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Review

A systematic review of methods for the analysis of total per- and polyfluoroalkyl substances (PFAS)

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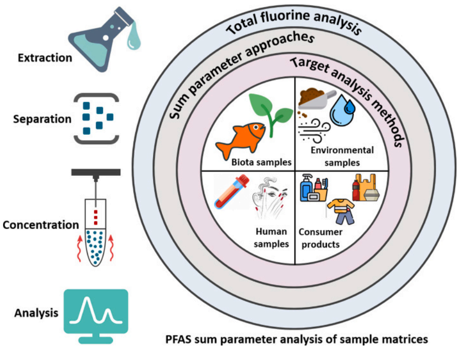
HIGHLIGHTS

- 156 articles on total PFAS identified by systematic review following PRISMA
- Total PFAS concentrations reported in varied units complicate interstudy comparisons
- TF (38% of studies) most reported parameter, followed by EOF (34%), and TOPA (31%)
- CIC (53% studies) most used analytical method, followed by TOPA by LC-MS/MS (31%), and PIGE (9%)
- Over 10 different calculations used to estimate total PFAS concentrations and mass balance

GRAPHICAL ABSTRACT



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ABSTRACT

This manuscript systematically reviews 156 peer-reviewed articles on methods for estimating total per- and polyfluoroalkyl substances (PFAS), following preferred reporting items for systematic reviews and meta-analyses (PRISMA) guidelines. Direct and indirect methods of estimating total PFAS include targeted analysis, total fluorine (TF), total organic fluorine (TOF), extractable organic fluorine (EOF), absorbable organic fluorine (AOF), and total oxidizable precursor (TOP) assay. Combustion ion chromatography (CIC) was the most utilized method (>50%), followed by particle-induced gamma-ray emission (PIGE, 9%) and high-resolution-continuum source graphite furnace molecular absorption spectrometry (HR-CS-GFMAS, 6%). Techniques like instrumental neutron activation analysis (INAA) and nuclear magnetic resonance (NMR) were less common.

A geographic bias was evident, with 69% of studies from the US (33%), Sweden (12%), China (12%), and Germany (11%). Most research targeted environmental samples (water, soil, sediments), while significant data gaps were noted in South America, Africa, and atmospheric PFAS. Challenges in inter-laboratory comparisons arise from inconsistent reporting units (e.g., mg/L, μg/m^3, %, etc.). About 75% of studies involved pre-treatment

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(e.g., solvent extraction, sorbents), while 25% did not. PFAS detection limit and observed concentrations varied widely, from low concentrations in water (ng/L) to higher levels in soil, biota, and products (mg/L).

Limitations of total PFAS methods include contradictory results when complementary techniques are applied to the same sample, potentially leading to over- or under-estimation. Across studies, a substantial fraction of TF remains unaccounted for, highlighting the need for non-targeted screening (NTS) to identify unknown PFAS (UPFAS or UOPFAS). Bridging these gaps is critical for advancing PFAS research and environmental risk assessment.

1. Introduction

Based on a revised definition by the Organization for Economic Cooperation and Development (OECD) in 2021, "per- and polyfluoroalkyl substances (PFAS) *are fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group* ($-CF_3$) *or a perfluorinated methylene group* ($-CF_2-$) *is a PFAS*" (Wang et al., 2021b; OECD, 2021). The newly revised definition contains over 7 million PFAS out of the 116 million compounds in PubChem (Schymanski et al., 2023). Over 4700 of these are likely of commercial importance (Wang et al., 2021b). Fluorinated compounds in the atmosphere occur as inorganic and organic compounds but primarily in mineral form. They originate from natural sources such as soil dust, marine aerosols, and volcanic eruptions (Jayarathne et al., 2014). Once in the atmosphere, these particles travel in gas and particle phases, depositing far from their sources through atmospheric deposition processes like rain, snow, and dust. Fluoride is a critical atmospheric pollutant, requiring comprehensive monitoring in air and deposition pathways due to its ubiquitousness. Distinguishing between natural and anthropogenic fluorinated compounds, particularly PFAS, is essential. Lin et al. (2022) pioneered efforts to quantify PFAS contributions to total organic fluorine in the atmosphere, advancing understanding of their environmental impact. Owing to their unique performance properties, such as stain resistance, water repellence, improved performance in electronics, and fire retardance, Glüge et al. (2020), PFAS have been utilized in numerous industrial and consumer applications. These include their utilization in oil and gas industries, semiconductors, aerospace, electronics manufacturing, coating products, cosmetics, pesticides, and pharmaceuticals.

The widespread occurrence and persistence of PFAS, especially long-chain perfluoroalkyl acids (PFAAs), have raised significant environmental and public health concerns. In response, global regulatory measures are being implemented to address the risks posed by PFAS contamination (Brennan et al., 2021; Schiavone and Portesi, 2023). For example, the Stockholm Convention on Persistent Organic Pollutants has sought to phase out or restrict the production and use of certain PFAS compounds, emphasizing the need for comprehensive monitoring and management strategies (UNEP, 2009). Also, the U.S. Environmental Protection Agency recently established maximum contaminant levels (MCLs) of 4–10 ng/L for certain PFAS in drinking water (including PFOA (perfluorooctanoic acid), PFOS (perfluorooctane sulfonic acid), (PFHxS perfluorohexanesulfonic acid), perfluorohexanoic acid (PFHA), and hexafluoropropylene oxide-dimer acid (HFPO-DA or GenX)), and set a hazard index of 1 (unitless) for mixtures of two or more of PFHxS, perfluorononanoic acid (PFNA), HFPO-DA, and perfluorobutane sulfonic acid (PFBS) (US EPA, 2024). In Europe, the Drinking Water Directive (2020/2184/EU) limits the sum of all targeted PFAS to 0.1 μg/L and total PFAS to 0.5 μg/L and requires member states to enforce these thresholds in national laws by 2023 (Shelor et al., 2024; Thomas et al., 2023). Additionally, new consumer products in the EU must meet specific limits of <25 ng/g for individual PFAS, <250 ng/g for the sum of target PFAS, and < 50 μg/g for total PFAS/total fluorine, including polymeric PFAS (Shelor et al., 2024, Thomas et al., 2023).

There is a growing recognition of the need for "total PFAS" analysis, which aims to capture the occurrence and potential risks of the entire class of PFAS (Androulakakis et al., 2022; Brunn et al., 2023). There are currently two approaches to achieving this: direct (specific) methods that target and quantify individual PFAS compounds, and indirect (non-specific) methods that measure parameters, such as total fluorine, to infer PFAS concentrations.

The simplest direct total PFAS method requires the summation of all PFAS concentrations measured from a targeted study and reporting as a total PFAS value. However, we have not included a detailed discussion on this method as we do not accept it as a viable way of reporting total PFAS concentrations due to the vast number of PFAS that need to be monitored. To overcome this limitation, the development of the total oxidizable precursor (TOP) assay (an indirect approach) using strong oxidizing agents like persulfate at high temperatures converts PFAS precursors into measurable terminal perfluorinated acids. The oxidation products are then analyzed by targeted methods such as liquid chromatography coupled with high-resolution or tandem mass spectrometry (LC-QTOF/MS, LC-orbitrap/MS, LC-MS/MS) or gas chromatography–mass spectrometry (GC–MS) to calculate a total PFAS concentration inclusive of precursors (Maldonado et al., 2022; Nickerson et al., 2020; Shojaei et al., 2022). A limitation of this method is the incomplete precursor conversion during the transformation process (Nikiforov, 2021). Another viable option used in total PFAS estimation by direct measurement involves non-targeted analysis (NTA) using high-resolution-mass spectrometry (HRMS)-based suspect and non-targeted screening methods. These methods quantify concentrations of individual PFAS in a sample; however, they are susceptible to errors as they do not account for all PFAS in a sample. Additionally, there are significant challenges with quantification due to a lack of commercially available standards for PFAS. These methods have been systematically reviewed in detail by Megson et al. (2025) as part of our complementary study, and so are not discussed further in this manuscript.

In indirect total PFAS analysis, individual PFAS compounds are not quantified; instead, the total fluorine (TF) content is measured after separation from the inorganic fraction. Various analytical techniques have been developed to characterize total PFAS; thereby, the gap in PFAS mass balance is bridged, and unknown, toxic, and persistent compounds are addressed (Gehrenkemper et al., 2021). The accuracy of these methods relies on effective sample preparation, appropriate solid-phase extraction (SPE) sorbents, and instrument capabilities. TF analysis, which quantifies organic and inorganic fluorine (IF), provides a broad overview of the fluorine content in samples (Roesch et al., 2024; Shen et al., 2023). Within this framework, Total Organic Fluorine (TOF) analysis and its derivatives – Extractable Organic Fluorine (EOF) and Adsorbable Organic Fluorine (AOF) – have been widely employed to measure total PFAS parameters (von Abercron et al., 2019; Nikiforov, 2021). TOF measures overall organic fluorine content, estimating the total PFAS burden; however, it should be noted that not all organic fluorine is regarded as PFAS (Lin et al., 2022; Liu et al., 2024a), while EOF and AOF isolate extractable and adsorbable fractions, respectively, for deeper insights into PFAS composition. For AOF determination, granular activated carbon (GAC) is commonly used, capturing all PFAS in a liquid matrix that adsorbs onto GAC (Forster et al., 2023; Gehrenkemper et al., 2021; Han et al., 2021). The range of PFAS detected with EOF depends on the SPE sorbent; WAX (weak anion exchange) sorbents are commonly used for selective extraction of anionic PFAS, but cationic, zwitterionic, or neutral PFAS could also be retained. For instance, recoveries of zwitterionic PFAS and neutral fluorotelomer alcohols by WAX have been reported at 77–87% and 48–55%, respectively (Boronow et al., 2019; Forster et al., 2023; Liu et al., 2024a). In contrast, HLB (hydrophilic-lipophilic balance) sorbents extract a broader PFAS spectrum due to their diverse retention mechanisms (Forster et al., 2023; Gehrenkemper et al., 2021; Metzger et al., 2019).

In the case of fluorine analysis for total PFAS determination, Combustion Ion Chromatography (CIC), and particle-induced gamma-ray emission (PIGE) techniques are widely used (Boronow et al., 2019, Forster et al., 2023, Liu et al., 2024a). Other less commonly applied instrumental techniques include high-resolution-continuum source graphite furnace molecular absorption spectrometry (HR-CS-GF-MAS) (Metzger et al., 2019), instrumental neutron activation analysis (INAA) (Muensterman et al., 2022), cyclic neutron activation analysis (CNAA) (Liu et al., 2020), fluorine nuclear magnetic resonance spectroscopy (^{19}F NMR) (Camdzic et al., 2023), x-ray photoelectron spectroscopy (XPS) (Wu et al., 2021), ion-selective electrode (ISE) (Gan et al., 2022), and inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) (Koch et al., 2020; Shen et al., 2023). These nuances in sample preparation and analysis indicate inequality in total PFAS methods.

While various excellent reviews on total PFAS parameters exist (Androulakakis et al., 2022; Ateia et al., 2023; Brunn et al., 2023; De Silva et al., 2021; Koch et al., 2020; McDonough et al., 2019; Shelor et al., 2024; Shen et al., 2023; Trojanowicz et al., 2011), they are either critical or opinion-based reviews, highlighting the need for a systematic evaluation. This manuscript, therefore, provides a systematic overview of total PFAS parameter research, assessing trends by sample type and geography. We examine analytical techniques for total PFAS parameters, covering sample preparation, instrumental analysis, quality control, and data analysis. Findings detail PFAS concentrations in different matrices, mass balance, quantification methods, and complementary analyses.

2. Methodology

2.1. Study selection

This systematic review was undertaken in line with the guidelines set by the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) (Page et al., 2021). The details of the study selection are provided in the Supplemental information (Fig. 1, Table S1).

2.2. Data collection

Data collection was focused on three areas: sample information, sample analysis, and data reporting. Information obtained about sample information includes the location of the study, sample type (matrix), sample year, and sample size (when available). Sample analysis information includes the sample processing (extraction method) and cleanup method, an instrument used for total PFAS determination, data processing method (formulas), QA/QC for calibration and validation, and detection limits when provided. Total PFAS concentrations were reported as TF, TOF, EOF, AOF, and hydrolyzable organic fluorine (HOF) for data reporting. Mass balance was also reported in articles where targeted PFAS analysis was quantified. Other complementary analyses reported in articles included inorganic fluorine (IF), non-extractable organic fluorine (NEOF), and nontargeted analysis (NTA). The detailed data collected are tabulated in the supplementary information (SI, Table S1).

3. Investigated sample types

3.1. Geographical location

Fig. 2 highlights eighteen (18) geographical locations worldwide where total PFAS concentrations have been reported. The majority of studies obtained samples from the United States (33%), followed by

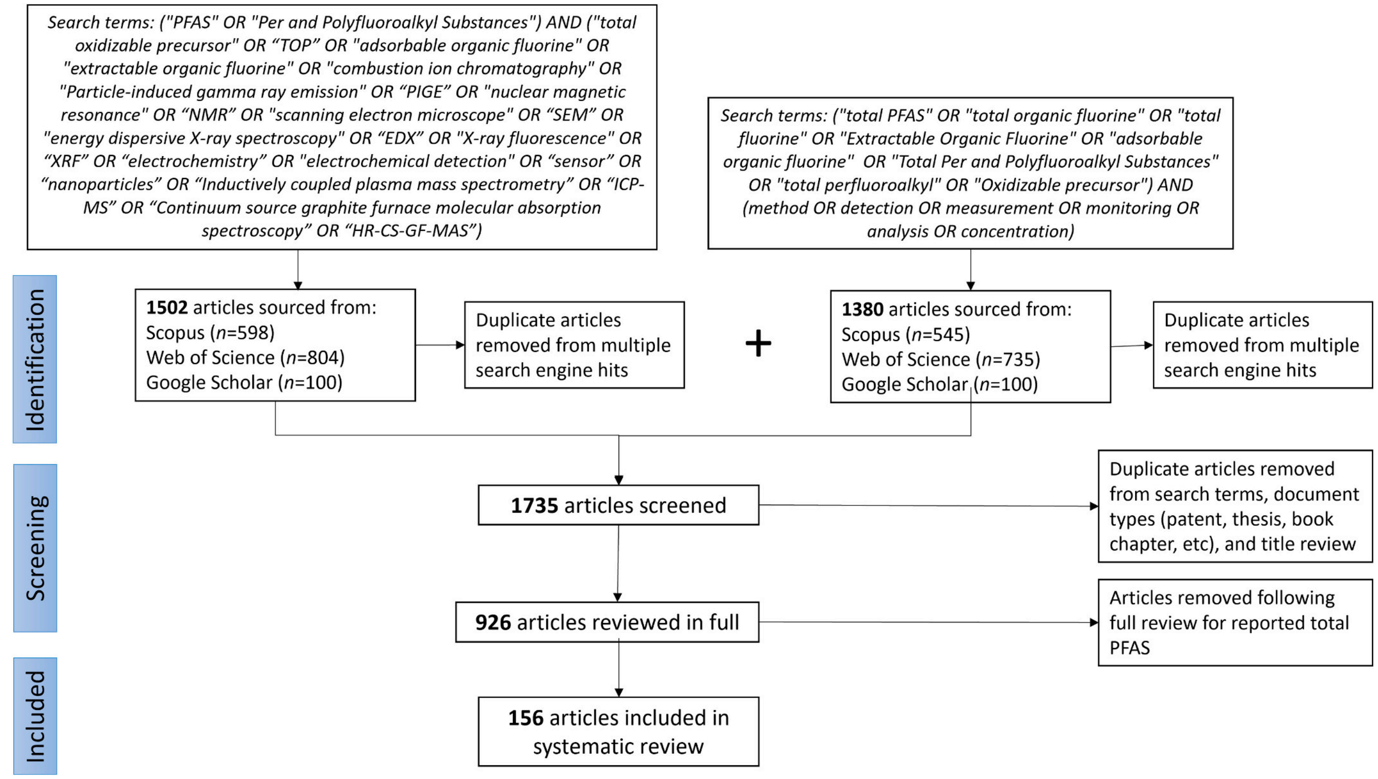

Fig. 1. Flow chart of manuscript identification, screening, and final selection process.

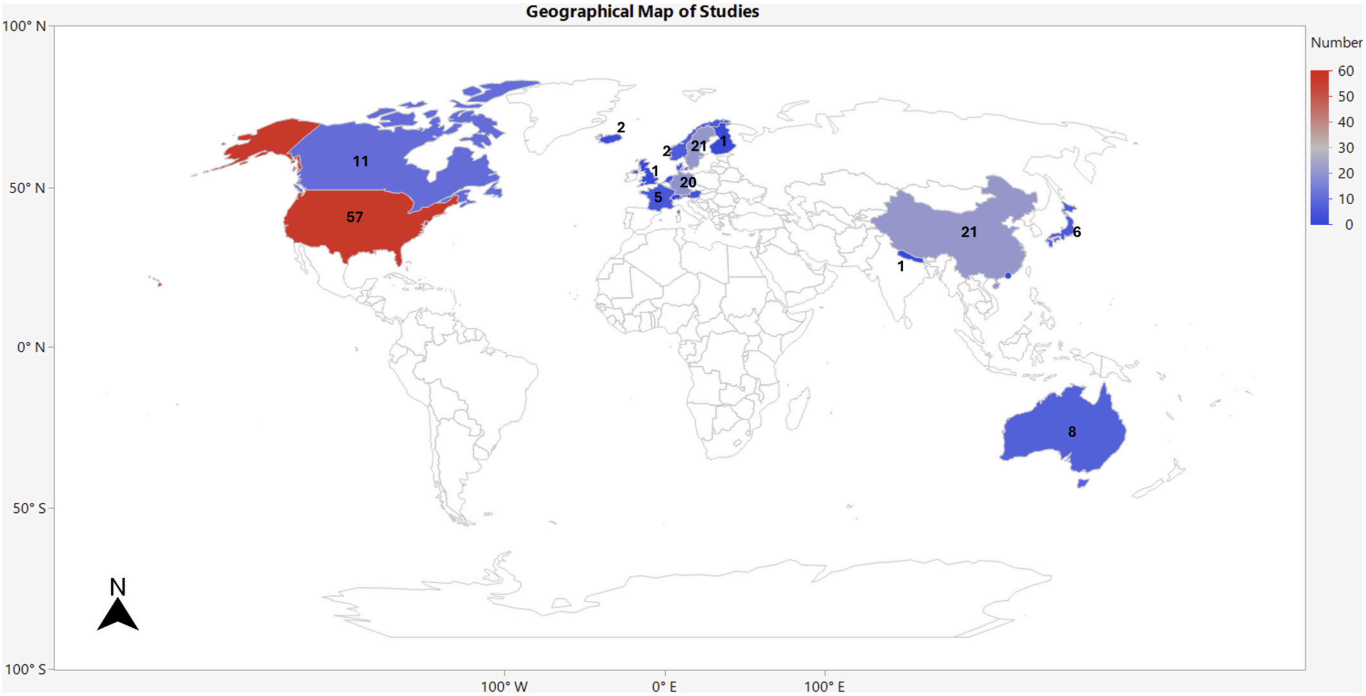

Fig. 2. The geographical location of the studies reviewed.

Sweden (12%), China (12%), and Germany (11%). North America, represented solely by the U.S. and Canada, accounted for 40% of the studies, while Europe contributed 33%, primarily from Sweden and Germany. Asian studies came from China, Japan, Hong Kong, and Nepal, with China comprising 70% of the region's data. Oceania contributed <5%, with eight studies from Australia. Transboundary studies included samples from Greenland and the U.S. Atlantic coast. No studies were identified from Africa, South America, or Antarctica, indicating a geographical bias toward Europe, North America, and Asia.

3.2. Sample type and sources

Water was the most studied sample type in this review, representing 34% of the articles. These included wastewater (effluents and influents from wastewater treatment plants, landfill leachate, and sewage) and "surface, groundwater, and drinking water" (lake water, river water, drinking water, surface water, seawater, groundwater, and brackish water surface). Seventeen (17) studies reported total PFAS in wastewater, and thirty-four (34) studies in surface, groundwater, and drinking water. Soils, sediments, and sludges comprised 26% (40/156) of studies. Samples in this category included soil samples, sediment cores, suspended particulate matter (SPM), sludges, and suspended solids.

Plants and animals were analyzed in 21/156 studies, with most focusing on fish and aquatic animals, and 2/156 studies examined blood from wild mammals (wild rats, mice, and whales). Five (5) studies provided concentrations in plants. 81% of the studies predominantly analyzed fish and other aquatic animals (16 studies). Human samples (blood, serum, placenta) were analyzed in 11/156 studies, primarily from Europe, the US, and Asia, while one study reported PFAS in human hair and nails.

The following industrial and commercial products were evaluated: AFFF (11 studies), textiles, paper, and food packaging (19 studies), and cosmetics and personal care products (5 studies). The atmosphere was studied less, with only four (4) articles on dust, three (2) on air samples, and one study on the WWTP stack gas. Similarly, two (2) studies analyzed total PFAS in food materials (e.g., tea and pet food). Other studies (13/156) analyzed total PFAS in dental floss, insecticides, face-mask photolithography materials, field sampling materials, solid ski wax, snowmelt, artificial turfs, fire suppression pipes, textile finishing agents and surfactants, technical mixture, and lubricating oil.

Table 1 summarizes the number of articles reported for each sample group. In summary, the main trend observed based on the data gathered for sample matrices shows sample size: water > soil, sediments, suspended solids, and sludges > Plants and animals > Textiles, paper, and food packaging > Aqueous firefighting foam (AFFF) > Human samples > Air/Dust/Gas > Cosmetics and personal care products.

4. Sample analysis, QA/QC, and data processing

4.1. Total PFAS methods

Sample preparation is a critical step in analytical method development, as it isolates analytes from matrix components that may interfere with the analysis (Wells, 2013) and adjusts analyte concentrations to a suitable range.

PFAS is typically measured by two approaches: direct (specific) and indirect (non-specific) methods (Fig. 3). Specific methods include targeted PFAS analysis and suspect/non-target (SNT) PFAS analysis. The PFAS-specific method evaluates the individual PFAS compounds or compound classes. In contrast, non-specific methods evaluate an alternative approach to fluorine content in matrices. These encompass TF, TOF, EOF, AOF, TOP assay, and HOF. Some methods, such as targeted/

Table 1
Summary of the significant sample matrix group in the review.

Sample group	Number of articles
Water samples (general)[a]	53
Soil, sediments, and sludges	40
Plants and Animals	21
Textiles, paper, and food packaging	19
Human blood/serum, placenta, hair and nails	12
Aqueous firefighting foam (AFFF)	11
Air/Dust/Gas	7
Cosmetics and personal care products	5

[a] Several studies simultaneously investigated multiple matrix types (e.g., wastewater, surface water, etc.).

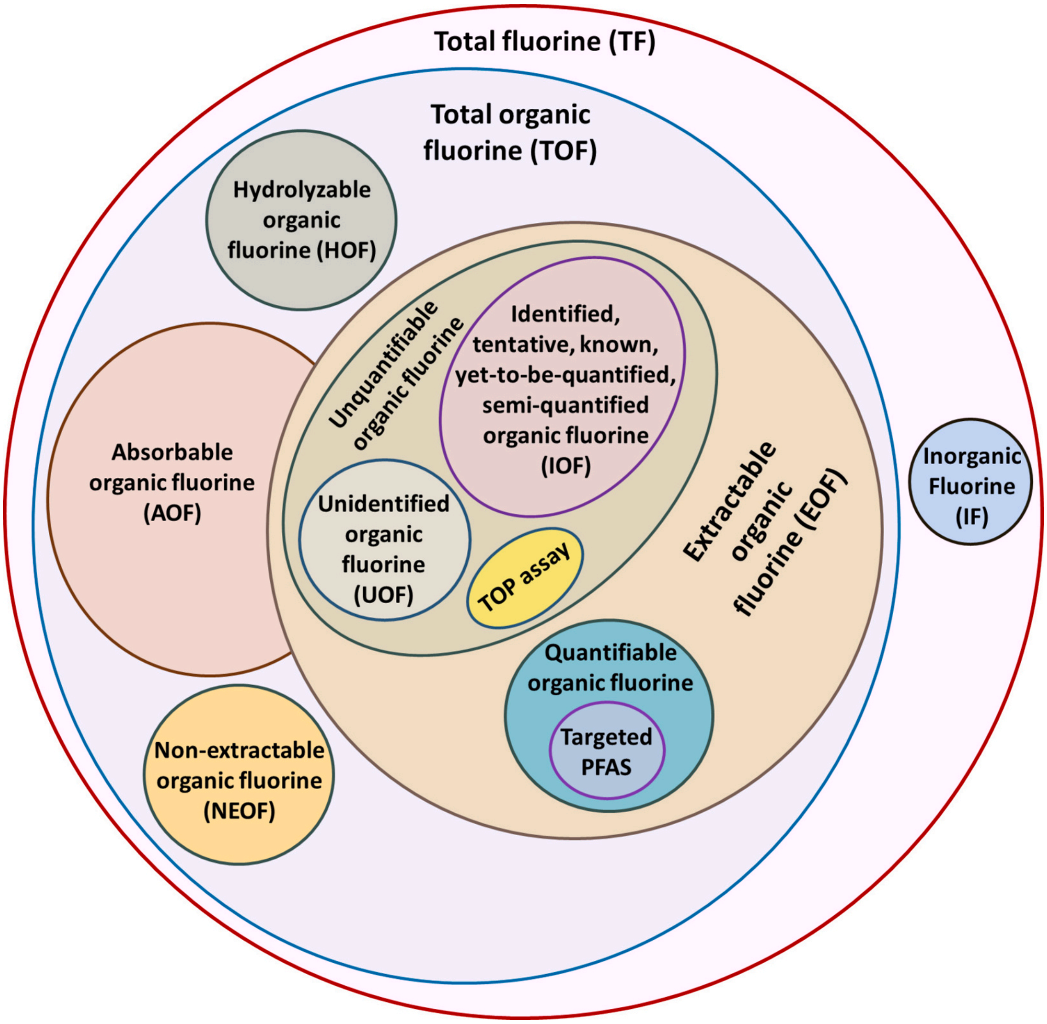

Fig. 3. An illustrative diagram showing the concept of total PFAS parameters.

SNT PFAS, TOP assay, and EOF, share similar extraction procedures, whereas others may not require sample preparation. Fig. 4 shows the conceptual workflow for assessing total PFAS parameters in various sample matrices.

4.1.1. *Direct (specific) PFAS methods*

The direct or specific PFAS methods measure known individual PFAS compounds or compound classes. The methods classified in this group include targeted PFAS analysis and SNT PFAS analysis. Targeted PFAS analysis is deemed insufficient for evaluating total PFAS concentrations in sample matrices. Hence, the sample preparation method for targeted PFAS analysis is not discussed here. However, it shares the same extraction procedure as EOF, which will be discussed later in this review. Due to the limitations of targeted PFAS analysis in capturing total PFAS, complementary techniques such as SNT analysis, TOP assay, and organofluorine analysis have been employed to detect additional PFAS compounds and concentrations. SNT analysis provides broader screening capabilities by detecting known and unknown PFAS compounds without requiring prior knowledge of specific analytes. This method enhances PFAS detection by relying on advanced analytical tools, such as HRMS, for comprehensive identification and quantification of PFAS compounds across diverse sample matrices. This was extensively reviewed in our recently published study (Megson et al., 2025).

4.1.2. *Indirect (non-specific) PFAS methods*

Non-specific or indirect PFAS methods are an alternative approach to evaluating PFAS concentration in different sample matrices. This includes the evaluation of parameters such as TF, TOF, EOF, AOF, IF, TOP assay, and HOF), etc. Depending on the method adopted, these methods can evaluate all fluorine/fluoride content, including those related to PFAS and non-PFAS substances.

4.1.2.1. Total oxidizable precursor (TOP) assay. The TOP assay is a notable example of an indirect PFAS method due to its reliance on chemical transformation to detect precursor PFAS compounds. While the TOP assay can complement target analysis by enhancing PFAS detection, its effectiveness depends on the target precursor compound class. The TOP assay converts PFAA precursors into quantifiable perfluorinated carboxylic acids (PFCAs) via hydroxyl radical-based oxidation. Persulfate is activated at 85 °C, producing sulfate radicals ($SO_4{\bullet}^-$), which react with hydroxide ions (OH^-) in alkaline conditions to generate hydroxyl radicals (•OH). These hydroxyl radicals are the primary oxidants responsible for the oxidative transformation of PFAA precursors into PFCAs. If PFAA precursors are present, the concentrations of PFAAs increase after oxidation, with the yield dependent on the specific precursor structure and reactivity (Houtz and Sedlak, 2012). A key parameter is pH, as acidic or neutral conditions can degrade PFCAs (Fan et al., 2021). Alkaline pH is critical, as it promotes the generation of hydroxyl radicals, while PFCAs remain stable under the conditions used in the TOP assay (Houtz and Sedlak, 2012). Pre- and post-oxidation of

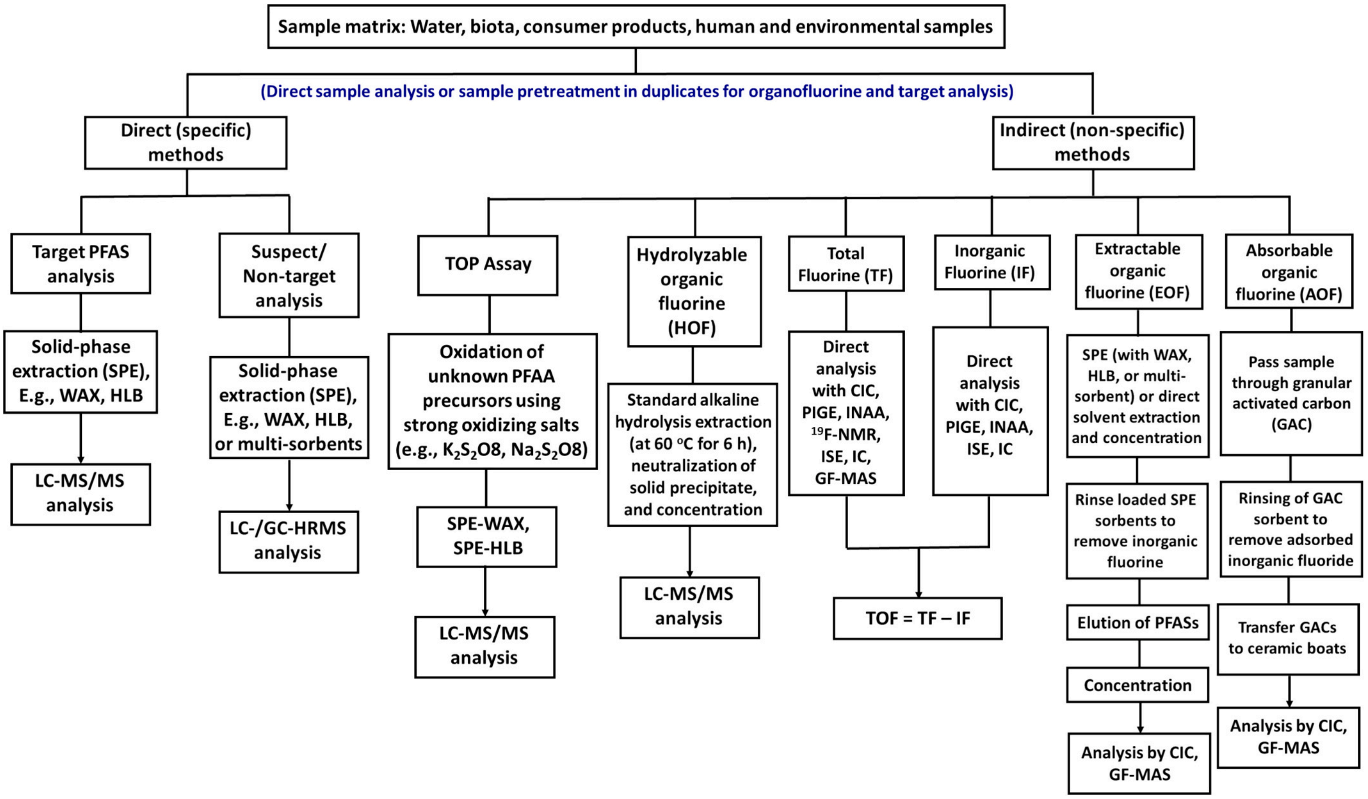

Fig. 4. Conceptual workflow for a systematic assessment of total PFAS parameters in various samples.

PFAS are measured using conventional LC-MS/MS techniques. To enhance PFAS detection and quantitation in sample matrices, Houtz and Sedlak (2012) developed the TOP assay using urban runoff samples. In our review, 48/156 studies used the TOP assay alongside targeted PFAS analysis, representing about 31% of our studies. The analysis was primarily reported in water samples (38%). In contrast, other sample matrices include soil, sediment, suspended solids and sludges (27%), industrial and personal care products (21%), landfill leachate (10%), biota, and paper/textile samples, each representing 6% of the studies reporting concentrations based on TOP assay, blood/serum samples (4%), two (2) studies investigated plants (4%), while one study each investigated house dust and pet food (2% in each case).

While the original TOP assay applied oxidation before sample SPE extraction, some studies, like Houtz et al. (2013), suggest post-extraction oxidation to minimize matrix effects (Houtz and Sedlak, 2012). Although post-extraction oxidation can minimize matric effects, it may also weaken the capture of non-anionic PFAS during SPE. Therefore, the use of more effective oxidation methods, such as a more concentrated oxidant and a UV-light/sulfite system, in the pre-extraction, is suggested. Göckener et al. (2021) demonstrated the use of a more concentrated oxidant to improve precursor extractability and oxidation efficiency(Göckener et al., 2021). Alternatives to thermal activation include a UV-light/sulfite (Fan et al., 2022; Tenorio et al., 2022) and the use of ozone as an oxidant at pH 7(Kaiser et al., 2021).

Despite its broad application, the TOP assay may overlook certain terminal products, and its ability to measure total PFAS is limited by the number of detectable PFAAs, incomplete oxidation of some precursors, and matrix effects (Guelfo et al., 2021). Ateia et al. (2023) highlighted these technical challenges in detail.

4.1.2.2. Total fluorine (TF) and total organic fluorine (TOF). TF analysis is straightforward and requires no sample pre-treatment. Solid or small-volume liquid samples are combusted at high temperatures for direct instrumental analysis. In this review, TF concentrations were reported in 38% of studies, primarily in textile, paper, industrial and personal care products, representing 53% of the total studies reporting TF concentration. TF was also measured in human and mammalian samples (i.e., blood/serum, hair, nails, 7%), soil, sediments, suspended solids and sludges (13%), biota (including plants, 15%), and surface, groundwater and wastewater (13%) samples. Dust, food materials (e.g., tea), and air (including stack gas) samples together accounted for 10% of studies reporting TF concentrations in the literature. It is important to ensure that TF measurements are IF-free to avoid positive bias.

TOF concentrations were less frequently reported, with 10/156 studies documenting TOF in nine (9) different sample matrices. Direct TOF determination is uncommon because current organofluorine analysis techniques cannot differentiate between organofluorine compounds and IF. The relationship between TF, IF, and TOF is given by TOF = TF – IF. Shelor et al. (2024) noted that TOF measurements are unreliable for trace analyses, as IF often constitutes nearly 100% of TF, limiting the precision of TOF determination.

4.1.2.3. Extractable organic fluorine (EOF) and hydrolyzable organic fluorine (HOF). Shelor et al. (2024) reviewed various extraction methods for EOF, highlighting the use of solvent extraction and solid-phase extraction (SPE). Liquid extraction suits solid samples, tissues, and complex liquids like blood, while SPE is ideal for dilute aqueous matrices. In liquid extraction, methyl tert-butyl ether (MTBE) combined with ion-pairing agents such as tetrabutylammonium (TBA) isolate anionic PFAS. Residues may be re-extracted with hexane to enhance recovery of other PFAS not accounted for with the MTBE/TBA solvent pair.

SPE for EOF commonly employs weak anion exchange (WAX) cartridges, such as Strata X-AW® and Oasis WAX®, for selective extraction of anionic PFAS. Non-WAX sorbents, such as SPE-HLB®, Florisil SEP®, and ENVI-Carb®, are also used in some workflows but rely on different retention mechanisms. Conditioning the WAX sorbents with an alkaline solvent (e.g., ammonium hydroxide (NH_4OH) in methanol) prevents the retention of solvent PFAS. Samples are then loaded, pH adjusted to 6–7 to optimize PFAS recovery, followed by elution with NH_4OH in water or methanol. Finally, PFAS are eluted with an alkaline solvent (e.g., methanol or acetonitrile with NH_4OH).

Our review identifies EOF as a critical method for determining total PFAS concentration, representing a significant portion of the articles reviewed (34%; 53/156). EOF was frequently assessed in various matrices. The observed trend decreased in samples in the order: surface, groundwater, and wastewater (26%) > soil, sediment, suspended solids and sludge (26%) > biota (23%) > industrial and personal care products (17%) > human and mammalian samples (including blood/serum, nail, and hair) (15 %) > paper, textile, dust, and tea (4%) across studies that evaluated EOF concentrations.

A procedural modification, referred to as "hydrolyzable organic fluorine" (HOF), employs strong alkaline hydrolysis to cleave polyfluoroalkyl side-chain polymers. This approach, as reported by Roesch et al. (2024) for applications in textiles, carpets, and food contact materials, represents the first and only study to date documenting this method.

4.1.2.4. Absorbable organic fluorine (AOF). In adsorbable organic fluorine (AOF) analysis, pre-packed columns or sorbents like granular activated carbon (GAC) are used in glass tubes. Ideal AOF sorbents should have low native fluorine content, produce no combustion by-products that interfere with analysis, and provide high PFAS retention capacity over inorganic fluorine (IF). Unlike EOF, AOF sorbents require no preconditioning before loading the sample, whereas PFAS are adsorbed from aqueous solutions. Sodium nitrate (10 mM $NaNO_3$) is added to reduce IF sorption. After extraction, the sorbent is rinsed with $NaNO_3$ or NH_4OH to remove residual IF while PFAS remains on the GAC. The sorbent is then transferred to a quartz or ceramic boat for further analysis. Alternatively, sorbents can be stirred or shaken with the sample, filtered, and rinsed. Shelor et al. (2024) reviewed emerging sorbents for the analysis of adsorbable organofluorine (AOF) and extractable organofluorine (EOF) and also compared the application of the two techniques alongside liquid chromatography-mass spectrometry (LC-MS) across various environmental matrices. The review highlighted the absence of studies applying AOF concentration reported in samples such as blood, serum, tissue, or biota, likely due to the unsuitability of these complex matrices, potentially leading to sorbent clogging. Conversely, AOF was more commonly reported in water samples, including unimpacted waters, waters affected by aqueous film-forming foams (AFFF), and those associated with fluorochemical manufacturing and industrial processes. Notably, Han et al. (2021) demonstrated that in impacted waters, AOF underestimated the true organofluorine content by over 70% in the most highly impacted samples. Our review identified AOF concentrations in 11 studies (~7%), with 91% focusing on water samples, while two studies investigated AFFF concentrates and photolithography materials.

4.2. Instrumentation for total PFAS analysis

Specific PFAS concentrations in various matrices are most commonly quantified using targeted analysis, focusing on a subset of individual PFAS. The standard method for quantification is liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS), as demonstrated by regulatory standards such as the German Institute for Standardization, DIN. 38407-42:2011-03 (2011) and DIN 38414-14:2011-08 (2011), and US Environmental Protection Agency (US EPA) methods 8327 (USEPA, 2021), 537.1 (USEPA, 2009), 533 (USEPA, 2019) and 1633 (USEPA, 2024).

Recently, high-resolution mass spectrometry (HRMS) has emerged as a valid and critical analytical approach for discovering unknown PFAS. This includes using instruments such as high-resolution quadrupole time-of-flight (HRqToF) and Orbitrap mass spectrometers. These instruments have been used to develop non-targeted analytical (NTA) methods capable of measuring a multitude of different PFAS in the same analytical run. This allows for analysis of individual PFAS beyond traditional targeted lists.

Beyond targeted and non-targeted analysis (NTA), indirect methods assess total PFAS through organofluorine measurement in various matrices. This section focuses on the instrumental methods for an indirect (non-specific) assessment of total PFAS in samples. TF is the sum of IF and TOF. TOF includes all PFAS and their precursors, while subsets like EOF and AOF focus on specific fractions. AOF measures highly fluorinated compounds adsorbed onto activated carbon, and EOF captures fluorinated compounds extractable by solvents through liquid extraction and solid phase extraction (Ateia et al., 2023). According to Koch et al. (2020), different extraction methods yield varying amounts of organic fluorine (OF), necessitating a distinction between non-extractable organic fluorine (NEOF) and EOF. EOF can be further categorized into quantifiable and unquantifiable OF, subdivided into unidentified and semi-quantified OF, aiding fluorine mass balance assessments in samples (Fig. 3).

Analytical methods used to quantify TF, TOF, EOF, or AOF in this review include CIC, particle-induced gamma-ray emission (PIGE), high-resolution graphite furnace molecular absorption spectrometry (HR-CS-GFMAS), neutron activation analysis (INAA), and ion-selective electrodes (ISE) (see SI Table S1). Additional methods include ICP-MS/MS, NMR, and X-ray photoelectron spectroscopy (XPS) (see SI Table S1). CIC and INAA assess bulk volumes, while PIGE and XPS target surface measurements. PIGE, INAA, and XPS are non-destructive and have high throughput, but only XPS and NMR can differentiate between TOF and IF. Accurate TOF measurement requires IF removal, although its contribution is often minimal in consumer products. Most concentrations are reported using CIC. This represents over 50% of the reviewed articles, with 82 out of 156 studies using CIC. The next most reported technique is PIGE, applied in 14 studies (9%), followed by HR-CS-GFMAS in 9 studies (~6%). Fig. 4 shows the conceptual workflow for systematically assessing total PFAS parameters in various samples.

4.2.1. Combustion ion chromatography (CIC)

Over 50% (82/156) of the reviewed articles used combustion ion chromatography (CIC) for quantifying EOF (56/82; 68%), TF (46/82; 56%), AOF (12/82; 15%) and TOF (7/82; 9%). CIC cannot differentiate between organic fluorine (OF) and inorganic fluorine (IF), so selectivity for the method for use for EOF and AOF depends on sample preparation. CIC applies to various matrices (solid, liquid, gas) by thermally oxidizing samples at 900–1100 °C in an oxygen/argon flow, converting OF to hydrogen fluoride (HF). The combustion gases are trapped in a Milli-Q water/NaOH solution absorber unit. In the absorber unit, the HF dissolves into H^+ and F^-. An aliquot of the absorption solution was injected into an ion exchange column for ion chromatography, followed by conductometric detection.

CIC offers high sensitivity, with limits of detection in the ng/L to μg/L range but lacks the specificity to distinguish between organic and inorganic fluorine without additional processing. According to Koch et al. (2020), while a powerful tool, CIC is prone to interference from chloride, which can displace fluoride in the ion exchange column, and from alkaline earth elements that may damage the combustion tube. Also, high instrument blanks, likely due to PFAS contamination in system components or gases, can also affect sensitivity. Minimizing blank contributions and exploring alternative mineralization techniques to improve sensitivity and accuracy when using CIC is crucial.

4.2.2. Particle-induced gamma-ray emission (PIGE)

PIGE is an ion beam technique that measures light elements in solid materials. Initially applied to quantify TF in PFAS-treated papers and textiles (Ritter et al., 2017). In this review, 14 studies (9%) reported TF concentrations using PIGE, with six (6) articles focusing on paper and textiles (including firefighter gear and fabric of children's car seats), two

(2) on food packaging, and one (1) study each on cosmetics, dental floss, AFFF, facemasks, dust, and field sampling materials.

PIGE involves direct sample measurement, where thin sections of sterilized samples are irradiated with proton beams. The method detects surface materials up to 250 μm, calibrating using sodium fluoride standards. However, calibrating for variable matrices like textiles can be challenging (Shelor et al., 2024). The use of PIGE does not require sample extraction; its strengths include high throughput and acceptable sensitivity at ppm levels. Its limitations include high detection limits (mg/L range); this makes it less effective for trace analysis. Additionally, it is unable to differentiate inorganic fluorine (IF) from total organic fluorine (TOF), making IF removal crucial for complex matrices like soil and biota (Koch et al., 2020). Despite these limitations, PIGE, like CIC, holds promise and could benefit from further optimization to improve sensitivity and applicability across various sample types.

4.2.3. Continuum source graphite furnace molecular absorption spectrometry (CS-GF-MAS)

High-resolution graphite furnace molecular absorption spectrometry (HR-MAS) is gaining prominence for PFAS monitoring across matrices. Nine (9) studies reported TF, TOF, EOF, and AOF concentrations using this method, with 44% focusing on water samples. Other matrices, including biota tissues, soil, ski wax, snow, and suspended particulates, were reported in single studies. HR-MAS is more sensitive and time-efficient than CIC, using online pyrolysis and forming metal monofluorides (e.g., AlF, GaF) for detection. According to Qin et al. (2012), the technique employs a high-pressure xenon short-arc lamp, a double monochromator system, and a CCD array detector. Fluoride detection, based on GaF at 1150 °C after pyrolysis at 550 °C, provides high resolution. Akhdhar et al. (2020) demonstrated HR-MAS's sensitivity for TF quantitation via CaF, while Zweigle et al. (2023) used it for EOF analysis by detecting GaF.

Advantages of HR-MAS include robustness, lower operational costs, high throughput, and minimal sample preparation, provided an optimized temperature program is used. However, as Koch et al. (2020) noted, better separation of compounds is needed to improve the identification of specific organofluorine compounds, as HR-MAS may detect multiple OFs under the same fluoride signal.

4.2.4. Fluorine nuclear magnetic resonance spectroscopy (^{19}F NMR)

One of the earliest uses of ^{19}F NMR in the determination of perfluorinated surfactants in biological samples (human serum) was in the 1970s by Guy et al. (1976). Weiner et al. (2013) employed this technique to analyze OF in samples of AFFFs. The NMR method is selective for different PFAS, including branched isomers (Schöpel et al., 2022). Our review identified only one (1) manuscript that evaluated total PFAS using NMR. Apart from the high equipment and operational costs, one of the method's downsides is its low sensitivity. Hence, sample preconcentration is required to determine perfluorinated surfactants in environmental matrices. Gauthier and Mabury (2022) addressed the issue of ^{19}F NMR sensitivity by optimizing parameters including needle calibration pulse angle, spin-lattice relaxation time, recyclic delay time, solvent choice, and the purposeful inclusion of paramagnetic material Cr (acac)$_3$. The advantages of using the ^{19}F NMR technique for analysis include sharp, well-resolved peaks, specificity to fluorine, and the lack of matrix interferences, which results in low signal-to-noise ratios. The absence of interferences is partly because multi-fluorinated compounds are not naturally occurring (Moody et al., 2001). Other applications of ^{19}F NMR spectroscopy for the analysis of PFAS include the combination of ^{19}F NMR with LC-MS to analyze the structural composition of compounds (Stefanac et al., 2018).

Other techniques are discussed in the Supplementary information (SI) section. A common challenge across all these techniques is the inability to differentiate between OF and IF, which often requires additional processing steps. High limits of detection (LOD) and quantification (LOQ) in some methods restrict their application to trace-level analysis. Additionally, the complexity of the sample matrix can pose significant challenges to achieving accurate and sensitive measurements. To improve PFAS monitoring, hybrid approaches that combine the strengths of multiple techniques should be explored for comprehensive PFAS profiling. Investments in enhancing sensitivity and matrix handling are essential, particularly for trace-level detection. Finally, reducing contamination sources is vital to ensure instrument reliability and accuracy across all methods.

4.3. Quality assurance/quality control

Quality assurance (QA) and quality control (QC) are crucial aspects of instrumental analysis, ensuring analytical results' reliability, accuracy, and precision. The key components of QA/QC in the sample pretreatment and instrumental analysis include calibration standards, control charts, quality control samples, method blanks, and several method performance characteristics, e.g., limit of detection/quantification, specificity, linearity, accuracy, and precision for method development, validation or verification. The QA/QC focuses on the operational techniques and activities used to fulfill requirements for quality.

In this review, 91% (142/156) of studies reported analysis on individual targeted PFAS with total PFAS from organofluorine evaluation as complementary analysis. For the articles reviewed, approximately 86% of the studies used calibration standards, method or procedural blanks, and laboratory control samples as quality control (QC) for their analysis. The abundance of fluorinated compounds in our environment makes the incorporation of QC important in analysis. Currently, analysis experiences high instrumental blanks, and a lack of labeled surrogates for analysis makes it more challenging to zero out interferences.

The LODs/LOQs were reported for targeted individual PFAS analysis (including TOP analysis) and total PFAS based on organofluorine analysis as represented by TF, TOF, EOF, and AOF (Fig. 5). The results show that the lowest detection limits were achieved for water samples, generally in the low to sub-ppb range. Limits of detection in blood samples were in the low ppb range, highlighting the potential of this method for human biomonitoring. Limits of detection in solid samples were generally in the ppm range, with ppb detection limits achieved in some studies involving personal care products and dust. Although the review's focus is not on targeted analysis, 56% (87/156) of the studies reported limits of detection for targeted analysis. OF this percentage, 54% (47/87) evaluated TOP assay analysis. Forty-nine percent (49%) of the articles (76/156) reviewed reported limits of detection for total PFAS as TF, TOF, EOF, and AOF. Only 29% of these studies (22/76) reported LODs and LOQs individually. Further evaluation of data obtained shows that 71% (54/76) of these studies reported LODs, and 56% (43/76) reported LOQs. A comparison of the LOD/LOQs reported for TOP assay analysis (SI Table S1, Fig. 5) shows considerably lower values than other organofluorine parameters. This is because the ranges reported are obtained from individual target PFAS compounds. The lowest ranges of LOD for TOP assay are reported for soil, sediments, suspended solids, and sludges with values ranging from 0.006 to 1.3 ng/g (ppm) and industrial and personal care products with LOD ranging from 0.01 to 8.6 ng/mL (ppb). Water samples show values ranging from 0.01 to 34 ng/L (ppt), with the exception of a study reporting concentrations of landfill leachates with LOD values in blank samples ranging between 10 and 80 ng/L (ppt).

Comparisons of LOD & LOQs within sample matrices are challenging due to a lack of data for many matrices. Water was the most studied matrix and included several studies where complementary methods were performed. LODs and LOQs were both reported in five (5) studies that evaluated river water: Metzger et al. (2019) – TF, EOF, Gehrenkemper et al. (2021) – TF, Akhdhar et al. (2020) – TOF, Willach et al. (2016) – AOF, and Nxumalo et al. (2023) – EOF. In Metzger et al. (2019), the LOD reported is 5.27 ng/L, while the LOQ is 17.57 ng/L using deionized water with an SPE enrichment factor. The direct method provided higher LOD and LOQ values, 880 ng/L and 2940 ng/L, respectively. The LOD and LOQ reported in Gehrenkemper et al. (2021) study is higher compared to Metzger et al. (2019), using deionized water, with a LOD ranging from 800 to 3200 ng/L and a LOQ ranging from 2700 to 10,700 ng/L. It is observed that higher LOD and LOQ values are reported without SPE enrichment. Both authors reported TF using the HR-CS-GFMAS. Nxumalo et al. (2023), using the same instrumentation for determining EOF, reported much lower LOD and LOQ at 1.2 ng/L and 4 ng/L, in surface water affected by sewage effluents, compared to Metzger et al. (2019). The LOD/LOQ reported by Akhdhar et al. (2020) using HR-CS-GFMAS for TOF is 300/1000 ng/L in measurements of blanks. Table 2 provides the LOD/LOQ for some of the reviewed samples. The detailed list is presented in SI Table S1. Depending on the sample matrix, CIC provided comparatively lower detection limits.

No clear trends in the LOD/LOQs were observed irrespective of the type of water or wastewater sample analyzed. Wang et al. (2021a) reported LOD values as high as 36,000 ng/L. LOD/LOQ for TF is generally higher compared to other OF analyses, TOF, and EOF, evaluated for values reported in water samples. Table 2 and SI Table S1 provide further details on the studies and LODs and LOQs for different water samples.

Only nine (9) studies reported LOD/LOQ in soil, sediments, suspended solids, and sludges. These values were reported in studies that evaluated EOF concentration in samples. No article in our review reported LOD/LOQ for TF and AOF in this sample group. Simon et al. (2022) reported a LOD value of TOF of 3.43 ng/g for soil sample analysis; Guckert et al., 2022 reported LOD of 5 ng/g for sediments and suspended sludges. For suspended particulate matter (SPM), Simon et al. (2023) reported an LOD value of 10.3 ng/g; a higher LOD value of 22 ng/g and 60 ng/g were detected for sediments and sewage sludge in studies of Aro et al. (2021a) and Vogel et al. (2023), respectively. LOQs for EOF reported in other studies were 10 ng/g in soil and sediment (Guckert et al., 2022; Simon et al., 2022; Yeung et al., 2013), 35 ng/g, as reported by Müller et al. (2023a). A much higher LOQ of 680 ng/g were reported for sludges by Müller et al. (2023b) for a wastewater plant in Austria. Despite the use of a similar instrumental method, CIC, to obtain EOF values, the LOQs reported in these articles have a wide range (Guckert et al. (2022), Müller et al. (2023a)).

For detection limits reported in biota samples, a high LOQ value of 5000 ng/g for TF was reported in Yeung and Mabury (2013) in Rainbow Trout. No LOD and LOQ were reported in biota for TOF and AOF analysis. Yeung and Mabury (2013) also reported LOQ for EOF values at 400 ng/g. A much lower LOQ was reported by Lauria et al. (2024) in liver samples from pilot whales and white-beaked dolphins, the EOF value is 29.3 ng/g. A comparatively low range was also reported in Langberg et al. (2020). In studies by Schultes et al. (2020) and Ruyle et al. (2023), LODs reported ranged from 19 to 84 ng/g for EOF, while Aro et al. (2021a) reported a range of 88–145 ng/g in fish liver.

In human serum and blood samples, LOD and LOQ values were not reported for TOF and AOF. LOD for TF was higher than other OF analyses. LOD captured for TF and EOF in human blood/serum samples ranged between 23 and 58 ng/g for TF, and between 4 and 20 ng/g for EOF (Yeung and Mabury, 2015; Yeung et al., 2008; Liu et al., 2020). Kaiser et al. (2021) reported even lower LOQ (0.92–2.7 ng/mL) for EOF values for the analysis of maternal blood, placental tissue, and cord blood. Other human sample matrices analyzed- hair and nails by Liu et al. (2020) had an LOD for TF data up to 610 ng/g. From Yeung et al. (2009b) analysis on wild rat blood, the reported LOQ for EOF was 32 ng/mL.

The data on commercial and personal products showed higher LODs and LOQs concentrations for TF analysis. The LODs reported for cosmetics and personal products were high, on comparison to other sample matrices. In a study by Pütz et al. (2022), the LOD concentrations ranged from 1000 to 1,310,000 ng/g, for personal care products. Other products evaluated, such as clothing and paper, adopted different

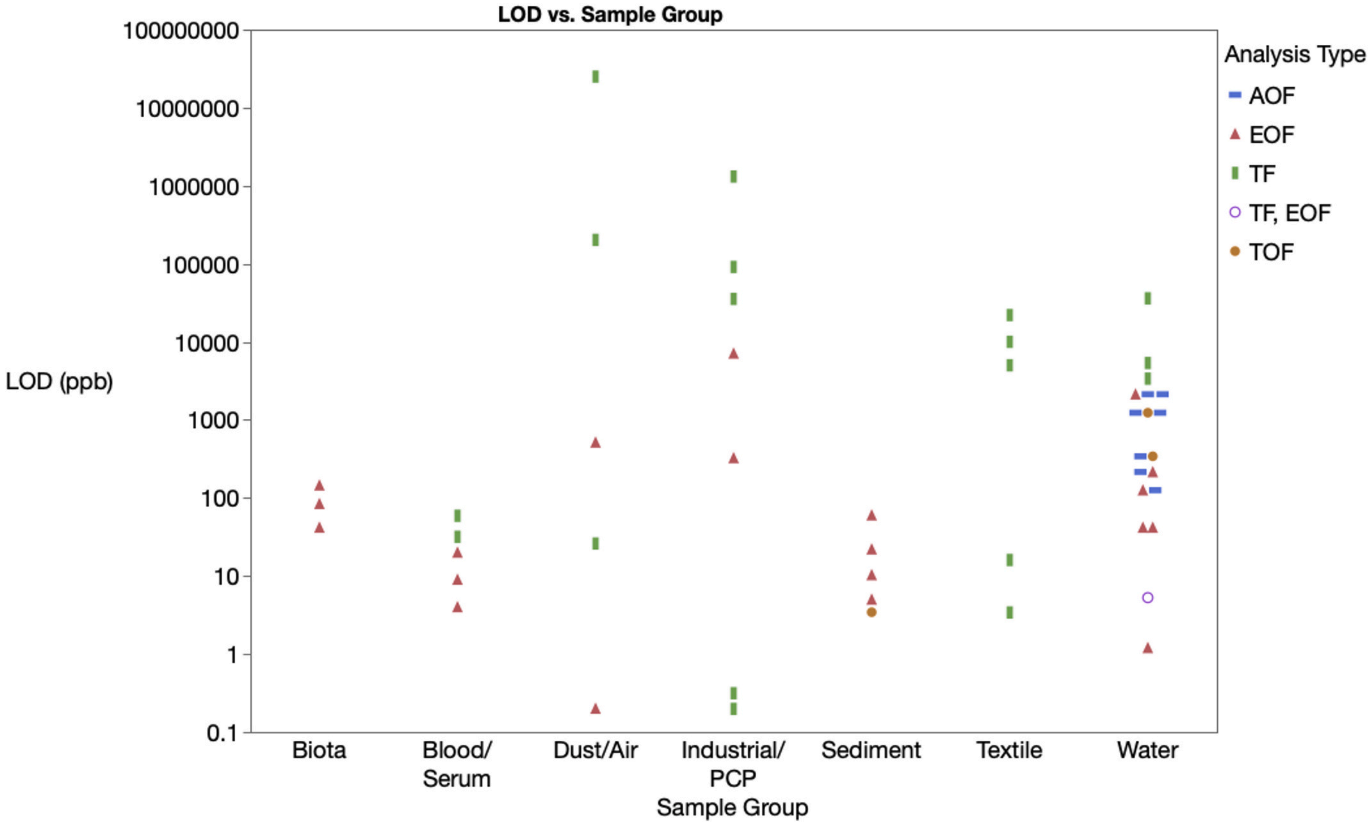

Fig. 5. Overview of LODs reported in different sample types by AOF, EOF, TF and TOF.

Table 2
LOD/LOQ of sample matrices.

Sample type	Instrumentation	Analysis type	LOD	LOQ	Unit	References
Water samples						
River/tap/lake/wastewater	CIC	TF	36,000	–	ng/L	Wang et al., 2021a, 2021b
Groundwater	CIC	TF	5000	–	ng/L	Singh et al., 2019
River water	HR-CS-GFMAS	TF, EOF	5.27	17.57	ng/L	Metzger et al., 2019
River water	CIC	TF	800–3200	2700–10,700	ng/L	Gehrenkemper et al., 2021
Sea/river/effluent/wastewater	HR-CS-GFMAS	TOF	300	1000	ng/L	Akhdhar et al., 2020
Wastewater	CIC	TOF	1000	–	ng/L	Verwold et al., 2023
Groundwater/soil	CIC	EOF	13–151	–	ng/L	Kärrman et al., 2021
Industrial/riverwater	CIC	EOF	200	–	ng/L	Forster et al., 2023
Tap water	CIC	EOF	25–43.5	–	ng/L	Jiao et al., 2023
Sewage water	CIC	EOF	36–40	123–200	ng/L	Aro et al., 2021a, 2021b
Surface/river water	HR-CS-GFMAS	EOF	1.2	4	ng/L	Nxumalo et al., 2023
Groundwater	CIC	EOF	680–2180		ng/L	Ruyle et al., 2023
Groundwater	CIC	EOF	7	–	μM	Ruyle et al., 2023
Wastewater effluent/influent	CIC	EOF	–	830	ng/L	Müller et al., 2023a, 2023b
Surface water	CIC	EOF	1.95–3.26	–	nM	Ruyle et al., 2021
AFFF/surface water	CIC	AOF	300	400	ng/L	Han et al., 2021
Municipal/groundwater	CIC	AOF	1300	2000	ng/L	von Abercron et al., 2019
Municipal/groundwater	CIC	AOF	230	770	ng/L	Willach et al., 2016
Surface water	CIC	AOF	2200	–	ng/L	Jones et al., 2022
Wastewater	CIC	AOF	1400	–	ng/L	Jones et al., 2022
Water	CIC	AOF	100	300	ng/L	Wagner et al., 2013
Groundwater	CIC	AOF	2000	–	ng/L	Ersan et al., 2024
Wastewater	CIC	AOF	–	1000	ng/L	Dauchy et al., 2017
Soil, sediments, suspended solids and sludges						
Suspended Particulate Matter (SPM)	HR-CS-GFMAS	EOF	10.3	–	ng/g	Simon et al., 2023
Sediments	CIC	EOF	5	10	ng/g	Guckert et al., 2022
Sediments	CIC	EOF	22	–	ng/g	Aro et al., 2021a, 2021b
Sewage sludge	CIC	EOF	60	–	ng/g	Vogel et al., 2023
Sludge	CIC	EOF	–	680	ng/g	Müller et al., 2023a, 2023b
Soil	CIC	EOF	–	35	ng/g	Müller et al., 2023a, 2023b
Soil	CIC	EOF	–	10.3	ng/g	Simon et al., 2022
Sediments	CIC	EOF	–	39–133	ng/g	Langberg et al., 2020
Sediments	CIC	EOF	–	10	ng/mL	Yeung et al., 2013
Soil	CIC	TOF	3	–	ng/g	Simon et al., 2022
Textiles, paper, and food packaging						
Paper and Textiles	CIC	TF	10,000	–	ng/g	Rodgers et al., 2022
Textile	PIGE	TF	16	–	ppm	Peaslee et al., 2020
Textile	PIGE	TF	5000	–	ng/g	Wu et al., 2021
Textile	CIC	TF	3	10.3	ng/g	Zweigle et al., 2023
Paper	PIGE	TF	13	42	nmol/cm^2	Ritter et al., 2017
Textile	PIGE	TF	18–45	42	nmol/cm^2	Robel et al., 2017
Textile	PIGE	TF	–	13–16.2	ppm	Muensterman et al., 2022
Textile	PIGE	TF	6.8	20	nmol/cm^2	Muensterman et al., 2022
Textile	CIC	TF	22,000		ng/g	Skedung et al., 2024
Textile	CIC	TF	–	100.6	ng	Schellenberger et al., 2019
Human samples						
Blood	CIC	EOF	–	107	ng/mL	Aro et al., 2022
Blood	CIC	EOF	–	0.92–2.7	ng/mL	Kaiser et al., 2021
Blood	CIC	EOF	4	4	ng/mL	Yeung and Mabury, 2015
Blood	CIC	EOF	–	6	ng/mL	Yeung et al., 2008
Serum	CIC	EOF	–	3.8	ng/g	Pennoyer et al., 2023
Serum	CIC	EOF	6–9	–	ng/mL	Cioni et al., 2023
Serum	CNAA	EOF	20	–	ng/mL	Liu et al., 2020
Blood	CIC	TF, EOF	–	6	ng/mL	Yeung et al., 2008
Serum	CIC	TF	23–25	–	ng/mL	Cioni et al., 2023
Serum	CNAA	TF	59	–	ng/mL	Liu et al., 2020
Nail	CNAA	TF	600	–	ng/g	Liu et al., 2020
Hair	CNAA	TF	610	–	ng/g	Liu et al., 2020
Nail	CNAA	EOF	200	–	ng/g	Liu et al., 2020
Hair	CNAA	EOF	240	–	ng/g	Liu et al., 2020
Plants and animals						
Blood (wild rat)	CIC	EOF	–	32	ng/mL	Yeung et al., 2009a, 2009b
Biota	CIC	TF	–	5000	ng/g	Yeung et al., 2013
Biota	CIC	EOF	19–84	–	ng/g	Ruyle et al., 2023
Biota	CIC	EOF	88–145	–	ng/g	Aro et al., 2021a, 2021b
Biota	CIC	EOF	41.8	–	ng/g	Schultes et al., 2020
Biota	CIC	EOF	–	39–133	ng/g	Langberg et al., 2020

(continued on next page)

Table 2 (*continued*)

Sample type	Instrumentation	Analysis type	LOD	LOQ	Unit	References
Biota	HR-CS-GFMAS	EOF	–	10.3	μg/L	Capozzi et al., 2023
Biota	CIC	EOF	–	400	ng/g	Yeung et al., 2013
Biota	CIC	EOF	–	29.3	ng/g	Lauria et al., 2024
Commercial products						
Artificial turfs	CIC	TF	0.0034–0.198	–	ng/g	Lauria et al., 2022
Field sampling materials	PIGE	TF	–	800	μg/m^2	Rodowa et al., 2020
Cosmetics	CIC	TF	91,000	–	ng/g	Schultes et al., 2018
Cosmetics	CIC	TF	35,450	–	ng/g	Namazkar et al., 2024
Cosmetics	CIC	TF	100–1,310,000	–	ng/g	Pütz et al., 2022
Cosmetics	PIGE	TF	–	3840	μg/m^2	Whitehead et al., 2021
Cosmetics	CIC	EOF	330–7100	–	ng/g	Namazkar et al., 2024
Cosmetics	CIC	EOF	162–325	–	ng/g	Pütz et al., 2022
Food packaging	CIC	TF	3580	10,800	μg/m^2	Schwartz-Narbonne et al., 2023
Food packaging	CIC	TF	0.1–0.3	–	ng/g	Yamazaki et al., 2019
Food packaging	PIGE	TF	–	50	nmol/cm^2	Schaider et al., 2017
Food packaging	CIC	EOF	400–700	–	μg/m^2	Schultes et al., 2019
AFFF	CIC	EOF	0.01	–	nM	Ruyle et al., 2021
AFFF	CIC	TF	0.007	–	nM	Ruyle et al., 2021
Tea	CNAA	EOF	0.2	–	μg	Zhang et al., 2017
Tea	CNAA	TF	0.58	–	ug	Zhang et al., 2017
Atmospheric samples						
Dust	CIC	TF	26	–	ng/mL	Young et al., 2022
Dust	PIGE	TF	25,000	–	ng/g	Young et al., 2021
Dust	CIC	EOF	514	–	ng/mL	Young et al., 2022
Air	CIC	EOF	0.2	–	μg/L	Forster et al., 2023
Air	CIC	TF	–	0.255–6.60	ng/m^3	Lin et al., 2022
Stack gas	CIC	TF	20,200,000	40,500,000	ng/m^3	Seay et al., 2023

instrumentation for analysis, reporting their limits of detection and concentration to units that are not directly comparable. A major challenge with analyzing these products is the lack of standardized methods for sample preparation and analysis based on the sample matrix. Table SI 1 highlights the LODs and LOQs of the different commercial and cosmetic products. One of the main challenges with total PFAS analysis is the laboratory blanks, which lead to high LODs/LOQs irrespective of the method used. The LODs/LOQs of different commercial products captured in the review are provided in Table 2.

4.4. Data processing

In the absence of a universal method for total PFAS calculation, challenges on data comparison are presented. Due to differences in total PFAS methods, a wide range of methods have been proposed (Dixit et al., 2024). The concentrations obtained from individual target PFAS analysis have been established to be inadequate in reporting total PFAS concentration due to the limited scope of compound detection (Ateia et al., 2023). In total, our review identified three (3) different calculations for total PFAS through direct measurements. Shojaei et al. (2022) provided these multiple approaches in an effort to estimate total PFAS concentration from targeted analysis and TOP assay. In addition, we identified 8 different calculations encompassing indirect PFAS measurements from the conversion of individual targeted PFAS concentration to fluorine and the calculation of mass balance (Supplementary Information SI Eq. 4–11). This dissimilarity in total PFAS calculation provides an extra layer of complexity when comparing total PFAS concentrations between studies. Any regulation that plans to encompass a total PFAS calculation, therefore, not only takes into account sample preparation and analytical procedures but also data processing and reporting methods.

5. Reporting the results of total PFAS studies

5.1. Total PFAS concentrations in different matrices

Concentrations of total PFAS parameters have been reported in various units, such as mg/L, μg/m^3, nmol/cm^2, μg/g, mMol/L, counts/μCoulomb, and percentages (%). To maintain consistency, this section focuses only on studies that use commonly reported units of mass per mass or mass per volume (e.g., ng/g, ng/L, ng/m^3), but all data is available in SI Table S1. A summary of the concentration range of total PFAS parameters in the matrices captured from this review is presented in Table 3. In general, the highest reported total PFAS concentrations were identified in water, with a maximum of 10,000,000,000 ng/L reported by Singh et al. (2020). The maximum concentrations in soils/sediments and dust were 7,209,000 ng/g (Roesch et al., 2022) and 17,800,000 ng/g (Young et al., 2022). The levels of total PFAS in biota were lower, with maximum concentrations of 1000,000 ng/g (Koch et al., 2021) reported in plants and animals and maximum concentrations in humans of 9500 ng/g in hair/nails (Liu et al., 2020) and 1160 ng/mL in blood/serum (Miyake et al., 2007).

5.1.1. Total oxidizable precursor (TOP) assay

TOP assay was the most widely used total PFAS method; this was noted to have been used in 48 studies (31%). Analysis has been conducted across a diverse number of samples, demonstrating the applicability of the method for a wide number of matrices. TOP assay is provided as a service by several commercial laboratories; this explains its wide adoption and usage. TOP assay is commonly used in isolation (51 instances) to provide an estimate of total PFAS concentrations; however, it has also been used in combination with other studies. When combined with TF analysis TOP assay concentrations were 0.1–13% of TF methods (Table 4).

5.1.2. Total fluorine (TF)

TF was the second most widely used parameter to report total PFAS concentrations and was used in 60 studies (38%). While TF can be used as a proxy for total PFAS concentrations in environmental and biological matrices, it often contains IF as an interference. Hence, TF concentration reported in the literature is the sum of organic fluorine and IF burdens, as TF determination does not require special sample preparation routine (Koch et al., 2020). The range of concentrations of TF is large; this presents a challenge when meaningful comparisons between techniques

Table 3
Concentrations of PFAS sum parameters in diverse matrices.

Sample type	Maximum values				Minimum values		
	Metric	Concentrations	Units	References	Concentrations	Units	References
Surface, groundwater, and drinking water	TF	5,000,000	ng/L	Singh et al., 2019	100	ng/L	Singh et al., 2019
	TOF	14,500		Akhdhar et al., 2020	1000		Akhdhar et al., 2020
	EOF	440,000		Han et al., 2021	<LOD		Aro et al., 2021a
	AOF	18,500		Bach et al., 2017	<LOD		Forster et al., 2023
	TOP	10,000,000,000		Singh et al., 2020	24		Qu et al., 2019
Wastewater	TF	–	ng/L	–	–	ng/L	–
	TOF	14,500		Akhdhar et al., 2020	1000		Akhdhar et al., 2020
	EOF	27,000,000		Forster et al., 2023	183		Aro et al., 2021a
	AOF	25,000		Forster et al., 2023	<LOD		von Abercron et al., 2019
	TOP	40,000		Wang et al., 2020	58.6		Kim et al., 2022
Biota (including plants)	TF	1,000,000	ng/g	Koch et al., 2021	210	ng/g	Yamazaki et al., 2019
	TOF	–		–	–		–
	EOF	16,000		Yeung and Mabury, 2013	<LOD		Aro et al., 2021a
	AOF	–		–	–		–
	TOP	13,979		Liu et al., 2024b	<LOQ		
Soil, sediment, suspended solids, and sludge	TF	1,322,000	ng/g	Codling et al., 2014	2.3	ng/g	Codling et al., 2018
	TOF	–		–	–		–
	EOF	7,209,000		Roesch et al., 2022	<LOD		Guckert et al., 2022
	AOF	–		–	–		–
	TOP	552		Zhao et al., 2023	<LOQ		Göckener et al., 2023
Dust	TF	17,800,000	ng/g	Young et al., 2022	<MDL	ng/g	Young et al., 2022
	TOF	–		–	–		–
	EOF	17,600		Young et al., 2022	<MDL		Young et al., 2022
	AOF	–		–	–		–
	TOP	62,300		Juhasz et al., 2023	91.5		Juhasz et al., 2023
Human hair/nails	TF	9500	ng/g	Liu et al., 2020	640	ng/g	Liu et al., 2020
	TOF	–		–	–		–
	EOF	4600		Liu et al., 2020	0.55		Liu et al., 2020
	AOF	–		–	–		–
	TOP	–		–	–		–
Human and mammalian blood/serum	TF	192	ng/mL	Yeung et al., 2008	59.9	ng/mL	Yeung et al., 2008
	TOF	1160		Miyake et al., 2007	140		Miyake et al., 2007
	EOF	1070		Miyake et al., 2007	<LOQ		Aro et al., 2021b
	AOF	–		–	–		–
	TOP	27.19		Coêlho et al., 2023	<LOD		Cioni et al., 2023
Food materials (e.g., tea, pet food)	TF	276,000	ng/g	Zhang et al., 2017	22,000	ng/g	Zhang et al., 2017
	TOF	–		–	–		–
	EOF	118,000		Zhang et al., 2017	4700		Zhang et al., 2017
	AOF	–		–	–		–
	TOP	14.3		Chinthakindi et al., 2021	0.6		Chinthakindi et al., 2021
Air (Gaseous phase)	TF	1100	ng/m^3	Lin et al., 2022	55.2	ng/m^3	Lin et al., 2022
	TOF	1100		Lin et al., 2022	52		Lin et al., 2022
	EOF	–		–	–		–
	AOF	–		–	–		–
	TOP	–		–	–		–

are sought after. However, for studies that performed complementary analysis of TF alongside other methods, TF concentrations were consistently higher than the other techniques used (Table 4).

5.1.3. *Extractable organic fluorine (EOF)*

EOF was the third most widely used parameter to report total PFAS concentrations and was used in 53 studies (34%). When compared against TF, calculated EOF concentrations were considerably lower (Table 4). EOF concentrations in soils and sediments were generally 3 or 4 orders or magnitude lower than TF (Wang et al., 2013; Tan et al., 2014; Spaan et al., 2023). EOF concentrations in water were generally 3 orders of magnitude lower than TF (Gehrenkemper et al., 2021; Miyake et al., 2007). EOF and TF concentrations were comparable in biota and commercial products; the best aligned examples included human, and cosmetics serum where EOF was 85 % and 82 % of TF, respectively (Table 4).

5.1.4. *Absorbable organic fluorine (AOF)*

AOF was not widely used; AOF results were reported in 11 studies (7%). Based on current methodology utilizing granular activated carbon (GAC) sorbent, AOF has so far only been measured in aqueous matrices (SI Table S1). Analysis has been performed on commercial products, as well as potentially contaminated water samples. Concentrations have been reported in AFFF concentrates (1100–4800 mg/L) (Jacob and Helbling, 2023), photolithography materials (180–2380 mg/L) (Han et al., 2021), surface, groundwater, and drinking water (ND-18,500 μg/L), and wastewater (<1.3–25,000 μg/L).

5.1.5. *Total organic fluorine (TOF)*

TOF has not been widely used and was only reported in 10 studies (6%). TOF is the organic fraction of TF devoid of the IF interference (Trojanowicz et al., 2011). TOF concentrations have been reported in several commercial products but have not been widely reported for environmental samples (Table 3 and SI Table S1). We were only able to identify two studies where TF and TOF had been conducted simultaneously. Surprisingly, the results showed TF and TOF concentrations to be nearly identical (Table 4). Total PFAS concentrations of 7.07 mg/L were reported in fire suppression pipes for both TF and TOF (Lang et al., 2022). Whereas Weiner et al. (2013) reported total concentrations of 18,000 μg/mL by TF and 17,800 μg/mL by TOF (Weiner et al., 2013).

5.1.6. *'Other' total PFAS parameters*

The literature encountered a variety of other terms related to total PFAS parameters. These included unidentified total fluorine (UTF),

Table 4
Comparison of TF total concentrations against other methods (TF = total fluorine, TOF = total organic fluorine, AOF = adsorbable organic fluorine, EOF = extractable organic fluorine, TOP = total oxidizable precursor assay).

		Maximum concentration reported by each method						Relative comparisons between methods (%)				
		TF	TOF	AOF	EOF	TOP	Unit	TF v TOF	TF v AOF	TF v EOF	TF v TOP	Reference
	Groundwater				4611	1793						Ruyle et al., 2023
	Surface and groundwater			110	440	340	μg/L					Han et al., 2021
	River water	269.8		1.5	0.22		μg/L		0.6	0.1		Gehrenkemper et al., 2021
	Industrial wastewater			25,000	27,000		μg/L					Forster et al., 2023
	Groundwater	5,000,000				100,000	ng/L			0	2	Singh et al., 2019
	River/drinking water			18,500			μg/L					Bach et al., 2017
Water	River water	110,000			270		ng/L			0.2		Metzger et al., 2019
	Fish	1,777,000			16,000		ng/g			1		Yeung et al., 2013
	Blood (wild rat)	192			134		ng/mL			70		Yeung et al., 2009a, 2009b
	Eggs	66.6			11.1		ng/g			17		Haque et al., 2023
	Eggs	4.38			6.35		ng/g			145		Haque et al., 2023
	Marine mammal liver	9196			3538		ng/g			38		Spaan et al., 2020
	Fish liver	9540			1590		ng/g ww			17		Yeung et al., 2009a, 2009b
	Aquatic biota	15,300			150		ng/g ww			1		Loi et al., 2011
	Human serum	1330			45	1.85	ng/mL			3	0.1	Cioni et al., 2023
	Human blood		1160		1070		ng/mL					Miyake et al., 2007
	Human blood	166			13.2		ng/mL			8		Yeung et al., 2008
Biota	Human serum	0.41			0.35		μg/g			85		Liu et al., 2020
	Soil	738,504			209		ng/g dw			0.03		Wang et al., 2013
	Surface soil	738,672			200		ng/g dw			0.03		Tan et al., 2014
	Suspended Particulate Matter (SPM)				695	220	μg/kg					Simon et al., 2023
	Sewage sludge	106,000			304		ng/g			0.29		Spaan et al., 2023
Soil/sediments	Sludge SRM 2781	813,000			3590		ng/g			0.44		Spaan et al., 2023
Dust	Dust SRM 2685	315,000			417		ng/g			0.13		Spaan et al., 2023
	Dust	17,800,000			17,600		ng/g			0.1		Young et al., 2022
	Textiles	5130				80	μg/g				1.6	Schellenberger et al., 2022
	Textile	1356			58		μg/g			4		Roesch et al., 2024
	Awing fabric	2064			64		mg F/kg			3		Zweigle et al., 2023
	Imitation linen	15			0.2		mg F/kg			1		Zweigle et al., 2023
	Outdoor fabric	126			4		mg F/kg			3		Zweigle et al., 2023
	Shower curtain	34			2		mg F/kg			6		Zweigle et al., 2023
	Cosmetic	6.01			4.93		mg/g			82		Pütz et al., 2022
	Cosmetic	10,581			3106		nMF			29		Namazkar et al., 2024
	Fire suppression pipe	7.07	7.07				mg/L	100				Lang et al., 2022
	AFFF	5370			840	724	mM F			16	13	Ruyle et al., 2021
	AFFF	18,000	17,800				μg/mL	99				Weiner et al., 2013
	Papers	430				7.8	nmol F/cm^2				2	Robel et al., 2017
	Brick tea	276			118		μg/g			43		Zhang et al., 2017
	Powders	19,200			296		μg/g			2		Schultes et al., 2018
	Photolithography materials	18.2		2.38			g/L		13.1			Jacob and Helbling, 2023
	Child car seat	9437				1260	ng/g				13	Wu et al., 2021
Commercial products	Food package	17.8			0.49		μg/cm^2			3		Schultes et al., 2019
Air	Air	1100	1100				ng/m^3	100				Lin et al., 2022

dw = dry weight, **ww** = wet weight

unidentified organic fluorine (UOF), identified organic fluorine (IOF), hydrolyzable organically bound fluorine (HOF), and unknown or unidentified PFAS (UPFAS). Cioni et al. (2023) reported that the serum concentrations of UTF (including inorganic fluoride and organic fluorinated compounds not extracted or partially extracted with organic solvent) ranged between 5 and 1194 ng/mL. In the case of UOF, some studies reported concentrations as a percentage, while others reported it as a concentration with units. In biota (liver samples of cetaceans) (Lauria et al., 2024) and sediment (Guckert et al., 2022), percentages ranging between 0 and 27% and 84–95% of UOF, were respectively reported. In human samples (comprising of blood and serum), the concentrations of UTF reported ranged from 0 to 34.8 ng/mL. IOF has been measured in human blood/serum and placental tissue at concentrations ranging from 0.53 to 58 ng (Kaiser et al., 2021; Liu et al., 2020), and concentrations of 10–160 ng/g in human hair and nails (Liu et al., 2020). HOF is a new total PFAS parameter recently introduced by Roesch et al. (2024). They compared HOF to other methods like EOF across different product types. They found that HOF generally yielded higher concentrations than EOF, especially for fluoropolymer-based products, suggesting it captures more PFAS. The following HOF concentrations were reported: Textile (1380–76,280 ng/g), food contact paper (70–79,730 ng/g), carpet (30–180 ng/g), and baking sheet (70–9200 ng/g). UPFAS was defined as TOF minus known PFAS; it was reported for fish samples in Canada as a percentage composition profile (32.3–97.7%) (Yeung and Mabury, 2013), as well as in AFFF samples as a total concentration (441–15,557 μg/mL) (Weiner et al., 2013).

5.2. *Mass balance and total PFAS parameters*

The fluorine mass balance approach is a fundamental analytical method used to account for the total fluorine content in various matrices. This method is particularly crucial in assessing per- and polyfluoroalkyl substances (PFAS), where a significant portion of fluorine often remains unquantified or unidentified. One hundred and six studies (68%) in this review made mention of the term mass balance. However, there were many different ways in which this was reported. It was most commonly referred to when comparing the sum of PFAS identified by a targeted HPLC-MS method against a total PFAS method. It was also commonly used to compare masses obtained by two total PFAS methods. Several specific instances were used to discuss changes between sample types or a form of remediation/treatment.

Due to the variability in methods used by different authors, it is challenging to draw strong conclusions about how the fluorine mass balance varies in different matrices. A common theme, however, was the many examples demonstrating how little we know about the composition of the total PFAS measurements being made. In seawater, 60–90% of the organofluorine fraction was unknown (Miyake et al., 2007). In river water, EOF and AOF accounted for only 0.04–0.28% and 0.14–0.81% of TF, respectively (Gehrenkemper et al., 2021). In diffuse contaminated surface water samples, >95% of AOF remained unidentified (Wagner et al., 2013). In industrial and municipal wastewater samples, only 10% of the total EOF was accounted for by 73 identified PFAS, leaving 90% unidentified (Aro et al., 2021b). Similar uncertainties were reported in biota, with 83.8% of total fluorine in fish liver samples unidentified (Aro et al., 2021a; Yeung et al., 2009a). Similarly, in shrimp samples, only 10–12% of EOF was comprised of known PFAS (Loi et al., 2011), and the contribution of EOF to TF in emergent aquatic insects ranged from 0.2 to 24% (Koch et al., 2021). Studies that used human samples reported some of the highest explained total fluorine proportions. In human serum and cord blood, only 24% and 9%, respectively, of EOF was unexplained (Kaiser et al., 2021). Similar results reported by Aro et al. (2022) showed that 84% of EOF could be explained by targeted analysis. The proportions of unknown fluorine in soil, sediments, and dust were generally higher than those reported for other matrices. In sediment samples from Lake Mjøsa and River Alna, 99.39% and 96.6% of EOF, respectively, were unidentified (Aro et al., 2021a). In soil samples, EOF accounted for a small proportion of TF, with percentages ranging from 0.01 to 1.75% (Roesch et al., 2022). Air and dust samples showed a high percentage of unknown organic fluorine. In air samples, the percentage of unknown organic fluorine ranged from 87% to over 99% (Forster et al., 2023). In dust samples, the results indicated that only 1.2% of total fluorine was accounted for by 24 targeted PFAS, suggesting a significant presence of unknown non-polymeric and polymeric PFAS (Young et al., 2021). Total fluorine measurements in many consumer products were also poorly explained. Textiles, clothing, and face mask analysis revealed that the fluorine attributable to methanol-extractable target PFAS analytes and oxidizable precursors did not exceed 0.1% of the total fluorine measured (Rodgers et al., 2022). This highlights the presence of a large fraction of unidentified fluorine in consumer goods and textiles, possibly due to fluoropolymers (Roesch et al., 2024; Young et al., 2021). The fluorine mass balance approach reveals significant gaps in our understanding of the full spectrum of fluorinated compounds in various matrices. While targeted PFAS analyses provide valuable insights, they often leave a substantial fraction of total fluorine unexplained, highlighting the presence of unidentified fluorinated substances. These findings underscore the need for advanced analytical methods and comprehensive studies to better quantify and identify the full range of fluorinated pollutants in the environment, consumer products, biota, and human samples.

6. Knowledge gaps and recommendations

Our systematic review synthesizes total PFAS concentrations reported across 156 peer-reviewed articles. The data shows a regional bias, with the majority of studies originating from North America, particularly the United States, while significant data gaps persist in South America and Africa. To achieve a more holistic understanding of PFAS distribution and its global environmental impact, future research must encompass all geographical regions. A predominant focus of the reviewed studies was on environmental matrices, particularly water samples (e.g., groundwater, surface water, rivers, tap water, leachates, and wastewater effluent/influent from municipal and industrial treatment plants) and solid samples (including soil, sediments, suspended particulate matter, and sludges). Additionally, ongoing research into other matrices shows concentrations reported from paper, textile, and food packaging materials, as well as biological matrices (biota), cosmetics (personal care products), and serum/blood samples. However, PFAS concentrations in air and dust remain significantly understudied, highlighting a critical gap in atmospheric PFAS research.

The concentrations reported for total PFAS parameters are highly diverse, spanning a myriad of reporting units across studies (e.g., mg/L, μg/m^3, nmol/cm^2, μg/g, mMol/L, counts/μCoulomb, %, etc.), thereby complicating the potential of inter-studies comparison. Therefore, future research should consider using generally acceptable reporting units to communicate their data (e.g., ng/g for solid samples, ng/L for water samples, ng/m^3 for air samples, ng/mL for serum/plasma or other aqueous samples, etc.). For reported mass balance, the percentage contribution of individual target PFAS parameters for matrices evaluated is smaller compared to the concentration obtained from parameters evaluating OF concentrations. The percentages obtained from parameters such as EOF, AOF, and HOF compared to the TF also show that there are unaccounted concentrations. After EOF or AOF analysis, target PFAS testing can be conducted to establish a mass balance, helping to estimate the amount of unquantifiable OF. For samples with a significant proportion of unquantifiable OF, methods like the TOP assay with tandem mass spectrometry, suspect screening, or non-target analysis can identify the unquantifiable OF.

A key issue discussed in several studies is the inadequacy of traditional targeted PFAS analysis to fully account for total PFAS concentrations. Organofluorine parameters, such as TF, TOF, EOF, and AOF, measured using diverse instrumental methods, may often overestimate PFAS concentrations due to the inability of these techniques to differentiate between PFAS-related and non-PFAS-related fluorine content. The CIC method, one of the instrumental methods, was predominantly used to evaluate TF and EOF, which are the most commonly assessed total PFAS parameters in the studies reviewed. Dixit et al. (2024) attempted closing the analytical gaps on total PFAS by evaluating nine (9) techniques for the determination of total organic fluorine in AFFF-impacted water. The authors observed that for the same sample, USEPA-targeted methods and AOF measured via PIGE and NME yielded estimates comparable to TF. In contrast, TOP assay, suspect screening, and

AOF assessed via CIC reported concentrations 2–3 times higher. This variability highlights the challenges in selecting appropriate methods for total PFAS quantification, especially across different methods and matrices.

We observed a broad range in the LODs across different sample matrices, both within and between matrix types. Water matrices generally showed the lowest detection limits with LODs of several thousand parts per trillion (ppt). In contrast, soil, sediment, suspended particulate matter, sludge, biota, and industrial/personal care products exhibited higher LODs, often in the parts per million (ppm) range. The detection limits for cosmetics (personal care products) were the highest of all matrices examined. Across all sample types, TF exhibited higher LODs compared to other organofluorine parameters. Organofluorine-based detection limits were consistently higher than those observed for targeted PFAS analysis and the TOP assay. This suggests that total PFAS concentrations could be underreported when relying solely on organofluorine measurements, especially when blank corrected.

There are calls to move toward regulations and legislation considering total PFAS concentrations. However, determining a total PFAS concentration is not straightforward. Careful consideration must be placed on selecting the most appropriate tool(s) for this task. Total fluorine methods have limitations, so the application of different methods on the same sample can generate results differing by several orders of magnitude. Applying the wrong method to calculate total PFAS in a sample could lead to over or underestimation, which would be detrimental to PFAS producers and the environment. There is a need for improved standardization of instrumental methods and reporting. This will aid these challenging decisions by ensuring consistency and comparability when comparing data across multiple studies.

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CRediT authorship contribution statement

Ifeoluwa Grace Idowu: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Okon Dominic Ekpe:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **David Megson:** Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Conceptualization. **Pennante Bruce-Vanderpuije:** Writing – review & editing. **Courtney D. Sandau:** Writing – review & editing, Resources, Funding acquisition.

Declaration of competing interest

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Data availability

Data is attached as supplemental information

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