Review

A Review of Analytical Methods and Technologies for Monitoring Per- and Polyfluoroalkyl Substances (PFAS) in Water

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Abstract: Per- and polyfluoroalkyl substances (PFAS) consist of a range of manufactured fluorinated chemicals that are used in a variety of household and waterproofing products, industrial processes, and firefighting foams. In the past few years, there has been increasing concern about PFAS in the environment, since they are difficult to break down through natural processes, are highly persistent in humans, animals, soils and waters, and can travel long distances in surface and groundwater. This has created an increased need for PFAS analysis. Most PFAS monitoring currently takes place using field sampling and chromatographic analytical methods, which are laboratory-based and are very costly when used to monitor PFAS in the environment. Using a semi-systematic literature review approach, a comparative study is conducted in this article on the available analytical methods and sensor technologies that can be used to monitor and detect PFAS in the environment, including chromatographic, instrumentation analysis, and sensor-based methods. This study considered four critical factors for effective and efficient monitoring methods, which include the type of PFAS detected, removing background levels, determining detection limits, and identifying samples. In general, other analytical instruments are used in conjunction with chromatographic techniques for detecting both target and non-target analytes at a lower level of detection (LOD). It is shown that even though some sensor types have a low LOD, they are only useful for detecting targeted PFAS in water samples. However, sensors are an emerging technology that could be developed to enable low-cost, portable methods for the remote detection of PFAS species on-site.

Keywords: PFAS; contaminants in water; environmental monitoring; chromatography technique; alternative methods and technologies; sensor-based technology

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a suite of anthropogenic organic compounds, most of which contain alkyl chains with carbon atoms bonded to fluorine atoms [1–3]. A number of sources of PFAS can be found in everyday life, such as firefighting agents, medical devices, and industrial applications that can include photo-imaging, photo-resist, waterproofing, and anti-reflective coatings, as well as carpet, textile, and leather treatments [4–6]. Table 1 provides a brief summary of the PFAS family and its classification.

Over the past decade, there have been increased detections of PFAS compounds in natural waters [7], wastewater, sludge [8], and aquatic [9] and land species [10]. Recently, there has been a shift from long-chained PFAS to short-chained PFAS [11] because short-chained PFAS have a shorter half-life [12] in the body and are less bioaccumulative [13]. However, with a shorter chain, these PFASs have higher water solubilities [11], vapour pressures [12], and weaker adsorption [13] to particles resulting in higher mobility [14], i.e.,

transported faster [15] and at greater distance from source. Biological transfer is also easier, for instance from maternal to cord serum in humans [4,15–17].

Table 1. An overview of the carboxylate and sulfonate PFAS groups and their classification [18–20].

Carbon Number	Type	Carboxylate Ion (or Acid Form)	Sulfonate Ion (or Acid Form)
4	Short chain	Perfluorobutanoate (PFBA)	Perfluorobutane sulfonate (PFBS)
5		Perfluoropentanoate (PFPeA)	Perfluoropentane sulfonate (PFPeS)
6		Perfluorohexanoate (PFHxA)	Perfluorohexane sulfonate (PFHxS)
7		Perfluoroheptanoate (PFHpA)	Perfluoroheptane sulfonate (PFHpS)
8	Long chain	Perfluorooctanoate (PFOA)	Perfluorooctane sulfonate (PFOS)
9		Perfluorononanoate (PFNA)	Perfluorononane sulfonate (PFNS)
10		Perfluorodecanoate (PFDA)	Perfluorodecane sulfonate (PFDS)

Given that the carbon–fluorine bond is very strong [21] and not normally broken down by natural processes, this has led to widespread concern over the persistence of PFAS in the environment [22]. Indeed, one recent study describes PFAS contamination as "cyclical", in the sense that any disposal technique returns either the original PFAS or its degradants to the environment [23,24]. Furthermore, the authors argue that standard methods for landfilling do not reduce or degrade PFAS species. In contrast, when a product that contains PFAS is disposed to landfill, the PFAS will remobilise into the landfill leachate and end up in the natural environment or wastewater treatment plants [23]. Due to its high resistance to degradation, PFAS can be transferred into sewage sludge and effluent, creating secondary PFAS impacts from the land application of sludge for agricultural purposes [25].

Recent studies report that PFAS species can be bioaccumulated in agricultural crops [25], contributing to PFAS transmission to humans [26] and animals through food consumption [27]. The sorption behaviour of PFAS is dominated by hydrophobic interactions with organic materials [28,29]. A number of studies have shown that highly hydrophobic PFASs tend to sorb to suspended solids (TSS), whereas the less hydrophobic compounds predominate in aqueous solutions [27,30–34]. Different factors such as the route of PFAS transport after use (runoff, seepage, direct discharge), the elapsed time since the end of firefighting activities, and the composition of the firefighting foam have an impact on the distribution of PFAS profiles [33].

Humans are vulnerable to PFAS exposure: different types of PFASs have been detected in clothes, footwear, and upholstery impregnated with PFAS [35]. Further, human consumption of fish, seafood, fruits, and their products has been shown to expose them to PFAS through the environmental intake of these organisms [35]. PFAS exposure has been linked to several health problems, including reduced kidney function, thyroid disruption, brain and behaviour disorder, induced obesity and type 2 diabetes, proteinuria, haematuria, immunosuppression, carcinogenic risks, and low birth weight [4,35,36].

According to the United States Environmental Protection Agency (US EPA), the health advisory level for perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), or their salts over a lifetime is 70 ng/L [2,37]. However, other states in the US have their own health-based monitoring standards for PFOA and PFOS, which range from 13 ng/L to 1000 ng/L [38]. More recently, New York State has set the maximum contaminant levels (MCLs) for drinking water standards as 10 ng/L each for PFOA and PFOS [39]. For 99 percent species protection, the Australian and New Zealand Environment Conservation Council (ANZECC) prescribes a limit of 0.23 ng/L for PFOS in fresh or marine waters [40]. This is of the same magnitude as the level of reporting (LOR) of PFOS and other PFAS species by commercial laboratories [41]. Moreover, Food Standards Australia New Zealand (FSANZ) has proposed trigger points for the investigation of PFOS and PFOS + PFHxS combined, which are for milk (0.4 g/kg), fruits and vegetables (0.6 and 1.1 g/kg), finfish (5.2 g/kg), mammalian meat (3.5 g/kg), and eggs (11 g/kg) [42]. A state or territory food jurisdiction could use FSANZ's proposed trigger points for PFOS + PFHxS combined and

PFOA to identify when PFAS levels exceed these values, and more research is needed to measure PFAS in food.

Since PFOA and PFOS are present at such low concentrations, it is necessary to develop highly sensitive techniques for their detection. In addition, the measurement of PFAS concentrations in environmental samples can be challenging, due to the variability in mobility of different PFAS species at a given contaminated site, and the low detection limits required to meet regulatory criteria [43–46]. In order to assess trends over time, a baseline of future monitoring activities needs to be established [47–49]. However, technological advancements have enabled the detection of PFAS at very low concentrations in waters and soils, leading researchers to explore the sources, fates, and impact of PFAS compounds [50–52]. The long persistence of PFAS in the environment and its consequent risks of human and ecological uptake make it imperative for researchers to develop improved methods for their monitoring.

The aim of this review is to provide a comprehensive overview of the evolution of methods and technologies that are used to monitor and detect PFAS in the environment, with a particular focus on water and soil, as they are the primary transport sites of PFAS. In this study, a semi-systematic literature review is conducted by collecting peer-reviewed sources in order to investigate the development of PFAS detection and monitoring methodologies and technologies in water and soil. To assist investigators in a more efficient PFAS environmental monitoring process, this study synthesises the current development of PFAS detection and monitoring methodologies, as well as the gaps and challenges that need to be taken into consideration for the future directions of PFAS environmental monitoring in order to help them make more efficient decisions.

2. Method

2.1. Semi-Systematic Literature Review

A semi-systematic literature review is conducted in this study to investigate methods and technologies for detecting and monitoring PFAS. A summary of the review methodology is shown in Figure 1.
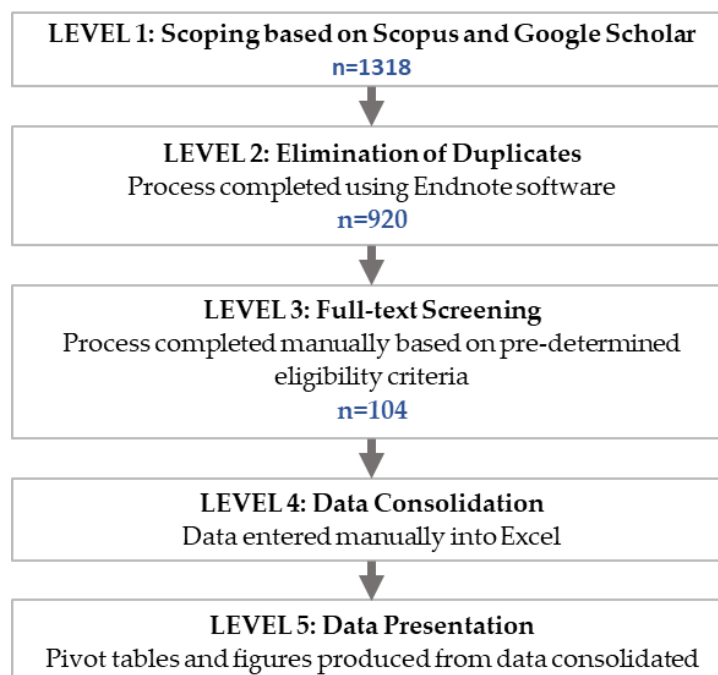

Figure 1. Flowchart of the semi-systematic literature review.

2.2. Sources of Information and Screening Process

In this study, peer-reviewed sources were retrieved from Scopus and Google Scholar, using the keywords "PFAS monitoring" and "PFAS detection", in the article title, abstract, and full manuscript, which were only published in journals and conference papers, in order to ensure that the selection process was limited to articles addressing PFAS-related research. As a result of the study, it was found that the first published article mentioning PFAS as a possible source of environmental contamination was published back in 2003. Up through June 2023, the search produced 1318 relevant documents, which were imported to reference management software EndNote^{X9} These documents were then filtered by the software to remove 398 duplicate and nonrelevant entries. A full-text screening was conducted based on a set of "Research Questions (RQ)" summarised in Table 2.

Table 2. Eligibility criteria used as methodical guidelines for full-text screening.

Research Questions (RQ)	Research Focus
RQ 1: What is the purpose of the study?	PFAS monitoring and detection methods
RQ 2: When were these data collected?	Studies conducted between 2003 to June 2023.
RQ 3: Which sources are considered for PFAS contamination?	Studies conducted on surface waters, tap waters, aqueous waters, soils, or sediments
RQ 4: What was the screening process?	Journal and conference publications, full manuscripts and written in English only.

Each of the 104 articles was coded into an Excel spreadsheet based on the following criteria: paper number, authorship, document title, year of publication, country of study, study type, methodology, sample, test location, detection limit, cost involved, type of PFAS detected, and comments on additional information. Pivot tables and figures were produced based on the data required for the presentation of results through a descriptive overview and a comparison study between existing methodologies.

The results of the Level 1 scoping process are presented in Figure 2, which gives a general overview of the timeline of studies that have been conducted to primarily detect and monitor PFAS, regardless of the type of sample investigated. This first review of PFAS as an environmental contaminant published in 2003 noted that there were not enough physicochemical data to provide a complete analysis of the fate of PFAS in the environment [53]. Figure 2 illustrates a rapid growth in interest in this topic from 2013, with 71% of articles published in the past three years under various topic areas related to it. The following sections analyse trends and the development of methods and technologies for monitoring PFAS in soil and surface water based on the 104 articles.
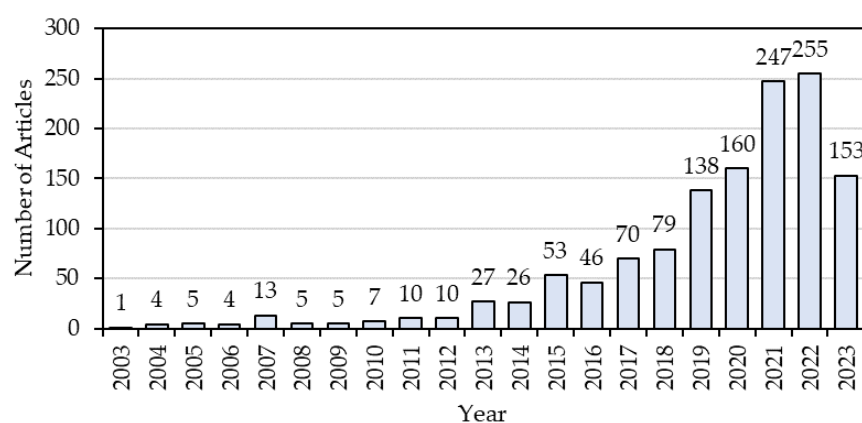

Figure 2. Distribution of publications on PFAS detection and monitoring (up to June 2023).

2.3. Publication Distribution

The compiled publications were categorised based on publication type: review papers, monitoring studies, and experimental studies. Among the publications, 56% reported results from environmental monitoring activities, 32% reported experimental results, and 12% reported literature reviews. It was found that most studies on PFAS in surface water and soil have been conducted in China, with 18 publications, followed by the USA with 15 publications. As of 2019, more countries have started publishing their monitoring reports, suggesting that environmental monitoring of PFAS and establishing baseline data have become more important. Furthermore, this is also a reflection of the actual shift in PFAS manufacturing from Western nations to Asian countries over the past few years [54].

Among publications categorised as 'experimental studies', the past five years have seen an increased focus on developing methods and technological advancements to detect and analyse PFAS. The increasing need to monitor PFAS worldwide has resulted in studies being conducted to improve current practices, whether through ease of analytical procedures, rapid analytical results, or reducing the overall costs.

The PFAS monitoring methods analysed in the selected publications were categorised into three categories: chromatographic techniques, alternative methods, and techniques and sensor-based detection techniques, as shown in Figure 3. The effectiveness of these methods must be assessed against the data quality objectives of the monitoring programme, so it is crucial to understand these objectives.
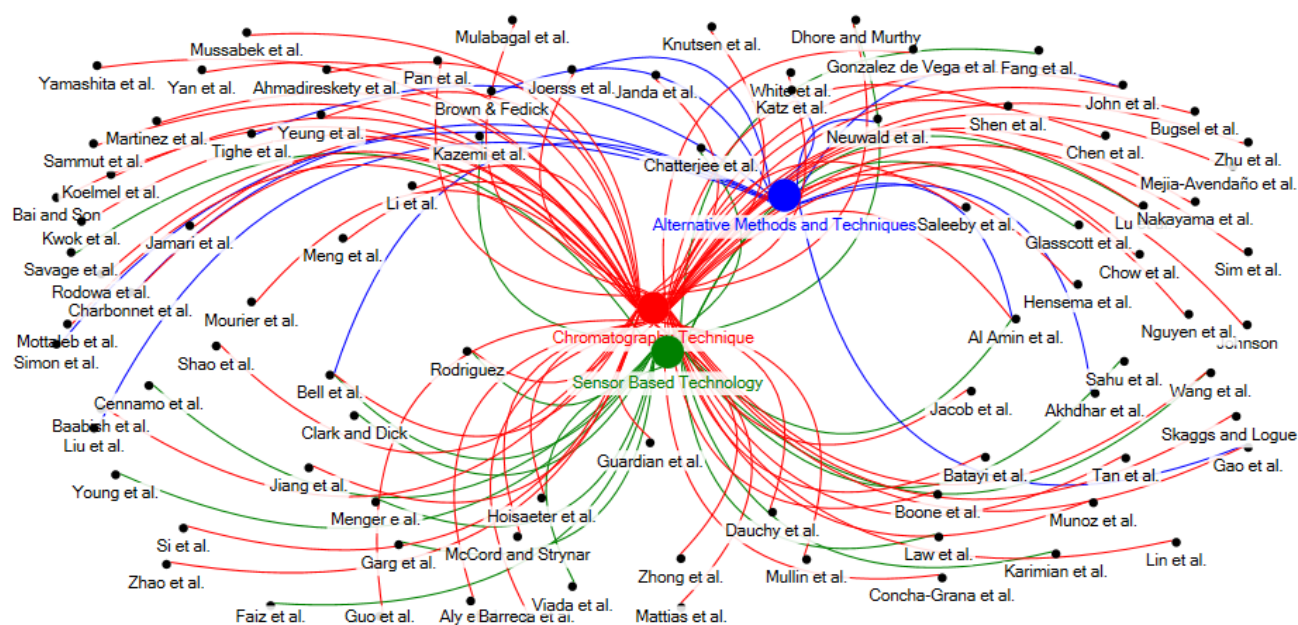

Figure 3. A network visualisation map of PFAS environmental monitoring methodologies and technologies.

3. Results and Discussion

3.1. PFAS Monitoring Methodologies and Technologies

There have been many standardised and non-standardised extraction and analytical techniques developed for PFAS analysis [55–62]. As a result of advances in instrumentation, chromatographic methods are now the preferred method for PFAS separation, as demonstrated by the monitoring studies identified [2,63]. This technique involves separating compounds by their selective adsorption onto a porous medium, which tends to separate the species by boiling points and mobilities [64]. This can be effected using liquid chromatography (LC) or gas chromatography (GC), depending on whether the compound is ionic or neutral [61]. Analysing PFAS in soil and sediments are generally similar to the ones described for water. Samples collected usually need to be dried, sieved, homogenised, ex-

tracted, and concentrated prior to the HPLC-MS analysis. However, for soil and sediments, some factors should be considered prior to LC analysis.

　　Based on the publications examined, approximately 71% of the studies were conducted using methodologies derived from liquid chromatography coupled with tandem mass spectrometry (MS). Those with a liquid mobile phase are commonly identified as LC-MS if they use a single mass spectrometry stage, or LC-MS/MS if they use two mass spectrometry stages.

　　From Figure 4, it can be seen that the majority of publications used some form of chromatographic technique to determine PFAS concentrations in either water or soil.
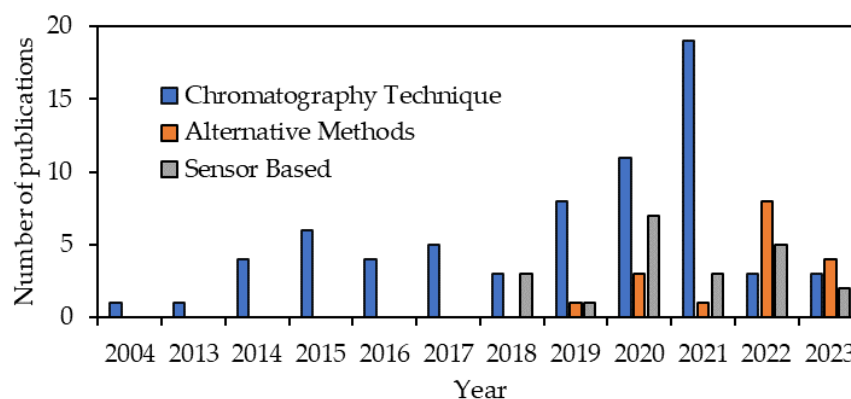

Figure 4. Distribution of publications used for environmental monitoring of PFASs.

　　The LC-MS/MS technique is usually used to measure targeted PFAS species, including known PFAS such as PFOA and PFOS. Due to the ever-increasing number of emerging PFAS being detected, non-targeted approaches have been used to improve environmental monitoring results.

　　The use of sensor-based technology for detecting PFAS in the environment is relatively new. The sensor-based technology uses water samples as the aqueous phase for an electrochemical-based sensor, making water samples a critical component of the instrumentation system [65]. The PFOS is then added to the aqueous phase where the surfactant is ionised and presents as an anionic form, PFOS, contributing to the study of matrix effects on electroanalytical signals. Similarly, for optical-based sensors, water samples are used as aqueous matrices of varying complexity in order to demonstrate the ability of the sensor to quantify precursor formation. As an example, water is required for hydroxylation to occur on the surface of nanoporous anodic alumina (NAA), which leads to fluorous interactions (F–F) when exposed to PFAS solutions. RIfS (reflectometric interference spectroscopy) can monitor this interaction under flow conditions in real time by quantifying changes in effective optical thickness (OTeff) [66].

　　The sensor-based technology can be categorised by the type of sensors used, which include optical-based sensors, fluorescence-based sensors, smartphone-based sensors, biosensors, and electrochemical sensors [64,67,68]. In each case, the outcomes of the categorisation vary slightly from one paper to the next. In some cases, categorisation can be a challenging task since some sensors have several characteristics that separate them into a number of different categories based on their characteristics. Table 3 attempts to classify sensors based on the information from the review publications. The two categories of sensors observed are the optical-based sensors and the electrochemical sensors.

　　Some examples of other methods that have been successfully used to detect PFAS are provided in Table 4. PFAS analyses utilising total oxidisable precursor (TOP) assays have been the most discussed and applied, with 12 publications mentioning or applying this methodology.

On the basis of the collected information on PFAS monitoring studies, it has been determined that four specific critical factors must be met in order for the monitoring methods and techniques to be effective and efficient.

Factor 1: Types of PFASs detected: Detection methods should be capable of detecting precursors and emerging PFAS species. This is an important factor that has been reported in the majority of the previous studies.

Factor 2: Elimination of background levels and/or pre-treatment: Methods should be able to reduce the potential effect of background contaminants that might affect the validity of the results.

Factor 3: Limit of detection: Methods should detect low levels of PFAS concentrations, which are sufficiently low to meet regulatory requirements.

Factor 4: Analysis of various types of samples: Methods should be able to analyse a wide range of environmental samples.

The following sections will use these critical factors in order to assess the effectiveness of different methodologies which are currently available for monitoring the effects of PFAS on the environment.

Table 3. Classification of sensor-based technology for PFAS detection as summarised from [2,39,63,64,67,68].

Sensor-Based Technology	Optical-based [67,68]	Using optical signals: • Absorbance • Raman scattering • Refractive index • Fluorescence Nanoparticles-based: • Gold (AuNP) • Quantum dot (QD) • Polystyrene modified • Magnetic iron oxide Dye: • Fluorescein • Cationic Optical fibre: • Silica-based • Plastic-based (POF)
	Electrochemical-based [63,64]	Using quantifiable electrical signals: • Potentiometric • Voltametric • Amperometric • Impedimetric • Conductimetric Electrode: • Molecularly imprinted polymers (MIP) • Metal: gold, platinum, nickel • Metal organic frameworks (MOFs) • Ion-selective electrodes (ISE)

3.2. Effectiveness of the Chromatographic Technique

3.2.1. Types of PFASs Detected

The standard method used to detect PFAS in groundwater, surface water, and wastewater samples is US EPA Method 8327 [69], which uses multiple reaction monitoring (MRM) LC-MS/MS to determine 24 analytes, including PFOS and PFOA. In drinking water, US

EPA Method 537.1 [70] has been approved for 18 different PFAS, and Method 533 [71] for an additional 11 PFAS, mostly short-chain species. The US EPA provides the full list of analytes that can be measured using both methods [72]. Various non-standardised methods are also constantly being developed by researchers to improve the detection of PFAS [55–58].

Chromatographic techniques have the advantage of detecting and quantifying more PFAS in a single analytical run but can experience difficulties in the analysis of varied sample matrices and in preparing efficient samples [20]. A quality assurance/quality control (QA/QC) procedure must be followed throughout the entire sampling and sample preparation process to minimise background contamination, since several factors can cause false-positive or false-negative PFAS concentrations [60–62]. For instance, it is essential that no contact be made with polytetrafluoroethylene (PTFE) or other fluoropolymer materials, as this will lead to overestimates [61,62].

3.2.2. Elimination of Background Levels and/or Pre-Treatment

To enhance selectivity, sensitivity, and clean-up of target analytes from background, sample preparation and/or pre-treatment is usually required before chromatographic analysis. Extraction techniques such as solid phase extraction (SPE), solid phase micro extraction (SPME), liquid–liquid extraction (LLE), and dispersive liquid–liquid micro extraction (DLLME) can be used for this purpose [20]. However, due to fluorinated materials in sample pre-treatment and instrumental determination, LC can overestimate analyte concentrations [20], while GC can underestimate analyte concentrations due to the inability to achieve 100% yield in derivatisation reactions or incomplete transfer of derivatised analytes to GC solvents [61]. The results suggest that stand-alone LC techniques are easily affected by background contaminants, and other instrumental methods are required to improve accuracy.

3.2.3. Limit of Detection

LOD is an important parameter used to indicate the lowest concentration of PFAS that can be detected using an analytical method. As fast liquid chromatography techniques are increasingly used for PFAS analysis, high-performance liquid chromatography (HPLC) is gradually being replaced with ultra-high-performance liquid chromatography (UHPLC) and ultra-performance liquid chromatography (UPLC) [64,73]. According to previous studies, UHPLC analysis had the best LOD for many analytes and improved analysis time [64]. In Table 4, the LOD achieved for water samples using chromatographic techniques are presented. These studies indicate that these techniques are capable of meeting the New York State low detection limit of less than 10 ng/L. Although these publications mainly address liquid chromatography techniques for water analysis, LC conditions for soil and sediment analysis are mostly similar.

3.2.4. Analysis of Various Types of Samples

Chromatography techniques have been successfully used to validate PFASs from a wide range of samples, including solid matrices, aqueous matrices, biological matrices, and air, dust, etc. [20]. Figure 5 illustrates the number of publications under monitoring studies based on the types of samples analysed. The number of publications on water monitoring is approximately 32% higher than the number of publications on soil monitoring, and about 23% of publications cover both water and soil monitoring. Generally, samples must be dried, sieved, homogenised, extracted, and concentrated before LC-MS analysis. However, for soil and sediments, several additional factors need to be considered prior to LC analysis. These include the following:

- Pre-treatment of soil samples should be focused on capturing PFAS with diverse properties, especially hydrophobic compounds, and cationic, anionic, or zwitterionic species [54].
- Background interferences should be cleaned up, as some recoveries can exceed 100%, showing high background interference [20].
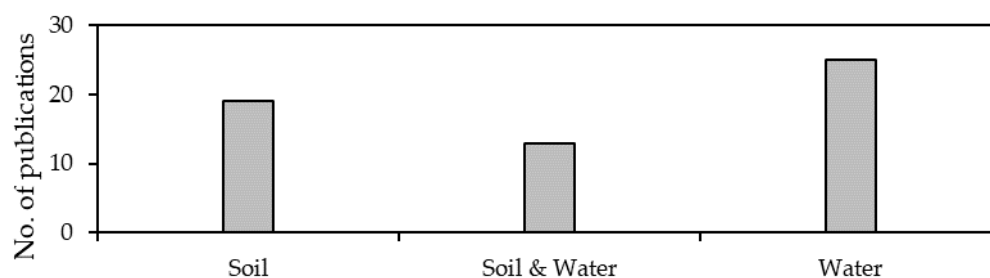
Figure 5. Types of samples analysed using chromatography techniques.

3.3. Effectiveness of Alternative Methods and Techniques

3.3.1. Types of PFAS Detected

It has been reported that many researchers are using TOP assays in conjunction with other methods to examine whether emerging PFAS species are present in the environment. For example, high-resolution accurate mass spectrometry (HRMS) and an improved TOP assay methodology are being used in Canada to examine surface and subsurface soil samples and groundwater samples [74]. In addition to TOP assays, mass spectrometry techniques have also been used to detect new PFAS compounds [75]. Some experimental testing on targeted PFAS has also been conducted to assess the validity of this new methodology. One study tested a new 3D-printed cone spray ionisation (3D-PCSI) technique using ambient ionisation mass spectrometry for detecting 11 targeted legacy PFAS [76]. Similarly, perfluorobutane sulfonate (PFBS) and perfluoropentanoic acid (PFOA) have been analysed using high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS-GFMAS) without additional SPE to test their liquid–solid extraction method [77]. With the development of portable reading kits for TOP assays, water samples have been spiked with PFOA before and after oxidation to study precursor concentrations [78]. Therefore, depending on methodology and combination of techniques, both targeted and non-targeted PFASs can be analysed; however, at present, identifying unknown precursors is proving to be the biggest challenge. Using these analytical tools along with UHPLC-HRMS will be a feasible solution [79].

3.3.2. Elimination of Background Levels and/or Pre-Treatment

Similar to chromatography, these alternative analysis techniques require sample preparation and/or pre-treatment to enhance selectivity, sensitivity, and clean-up of target analytes from the sample background. Therefore, the extraction step for PFAS analysis will be similar prior to using either chromatographic technique, HRMS techniques, TOP assays, and other total organic fluorine (TOF) techniques.

3.3.3. Limit of Detection

In contrast to chromatography, other techniques do not collect as much data as chromatographic techniques. A summary of LODs for PFAS measurements produced by notable experimental and environmental techniques is presented in Table 4. Similar to the observation about chromatography techniques, more studies were conducted for water samples than soil samples.

3.3.4. Analysis of Various Types of Samples

From the limited published studies using alternative analytical methods, Figure 6 represents the trends of PFAS monitoring and research activities using alternative instruments to chromatography. Similar to what was observed regarding the type of samples used for chromatography techniques, more studies were conducted on water samples (78% of the total publications under these two categories) than on soil samples. It is important to note that other types of samples have been used, such as biological matrices (blood, plasma, serum, urine, and saliva), fish, seafood, textiles, and paper [20], indicating that

these methods have a broad range of monitoring applications similar to chromatographic techniques.
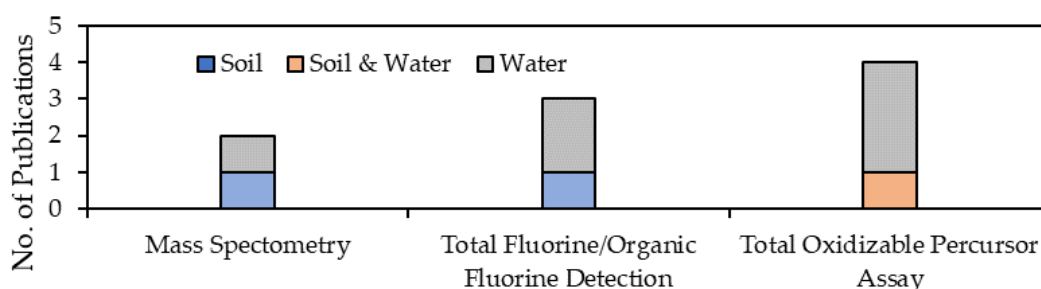

Figure 6. Types of samples analysed using alternative techniques.

3.4. Effectiveness of Emerging Sensor-Based Technology

3.4.1. Types of PFAS Detected

Unlike chromatography and other instrumental analysis techniques, sensor-based technology detects only targeted PFAS. With the efforts to replace PFOA and PFOS in a broad range of applications with alternative molecules, hexafluoropropylene oxide dimer acid (HFPO-DA, known as GenX), formed by hydrogenating ammonium perfluoro (2-methyl-3-oxahexanoate), has been found to be more toxic than PFOA [80].

In order to detect this specific contaminant, one study used molecularly imprinted polymer (MIP) electrodes on which HFPO-DA was extracted from the polymers and bound to the electrode surfaces [80]. As sensor devices are developed to be sensitive to certain types of targeted molecules, selectivity on other types needs to be enhanced, as highlighted in a previous study [81]. In order to detect PFOA, PFOS, and 6:2FTS in a smartphone-based/fluoro-SPE sensor, the authors found that improving the selectivity for particular anionic surfactants would be of benefit to future research [81]. Considering this, sensor-based techniques can be used for initial screening procedures to detect targeted PFAS at this stage.

3.4.2. Elimination of Background Levels and/or Pre-Treatment

Sensor-based technologies for PFAS detection also require extraction to clean up background levels as discussed previously. There are several types of water contaminants that contribute to these background levels, for example, surfactant anions such as ethylenediaminetetraacetic acid (EDTA), sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfonate (SDBS), and metallic cations such as Ca^{2+}, Mg^{2+}, F^-, and Cl^- [68]. They may interfere with signal generation by blocking the detection sites on probes, resulting in ambiguous results or false negatives, as well as hindering the selectivity of the sensor. Prior to quantification of PFAS by sensors, solid-phase, liquid–liquid, and solid–liquid extractions can be used as a pre-concentration step to reduce the effect of interferences like inorganic ions [68].

3.4.3. Limit of Detection

By eliminating background interference and sample pre-treatment, the sensitivity of the instruments can be lowered to the required limit of detection. Solid phase extraction (SPE) is capable of lowering the LOD for PFOA and PFOS in spiked tap and groundwater from 10 ppb to 0.5 ppb [82] Also, an efficient concentration procedure based on electrochemical aerosol formation can concentrate 10 common PFAS 1000-fold within 10 min [67]. AstkCARETM reagents (cationic dyes containing ethyl acetate and ethyl violet) have also been used in the extraction step for a sensor-based methodology developed by CRC CARE Australia [2]. Prior to the smartphone-based PFAS detection technique, astkCARETM reagents were used to remove background interferences from inorganic ions and other elements. Nano-enabled sensing can also address the issues of extensive sample preparation

and selectivity, as nanomaterials can be specifically designed to target particular analytes. For example, Ba^{2+} can be added to successfully complex non-fluorinated surfactants (for example, SDS and SDBS) in aqueous solutions to impede non-specific bindings during PFAS sensing.

In the case of smartphone app-based sensor technology, PFAS can be detected in soil samples and water samples after dual- or tri-extraction. During the extraction process, anionic surfactant (PFOA or PFOS) reacts with cationic dye to form an ion pair. With the smartphone app-based sensor, the anionic surfactant concentration can be monitored. While there is a lack of information on sensors used on soil samples, in the future, it is likely that advancements in sensor-based technology for PFAS detection will involve sample types other than water.

In the 22 collated publications, 100 data on LOD for different types of sensors used in PFAS quantification were extracted. More studies have been conducted on the LOD of fluorescence-based and electrochemical-based sensors, likely due to their potential to achieve low LODs [2,20,39,63–66,68,80,81,83–94].

3.4.4. Analysis of Various Types of Samples

Based on the reviewed publications, 91% of PFAS detection data was collected for water samples, while only 1–2% were collected from biological, textile, wastewater, aqueous film-forming foam (AFFF), or synthetic samples. An app-based reading kit developed in a previous study allowed PFAS to be analysed in water and soil samples after dual- or tri-extraction [20]. The anionic surfactant (PFOA or PFOS) reacted with the cationic dye to form ion pairs during the extraction process. Using an app-based smartphone sensor, the concentration of anionic surfactant was monitored [20].

Despite the lack of information on the type of sensors used in soil samples, there is a strong likelihood that sensor-based technology will become increasingly incorporated into PFAS detection in the future for soil and other samples other than water samples.

A brief summary of the results of the comparative study that was undertaken as part of this semi-systematic literature review can be found in Table 5. The baselines for comparison for all four critical factors are established based on the chromatography technique capability.

Table 4. LOD comparison reported from the collated publications.

Item	Type of PFAS	Samples	(LOD)	References
Chromatographic Technique				
Multiple monolithic fibre solid-phase microextraction (MMF-SPME)-HPLC-MS/MS	PFCA	Tap water, river water, wastewater, and milk samples	0.4–12.1 ng/L	[39,95]
Dispersive liquid–liquid microextraction (DLLME)-HPLC-MS/MS	Medium- and long-chain PFASs (CF$_2$ > 5)	Water and urine samples	0.6–8.7 ng/L	[20,96]
Vortex-assisted liquid–liquid microextraction (VALLME)-LC-MS	PFOS	Tap, river, and well water samples	1.6 ng/L	[54,97]
Ice concentration linked with extractive stirrer (ICECLES)-HPLC-MS/MS	PFHxA, PFOA, and PFHpA	Drinking water samples	0.05–0.3 ng/L	[98]
Acrodisc Filter multiple reaction monitoring (MRM)-UPLC-MS/MS	PFOS, PFOA, PFNA, and PFBS	Tap water and surface water samples	7–40 ng/mL	[99]
SPE extraction- UHPLC/(-) ESI-MS/MS	PFCAs, PFSAs, and perfluoro ethers	Surface water samples	0.48–1.68 ng/L	[100]
Sensor-based technology				
Biosensor, Colorimetric, Electrochemical, Electrochemiluminescence Fluorescence Nanoparticle Optical Fibre Photoelectrochemical Spectrophotometric	PFOS, PFOA, PFBS, GenX, 6:2 FTS, and others	Mostly water samples	Below 10 ng/L but mostly by incorporating chromatographic techniques	[20,65,66,85,94]
Alternative methods and techniques				
Total oxidisable precursor (TOP) assays	Total oxidisable PFASs	Water, surface/subsurface soil and groundwater samples	0.5–7.9 ng/L	[2,6,20,54,64,67,74,78,101–104]
Fluorine-19 nuclear magnetic resonance (19F NMR) spectroscopy	Total organic fluorine (TOF) and total fluorine (TF, organic and inorganic)			[2,20,54,102]
Inductively coupled plasma mass spectrometry (ICP-MS)	Fluorine-specific detection of PFASs after LC separation			[102]
Continuum source molecular absorption spectroscopy (CS-MAS)	Total fluorine			[102]
X-ray photoelectron spectroscopy (XPS)	Fluorine/organic fluorine detection			[20]
Particle-induced gamma-ray emission (PIGE) spectroscopy	Total fluorine measurements of HFPO-DA, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, and PFDA	Drinking water samples	<50 ng/L	[2,20,54,105]

Table 4. *Cont.*

Item	Type of PFAS	Samples	(LOD)	References
Chromatographic Technique				
3D-printed cone spray ionisation (3D-PCSI)	PFBA, PFHpA, PFOA, 6:2FTS, PFNA, PFOSA, PFOS, PFDA, PFUdA, PFDoA, and PFTrDA	Soil and sediment matrices	100 ng/L	[76]
High-resolution graphite furnace continuum source molecular absorption spectrometry (HR GF-MAS)	Total fluorine measurement of PFCA	Seawater, river water, and effluent samples	Without SPE: 0.1 mg/L With SPE: 300 ng/L	[106]
Laser thermal desorption (LDTD) coupled with Orbitrap HRMS	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, PFOS, PFDS, FOSA, 6:2 FTS	Surface water samples	0.03–0.2 ng/L	[61,107]
Total oxidisable precursor (TOP) assays	29 target analytes including PFUnDA, PFOA, and PFOS	Surface water samples	Method detection limit (MDL): 0.5–7.9 ng/L	[6]

Table 5. Comparison of the performance of various PFAS monitoring methods and techniques.

Methods/Techniques	Factor 1	Factor 2	Factor 3	Factor 4	Disadvantages
Chromatography	Targeted and non-targeted analytes	Sample extraction and clean-up required	Able to detect analyte concentrations below 10 ng/L	Soil, water, and other various sample types	• Unable to meet the growing demand for low-cost, portable, in situ, and rapid PFAS detection methods • Relies mostly on highly sophisticated instruments. • Analyses data in a highly time-consuming pro-cess
Other instrumentation analysis	Targeted and non-targeted analytes	Sample extraction and clean-up required	Some analyses are able to detect analyte concentrations below 10 ng/L (examples: LDTD, TOP), but mostly by incorporating chromatography techniques	Soil, water, and other various sample types	• It is difficult to identify unknown precursors of tar-geted and non-targeted PFAS • It can detect low levels of PFAS but still relies on chromatography to monitor PFAS levels below 10 ng/L
Sensor-based technology	Targeted analytes only	Sample extraction and clean-up required	Some sensors are able to detect analyte concentrations below 10 ng/L (examples: sensors based on biosensors, and electrochemical, electrochemiluminescence, fluorescence, photoelectrochemical and nanoparticle sensors)	Mainly water, potential for use with soil and other sample types	• Only targeted analytes can be quantified • Use in soil sample analysis is very limited

4. Conclusions

This study used a semi-systematic literature review approach to review the required outcomes from monitoring studies for PFAS in the environment. Using the collected information, four outcomes were identified as relevant to the monitoring methods and techniques. The monitoring method used will need to meet specific factors, including the type of PFAS detected, elimination of background levels, device detection limits, and types of samples analysed. Comparisons were made between current methodologies, including chromatography techniques, alternative instrumental analysis, and sensor-based technologies. Chromatography and, to some extent, other instrumentation techniques have some disadvantages, too. In particular, they cannot meet the growing demand for an easy-to-use, low-cost, portable, in situ, and rapid PFAS detection techniques, since these techniques require highly sophisticated instruments along with a generally lengthy analytical process [20,63]. As a result, research is focusing more on sensor-based technologies for environmental monitoring of PFAS. For PFAS monitoring to be successful in the future, portability and lower cost are two important factors to consider. They are particularly important for supporting PFAS monitoring activities in remote and developing countries where samples need to be sent over long distances to specialised laboratories.

4.1. Limitations

The use of chromatography-based methodologies for the measurement of PFAS has been widely acknowledged as the most accurate and reliable method for quantifying the amount of PFAS in the environment, so other methods have been compared to chromatography-based methodologies. It was found that other analytical methods are mostly used in conjunction with chromatography to detect both targeted and non-targeted analytes at lower levels of detection. In order to improve the reliability of the results of the PFAS detection procedure, all methodologies generally require extraction steps prior to PFAS detection. The sensor-based technology includes a number of sensor types that are capable of detecting PFAS levels at low concentrations. However, these devices can only be used to detect key PFAS targets and have been extensively used only for water samples under certain conditions.

4.2. Future Direction

There is a growing interest among researchers to develop sensors or sensor-based fast technologies for monitoring the environmental concentration of PFAS in order to achieve the following objectives [68]:

- Field test device: portable and capable of in situ PFAS analysis.
- Rapid analysis: detecting PFAS at its source in time to take immediate action. Laboratory results for remote sites can take a week or more to arrive.
- Continuous monitoring of a polluted site: ensuring compliance with regulatory standards by monitoring soil, water, and wastewater remediation processes.
- Capable of speciating PFAS molecules: specific, sensitive, and selective against competing ions or molecules to enable operation in harsh environments containing high concentrations of interfering compounds.

It can be noted that none of the monitoring studies reviewed in this study employed an in situ methodology to quantify PFAS, and instead relied on laboratory equipment for PFAS quantification. It indicates that deployable devices are still in the experimental stage. However, most experimental studies claim potential for in situ or on-site application but are still conducted in laboratories. There has also been a great deal of interest in incorporating smartphones into on-site monitoring of PFAS. This technology has the potential to accomplish the following:

- Integrating into a network of smart sensing technology, allowing PFAS contamination mapping and monitoring.

- Using high-resolution cameras and custom applications to analyse sample images and compare them to a calibration curve.
- Utilising GPS tracking and an internet connection to upload results and access online help for on-site assistance, providing rapid and remote response to PFAS monitoring works.

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Glossary

PASF	Perfluoroalkane sulfonyl fluoride
PFAAs	Perfluoroalkyl acids
PFAIs	Perfluoroalkyl iodides
PFCAs	Perfluroalkyl carboxylates (or acid forms)
PFSAs	Perfluoroalkane sulfonates (or acid forms)
PFPAs	Perfluroalkyl phosphonates (or acid forms)
PFPiAs	Perfluroalkyl phosphinates (or acid forms)
FTIs	Fluorotelometer iodides
PFECAs	Per- and polyfluoroether carboxylates (or acid forms)
PFESAs	Per- and polyfluoroether sulfonates (or acid forms)
FPs	Fluoropolymers
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
FEP	Fluorinated ethylene propylene
PVF	Polyvinyl fluoride

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