water from Nordic countries (Sweden (n=3), Norway (n=2) and Denmark (n=1)). TFA_{target} ranged from 68.3 ng L⁻¹ (Copenhagen) to 305 L⁻¹ (Örebro) and EOF ranged from 68.1 ng F/L (Bergen) to 350 ng L⁻¹ F (Örebro). TFA_{EOF} concentrations were 36-89% lower compared to TFA_{target}, where TFA_{EOF}

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levels ranged from 7.42 to 128 ng L⁻¹ and TFA_{target} concentrations were between 68.3-305 ng L⁻¹. EOF were below MDL (250 ng/L) in all samples collected from Germany (n=4) and Austria (n=1). Therefore, these samples were not further analyzed for TFA, BF₄⁻ and PF₆⁻.

Two inorganic fluorinated anions (BF₄⁻ and PF₆⁻) were included in the analysis of samples with detectable EOF, since previous studies have shown that tap water from Shanghai³¹ contains BF₄⁻ and PF₆⁻, which can account for a substantial fraction of the EOF mass balance (>44%) and potentially result in overestimation of the PFAS Total parametric value. No detectable levels of BF₄⁻ and PF₆⁻ were found in this study.

Table 2. TFA (ng L⁻¹) and EOF (ng L⁻¹ F) concentrations in drinking water collected from Nordic countries.

Country	Locations	EOF extract		Target analysis
		EOF (ng L ⁻¹ F)	TFA _{EOF} (ng L ⁻¹)	TFA _{target} (ng L ⁻¹)
Sweden (n=3)	Lidköping	319	44.6	148
	Örebro	350	95.7	305
	Malmö	203	41.8	208
Norway (n=2)	Oslo	324	128	199
	Bergen	68.1	59.7	94.6
Denmark (n=1)	Copenhagen	168	7.42	68.3

3.2 Differences between the concentrations of TFA_{target} and TFA_{EOF}

The measured concentrations of TFA_{EOF} were lower than those of TFA_{target} in all samples, indicating a systematic loss of TFA during EOF extraction. The magnitude of this difference varied considerably between samples, suggesting that TFA losses during extraction are both significant and sample dependent. This variability is expected, as the mass-labelled TFA standard in the TFA_{EOF} approach is added after extraction and therefore does not correct for extraction losses. The TFA_{EOF} extraction method contains an additional washing step compared to TFA_{target}, that is required to avoid the interference of inorganic fluoride, including free fluoride, in the CIC analysis. Previous studies have shown poor extraction recovery of TFA (~5%) when this additional washing step^{31, 35} was included. Differences in washing volumes, as reported in literature^{32, 36, 37}, may also influence TFA recovery. The extraction recovery of TFA could further be influenced by other factors, e.g., sample type (e.g., drinking water, groundwater)³⁸. In this context, TFA_{EOF} does not reflect the actual concentration of TFA in the sample, and PFAS Total assessed by EOF-CIC therefore underestimates the contribution of TFA.

It is also important to note the differences and similarities between TFA_{target} , TFA_{EOF} and TFA_{direct} as shown in SI Table S4. TFA_{direct} and TFA_{target} both provide reliable estimates of TFA concentrations, as they either avoid extraction (TFA_{direct}) or correct for extraction losses using mass-labelled internal standards (TFA_{target}). Conversely, in TFA_{EOF} , only post extraction-losses or artefacts are accounted for (e.g., instrumental matrix effects), and extraction-related losses are not corrected.

The discrepancy between TFA_{target} and TFA_{EOF} indicates that TFA is not quantitatively recovered using the EOF extraction method, likely due to its high polarity and poor retention on SPE sorbents. Comparison with TFA_{direct} (Table S4) further supports this interpretation. As TFA_{direct} bypasses extraction, it provides a direct measure of TFA in the samples and can be considered a reference for evaluating extraction-based methods. The agreement between TFA_{direct} and TFA_{target} indicates that both approaches provide consistent estimates of TFA concentrations, whereas the substantially lower TFA_{EOF} concentrations confirm significant and variable losses of TFA during EOF extraction.

The separation of TFA from inorganic fluoride remains a significant analytical challenge in EOF-CIC workflows due to their similar physicochemical properties, including high polarity and weak retention on commonly used sorbents. While modifications to extraction procedures (e.g., adjustment of washing steps, sorbent selection, or elution conditions) could potentially improve TFA recovery, such approaches typically involve a trade-off between retaining highly polar PFAS and effectively removing inorganic fluoride, which is essential to avoid interference in CIC analysis. Within the scope of this study, no further optimization of the extraction method was performed, as the objective was to evaluate EOF-CIC as a proxy for PFAS Total using currently available methodologies. These limitations highlight the need for future method development aimed at improving the simultaneous retention of highly polar PFAS while excluding inorganic fluorinated species. These limitations highlight the need for future method development aimed at improving the simultaneous retention of highly polar PFAS while excluding inorganic fluorinated species. Alternative total-parameter approaches, such as AOF-CIC or the TOP assay, could provide complementary information for PFAS total assessment. However, these methods were beyond the scope of the present study, which focused on evaluating EOF-CIC using currently available workflows.

3.3 Conversion of EOF-CIC concentration to PFAS Total parametric value

Although EOF-CIC intrinsically measures fluorine on a molar basis, results are conventionally converted and reported as mass concentration (e.g., $\text{ng L}^{-1} \text{ F}$)^{24, 35, 37}. Because the fluorine mass percentage (i.e., derived from the sum mass of fluorine atoms divided by the molecular mass)

of unknown PFAS combusted in EOF-CIC is not known, the conversion of ng L^{-1} F to the DWD parametric value (ng L^{-1}) (and vice versa) creates an ambiguity that needs to be considered. For example, a compound with higher fluorine mass percentage will have a closer EOF-CIC (ng L^{-1} F) equivalent limit value to the DWD PFAS Total parametric value (500 ng L^{-1}). This can be exemplified by TFA (250 ng L^{-1} F equivalent limit value) and PFOA (345 ng L^{-1} F) by using their respective fluorine mass percentages of 50% (TFA) and 67% (PFOA).

An upper-bound, a less conservative conversion factor assumes that the measured unknown fluorine originates from compounds with a high fluorine mass fraction (i.e. a high number of fluorine atoms relative to molecular weight). In contrast, a lower-bound conversion factor assumes that unknown fluorinated compounds are dominated by a lower fluorine mass fraction, which results in a lower CIC-derived ng L^{-1} F-equivalent threshold required to comply with the 500 ng L^{-1} PFAS Total parametric value.

Although a chemical definition of PFAS is essential for interpreting the scope of the PFAS Total parameter, the DWD does not specify such a definition. However, as previously mentioned, the technical guidelines assumed the current OECD definition²⁸, and it is the definition used for discussion herein. It is not practical to assign a definitive lower or upper bound of fluorine mass percentage constituting a PFAS according to the OECD. However, the fungicide fludioxonil, containing 15% F, could serve as an example for a lower bound estimate of fluorine mass percentage. Fludioxonil is a benzodioxole derivative containing two fluorine atoms and was not considered a PFAS under the 2018 OECD definition²⁷, but is consistent with the broader updated OECD 2021 definition.

Using this lower-bound fluorine mass percentage (15% F), the CIC-EOF derived equivalent limit value of the DWD PFAS Total limit correspond to around 75 ng L^{-1} F. The technical guidelines specify that no higher than 30% of the limit value is the criterion for limit of quantification. Notably, although likely technically possible, it may be practically challenging for commercial laboratories to comply with this based on results from EOF-CIC method performance in interlaboratory trials^{35,37}. For example, in the first interlaboratory trial published in 2021, only one participant reported a sufficiently low method reporting limit (MRL) of 13 ng L^{-1} F, based on the average plus three times the standard deviation in blanks; consisting of procedural blanks (no water matrix) and ultrapure water (500 mL). The MRLs of the other two participating laboratories were 151 and 124 ng L^{-1} . Furthermore, in a later interlaboratory study published in 2023, similar extraction blank-based MRL (50 mL ultrapure water) ranged from 680 to 2180 ng L^{-1} F between the seven participating laboratories. The higher reported MRL in latter study likely stems from lower sample volume used. Importantly, these values originate

from interlaboratory studies and do not reflect the performance of the present study. In the present study, the reported MDLs ranged from 50 - 250 ng L⁻¹ F, based on the extraction volume (500 mL or 100 mL).

By comparison, highly fluorinated perfluoroalkyl acids such as PFOA (69% F), PFOS (65% F) and TFA (50% F) equal a derived PFAS Total parametric limit value of 344 ng L⁻¹ F, 323 ng L⁻¹ F and 250 ng L⁻¹ F, respectively. To assess the effect of using different conversion factors of % F, the results from table 2 and table 3 (Shanghai (China) samples)³¹ were converted from EOF-CIC (ng L⁻¹ F) to PFAS Total parametric value (ng L⁻¹); these results can be found summarized in figure 1. Importantly, using a low fluorine mass percentage as a conversion factor would give low-fluorinated compounds high impact and would lead to an exceedance in all tested tap waters from the Nordic countries.

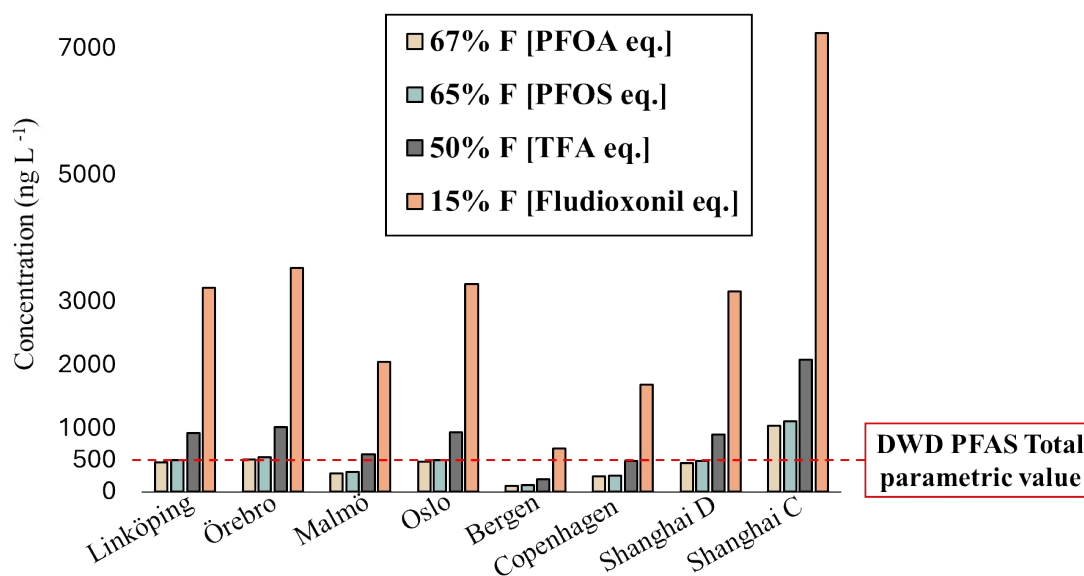


Figure 1. The effect of different conversion factors, based on fluorine mass fraction of PFOS, PFOA, TFA and Fludioxonil, for converting CIC-EOF concentrations (ng L⁻¹ F) to the DWD PFAS Total parametric value (ng L⁻¹). EOF-CIC concentrations presented in table 2 (Nordic countries) and table 3 (China) were used as the illustrations.

Beyond technical aspects, selection of an appropriate conversion factor may also take into account the fluorine mass percentage of PFAS commonly detected in drinking water, particularly compounds with high detection frequency and concentration. TFA has been measured in sources to drinking water with a high detection frequency at concentration exceeding other PFAS by orders of magnitude^{39, 40}.

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Toxicological relevance may also be considered when deriving a suitable conversion factor. Although the PFAS Total parametric value in the DWD is not based on a formal health-based risk assessment, the overarching purpose of the DWD is the protection of human health within the Member States. PFOA has been extensively evaluated with respect to human toxicological effects and has been used as a reference compound for deriving relative potency factors (RPFs) for PFAS mixture risk assessment^{41, 42}. PFOA is also one of the four PFAS for which the EFSA has established health-based guideline values⁴³. In general, longer-chain perfluoroalkyl acids are expected to be more bioaccumulative than their shorter-chain analogues and are often considered more hazardous⁴⁴.

Taken together, adopting low fluorine mass percentage as a conversion factor may lead to analytical challenges as well as exceedance in many drinking waters. When considering perfluoroalkyl acids, a low fluorine mass percentage may also overstate the significance of e.g., TFA whose relative toxicity may be lower than that of longer chain perfluoroalkyl acids with higher bioaccumulative potential.

In this context, the selection of an appropriate fluorine mass fraction for conversion of EOF-CIC results to PFAS Total remains uncertain and may depend on the assumed composition of the underlying organofluorine mixture. From an analytical perspective, a compound such as TFA (50% F) could be considered more representative in drinking water, given its frequent occurrence and often dominant contribution. However, the purpose of this discussion is not to define a single optimal conversion factor, but rather to illustrate the substantial impact that different assumptions of fluorine mass fraction can have on the derived PFAS Total concentration.

PFOA was selected in this study as a reference compound in accordance with the EU technical guidelines and due to its well-characterized toxicological and regulatory relevance. It should be noted that PFOA may not reflect the actual composition of the unknown organofluorine fraction in drinking water. Therefore, the use of PFOA as a conversion factor should be regarded as a guideline-consistent choice and not a representative descriptor of the PFAS mixture. These considerations highlight a key limitation of EOF-CIC-based PFAS Total assessment, where the lack of compositional information introduces uncertainty in the conversion from fluorine mass to mass concentration.

3.4 Evaluation of PFAS Total following Technical Guidelines and an improved approach

The evaluation of PFAS Total in drinking water was conducted following the EU technical guidelines⁴⁵. First, EOF-CIC (PFAS Total_{EOF-CIC}) is determined and its concentration converted

into a ng L^{-1} PFOA equivalent (PFAS Total_{EOF-CIC PFOAeq}). Secondly, TFA concentration in the samples (TFA_{target}) were determined separately using a targeted analysis. Subsequently, difference between TFA_{target} was subtracted from PFAS Total_{EOF-CIC PFOAeq} and evaluated whether the results were inconclusive. Using the results of tap water from the Nordic countries in section 3 and tap water from China (Shanghai) in our previous study³¹ as examples, the evaluation of PFAS Total was conducted following the steps described above; the results are summarized in Table 3. In Nordic countries, all samples except for Örebro were compliant for PFAS Total_{EOF-CIC PFOAeq}, while if TFA (TFA_{target}) was subtracted (PFAS Total-TFA), all were below the limit value. Notably, in drinking water samples from China, TFA_{target} alone exceeded the PFAS Total parametric value and subtraction of TFA_{target} led to negative values and therefore should be reported as inconclusive according to the technical guidelines.

Given the fact that TFA alone showed exceedance of PFAS Total, e.g., tap water from China (Shanghai)³¹ and in some samples from Sweden (see table S1) as well as in sources to drinking water in Germany in previous studies^{30,46}, TFA is important in the context of PFAS Total. The approach in EU technical guidelines may lead to inconclusive results due to the difference in TFA recovery in a targeted TFA analysis and EOF analysis, which requires a fluoride removal step that also partly removes TFA. Importantly, the guidance document does not describe what an inconclusive result asserts to and how such results should be handled.

Table 3. The evaluation of PFAS Total following the steps in the EU DWD technical guidelines⁴⁵.

Country	Locations	Step 1	Step 2	Step 3	Step 4
		The determination of PFAS Total _{EOF-CIC}	The determination of TFA using target method	The analytical report*	Recognition of inconclusive results
		[PFAS Total _{EOF-CIC PFOAeq}] (ng L^{-1})	[TFA] (ng L^{-1})	[PFAS Total-TFA] (ng L^{-1})	[PFAS Total-TFA] <500 ng L^{-1}
Sweden (n=3)	Lidköping	464	148	316	OK
	Örebro	508	305	203	OK
	Malmö	296	208	87	OK
Norway (n=2)	Oslo	470	199	271	OK
	Bergen	98.9	94.6	4	OK
Denmark (n=1)	Copenhagen	244	68.3	176	OK
China (n=30) ³¹	Shanghai reservoir D (n=20)	455	1762	-1307	Inconclusive
	Shanghai reservoir C (n=10)	1042	7076	-6034	Inconclusive

*The technical guideline recommends the analytical report to also include PFAS Total_{EOF-CIC}

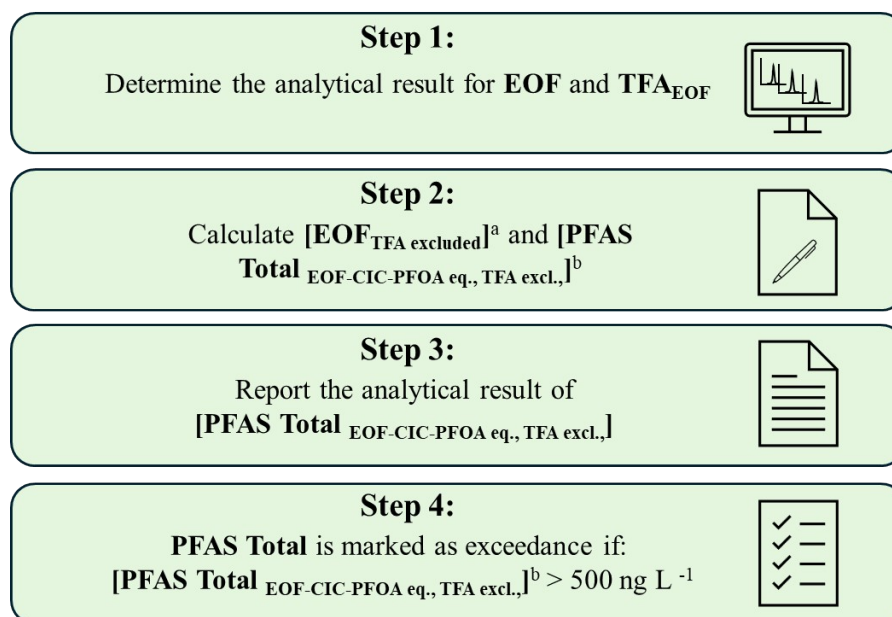
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and $Target_{TFA}$.

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An improved reporting system is proposed to better evaluate PFAS Total_{EOF-CIC} and remove the ambiguity of potential inconclusive results. First, EOF-CIC should be determined according to current technical guidelines, followed by TFA_{EOF} , i.e., concentration of TFA in the EOF-CIC fraction. Subsequently, $EOF_{TFA\ excluded}$, should be calculated by subtracting the fluorine equivalent concentration of TFA_{EOF} from EOF (i.e., subtraction of TFA in the EOF-CIC fraction). Finally, PFAS Total_{EOF-CIC-PFOA eq. TFA excl.} should be evaluated against the PFAS Total parametric value (500 ng L⁻¹). While TFA could be included in a PFAS Total reporting by addition of TFA_{target} concentration to the calculated PFAS Total_{EOF-CIC-PFOA eq. TFA excl.}, given the high concentration of TFA in drinking water, its separation of the PFAS Total limit value is proposed. Thus, TFA is proposed to be evaluated based on its own limit value in drinking water. Though no limit values for TFA in drinking water are in effect on the European level, certain Member States have implemented advisory thresholds (Netherlands, RIVM: 2 200 ng L⁻¹) and health-based guideline values (Germany: 60 000 ng L⁻¹).

Following the above improved steps, the evaluation was updated using the same data as table 3. PFAS Total was below 500 ng L⁻¹ in tap water samples from Nordic countries and was above the parametric value in tap water from reservoir C, Shanghai. Because the TFA_{target} subtraction of PFAS Total was replaced with TFA_{EOF} subtraction, the potential for inconclusive results is eliminated. A summary of the improved workflow to assess PFAS Total under the EU DWD is presented in figure 2.



Note: ^a: $EOF_{TFA\ excluded} = EOF - n_{F(TFA)} \times MW_F / MW_{TFA} \times TFA_{EOF}$;

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$$b. PFAS\ Total_{TFA\ excluded, PFOA\ eq} = EOF_{TFA\ excluded} \times MW_{PFOA} / (n_F(PFOA) \times MW_F);$$

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Figure 2. An improved approach for reporting PFAS Total based on EOF-CIC method.

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Table 4. Evaluation of PFAS Total_{EOF-CIC} based on the improved approach

Country	Locations	Step 1			Step 2	Step 3		Step 4	
		The determination of EOF, TFA _{target} and TFA _{EOF}			The calculation of EOF _{TFA excluded}	The analytical report		Recognition of exceeding results	
		[EOF]	[TFA _{target}]	[TFA _{EOF}]	[EOF _{TFA excluded}]	[PFAS Total _{TFA excluded, PFOA eq}]	[TFA _{target}]	[PFAS Total _{TFA excluded} <500 ng L ⁻¹]	[TFA _{target} <2200 ng L ⁻¹]
		(ng F L ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)	(ng F L ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)		
Sweden (n=3)	Lidköping	319	148	44.6	297	431	148	OK	OK
	Örebro	350	305	95.7	302	438	305	OK	OK
	Malmö	203	208	41.8	183	265	208	OK	OK
Norway (n=2)	Oslo	324	199	128	260	377	199	OK	OK
	Bergen	68.1	94.6	59.7	38.3	55.6	94.6	OK	OK
Denmark (n=1)	Copenhagen	168	68.3	7.42	164	239	68.3	OK	OK
China (n=30) ³¹	Shanghai reservoir D (n=20)	313	1762	76	275	399	1762	OK	OK
	Shanghai reservoir C (n=10)	717	7076	150	642	933	7076	Exceedance	Exceedance

Note: EOF-related parameters are expressed as fluorine equivalents (ng F L⁻¹), while TFA and PFAS Total values are expressed as mass concentrations (ng L⁻¹).

3.5 Understanding exceedance of PFAS Total parametric value

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Any exceedance of the DWD PFAS Total parametric value must be investigated according to procedures implemented by affected drinking water works. In the following section, potential reasons for exceedance, including the potential of false positive results, are discussed.

Given the EOF-CIC methods' broad coverage i.e., its aggregation of all extracted fluorine species into a single fluoride concentration, overestimation of PFAS Total can occur. Presence of organofluorines, other than PFAS, may inflate and lead to a false exceedance of the Directive's PFAS Total parametric value. For example, CF groups are common in agrochemicals⁴⁷ and pharmaceuticals⁴⁸ and may fall outside of the Directive's definition of a PFAS. In fact, a large range of fluorinated pesticides and pharmaceuticals have been shown to be quantitatively recovered in wastewater using EOF-CIC methods⁴⁹. Moreover, while the inorganic compounds BF_4^- and PF_6^- were not detected in samples from the Nordic countries in the current study. In contrast, in the samples from Shanghai³¹, they were shown to substantially contribute to the fluorine mass balance with BF_4^- accounting for 3-40% and PF_6^- 24-82%. To further verify the extraction recoveries of inorganic species and fluorinated pharmaceuticals in tap water, follow-up spike tests were performed. These experiments showed that PF_6^- was recovered quantitatively (76-78%) using WAX sorbent, while a minor fraction (12%) was recovered with an HLB sorbent method. In contrast, BF_4^- recovery was 5-45% with WAX and <1% with HLB. Moreover, selected fluorinated pharmaceuticals (n=6), including mono-fluorinated, and one pesticide displayed a recovery between 60-108% (HLB) and 24-103% (WAX), demonstrating that also low-fluorinated compounds may be recovered in tap water using common EOF-CIC extraction methods. Detailed information of the spike tests together with recovery data of perfluorinated acids and precursors can be found in SI tables S9-11. Notably, BF_4^- and PF_6^- were recently detected in tap water from Stockholm⁵⁰, and another inorganic anion, hexafluoroarsenate (AsF_6^-) was detected in European wastewater⁵¹, underscoring the importance of inorganic fluorinated compounds in the context of European drinking water. Although there are known industrial uses of these anions, e.g., lithium-ion batteries⁵² and various other industrial and consumer product applications, it remains unclear to what extent they occur naturally in the environment. For example, BF_4^- has been shown to occur naturally in areas around volcanoes. In particular, in hot spring water from the island of Iwo-Jima⁵³, up to nearly 50% of fluoride was detected as BF_4^- at a concentration of 7 mg L⁻¹. For the two other anions mentioned here (PF_6^- and AsF_6^-), their natural formation and occurrence remain largely unknown. Further monitoring data is required to understand the contribution of these species to EOF-CIC measurement of European drinking water.

Furthermore, it should be noted that the unidentified organofluorine (UOF) fraction derived

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3 from EOF-CIC analysis cannot be assumed to represent unknown PFAS exclusively. Instead, it may comprise of a mixture of PFAS, non-PFAS organofluorine compounds (e.g., fluorinated
4 pharmaceuticals and pesticides), and potentially inorganic fluorinated species. Therefore, UOF
5 should be interpreted as a method-defined parameter rather than a direct surrogate for unknown
6 PFAS, highlighting the need for further chemical characterization of this fraction.
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12 A “true” exceedance of PFAS Total via EOF-CIC proxy presents unique challenges in how to
13 remediate a non-compliant water supply as physicochemical properties of the compound(s)
14 driving the exceedance is not known. Thus, without knowing the chemicals’ identity, actions
15 targeting a certain removal technique relying on certain physicochemical properties may or may
16 not be successful. In general, it is likely necessary to further elucidate the chemical properties
17 via identification of the unknown compound(s) to better implement corrective actions. For
18 example, in conjunction with a source investigation aimed to understand local potential point
19 sources of an affected water supply, a targeted analysis of e.g., the Directive’s “Sum of PFAS”,
20 combined with an expanded list of analytes, could be performed. Furthermore, more extensive
21 analysis could involve e.g., TOP assay^{54, 55}, or advanced identification techniques based on
22 HRMS⁵⁶⁻⁵⁸ or fluorine nuclear magnetic resonance (¹⁹F-NMR) spectroscopy⁵⁹. The latter has
23 seen recent advancements in sensitivity, which can be especially useful for drinking water
24 where organofluorine contaminants may be expected to be present at relatively low
25 concentrations. For example, ¹⁹F-NMR has been used to identify and characterize
26 organofluorine not detected by targeted PFAS analysis, including wastewater, surface water,
27 rainwater and biological samples^{48, 60}. These applications demonstrate the potential of ¹⁹F-NMR
28 as a complementary technique for assessing unknown organofluorine in environmental samples.
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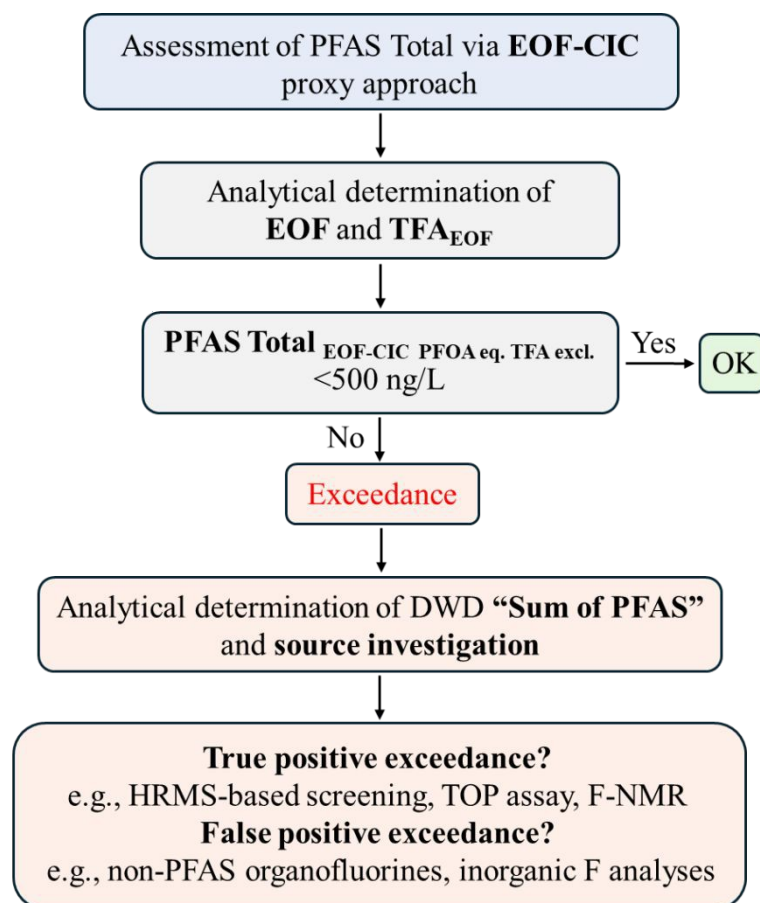


Figure 3. A possible workflow for assessment of PFAS Total by EOF-CIC and actions following exceedance.

4 Conclusions and perspectives

Evaluation of PFAS Total proxy determination using EOF-CIC, following the EU technical guidelines, indicates that the method in its current form carries a risk of inconclusive results due to its limited ability to accurately assess and include TFA in the PFAS Total determination. To address this limitation, an alternative workflow was developed in which TFA is quantified separately within the EOF fraction and excluded from the PFAS Total calculation. This approach streamlines reporting and reduces the risk of inconclusive interpretation. The separation of TFA from the PFAS Total parametric value is further supported by its low extraction recovery in EOF-CIC and its widespread occurrence in drinking water at concentrations that warrant consideration of a separate guideline value.

The EU technical guidelines for methods of analysis of PFAS Total state that EOF-CIC should not be used as a direct quantitative method but rather as a proxy. Understanding the suitability of EOF-CIC as a proxy therefore requires careful consideration of its limitations. Due to its non-specific nature, EOF-CIC may overestimate PFAS Total by including contributions from non-PFAS organofluorine or inorganic fluorinated compounds. Conversely, the low recovery

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of TFA suggests that other highly polar PFAS with similar physicochemical properties may also be poorly recovered, potentially leading to underestimation of PFAS Total. Although recent methodological improvements have increased TFA recovery, a robust extraction or preconcentration approach capable of quantitatively retaining very polar PFAS while simultaneously excluding inorganic fluorine remains a key development need. Further methodological advances are also required to better differentiate low-fluorinated organofluorine compounds from highly fluorinated species, such as perfluoroalkyl acids, to improve the accuracy of PFAS Total determination by EOF-CIC.

In addition, validation of method specificity and selectivity ultimately depends on clarity regarding which compounds are considered PFAS. Clear definition of PFAS for the purpose of the PFAS Total parametric value is therefore essential. More extensive interlaboratory trials are also needed to evaluate method accuracy and precision in drinking water and to establish realistic practical detection limits.

Taken together, the inherent characteristics of EOF-CIC suggest that it may be more appropriate to treat the method as a method-defined EOF parameter, primarily serving as a screening and early-warning tool. While its broad analytical scope presents challenges for direct regulatory compliance, it enhances the method's value for identifying potential fluorinated contamination and informing risk assessment, without imposing immediate legal consequences.

Although it is outside the scope of this study to evaluate other potential approaches for PFAS Total within the scope of the EU DWD, it is important to acknowledge that other, alternative analytical techniques may be more suitable or complementary in certain contexts. For example, a TOP assay approach addresses several key limitations of EOF-CIC including reducing uncertainty associated with precursor compounds and avoiding the need to derive a fluorine mass percentage for conversion to the parametric value, as required in the EOF-CIC approach. However, it should be noted that the TOP assay is limited to oxidizable precursors and does not capture all PFAS. Other approaches, e.g., AOF-CIC, likely exhibits similar limitations to EOF-CIC because of its broad, non-specific coverage, including potential contributions from non-PFAS organofluorine compounds and incomplete recovery of highly polar species.

Future methodological improvements should focus on enhancing extraction strategies to improve retention of highly polar PFAS (e.g., TFA) while effectively removing inorganic fluorides, as well as developing approaches that better constrain the composition of the measured organofluorine fraction. In this context, combining multiple analytical approaches (e.g., EOF-CIC, TOP assay, and targeted analysis) may provide a more comprehensive



understanding of PFAS occurrence and improve confidence in PFAS Total assessments.” View Article Online
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Supporting information

*Information on chemicals, instrumental settings, example chromatograms of TFA, results from TFA screening of Swedish and Norwegian drinking water samples, extraction recovery test can be found in supporting information (docx)

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Data Availability Statement

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The data supporting this article have been included in the tables in the main manuscript and the supplementary information. Further data are available upon request.

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