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A national-scale preliminary overview study of poly- and perfluoroalkyl substances (PFAS) occurrence in aquatic environments of England, UK

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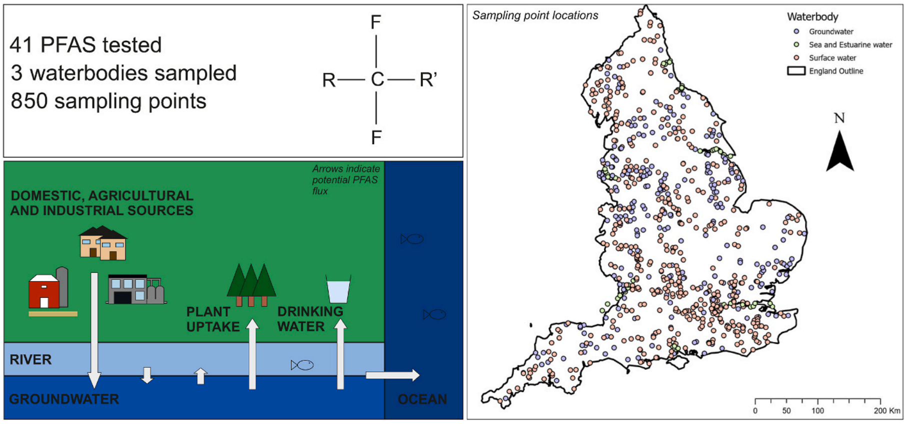
HIGHLIGHTS

- We studied the occurrence and distribution of 41 PFAS in 3 waterbodies in England (n = 850).
- 475 sampling points had at least one detection throughout England.
- Detections may be affected by spatial and physiochemical factors which are discussed.
- Future research objectives are suggested to increase the understanding of aquatic PFAS occurrence.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are emerging contaminants, where some are known to harm ecological and human health. Due to their widespread use, PFAS have become commonly detected in aquatic environments, which serve both as pathways and as reservoirs for these pollutants. This study provides the first full quantitative national overview of 41 PFAS compounds in English waterbodies (surface water, groundwater, coastal, and estuarine; n = 850), using High-Performance Liquid Chromatography-Triple Quadrupole Mass Spectrometry (HPLC-QQQ). Individual PFAS concentrations at 475 sites ranged from 0.0052 to 480 ng/L while ΣPFAS concentrations per site ranged from 0.024 to 2021 ng/L. Monitoring detected the highest concentrations near large distinct urban areas, though PFAS were also present in rural and undeveloped regions, highlighting the importance of detections across different land use. PFOA was one of the most frequently detected PFAS across all waterbodies, consistent with other studies. No clear correlations were found between

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PFAS physiochemical properties (chain length and functional group) and concentrations, this may be due to the sampling approach focused which focused on an assessment of background concentrations, rather than point-source, pollution. However, shorter chain PFAS compounds dominated detections in surface waters compared to groundwater. Physical properties and PFAS exposure in waterbodies may play a large role in PFAS detections, as higher concentrations were found in surface water relative to groundwater. Future research should explore PFAS trends over time, consider groundwater sampling depths, examine a broader range of land uses, and assess transboundary PFAS transport to better understand PFAS flux in aquatic systems.

1. Introduction

Monitoring pollution in waterbodies is essential for maintaining water quality and reducing risks to human and ecosystem health. The use of novel compounds in industrial and domestic settings can introduce pollutants which have not been previously studied. In the UK, as in many other countries, contamination of water resources by Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) is a growing issue. This raises concerns about the sources, presence, and impact of PFAS on both humans and the environment (Abunada et al., 2020; Pemberton, 2021). PFAS are of global concern, with monitoring practices potentially underestimating their concentrations (Ackerman Grunfeld et al., 2024).

With over 4,000 known variants, PFAS are used in more than 200 product types (Brennan et al., 2021; Glüge et al., 2020). Their hydrophobicity, lipophobicity, and resistance to temperature and chemicals make them highly useful in many applications. These properties are due to their perfluorocarbon moieties, which resist degradation, especially in environmental conditions (De Silva et al., 2021; Kwiatkowski et al., 2020). The widespread use and persistence of PFAS have attracted significant global attention in recent years due to concerns about their potential risks to human and environmental health (Abunada et al., 2020; Kurwadkar et al., 2022; Pemberton, 2021).

PFAS are often called "forever chemicals" due to their resistance to degradation (Renfrew and Pearson, 2021). They have been widely detected in plants, animals, soils, air, water, and humans worldwide (Abunada et al., 2020; Ahrens, 2011; De Silva et al., 2021). Some PFAS are highly mobile and accumulate in various aquatic environments, including surface waters, groundwater, oceans, and drinking water (Lyu et al., 2022; Sims et al., 2022). PFAS and its volatile precursors are also found in rainwater and oceans, enabling long-distance transport via atmospheric and oceanic circulation (De Silva et al., 2021; Faust, 2023).

The current understanding of PFAS in English waterbodies is limited, and currently there are no published national assessments of full quantitative PFAS sources and occurrences in English aquatic environments. With perfluorocarbons synthesis introduced during the 20th century (Gaines, 2023), PFAS may have entered the UK after 1950, following a significant rise in their production for commercial products after World War II. This increase, along with the expansion of PFAS-producing companies' facilities in the UK (3M Company, 2023; DuPont, 2023; Renfrew and Pearson, 2021), suggests that PFAS may have been circulating in English waterbodies for decades.

Currently, few comprehensive surveys have addressed aquatic PFAS contamination on a national scale in other countries (Li et al., 2022; Munoz et al., 2015). Additionally, some regional focus has been on soils and sediments (Beriro et al., 2025; Brusseau et al., 2020; Macorps et al., 2023). A previous report by the Environment Agency (Environment Agency, 2021) reviewed PFAS concentrations in aquatic water bodies across England. However, the present study differs from that report in several key aspects: i) The EA report employed a semi-quantitative screening approach, which provides only estimated (approximate) PFAS concentrations and does not yield validated absolute values with known accuracy or precision. In contrast, this study presents quantitatively validated data in a more comparable format, following a peer review process. ii) This study also includes comparisons with relevant peer-reviewed literature utilizing similar scopes of study. iii) This study encompasses a broader range of analytes (41 compared to 16) and covers a different sampling period (2023 versus 2014–2019).

Understanding the extent of PFAS contamination in water is essential for targeting remediation and reducing risks to the aquatic environment. Existing literature studying PFAS sources in England, as well as globally, report multiple point sources that contribute to aquatic contamination. These include landfills (via leachate and ambient air) (Hamid et al., 2018; Weinberg et al., 2011), waste-water treatment plants (Lenka et al., 2021; Tavasoli et al., 2021), biosolid application (Johnson, 2022), aqueous film-forming foams (Anderson et al., 2016), PFAS manufacturing facilities (Bach et al., 2017; Jia et al., 2023), atmospheric deposition (Faust, 2023; Pfotenhauer et al., 2022), industrial facilities (Megson et al., 2024), and a wide variety of consumer products (Gaines, 2023; Glüge et al., 2020; Sims et al., 2022). Fig. 1 illustrates these interconnections which can cause aquatic pollution.

Furthermore, studies have linked PFAS exposure to harmful health effects in humans and ecosystems, demonstrating that PFAS bioaccumulation can occur in living organisms due to direct or indirect interactions with water bodies (Barton et al., 2020; Christensen et al., 2017; Crone et al., 2019; Dassuncao et al., 2018; Herrick et al., 2017).

Some PFAS (perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS) and their derivatives) are classified as Persistent Organic Pollutants (POPs) and Emerging Organic Contaminants (EOCs) (OECD and UNEP, 2013). They are often categorised by carbon chain length and functional group, which affect their physiochemical properties and environmental behaviour. Longer-chain PFAS ($C \geq 8$) tend to attenuate more in the subsurface than shorter chains ($C < 8$) (Cai et al., 2022; Sima and Jaffé, 2021; Zhao et al., 2016). This paper uses this chain length definition provided. However it is acknowledged that some governmental organizations define short-chain PFAS as $C < 7$ for PFCAs (perfluoroalkyl carboxylic acids) and $C < 6$ for PFSAs (perfluoroalkane sulfonic acids) (OECD and UNEP, 2013; REACH, 2007).

Currently in the UK, PFOS and PFOA are restricted under the Persistent Organic Pollutants regulation, (Health and Safety Executive, 2023). England follows tiered, non-statutory guidelines that cap the sum of 48 named PFAS concentrations in drinking water at 0.1 μg/L (DWI, 2025) but does not have statutory drinking water standards for other PFAS unlike many countries in the Global North.

Here, we examine PFAS occurrences and distribution across the English Water Quality Monitoring Network (WQMN). The Environment Agency (EA) conducted a national PFAS monitoring program in English waters during 2023 (Environment Agency, 2023). This dataset is used here to assess PFAS presence on a national scale in surface waters, coastal waters and groundwater. The data is freely available for download from the UK Government website as part of its open data commitments.

The overall aim of this paper is to obtain an exploratory and observational understanding of PFAS contamination in aquatic environments of England by providing its first comprehensive regional study. Due to the nature of this extensive dataset and its first interpretation, to keep the scope reasonable, the study will provide a preliminary overview to guide future research priorities. Our objectives are to:

- Evaluate the spatial occurrence of 41 PFAS across 3 different waterbodies (Table 1 in Materials and methods).

- Demonstrate the magnitude of aquatic pollution within English waterbodies.
- Identify potential factors influencing PFAS occurrence and distribution based on current knowledge of their environmental fate.
- Assess results against comparable studies of similar scale globally.
- Propose future research directions to improve understanding of PFAS in aquatic environments.

2. Materials and methods

2.1. Data collection

Samples were collected as part of the EA WQMN. The samples were collected throughout the period of February to December 2023 and collated in the EA's Water Quality Archive (Environment Agency, 2023) retrieved from the 2023 data selection. The purpose of this archive is to have a publicly accessible database for water quality parameters across aquatic environments in England. The water network is used for distinguishing the environmental condition or "status" of water bodies from long-term monitoring.

In 2023, the EA began monitoring for an extended suite of PFAS, where the overall objectives of this monitoring programme were to better understand the risks of PFAS in the environment. Sites (Fig. 2) were selected based on their suitability to represent regional conditions of catchments and to identify potential risk from PFAS sources. Sampling points near obvious point sources of pollution, such as landfill, have been excluded from this network. Funding was provided by the Department of Environment, Food and Rural Affairs (DEFRA) to undertake a sampling programme for PFAS using a newly developed analytical methodology.

Groundwater and surface waters were sampled for 41 PFAS at 277 and 526 sites respectively. Surface waters consisted of samples from rivers, lakes, ponds and reservoirs. The full analyte list can be found in Table S1 (in Supplementary Information). Coastal waters (which consists of both coastal and estuarine samples) were only sampled for 2 PFAS as part of a different analyte suite at 47 sites (PFOA and PFOS), due to project and funding limitations. locations were selected to represent significant estuarine environments around the English coast.

Field sampling procedures followed EA internal documents: (i) Operational instruction 275_04 'Sampling groundwater' (Issued 1/7/2016), which describes the methods the EA uses to sample groundwater; (ii) Operational Instruction 19_09 'Chemical and microbiological sampling of water' (Issued 17/2/2018), which describes how the EA samples controlled waters, discharges and associated material for chemical and biological analysis. These procedures are internal and cannot be provided.

Samples were deposited at agreed sites and stored in a refrigerator or cold room prior to collection by couriers. Samples were stored in compartments where the temperature is controlled between 2 and 8^{o}C. throughout their journey. Any transfers between vehicles 'en-route' were made directly between the chilled compartments of the vehicles. Samples were not left in an uncontrolled environment during their journey.

2.2. Sample analysis and quality control

The EA laboratory analysis utilised High-Performance Liquid Chromatography-Triple Quadrupole Mass Spectrometry (HPLC-QQQ). This approach or similar are used commonly to quantify PFAS in environmental samples to detect multiple variants of PFAS (Backe et al., 2013; Coggan et al., 2019; Gremmel et al., 2017; Huset and M. Barry, 2018; Mulabagal et al., 2018).

Storage and preservation were maintained in 125 ml Polyethylene bottles at 5 °C ± 3 °C to minimize risks of contamination and ensure stability of PFAS. An unfiltered 500 μl of each water sample was transferred to a polypropylene vial, followed by the addition of 10 μl internal standard solution. The internal standard solution contained a mix of 24 mass labelled PFAS compounds (Table S2 in Supplementary Information) to cover the range of target compounds analysed. For each batch of samples, internal standard tolerances were established by averaging peak areas for each of the internal standards, in the seven calibration standards and a blank. If the internal standard response for a sample deviate by ±50 % from the average established, the result is rejected. A minimum peak area is also established during validation for select compounds, where a repeat analysis is conducted for results that fail to meet the threshold.

An 80 μl aliquot was introduced onto the HPLC analytical column, facilitating the separation of PFAS compounds. This analytical method was used as it is capable to provide high sensitivity and accuracy in quantifying PFAS (analyte suite and LODs in Supplementary Information).

To resolve individual PFAS, chromatographic separation within the

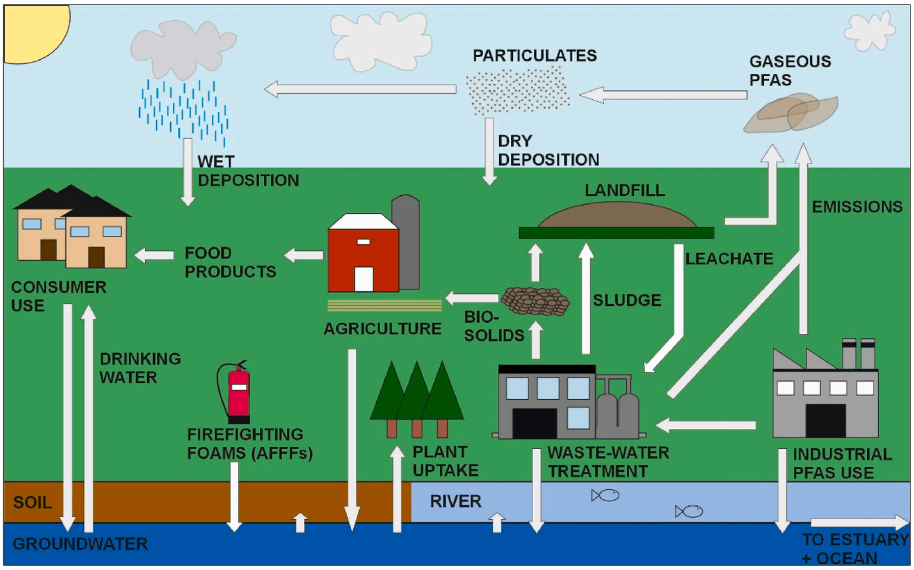

Fig. 1. Typical sources, occurrence, and transport pathways of PFAS. Arrows through soil/river into groundwater indicate the ability of PFAS which can move into both soil/river and groundwater.

HPLC system was followed by mass spectrometric analysis in a Triple Quadrupole Mass Spectrometer. This system is able to detect trace concentrations of PFAS. Compound identification (fingerprints) relied on Multiple Reaction Monitoring (MRM) transitions, with quantification achieved through this process. The method demonstrated a typical application range up to 200 ng/L of PFAS compounds, extendable through sample dilution, if concentrations exceed this upper limit.

Interferences, including compounds with identical MRM transitions and retention times, were considered, to reduce false positives. The method was fully validated using an 11 × 2 procedure for each representative ample matrix following the United Kingdom Accreditation Society (UKAS) ISO 17021-1:2015 guidelines although the method has not been formally accredited.

For Quality Control (QC), one control sample was run for every ten samples, with a minimum of two for each batch of samples. One of the control samples was positioned at the end of the run to ensure instrument performance. QC limits were generally based on statistical analysis of QC results. The laboratory analysed control samples with each batch of analysis, using the results to establish routine QC procedures. These procedures, maintained and updated for every batch, formed the basis of routine Analytical Quality Control (AQC) and were essential to the ongoing control of error and the demonstration of adequate accuracy. These AQC procedures, including control charts, demonstrated whether the system remained in a state of statistical control or required corrective action.

Control samples were analysed in a random order on the same basis as real samples. Initially, control limits were calculated from the total standard deviation (SD) of at least 20 results for each representative sample matrix, produced while the method was 'in control'. Results from performance testing were used for new methods where available.

2.3. Data treatment

Data were collated from the most recent round of sampling for each monitoring point (Environment Agency, 2023). The program RStudio (v4.2.2) was utilised for data manipulation and analysis. The dataset was initially scrubbed for duplicated or erroneous data and then targeted towards the relevant waterbodies and sampling objectives. When calculating the site-total, medians and 95th percentiles of the PFAS concentrations, non-detects were set equal to half of the limit of detection (LOD), consistent with Water Framework Directive (WFD) approaches. We confirmed that the decision to treat non-detects as zeros, equal to LOD or half of LOD, had negligible impact on the total PFAS concentrations at a site. Within each waterbody, there were a small number of sites where the analyte suite slightly differed from the standard suite, where up to three substances were not accounted for, due to unknown reasons. However, we also confirmed this had negligible influence on results. Results are presented on a logarithmic scale to represent the high variability across magnitudes in a clearer fashion for visualization purposes.

Three sampling points appeared to be anomalous and were not representative of background concentrations. Therefore, these were omitted from the results. These sites accounted for the anomalous detections of seven additional PFAS within the suite at concentrations magnitudes higher. The sites were i) a surface water sampling point situated within close proximity to a firefighting college. Firefighting foams are known to be a source of PFAS, defeating the purpose of this study. This site contained very high concentrations of PFAS (in some cases, 1000 times larger than the median), including some variants that were not detected elsewhere. ii) A rural groundwater sampling point that contained a greater number of PFAS detected with no obvious local source. This site also contained PFAS that were not detected elsewhere in the dataset. iii) A groundwater site was also removed from the analysis since only a single PFAS was measured, and this substance was not measured at other groundwater sites, therefore hindering comparability of total sums across sampling points. After data treatment and QA, the total site count reduced from 850 to 631.

3. Results

3.1. Variation in concentrations and detection frequencies

Across the three types of waterbodies, 475 sites had positive detections. The concentrations of individual PFAS varied substantially between waterbodies. Eighteen of the forty-one PFAS sampled were detected. Table S3 (in Supplementary Information) shows that PFOA and PFOS had the highest detection frequencies (DF), particularly in coastal waters, both at 91 %. Notably, PFBA (perfluorobutanoic acid) had the highest median concentration in surface waters at 2.25 ng/L and the highest maximum concentration in groundwater at 370 ng/L, with a detection frequency of 20 %. In surface waters, PFOS (L) and PFHxS-L exhibited the highest overall maximum concentration of 480 ng/L. The substances with the highest detection frequencies in surface waters followed this sequence: PFBA & PFOA (72 %) > PFHxA (perfluorohexanoic acid, 68 %) > PFPeA (perfluoropentanoic acid, 65 %) > PFOS (L) (65 %).

Surface waters consistently showed higher detection frequencies, median concentrations, and maximum concentrations for each PFAS compared to groundwater, except for the 95th percentile of 6:2 FTS (17 ng/L in groundwater versus 7.7 ng/L in surface waters). Due to low detection frequencies in groundwater (<25 %), median concentrations were below the limit of detection, rendering all median values equivalent to non-detections.

In coastal waters, PFOS and PFOA had notably higher detection frequencies (91 %) compared to other PFAS in the different waterbodies. In contrast, surface waters and groundwater, tested for 41 substances, which had overall lower detection frequencies.

Across all waterbodies, seven long-chain and eleven short-chain PFAS were detected. The only PFAS with chain lengths of nine or more carbons were two PFCAs: PFNA (C9) and PFDA (C10). Of the seven C8 PFAS sampled, six were detected. Fig. 3 shows that detected PFAS concentrations were analogous between all waterbodies, with most falling within the range of 1–10 ng/L groundwater and surface waters detected the same number and types of substances, but the most

Table 1
Summary statistics for waterbodies sampled (Environment Agency, 2023).

Waterbody	Total samples before QA	Total samples[a]	Total sites with detections[b]	Detection frequency (%)[c]	PFAS sampled[d]	PFAS detected[e]
Coastal waters (coastal and estuarine)	47	47	47	91	2	2
Groundwater	277	275	148	6.1	41	18
Surface waters (rivers, lakes, ponds and reservoirs)	526	309	279	18	41	18

[a] Total samples – count of all sampling points after data treatment and QA;
[b] Total sites with detections – count of all sampling points containing a minimum of 1 detection;
[c] Detection frequency – ratio of detected PFAS against total PFAS sampled, irrespective of sites;
[d] PFAS sampled – number of compounds sampled for;
[e] PFAS detected – number of compounds detected. Note, coastal waters have a separate analyte suite.

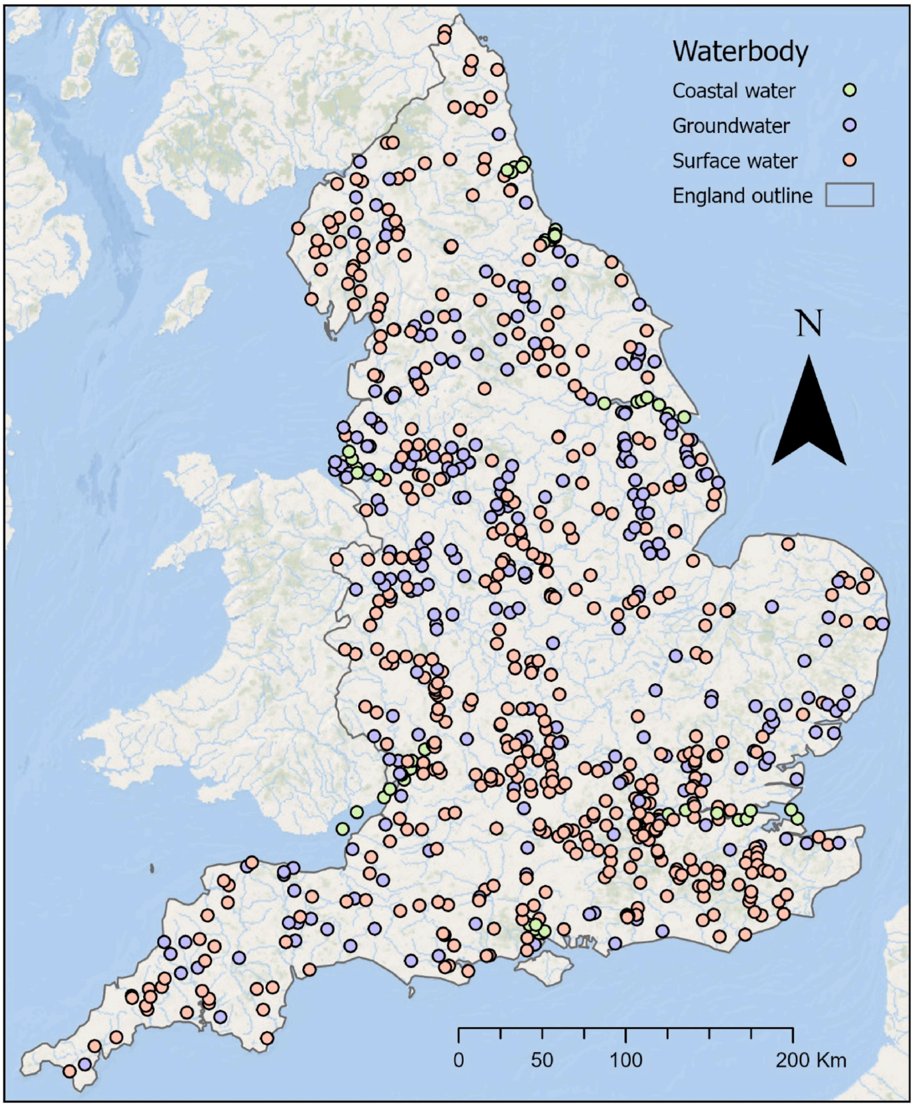

Fig. 2. All sampling points used in the survey, categorised by waterbody. Contains basemap data sourced from Esri, GEBCO, NOAA, National Geographic, DeLorme, HERE, Geonames.org, and other contributors (Esri, 2025).

substantial difference was in PFHxSA, with an 8 ng/L variance. Fig. 3 also highlights numerous outliers in surface waters compared to groundwater, based on the interquartile range (IQR). This is calculated by the determining the first quartile (Q1) and third quartile (Q3), being the lower and upper limit respectively as Q1 – 1.5IQR, Q3 + 1.5IQR. Anything below or above these limits is typically treated as an outlier.

Fig. 4, however, shows that groundwater had more outliers when comparing carbon chain length ratios to surface waters. Additionally, the median PFAS ratio in groundwater (0.44) and its interquartile range were lower than those in surface waters (2.16). Inspection and analysis of Fig. 3 revealed no clear relationship between median PFAS concentrations, carbon chain length, or functional group in either groundwater or surface waters. Statistical analysis, including (i) t-tests between median PFAS concentrations and chain length, and (ii) t-tests comparing median PFAS concentrations by functional group, observed no significant relationships ($p > 0.05$).

3.2. Spatial distribution

The spatial distribution of total PFAS concentrations across different water bodies is shown in Fig. 5. In surface waters, higher concentrations were observed in large distinct urban areas, often several orders of magnitude higher than those in surrounding rural areas. The highest concentrations were found within the proximity of London, reaching a maximum of approximately 720 ng/L, and one measuring 2021 ng/L. Other high-concentration areas, with values up to 33.1 ng/L, were clustered around large conurbations in northwest England, where population densities averaged 4500 ± 200 people per km^2, and a smaller conurbation with ~2100 people per km^2 (Office for National Statistics, 2022). Some non-urban areas in the Midlands, East, and Southeast England exhibited PFAS concentrations comparable to urban areas. In contrast, large regions along the Welsh border in southwest England showed low concentrations, as did rural, elevated areas around the English Midlands. The lowest concentrations reached 0.024 ng/L.

For sampling points along river profiles and estuaries, PFAS concentrations generally decreased downstream (Fig. S1). This trend was particularly evident in urban areas, where upstream concentrations were relatively high. For instance, the River Severn had an upstream sampling point near a large conurbation (population density of ~3300 people per km^2), where concentrations measured 8.0 ng/L, while the most downstream estuary sampling points had an average concentration of 1.25 ng/L.

In contrast, the spatial distribution of groundwater sites did not follow a clear pattern, with a mix of sites showing both high

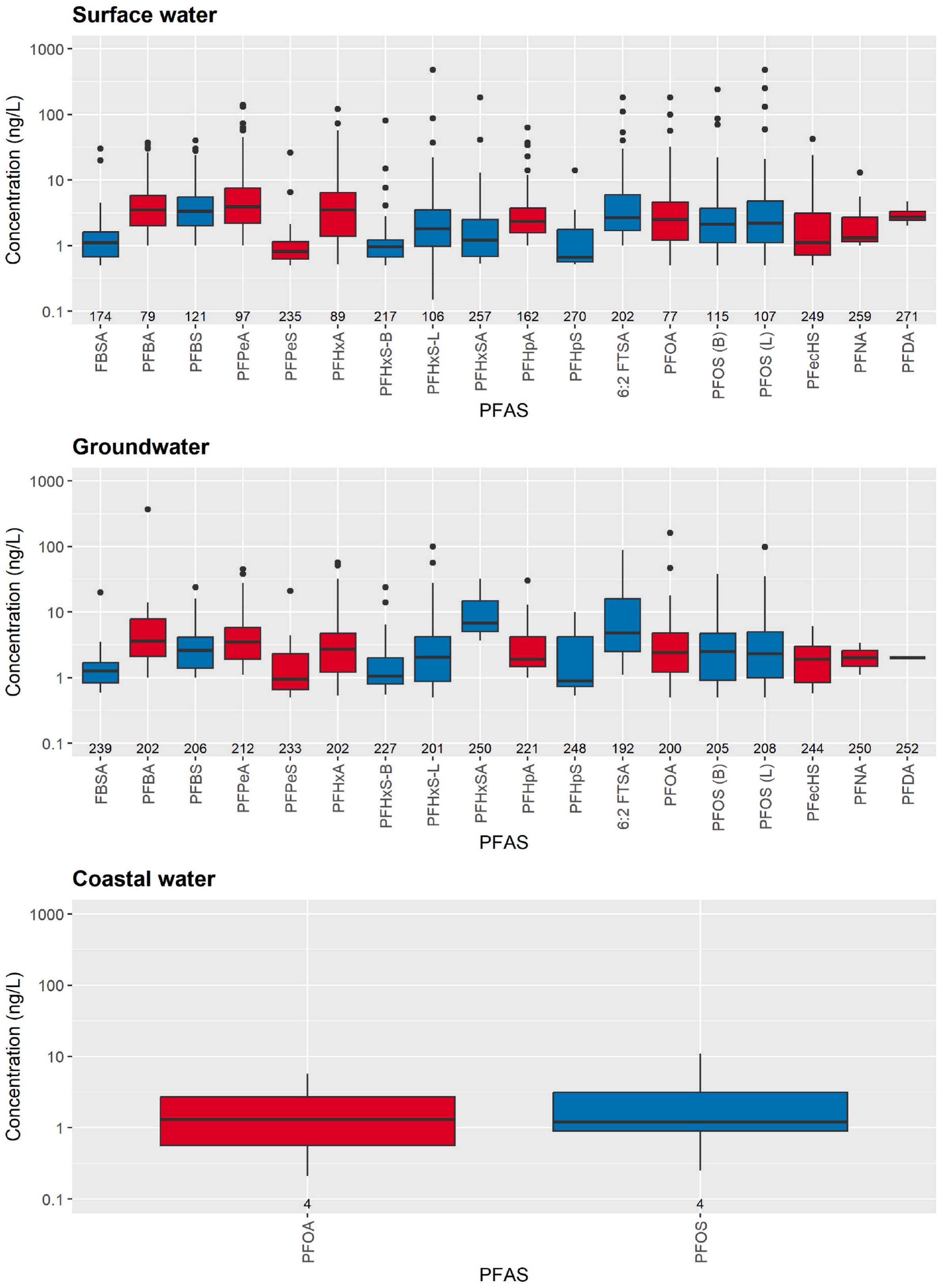

Fig. 3. Box and whisker plots representing the distribution of detected PFAS concentrations (log10 scale) categorised into waterbody types (n = 309 and 275 for surface water and groundwater respectively, Environment Agency, 2023). Red boxes are carboxylates, and blue boxes are sulfonates, ordered in ascending chain length. The boxes represent the interquartile range with a horizontal line within representing the median; whiskers represent the range of the first and third quartile; and dots represent outliers. Numbers along the x axis indicate the number of non-detects across all sampling points per waterbody per PFAS. See supplementary information for individual datum.

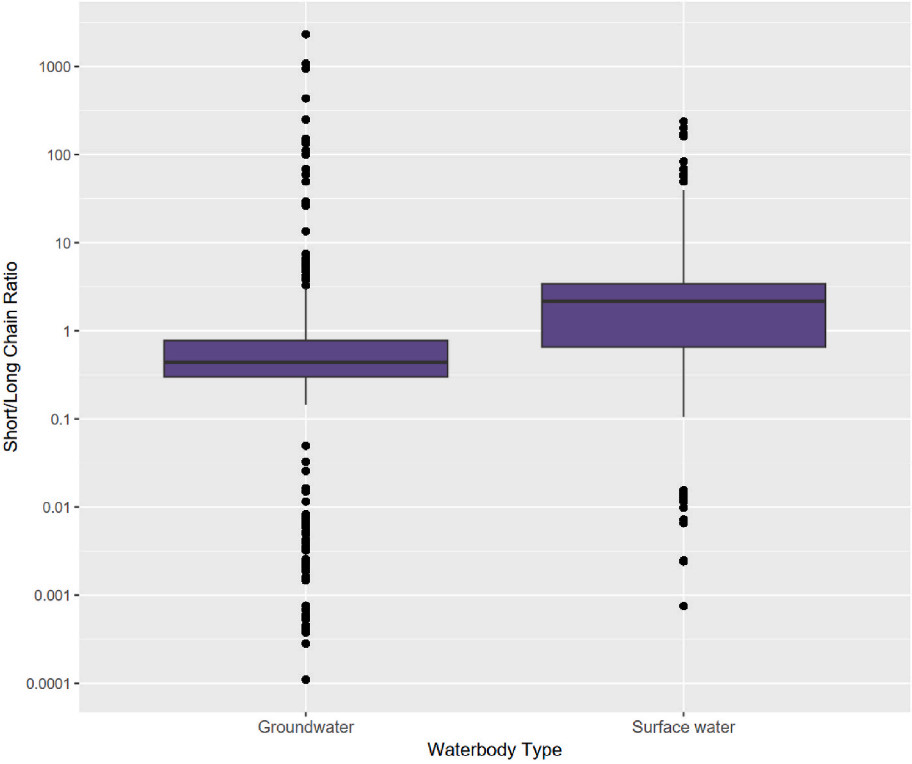

Fig. 4. Box and whisker plot representing the ratio of short chain to long chain PFAS concentrations in sampling points with positive detections (log10 scale) categorised by waterbody (Environment Agency, 2023). The boxes represent the interquartile range with a horizontal line within representing the median; whiskers represent the range of the first and third quartile; and dots represent outliers.

concentrations and many sites with no detections, resulting in considerable variability, as also reflected in Fig. 4.

4. Discussion

The selected sites were intentionally chosen to understand presence of PFAS concentrations at the national level, without focusing on specific pollution sources. Consequently, the approach to the data is heuristic and represents the “background” concentration of PFAS in English waterbodies. Sites within proximity of point-source pollution were avoided, as it can lead to elevated contaminant loading at local receptors and consequently higher PFAS concentrations (Johnson et al., 2022; Park et al., 2023).

The discussion presents additional aspects of data analysis not included in the previous EA report (Environment Agency, 2021). These encompass extended statistical analyses and assessments of chain length ratios, along with an examination of waterbody properties and spatial characteristics that may influence PFAS fluxes in aquatic environments.

4.1. Variation in detection frequency

There is no evidence of relationships between PFAS physiochemical properties, carbon chain length, functional group, against detection frequency, and concentration. However, literature indicates that PFAS profiles near point pollution sources are dominated by short chains, which are detected more frequently and at higher concentrations than long chains (Dasu et al., 2022; Joerss et al., 2022; Möller et al., 2010). This disparity arises because long-chain PFAS exhibit higher hydrophobicity, leading to lower water solubility and pKa (acid dissociation constant) values, which diminish with increasing chain length (Li et al., 2020; Phong Vo et al., 2020). Consequently, long-chain PFAS are more likely to attenuate in the subsurface via attenuation processes (Cai et al., 2022). Industrial shifts favouring short-chain PFAS may also lower short/long chain ratios in environmental matrices. This is illustrated in Fig. 4, where groundwater has a lower short/long chain ratio compared to surface waters (0.44 vs. 2.16), reflecting groundwater buffering properties further discussed in Sections 4.1 below and 4.3.

Literature which has studied point pollution demonstrate general spatial characteristics (described above) of PFAS contamination pollution sites that do not align with our results, which may suggest that “background” concentrations may account for a lack of discrepancy between short and long chain detection frequencies and concentrations within waterbodies. This study may highlight dissimilarities of PFAS contamination on different spatial scales, between point pollution and diffuse pollution on a regional scale and the role of transboundary flux (PFAS transport across conjunctive waterbodies).

Our study shows a clear distinction in PFAS detection frequencies across different waterbodies. This may be due to each waterbody having distinguishable properties and pollution sources that can affect the transport and fate of PFAS. For groundwater, Lasagna et al. (2013), discusses in depth how dilution is able to have a large role in lowering concentrations for non-reactive and non-sorbing contaminants in groundwater - primarily caused by molecular diffusion of compounds moving from volumes of high concentration to lower concentrations. Consequently, dilution can prevent the net increase of contaminants in shallow aquifers and overall obtains the ability to reduce contaminant concentrations, hence may contribute to relatively lower concentrations and detection frequencies in groundwater. However, given the absence of contextual data for groundwater, understanding the role of lithology or other hydrogeological properties is limited in this study but should be explored further.

In a global review by Sims et al. (2022), groundwater showed lower PFAS detection frequencies than surface waters, consistent with this study. The ability of groundwater to buffer contamination can result in longer residence times allow for greater attenuation of contaminants over time (Lapworth et al., 2022; Sunderland et al., 2019). However,

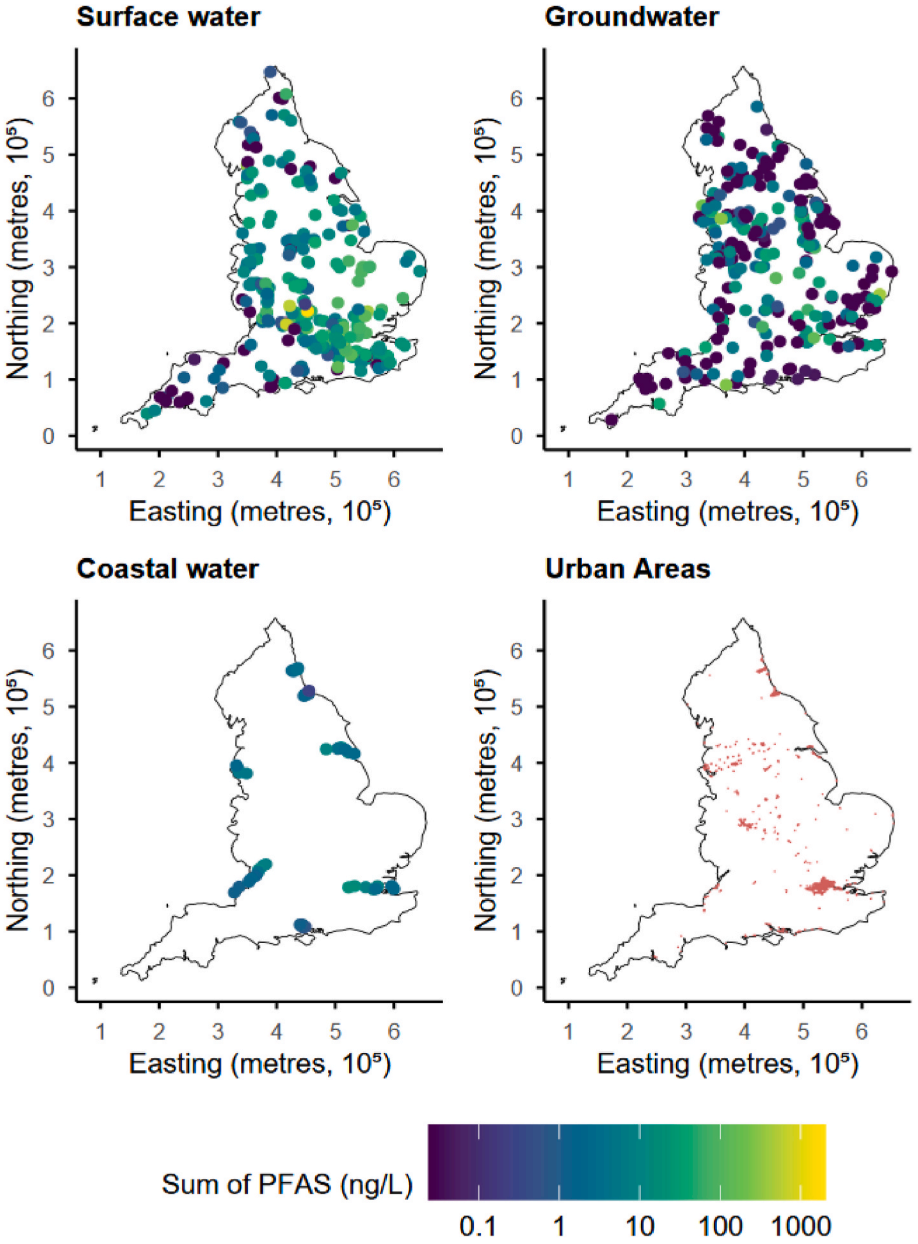

Fig. 5. Spatial distribution of detected PFAS (log10 scale) across English waterbodies (Environment Agency, 2023). Each sampling point shown is the sum of all PFAS detected taken from the most recent sampling round respectively. A full list of exact concentrations is given in Table S4. Urban areas is from derived from a raster dataset from the 2021 UK land cover map produced by Marston et al. (2022) for context - acknowledgement: Data owned by UK Centre for Ecology & Hydrology © Database Right/Copyright UKCEH. Displayed in a standard British National Grid (BNG) projection in unit metres - easting and northing denote horizontal (x) and vertical (y) coordinates. Contains National and Ordnance Survey (OS) data © Crown copyright and database right (2024).

processes like desorption can still release unaltered PFAS over time, though this is not well understood (Kookana et al., 2022; Umeh et al., 2023). These factors could provide plausible justification of lower PFAS detection frequencies in groundwater relative to surface waters.

Surface waters have about three times the detection frequency of groundwater, with all PFAS showing higher detection rates. The characteristics of surface waters may influence PFAS fate on a spatiotemporal scale, as noted in Podder et al. (2021), with exposure to effluent discharge, surface runoff, and point pollution sources. Literature suggests that surface waters are also susceptible to diffuse pollution (Clara et al., 2009; Kittlaus et al., 2022; Möller et al., 2010). On a regional scale, the mixture of source and diffuse pollution can coexist to PFAS to accumulate in surface waters. In addition, temporal factors like seasonal variation, temperature, rainfall, and dissolved organic matter, along with surface waters shorter residence time, may further influence the higher detection frequencies. However, results reflect a single sampling period that can vary over time.

4.2. Spatial variation

The results suggest a broad association where larger areas of urban classification density tended to demonstrate elevated PFAS concentrations. This aligns with some existing literature which study contamination of regional scales in environmental matrices. Previous studies strongly suggest that urban areas have influence over PFAS pollution on a spatial scale (Johnson et al., 2022; Lenka et al., 2022; Macorps et al., 2023). One notable study is a national of lakes in France (n = 133) by Munoz et al. (2015), who demonstrates that PFAS concentrations were characteristically higher in urban or industrial sites relative to “reference” sites, which are supposedly “pristine”, suggesting widescale diffuse pollution. Another study from Sardiña et al. (2019) who studied contamination across a gradient of land-use intensity, demonstrated that urban land use (residential and industrial) provided to act as pollution hotspots and are potential important large-scale sources of PFAS. These similar findings may show that urbanization on a regional scale can play a large role in PFAS contamination. As PFAS are widely used in industrial, commercial, and domestic activities (Glüge et al., 2020), one could presume urban areas, small or large, have varying potential in being a source of PFAS contamination. Further analysis would be required to confirm this trend but has not been conducted to adhere to the observational approach and scope of the paper.

Urban areas can contain mixtures of multiple sources such as the ones shown in Fig. 1, and so, are likely to contribute to higher PFAS concentrations and diversity. Urbanization, specifically urban drainage systems may also alter pollutant transport by reducing water infiltration into the subsurface, limiting environmental attenuation processes, and increasing runoff through sewer systems where PFAS are not treated (Yang et al., 2022).

Our study detected notable PFAS concentrations in rural areas, including areas such as National Parks, where land use is relatively undeveloped for conservation purposes, disseminating the contribution of rural detections on a regional scale. This may suggest long-range PFAS transport, as fewer local sources are expected (Brusseau et al., 2020; Cousins et al., 2022; De Silva et al., 2021). Conversely, it may show that small-scale sources, such as septic tanks, sewage discharges, and biosolid applications, could also contribute to rural detections. While literature supports regional long-range PFAS transport as a pathway for rural contamination, insufficient data on rural sources in this dataset make it difficult to confidently attribute these detections to specific causes.

Coastal waters show downstream dilution towards the sea (Fig. S1 in Supplementary Information) with higher concentrations upstream, particularly rivers and estuaries with urban areas, but due to a limited analyte suite and few samples per estuary, no statistical relationships were found. Yan et al. (2015) observed similar dilution trends for sediment of the East China Sea. Boiteux et al. (2012) also observed another similar trend to our study, where rivers which crossed high population densities exhibited higher PFC contamination. Like surface waters, coastal waters are often impacted by point pollution sources within the vicinity of manufacturing and wastewater treatment plants (Clara et al., 2009; Sánchez-Avila et al., 2010; Wang et al., 2011). Therefore, the trend of decreasing concentration is likely to be dependent on the potential absence of local pollution source point conditions for each estuary. Continued PFAS loading into the sea enables seawater to exist as a long-term sink, which could rationalise high C8 legacy PFAS detection, where salinity is known to affect PFAS fate by influencing sorption behaviour (Jeon et al., 2011; Navarro et al., 2022). While results align with some existing literature, Muir and Miaz (2021) highlight there is limited data on broad spatial and temporal PFAS trends in coastal waters.

4.3. *Wider implications and regional research priorities*

This unique dataset allows for a large scope of analysis, representing the importance of regional studies without explicit focus on point pollution, and is also difficult to fully interpret through the scope of a singular paper. There is extensive research on PFAS contamination near primary or secondary sources, but fewer studies focus on background levels in aquatic matrices. Though it is widely understood that local PFAS contamination is high near primary sources, on a national scale, widespread use, long-range transport, and the accumulative nature of PFAS highlight the need to examine anthropogenic background concentrations. This broader focus would improve understanding of PFAS in aquatic environments at a national scale. Brusseau et al. (2020) similarly emphasize the importance of studying background PFAS contamination in remote areas to fully grasp its environmental impact. This context is also applicable on a catchment-scale approach where notable discrepancies in concentration are possible.

Large, comprehensive studies can also allow for an anthropogenic ‘baseline’ to be determined which is highlighted comprehensively by Edmunds et al. (2003). Such a baseline offers a foundational reference point for long-term PFAS monitoring, supporting both regulatory and legal objectives. This foundation enables long-term monitoring of PFAS in aquatic environments, allowing researchers to identify temporal trends and detect shifts in water quality over time. For example, given that PFAS have been in use for decades as legacy contaminants, their production and application have also evolved, shifting from long-chain to short-chain PFAS (Phong Vo et al., 2020).

Complementary to this, it would be important to examine PFAS sources and presence in differing land uses on a regional scale, where it is understood that land use can influence PFAS occurrence (as discussed in section 4.2). This research would offer valuable insight into the influence of both commercial and household sources may contribute to contamination, shifting focus away from solely studies point pollution sources which typically focus on industrial sources, especially at larger scales. Additionally, understanding PFAS fingerprint profiling based on source helps develop targeted remediation strategies by revealing how specific PFAS properties and usage may affect their environmental presence (Joerss et al., 2022; Jonker, 2024; Langberg et al., 2022).

Studies discussing interactions between different water bodies are rare, yet crucial for understanding PFAS flux within the broader water cycle (Briggs et al., 2020), limiting depth of analysis on large scale studies. Properties of waterbodies (discussed in section 4.1) are known to have influence on PFAS fate. Examining these interactions can help identify key areas for remediation and predict pathways and receptors of PFAS concentrations, across catchment or regional scales. This includes quantifying PFAS flux and understanding partitioning behaviour during transboundary transport, which is essential for effective environmental management over large spatiotemporal scales. Climate change impacts, such as increased dissolved organic carbon affecting pH and PFAS behaviour, are also relevant (McDonough et al., 2020; Umeh et al., 2023).

Though groundwater contribution to the freshwater resource via baseflow is large, PFAS spatiotemporal variability in groundwater remains less studied compared to surface water (Munoz et al., 2017). While some research addresses PFAS attenuation, few examine changes across broad spatial or temporal scales or in diverse settings (urban, industrial, rural). Xu et al. (2021) also advocates for increased global PFAS monitoring in groundwater to capture these trends. Sampling depth is an important factor when evaluating groundwater contamination, as shallow depths face higher contamination risks, while deeper layers allow for greater attenuation through dilution and sorption (Lapworth et al., 2022). Lithology, especially in formations like fractured chalk, affects PFAS fate through dual-porosity mass transfer, significantly enhancing attenuation (Farhat et al., 2022; Lukač Reberski et al., 2022; Newell et al., 2021). Understanding groundwater’s buffering of PFAS is essential for spatiotemporal studies, as PFAS can desorb over time, leading to prolonged contamination.

Table 2 offers a comparative analysis of PFAS studies across waterbody types, highlighting patterns and challenges. Studies were selected for their similar sampling scales, with those focused on point pollution excluded to ensure broader comparability. Despite inherent limitations, such as differences in PFAS analyte suites, non-detect treatment methods, and spatial scales, several insights emerge from studies with generally similar methodologies.

In coastal waters, detection frequencies remain high for certain PFAS, with our study showing 91 % DF for PFOA and PFOS. Other studies, like Shao et al. (2016) in China, report 100 % detection for a broader set of compounds, including PFPeA and PFHxA, which are also detected at higher frequencies in the other coastal water studies. Such findings may reflect overall PFAS loading into oceans, regional usage patterns or differences in the analytical focus.

Table 2

– Comparison of relevant literature categorised by waterbody in descending publication date. PFAS sampled - number of PFAS analysed in the paper: PFAS detected – number of PFAS sampled that were detected; n = number of samples taken across all sampling points, DF = detection frequency; Min, Median, Mean, Max, SD – respective statistic calculated from all individual PFAS samples (irrespective of sampling point); Dominant PFAS – PFAS that were most commonly detected in descending order with respective detection frequencies.

Author	Region	PFAS sampled	PFAS detected	n	DF	Min	Median	Mean	Max	SD	Dominant PFAS (%DF)
Coastal waters											
This study	England	2	2	47	91	<LOD	1.2	1.95	11	2.13	PFOA (91) & PFOS (91)
Shao et al. (2016)	China	15	15	22	62	<LOD	0.33	7.62	98.8	16.8	PFPeA & PFHxA & PFHpA & PFOA & PFNA & PFBS (100), PFBA (86)
Takemine et al. (2014)	Japan	12	10	38	29	<LOD	<LOD	4.7	510	31.9	PFHxA (100), PFOA (97), PFPeA (34)
McLachlan et al. (2007)	Europe	6	4	15	83	<LOD	1.48	7.58	200	25.9	PFHpA (100), PFNA (87), PFHxA & PFOA (73)
Surface waters											
This study	England	41	18	309	18	<LOD	<LOD	1.05	480	9.11	PFBA & PFOA (72 %), PFHxA (68 %), PFPeA % PFOS (L) (65 %)
Munoz et al. (2017)	French Territories	21	15	75	–	<LOD	1.8	–	20	12	PFOS (79), PFOA (65)
Lam et al. (2017)	Vietnam	13	11	47	30	<LOD	–	14	–	–	PFOA (81), PFNA (72), PFOS (51), PFHxS (47), PFHxA (45)
Munoz et al. (2015)	France	22	19	333	45	<LOD	7.9	28.2	217	75.3	PFOS (89), PFOA (84), PFHxS (81.1)
Boiteux et al. (2012)	France	10	9	99	21	–	<1	<1	–	–	PFOA & PFOS (53), PFHxS (48), PFHxA (28)
Groundwater											
This study	England	41	18	275	6.1	<LOD	<LOD	0.4	370	5.01	PFOS (B) (25 %), PFOS (L) & 6:2 FTSA (24), PFHxS-L (21)
Munoz et al. (2017)	French Territories	21	17	80	–	<LOD	0.56	–	213	119	PFBS (45), PFHxS (44), PFOA (40)
Lopez et al. (2015)	Europe	11	11	954	6.8	<LOD	–	13.16	–	–	PFHxS & PFOS (20), PFOA (11.2), PFHxA (9)
Boiteux et al. (2012)	France	10	10	163	14	–	<1	<1	–	–	PFHxS & PFOA (31), PFOS (24), PFHxA (13)
Loos et al. (2010)	Europe	7	7	164	33	–	<1	1.3	–	–	PFOA (66), PFOS (48), PFHxS (35)

In surface waters, our study in England demonstrates lower overall detection frequencies (18 %) for 41 PFAS compounds, compared to studies with smaller analyte sets presented in Table 2. This pattern may result from different detection levels or methodologies which may include more contaminated sites. Other studies in this category report notably high DFs for PFOS and PFOA; for instance, Munoz et al. (2015) in France found DF values over 80 % for these compounds, and Lam et al. (2017) in Vietnam recorded a DF of 81 % for PFOA. Similarly, Boiteux et al. (2012) observed PFOA and PFOS as the most frequently detected, with DFs of 53 %. However, it is important to note that there is a phase out of PFOS, PFOA and PFHxS in the UK due to the Stockholm Convention (Stockholm Convention, 2024), which could contribute towards discrepancies between past studies.

Groundwater studies similarly show consistently lower DF values compared to coastal waters and surface waters, where dominant PFAS found in these studies also exuded lower DFs, highlighting variation of PFAS detection within the subsurface.

Detection frequency exhibits the most notable trends across the studies in Table 2. Other statistical measures like minimum, median, mean, and maximum values are challenging to show correlations across studies, likely due to variability in PFAS distribution and environmental conditions. While DF offers more comparable insights, these descriptive statistics tend to vary widely, likely to be more influenced by regional factors, analytical methods, and sample characteristics, making it difficult to draw consistent conclusions across studies.

5. Conclusion

This study is the first comprehensive assessment of PFAS in English waterbodies. Analysing a set of 41 PFAS compounds provided by the Environment Agency (EA) through its Water Quality Monitoring Network (WQMN), we found frequent detections across estuaries, seawater rivers, lakes, ponds, reservoirs and groundwater. Among 475 sites with positive detections with PFOA, PFOS and PFBA being most commonly detected. ΣPFAS concentrations ranged from 0.024 to 2021 ng/L, with surface water concentrations higher near large significant urban areas and coastal waters showing dilution towards the sea.

The findings suggest that both point, and diffuse pollution contribute to long- and short-range PFAS transport, leading to contamination that could reach rural or undeveloped areas, highlighting the contribution of such detections on a regional scale. Variations in PFAS concentrations across waterbody types may be influenced by specific properties of each type or differences in sampling approaches, particularly for coastal waters. Although PFAS properties, such as carbon chain length and functional groups, can affect their environmental behaviour, these factors were not clearly correlated with concentration or detection frequency, likely due to the broad influence of diffuse pollution rather than specific point sources though some detection frequencies across waterbodies have correlated with other large-scale studies. Notably, many long-chain PFAS were not detected within this suite.

PFAS concentrations across England vary due to multiple factors influencing their distribution over time and space. Assessing contamination concentrations nationwide is challenging, given the diversity of environmental conditions and the limitations of sampling within a single time period. Further research is recommended to explore spatiotemporal trends, especially in both urban and rural contexts, as well as PFAS transport dynamics, including the role and magnitude of PFAS flux in transboundary transport, and the impact of geological properties on groundwater contamination. Understanding the behaviour and fate of PFAS in the wider aquatic environment can assist in remediation efforts. Overall, this study highlights the widespread occurrence of PFAS in English waters, posing potential ecological risks due to the hazardous concentrations detected as well as highlighting the importance and approaches for further regional studies.

CRediT authorship contribution statement

R.J. Patel: Writing – original draft, Visualization, Software, Formal analysis, Data curation, Conceptualization. **D.C. Gooddy:** Writing – review & editing, Validation, Supervision. **B. Marchant:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Conceptualization. **D.J. Lapworth:** Writing – review & editing, Validation, Supervision. **A. James:** Writing – review & editing, Resources, Methodology, Investigation. **M. Cook:** Writing – review & editing, Resources, Methodology. **K. Darby:** Methodology, Investigation. **T. Besien:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2025.144804.

Data availability

Data is publicly available here: https://environment.data.gov.uk/water-quality

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