

Partitioning and removal of per- and polyfluoroalkyl substances (PFAS) in full-scale surface flow treatment wetlands with different upstream wastewater treatment[☆]

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ABSTRACT

The performance of treatment wetlands (TWs), as a nature-based solution, in mitigating persistent per- and polyfluoroalkyl substances (PFAS) and their interactions with existing treatment flowsheets remain unclear. This study investigated PFAS removal in two full-scale surface flow TWs treating secondary effluent from different domestic wastewater treatment plants (WWTPs). The systems demonstrated their capacities to safeguard natural water bodies by achieving discharge levels of the legacy PFOS (4–4.6 ng L⁻¹) and PFOA (1.79–3.27 ng L⁻¹) with removal efficiencies of 29%–38% and 15%–34%, respectively. Further upstream and downstream water quality monitoring in receiving waters is required to accurately evaluate PFAS contributions from WWTP effluents. Partitioning behaviour analysis revealed that sediment adsorption was the dominant removal pathway, achieving removal rates 16–61 times higher than plant uptake for PFOS and 1.8–6 times higher for PFOA. Sediment iron content, depth, and bulk density were positively correlated with PFAS sequestration, highlighting their importance in controlling PFAS mobility. PFOS accumulation in the sediment was greater in the TW for the WWTP dosing with ferric sulphate than the WWTP without chemical dosing (2.80 mg m⁻² y⁻¹ vs. 1.34 mg m⁻² y⁻¹). Notably, a conventional mass balance analysis was challenged by the transformation of PFAS precursors into terminal compounds, including PFOS and PFOA, potentially inflating input concentrations and contributing to mass imbalance during treatment. Further research is necessary to address these complexities, but the findings are encouraging for the use of TWs as scalable, eco-friendly solutions for mitigating PFAS pollution and are instructive for optimising wetland design and operation to safeguard aquatic ecosystems.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds extensively used in industrial processes and consumer products [1]. Due to their resistance to natural degradation, PFAS are often referred to as 'forever chemicals'. Their accumulation in the environment presents persistent challenges to water quality and ecological health. Additionally, PFAS pose risks of biomagnification within food chains, with significant implications for human and environmental safety [2,3]. PFAS have been identified in a wide range of environmental matrices, including urban rivers [4] and coastal ecosystems [5], as well as remote locations with minimal human activity, such as Mount Everest [6]. Alarming, these compounds have also been identified in human

biological systems, including the placenta during pregnancy [7]. Therefore, stringent regulations have been implemented globally to limit PFAS concentrations, particularly in drinking water supplies.

The USA is at the forefront of PFAS regulatory framework in drinking water, where the Environmental Protection Agency (EPA) introduced the first nationwide PFAS regulation in April 2024 setting maximum contaminant levels of 4–10 ng L⁻¹ for six PFAS compounds [8]. The most recent European Union (EU) Drinking Water Directive (DWD) has established a maximum threshold of 0.5 µg L⁻¹ for total PFAS, while also restricting 20 specific PFAS compounds to a total concentration of 0.1 µg L⁻¹ [9]. In the UK, the Drinking Water Inspectorate (DWI) has issued guidelines for England and Wales, requiring the cumulative concentration of 48 PFAS to remain below 100 ng L⁻¹ in drinking water [10]. All

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these legislative measures focus on drinking water quality, but there are no established limits for the discharge of PFAS from wastewater treatment plants (WWTP). WWTPs receive and process contaminants originating from domestic and industrial sources, including nutrients, microorganisms, and chemical micropollutants [11,12]. Among these, PFAS are of particular concern as newly recognised legacy compounds. Therefore, proactive efforts to assess the dynamics of PFAS in WWTPs are essential for evaluating existing treatment performance and proposing alternative enhancement strategies.

PFAS have been frequently detected in WWTP effluents vary significantly depending on their influent sources and treatment processes, with reported ranges up to $28 \mu\text{g L}^{-1}$ in China [13,14], $3\text{--}1690 \text{ ng L}^{-1}$ in the USA [15], $5\text{--}137 \text{ ng L}^{-1}$ in Italy [16], and $1\text{--}213 \text{ ng L}^{-1}$ in Sweden [17], with the majority of the studies employing conventional treatment technologies. Nature-based solutions, particularly treatment wetlands (TWs), have been widely implemented in sewage works, not only for wastewater treatment but also for providing multiple co-benefits such as supporting biodiversity and carbon sequestration [18]. Previous studies have shown that TWs can be a promising alternative for the removal of micropollutants, including pharmaceuticals and personal care products [19]. In terms of PFAS removal, several lab-scale [20,21] and pilot-scale [22] studies have reported removal rates exceeding 80% in TWs. However, these exceptional performances are often attributed to controlled experimental conditions, relatively short operational durations, and the use of synthetic wastewater, which may not accurately reflect real large-scale scenarios. Among the limited studies on full-scale systems, PFAS removal rates have shown significant variability. For instance, a surface flow wetland treating stormwater runoff in the USA reported removal efficiencies ranging from negative values to 67% [23,24], while wetlands in China treating a mix of industrial and domestic wastewater demonstrated rates between -284% and 63% [25]. Similarly, Yin et al. (2017) observed a 61% removal rate over several years in a large-scale hybrid wetland treating landfill leachate [26]. However, limited studies have investigated PFAS removal in full-scale TWs designed specifically for domestic wastewater.

TWs are primarily employed for tertiary treatment, serving as the final safeguard for natural water bodies. The composition and flow of effluent entering TWs, which are largely influenced by the upstream treatment processes in WWTPs, potentially play a critical role in determining PFAS removal performance. For instance, chemical dosing with iron (Fe) or aluminium (Al) salts is commonly used in many WWTPs to achieve extremely low phosphorus discharge limits. The resulting iron residues and precipitated flocs may enter tertiary TWs, altering pollutant removal through microbial-mediated degradation and precipitation processes [27]. Specific PFAS-degrading bacteria, such as *Acidimicrobium* sp. *Strain A6*, have been identified in iron-rich sediments [28] and enhanced PFAS removal has been reported in TWs containing iron mineral-based substrate [29]. PFAS exhibit both hydrophobic and hydrophilic characteristics due to their unique structure and physico-chemical properties, thus, numerous studies have suggested that sediment adsorption and plant uptake play significant roles in PFAS removal in TWs [24]. Factors such as sediment properties (e.g., particle size, organic matter content, and density) and plant traits (e.g., root structure and biomass) are critical to their removal. However, research on large-scale TWs is extremely limited, and the mechanisms and dynamics of PFAS retention within these systems are not fully understood. This represents a significant limitation in the advanced design and optimisation of TW technology for PFAS mitigation.

To address the aforementioned knowledge gaps, this study focused on two large-scale surface flow TWs constructed as tertiary treatment systems to polish effluent from long-term operated domestic WWTPs in Norfolk, UK. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), two of the most well-known and regulated PFAS compounds, were selected as target PFAS compounds to evaluate their occurrence and removal in both TWs. Moreover, the removal mechanisms and partitioning behaviours of PFAS driven by sediment and plant

characteristics were also investigated. The ultimate aim of this research is to enhance the understanding of PFAS dynamics within TWs, thereby providing insights to inform the design and operation of nature-based solutions for effective PFAS micropollutants management.

2. Materials and methods

2.1. Target two surface flow TWs

This study investigated two full-scale surface flow TWs, also referred to as Integrated Constructed Wetlands (ICW), located in Norfolk County, UK (Fig. 1). Both systems were designed and constructed collaboratively by Anglian Water and the Norfolk Rivers Trust to serve as tertiary treatment systems for polishing effluent from nearby long-term operated Anglian Water WWTPs.

The Ingoldisthorpe WWTP (52.865779, 0.521202) serves a population equivalent (PE) of approximately 6000 with a designed dry weather flow of $1400 \text{ m}^3 \text{ d}^{-1}$ and a peak flow capacity of up to $3640 \text{ m}^3 \text{ d}^{-1}$ during wet weather, beyond which flows are diverted to storm tanks. The biological treatment process includes primary settlement tanks, trickling filters, humus tanks, and a nitrifying sand filter. Additionally, ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) is dosed to reduce phosphorus and suspended solids through coagulation and flocculation. The associated Ingoldisthorpe wetland (1.08 ha) became fully operational in April 2018 (Fig. 1a). It comprises four consecutive cells with areas of 1972, 2450, 3560, and 2806 m^2 , respectively, and a maintained water depth of approximately 0.2 m. The wetland has been planted with 25,000 native aquatic plants and designed to have a hydraulic loading rate of 0.2 m d^{-1} and a hydraulic retention time of 1.35 d.

The second wetland (Fig. 1b) under investigation is located near the village of Binham in Norfolk County, UK, at Langham (52.927697, 0.971389). This system was commissioned in 2022 and received effluent from Langham WWTP, which serves a PE of 2000. The biological treatment train at Langham includes primary settling tanks, trickling filters, and a humus tank. In contrast to the Ingoldisthorpe site, the Langham system does not utilise chemical dosing as a treatment step. The tertiary Langham wetland covers a total area of 1.05 ha and comprises three consecutive cells, with areas of 2988, 3244, and 4282 m^2 , respectively. The water depth was maintained at approximately 0.2 m, with a hydraulic loading rate of 0.03 m d^{-1} and a hydraulic retention time of 6.52 d. The final treated effluent was discharged into Binham Stream, a tributary of the River Stiffkey.

2.2. Sample collection

Five monthly sampling campaigns were conducted during the spring and summer of 2024, from March to July, to collect water samples from each cell of the two surface flow TWs. To understand the PFAS removal mechanisms and partitioning behaviours within the TWs, sediment and plant samples were collected from various locations in June for further analysis.

2.2.1. Water samples

During each field sampling campaign, grab water samples were collected at the inlet of the first cell and the outlet of each subsequent cell in both systems. Physio-chemical parameters, including conductivity, pH, temperature, and dissolved oxygen (DO), were measured in situ using an optical double-probe sensor (Hach Company, Loveland, Colorado, USA). Water samples were collected in clean and pre-rinsed 500 mL high-density polypropylene (HDPE) bottles and transported to the lab immediately and stored at 4°C . These samples were analysed for phosphorus, nitrogen, and trace metal concentrations within 48 h of collection to ensure the stability of analytes. Additional samples for PFAS analysis were collected in 250 mL bottles and frozen until analysis in accordance with EPA 1633 guidelines. The exact volume of each sample was determined by weighing the bottles before and after sample



Fig. 1. Aerial views of Ingoldisthorpe (a) and Langham (b) treatment wetlands. Yellow lines outline the boundaries of each cell in the systems. The yellow map pointer marks the outlet of the final cell in each wetland and the light blue arrows indicate the water flow direction.

preparation.

2.2.2. Sediment samples

For the sediment collection, the first cell (cell 1) of each system was divided into three zones: inlet, middle, and outlet, using an imaginary grid. Sediment samples (500 mL) were collected from three different points within each zone of cell 1. Sediment was also sampled from the outlet zone of the final cell in each wetland (i.e. the 4th cell for Ingoldisthorpe and the 3rd cell for Langham). Sediment sampling was performed using a gravity-type sediment corer. Sediment depth was measured directly by recording the height of the sediment column within the corer. Sampling procedures were conducted to minimise disturbance to the sediment structure. All sediment samples were transferred to 500 mL sterile polyethylene containers and transported to the laboratory for subsequent analysis.

2.2.3. Plant samples

For plant collection, the first cell of each wetland system was divided

into three zones (inlet, middle, and outlet) using an imaginary grid. Entire plants were carefully collected from three different points within each zone, covering an area of 0.25 m^2 at each point. The extraction of roots from the sediment was conducted rigorously to ensure the complete collection of belowground material for subsequent analysis. The samples were placed in low-density polyethylene (LDPE) zip-lock bags and transported to the laboratory under refrigerated conditions (4°C) to maintain sample integrity. In the laboratory, the plants were thoroughly rinsed to remove any attached sediment or debris and then divided into aboveground (stems and leaves) and belowground (roots) compartments. Roots were further washed under running deionized water and gently scrubbed with a soft brush to remove visible sediment and fine-grained particles lodged in root crevices, following previously established methodologies [30–32]. After rinsing, they were visually inspected under magnification to confirm the absence of residual sediment.

2.3. Sample analysis

2.3.1. Nutrient and metal analysis

Nutrients, such as total nitrate/nitrite (N) were quantified in water samples using a segmented flow analyser (SEAL Analytical Ltd., Mequon, WI, USA). Total phosphorus was determined by digesting water samples with perchloric and nitric acids, followed by spectrophotometric analysis. Total suspended solids (TSS) were calculated gravimetrically by filtering samples, drying the retained solids, and determining weight differences. Quality control measures, including reagent blanks, calibration standards, and triplicate analyses, were implemented to ensure accuracy and consistency in line with APAH guidelines. Fe and Al concentrations were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (NexION 350D, PerkinElmer Inc., Waltham, MA, USA). The chemical composition of the sediments was determined by SEM analysis (Tescan VEGA 4 equipped with Oxford Instruments EDS, using AZtec software) of dried and ground samples. P, Fe and Al in sediments were also quantified by ICP-OES. Plant samples were additionally analysed by ICP-OES to quantify key nutrient indicators such as P and Fe.

2.3.2. PFAS analysis

Previous studies on PFAS analysis, including the US EAP 1633 method, have primarily focused on water and sediment samples, with plant tissue analysis posing greater challenges due to high pigment content. In this study, all samples were processed using dual-phase solid-phase extraction (SPE) cartridges containing both Weak Anion Exchange (WAX) and Graphitized Carbon Black (GCB) sorbents, supplied by Water Corporation (Milford, MA, USA). Specific protocols for sample cleaning and concentration tailored to each environmental matrix are detailed in Section S1 (Supplementary material).

An HPLC system (ExionLC, AB SCIEX, Concord, Canada) was used in conjunction with a QTrap 6500⁺ (AB SCIEX, Concord, Canada) triple-quadrupole linear ion trap tandem mass spectrometer equipped with an ESI source in negative ion mode ($V = -4.0$ kV). Data acquisition and analysis were performed using Analyst® software, version 1.6.3 (AB SCIEX, Concord, Canada). Chromatographic separation was carried out using a reversed-phase C₁₈ column (Kinetex 2.6 μ m C₁₈ 100 Å, 50 mm $\times$ 2.1 mm, Phenomenex, Torrance, CA, USA) along with a delay column (PFAS delay Phase, 5 μ m, 50 mm $\times$ 2.1 mm, Restek Corp., Bellefonte, PA, USA). The columns were thermostatic at 40 °C with a mobile phase flow rate of 0.4 μ L min⁻¹. The mobile phases consisted of MeOH containing 5 mM ammonium acetate (solvent A) and H₂O with 5 mM ammonium acetate (solvent B). The injection volume was set to 5 μ L, and the autosampler temperature was maintained at 15 °C. The gradient elution programme for the HPLC-MS/MS method started at 40% solvent B with a flow rate of 400 μ L min⁻¹ for 0.5 min, transitioned to 100% solvent B over 5 min, and was maintained at this level for 3 min. At the end, the gradient returned to the initial conditions and was equilibrated for 3 min, resulting in a total run time of 11 min. Additional details on the instrumental conditions are provided in Section S2 (see Table S1). The limits of detection (LODs) of PFOS and PFOA were determined to be 0.03 and 0.17 ng L⁻¹ in water samples, 2.4 and 7.2 pg g⁻¹ in dry sediment samples, and 0.13 and 0.64 ng g⁻¹ in dry plant samples, respectively.

2.4. Mass balance calculation

The mass balance calculation in this study focused exclusively on the first cell of each surface flow TWs, as sediment accumulation in the subsequent cells was insufficient for collection and subsequently PFAS analysis. For these calculations, the inflow and outflow concentrations of PFOS and PFOA in water samples were measured, and their mass fluxes were determined by multiplying each concentration by the corresponding flow rates. Adjustments were made to account for variable flow conditions, ensuring an accurate representation of contaminant

dynamics throughout the treatment process. To thoroughly assess PFAS retention in the first cell, sediment samples were analysed for PFOS and PFOA concentrations. Sediment density and depth measurements were taken at each sampling point to estimate the total mass of contaminants adsorbed within the wetland compartment. In addition, PFAS accumulation measured in plant biomass was quantified by combining PFOS and PFOA concentrations measured in different plant compartments, percentage plant coverage, and average plant mass. This approach provided a comprehensive assessment of PFOS and PFOA behaviour in TWs, considering variations in water flow, sediment accumulation, and plant uptake capacity.

2.5. Data analysis

Kruskal-Wallis tests were performed to compare water quality parameters and influent/effluent pollutant concentrations across different cells with a significance level set at $p = 0.05$. To identify the key factors influencing PFAS removal in TWs, Pearson correlation analysis was used to assess the relationships between PFOS and PFOA concentrations and physicochemical indicators. Prior to correlation analysis, data were standardised using the autoscaling method to ensure that each variable had an equal influence in the analysis [33]. All statistical and data analyses were performed using Origin 2024.

3. Results and discussion

3.1. PFAS occurrence in water samples and removal in TWs

PFAS, including PFOS and PFOA, have been reported in treated domestic wastewater, with concentrations ranging from 1–75 ng L⁻¹ for PFOS and 0.2–145 ng L⁻¹ for PFOA [34,35]. The influent concentrations observed in the two tertiary TWs were consistent with these reported ranges (Fig. 2). The mean influent PFOS concentrations (Fig. 2a) in the Ingoldisthorpe and Langham TWs were 6.50 ± 0.63 and 6.48 ± 2.83 ng L⁻¹, respectively. Although variability was noted across the sampling campaigns, a general trend of PFOS reduction was observed across the subsequent treatment cells, resulting in final effluent concentrations of 4.0 and 4.6 ng L⁻¹ for the two systems. The mean influent PFOA concentrations (Fig. 2b) were lower than those of PFOS, measuring 3.87 ± 0.86 ng L⁻¹ in Ingoldisthorpe and 2.70 ± 0.81 ng L⁻¹ in Langham. Despite these lower initial concentrations, both systems exhibited a gradual decrease in PFOA levels across all cells, with final effluent concentrations ranging from 1.79 and 3.27 ng L⁻¹, which were within the limits set by most international drinking water guidelines. The findings indicated that the two TWs effectively reduce PFAS concentrations in treated effluent to safe levels, thus contributing to the protection of receiving water bodies.

Notably, while it is generally acknowledged that the pollutants (e.g. phosphorus and nitrogen) from WWTP effluent are further diluted in receiving waters, this may not always be the case for trace levels of PFAS compounds. PFAS in natural waters can also arise from diffuse sources such as agricultural and urban runoff, atmospheric deposition, and industrial discharge [36]. These sources can significantly contribute to PFAS levels in rivers and other natural water bodies, raising concerns about cumulative contamination [37]. Consequently, while the TW effluent may present low PFAS contamination, overall PFAS concentrations in natural waters could still be influenced by upstream or adjacent inputs. Comprehensive monitoring of upstream and downstream of discharge points is therefore essential to fully clarify the contributions of treated sewage and other sources to PFAS levels.

The average PFOS removal rates in the Ingoldisthorpe and Langham TWs were 38% and 29%, respectively, while PFOA removal rates were 15% and 34%. These removal efficiencies were consistent with previous studies on full-scale TWs, which often report significantly lower rates than those observed in controlled lab/pilot-scale systems [24]. For instance, a surface flow TWs treating domestic and industrial

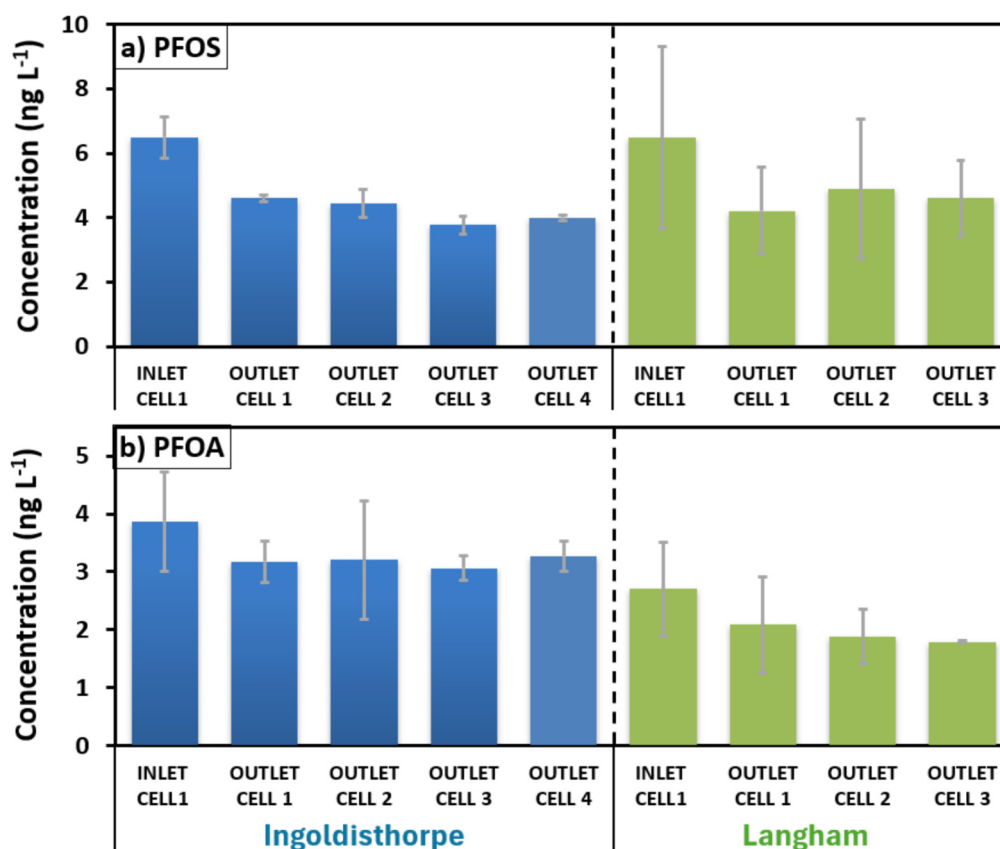


Fig. 2. Mean concentration of PFOS (a) and PFOA (b) in water samples at different sampling points of Ingoldisthorpe (blue) and Langham (green) surface flow treatment wetlands.

wastewater near a fluorochemical industry reported PFOA removal rates ranging from -199% to 63% and PFOS removal rates from -284% to 63% [25]. In Ingoldisthorpe TW, PFOS removal exhibited higher efficiency compared to PFOA, which may be attributed to upstream ferric sulphate dosing. PFOS facilitates strong electrostatic interactions and hydrogen bonding with adsorption sites due to its larger and more polarisable sulfonate group [38], while PFOA's less polarisable carboxylate group and slightly higher water solubility [39] reduce its affinity for iron-rich sediments, increasing its mobility in wetlands. The variability of treatment performance highlighted the importance of upstream treatment approaches in the removal of PFAS.

In terms of the water quality dynamics (Table S2), the lower TSS levels observed at each sampling point in the Ingoldisthorpe TW supported the influence of the coagulation pre-treatment (chemical dosing), which was not implemented at Langham. Although both sites exhibited a consistent decrease in TSS across the treatment cell, a slight increase was noted in the final effluent. This increase may be attributed to the resuspension of fine particulates during the later treatment stages. The dynamics of suspended particles can influence PFAS behaviour in TWs, as such particles can act as carriers for these contaminants. This emphasised the necessity of investigating the adsorption behaviour of PFAS on particulates and sediments, as PFAS bound to resuspended particles could reduce overall removal efficiency and adversely affect effluent quality. Given the critical role of TSS dynamics in PFAS retention, the adsorption rates of PFAS onto particulate matter and sediments were further analysed and discussed in Section 3.3.

3.2. PFAS accumulation in sediments

The partitioning of PFAS compounds in sediments and plants was assessed to gain a comprehensive understanding of their removal

pathways in TWs. The accumulation of sediment in surface flow TWs was found to be $0.5\text{--}2\text{ cm}$ per annum, with significantly lower rates observed in tertiary treatment systems [40]. In line with these findings, sediment samples were collected for the analysis of adsorbed PFOS and PFOA at varying points within the first cell, with additional composite samples collected from the outlet of the final cell in each TW (Section 2.2.2). Although the influent PFOS concentrations were similar for both wetlands (Fig. 2a), sediment concentrations showed significant variation (Fig. 3a). In the inlet zone of the first cell, the Ingoldisthorpe system recorded significantly higher PFOS levels ($235 \pm 84\text{ ng g}^{-1}$) compared to the corresponding inlet area at Langham ($49 \pm 23\text{ ng g}^{-1}$). While PFOS concentrations remained relatively stable within Cell 1 at Langham (with a mean value of $48 \pm 14\text{ ng g}^{-1}$), and a distinct decreasing trend was observed in Ingoldisthorpe TW. In this case, PFOS levels declined from 235 ± 84 to $17 \pm 2\text{ ng g}^{-1}$ along with the water flow pathway.

A considerably lower magnitude of PFOA concentrations was observed in the sediment compared to PFOS (Fig. 3b). This was partly due to the relatively low PFOA loading in the systems (Fig. 2) and also to its weaker binding affinity to sediment, which is influenced by its lower hydrophobicity compared to PFOS [39]. Nevertheless, the trend of PFOA concentrations in sediments in both systems was similar to PFOS with the highest PFOA concentration ($6.6 \pm 1.4\text{ ng g}^{-1}$) detected in the inlet zone of Ingoldisthorpe's first cell, gradually decreasing in the middle and outlet zones ($3.4 \pm 0.5\text{ ng g}^{-1}$ and $2.1 \pm 0.4\text{ ng g}^{-1}$, respectively). The PFOA concentration ($2.7 \pm 1.7\text{ ng g}^{-1}$) in the inlet area of Langham's Cell 1 was lower compared to Ingoldisthorpe, with relatively uniform levels throughout the cell.

A significant reduction in both PFOS and PFOA concentrations adsorbed in sediments was found near the discharge points of the final effluent at both sites. At Ingoldisthorpe, mean PFOS concentrations were

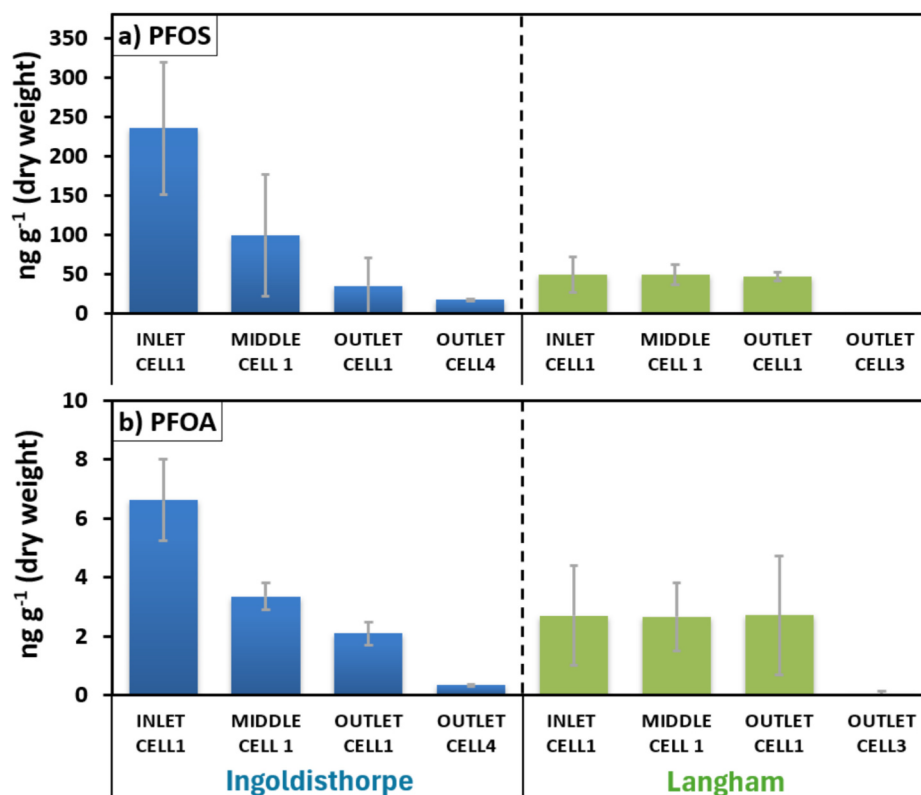


Fig. 3. Dry weight concentrations of PFOS (a) and PFOA (b) in sediment samples at different sampling points in Ingoldisthorpe (blue) and Langham (green) surface flow treatment wetlands.

$17.0 \pm 1.7 \text{ ng g}^{-1}$, while PFOA levels were $0.3 \pm 0.03 \text{ ng g}^{-1}$. In contrast, at Langham, both PFOS and PFOA concentrations were below the limit of detection (LOD) (Fig. 3a and b). This marked decrease may be attributed to the specific characteristics of the final cell of the wetlands, characterised by a scarce sediment accumulation, which also leads to the need for composite sediment samples. The reduction in the volume of sediment may result in lower concentrations of adsorbed PFOS due to the limited capacity of less well-consolidated or loosely compacted sediment for PFAS adsorption and retention. Nevertheless, over long-term operation, the gradual particulate accumulation in the final cell may lead to an increase in the concentrations of PFOS and PFOA in sediment.

3.3. Impacts of sediment characteristics on PFAS retention

The distinct dynamics of sediment PFAS concentrations were observed in the Ingoldisthorpe (significantly higher level in the inlet zone followed by a significant reduction along the flow path, Fig. 3a) and Langham TWs (homogeneous distributions across the cells, Fig. 3b). As highlighted in Fig. 4a, the decreasing trend of PFAS concentrations in the first cell of Ingoldisthorpe TW corresponded with a similar pattern of sediment accumulation. This was attributed to the presence of upstream ferric sulphate dosing, which promoted the rapid settling of flocs upon entering the wetland [41]. This association is further reinforced by the Pearson correlation analysis (Fig. 4b), which demonstrated strong positive correlations between sediment depth and PFOS (0.81) and sediment depth and PFOA concentrations (0.73). The results align with prior studies [20], which identified sediment adsorption and accumulation as primary pathways for PFAS removal in TWs. Mechanisms such as electrostatic and hydrophobic interactions [42], anion exchange, surface complexing, and hydrogen bonding (Sima and Jaffe, 2021) play critical roles in PFAS retention. Additionally, the positive correlations with bulk density (0.77 for PFOS and 0.62 for PFOA) indicated that both

compounds preferentially adsorb onto more compact sediment layers. Sediments with higher bulk density, often correspond to less porous and fine-grained, such as clay-rich layers, provide a greater capacity to retain trace hydrophobic contaminants through noncovalent interactions [28]. At Ingoldisthorpe, ferric sulphate dosing could introduce ferric ions (Fe^{3+}) into TWs, which could enhance the adsorption of PFOS and PFOA. Fe^{3+} interacts more strongly with PFOS than PFOA due to the sulfonate group's higher affinity, explaining the approximately two orders of magnitude higher PFOS concentrations in Ingoldisthorpe sediments [21].

Over time, Fe^{3+} can precipitate as iron oxides or hydroxides, which possess large surface areas and high sorption capacities. These precipitates can act as stable, long-term adsorption sites, further reduce PFAS mobility. This tendency has been proved by several lab-scale studies, highlighting the potential of iron amendments to improve PFAS retention in wetlands. For instance, Ma et al. (2023) demonstrated a 30.7% and 35.5% increase in PFOS and PFOA removal, respectively, when Fe mineral amendments were applied to TW substrates [29]. This improvement was attributed to a higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, which facilitates both adsorption and microbial degradation pathways. Similarly, Yu et al. (2023) reported that integrating iron-carbon substrates into wetland design increased PFAS adsorption by 17.9% for PFOS and 15.9% for PFOA, owing to enhanced surface area and electrostatic interactions [21]. Additionally, ferric ions can contribute to microbial degradation of PFAS by supporting iron-reducing bacteria (FeRB) such as *Pseudomonas* and *Burkholderia* [29]. These microbial communities facilitate PFAS degradation through electron transfer processes. These studies reported that combining iron oxides with FeRB significantly improved PFAS removal in TW microcosms, particularly under anaerobic conditions.

However, adsorption competition may occur due to the presence of other anions, such as phosphate (P), which are typically present at significantly higher concentrations than PFAS. These anions have a

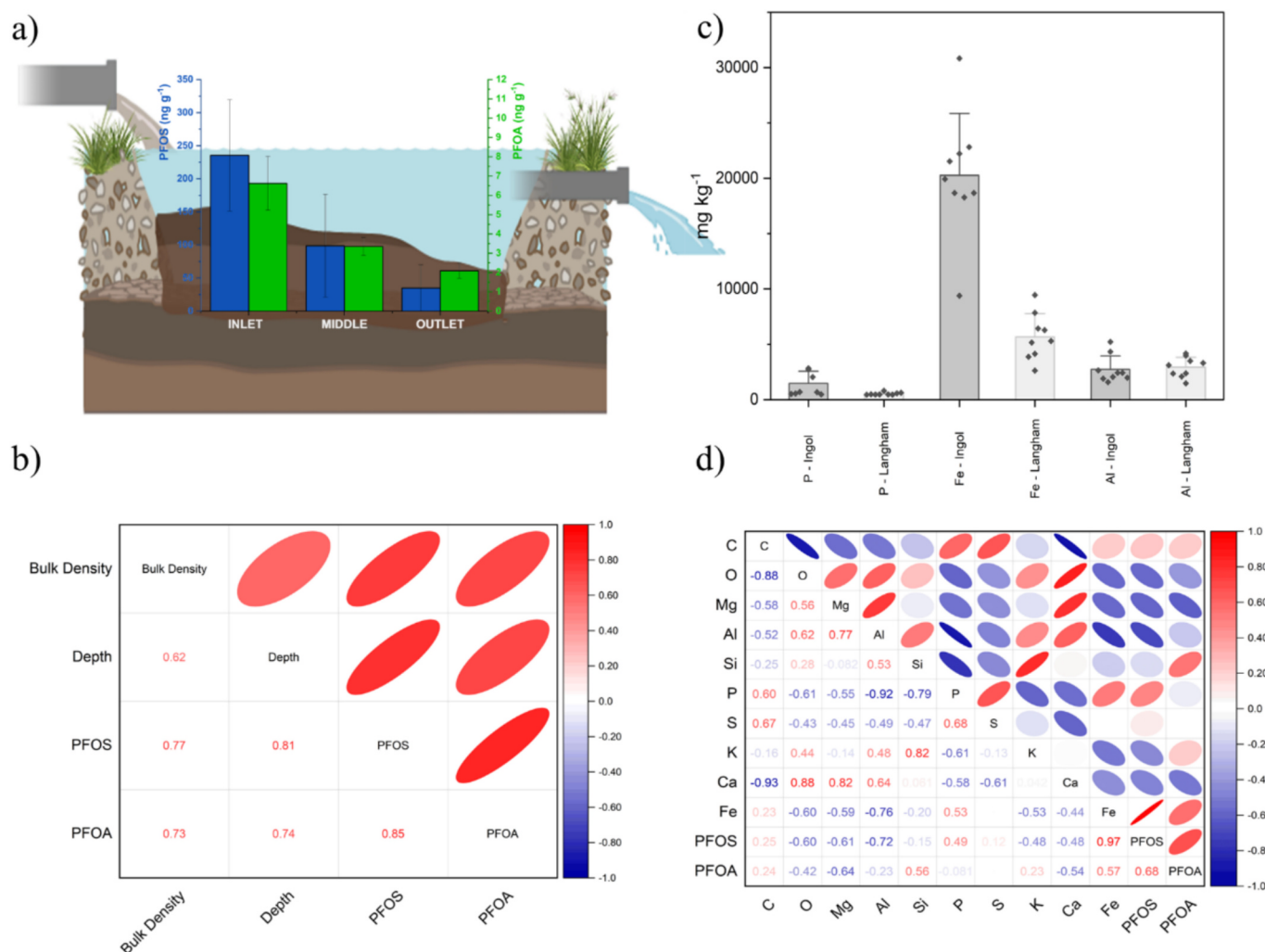


Fig. 4. Variation in sediment depth and mean concentrations of PFOS (blue) and PFOA (green) in ng g^{-1} (dry weight) in sediment samples collected at different points within cell 1 of the Ingoldisthorpe wetland (a). Pearson correlations between PFOS and PFOA concentrations, bulk density, and sediment depths (b). Statistical representation of dry weight concentration of total phosphorus (P), total iron (Fe), and total aluminium (Al) in sediment samples from the first cell of the Ingoldisthorpe (dark grey) and Langham (light grey) wetland (c). Pearson correlations between PFOS and PFOA concentrations in sediments and sediment chemical composition (d).

similar strong affinity for Fe, thereby reducing the available binding sites for PFOS and PFOA. To validate these hypotheses, an ICP-OES analysis was conducted on sediment samples from both TWs to quantify the concentration of Fe, P, and Aluminium (Al). Al was included as a reference element, as it exhibits a similar positive charge to Fe but was not employed in the chemical dosing process, allowing for a comparison of natural versus augmented adsorption contributions. As expected, Fe concentrations were significantly higher in the sediments from Ingoldisthorpe than in those from Langham (Fig. 4c). In contrast, Al concentrations were comparable between the two sites (Fig. 4c), aligning with its exclusion from the dosing strategy. The sediments from Ingoldisthorpe also exhibited elevated P levels in Cell 1 (Fig. 4c), indicating that negative charged phosphate ions exhibit a strong affinity for ferric ions, thereby facilitating their adsorption.

Additional data on the elemental composition of the sediments was obtained through SEM analysis (Fig. S1). Pearson correlation analysis ($p < 0.05$) provided further insight into the relationships between sediment chemical composition and PFAS concentrations (Fig. 4d). The expected strong positive correlation between PFOS and Fe (0.97) confirmed the crucial role of Fe in retaining PFOS within the sediment matrix. Similarly, Fe also exhibited a positive correlation with PFOA (0.57), although the interaction was relatively weaker likely due to the lower affinity of

carboxylate groups in PFOA compared to the sulfonate groups in PFOS. The observed positive correlation between PFOS and P (0.49) can be attributed to the shared affinity of phosphate and PFOS for ferric ions. Both phosphate ions and PFOS are negatively charged and strongly adsorb onto iron oxides, resulting in co-adsorption effects in iron-rich sediments that explain the moderate positive correlation. In contrast, negative correlations between magnesium (Mg) and both PFOS (−0.61) and PFOA (−0.64) suggest Mg does not support PFAS retention.

The results revealed weak positive correlations between PFOS and PFOA and carbon (PFOS: 0.25, PFOA: 0.24), indicating a limited yet discernible relationship with organic matter in the sediment. Organic matter can provide hydrophobic sites that may facilitate the binding of PFAS molecules, enabling interactions with carbon-based materials. Nevertheless, the weak correlation suggested that organic matter may only play a secondary role in PFAS retention compared to other mechanisms, such as adsorption to iron-rich substrates. A negative correlation between PFOS and PFOA and Al (−0.72 and −0.23, respectively) contrasts sharply with the strong positive correlation with Fe, highlighting differences in their surface chemistry and adsorption behaviour. Ferric iron forms oxides and hydroxides with high surface charge density, creating numerous positively charged sites that effectively bind negatively charged PFAS molecules, such as PFOS and PFOA. In contrast, Al

compounds exhibit lower surface charge density and a weaker affinity for PFAS. The stronger correlation with Fe is also attributed to its higher concentrations, particularly at Ingoldisthorpe, where chemical dosing increases available adsorption sites. Conversely, the lower Al concentration likely leads to greater competition with other anions, such as phosphate and sulphate, which preferentially occupy Al's limited adsorption sites, reducing its effectiveness in retaining PFAS.

The positive correlation (0.68) between PFOS and PFOA indicates a possible shared environmental pathway or source within the sediment, potentially influenced by analogous adsorption mechanisms in CW systems. These findings highlight the pivotal role of Fe-rich sediments in PFAS retention, offering critical insights into optimising wetland systems for effective contaminant management. As global efforts increasingly focus on reducing or eliminating chemical dosing to mitigate environmental impacts, understanding the potential consequences for PFAS retention becomes essential. Without chemical dosing, Fe concentrations in sediments are likely to decline, which could significantly diminish the adsorption capacity for PFOS and PFOA, given their strong affinity for ferric oxides and hydroxides. To address these challenges, alternative strategies for enhancing long-chain PFAS retention in wetlands are needed. Incorporating natural Fe-rich materials, such as iron-bearing clays or iron-coated sands, could provide a sustainable solution to maintain high adsorption capacity. These materials could be integrated into CW substrates to mimic the benefits of chemical dosing without introducing synthetic chemicals. Moreover, optimising wetland designs to increase retention time and maximize sediment-water interactions could enhance PFAS adsorption. Innovative configurations, such as multi-layered substrates or zoned treatment cells with Fe-enriched materials, might improve efficiency and adaptability in response to evolving environmental challenges.

3.4. PFAS accumulations in plant samples

In accordance with the pattern of PFOS retention observed in sediments (Fig. 3), the accumulated PFOS in plants was significantly higher ($225 \pm 89 \text{ ng g}^{-1}$) at the inlet of Ingoldisthorpe's first cell compared to the middle ($151 \pm 129 \text{ ng g}^{-1}$) and the outlet zone ($89 \pm 54 \text{ ng g}^{-1}$) (Fig. 5a). Similarly, lower PFOS concentrations were detected in plant samples in Langham, with values of 137 ± 128 , 40 ± 12 , and $70 \pm 82 \text{ ng g}^{-1}$ for the inlet, middle, and outlet zones, respectively. On the contrary, PFOA data demonstrated a less defined trend with concentrations of 137 ± 17 , 115 ± 34 , and $123 \pm 38 \text{ ng g}^{-1}$ at Ingoldisthorpe and 55 ± 60 , 37 ± 31 , and $104 \pm 78 \text{ ng g}^{-1}$ at Langham, for inlet, middle, and outlet zone of Cell 1, respectively (Fig. 5c). The observed higher PFOS concentrations align with the established understanding that root absorption is a primary pathway for the uptake of chemical micropollutants in plants [43]. Elevated sediment PFOS levels likely enhance its bioavailability, resulting in greater accumulation in plant tissues.

Further compartmental analysis confirmed that PFOS is predominantly retained in the roots, with much lower concentrations observed in the stems and leaves (Fig. 5b). In contrast, the distribution of PFOA, while still demonstrating a greater accumulation in roots, is less presented (Fig. 5d). This disparity is more evident for PFOS due to its higher partitioning coefficient (K_d), which enhances PFOS sorption to both root surfaces and soil particles compared to PFOA [44]. The uptake and translocation of PFAS are influenced by chain length and octanol–water partition coefficient ($\log K_{ow}$). Short-chain PFAS more readily cross cell membranes via passive diffusion, while long-chain PFAS depend on active transport, limiting their mobility to aboveground tissues [43,45]. Hydroponic studies support these findings, showing that the translocation factor (TF), or shoot-to-root concentration ratio, decreases with increasing PFAS chain length with values consistently below 1 for PFOA

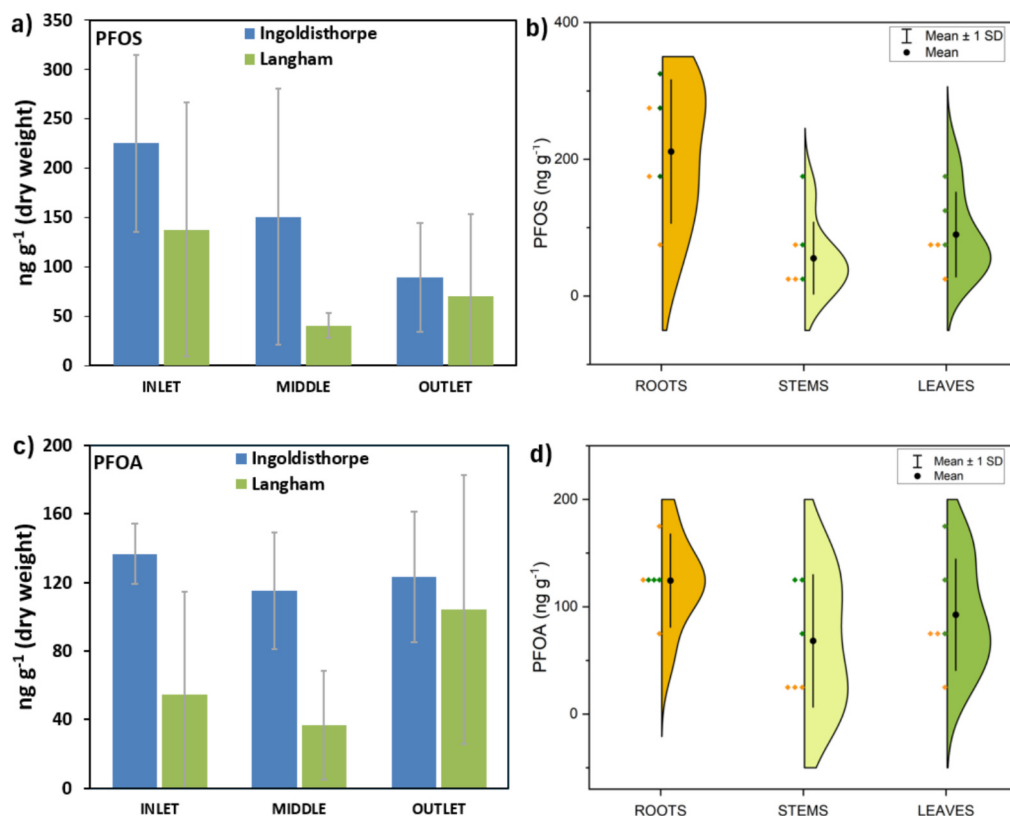


Fig. 5. Dry weight concentration of PFOS (a) and PFOA (b) in sediment samples at different sampling points of the first cell of Ingoldisthorpe (blue) and Langham (green) wetlands, with the first histogram of each series representing the mean concentration in the inlet zone, the second one the mean concentration in the middle zone and the third one the mean concentration in the outlet zone of Cell 1. Statistical representation of PFOS (c) and PFOA (d) in different plant compartments for Ingoldisthorpe (green dots) and Langham (orange dots) wetlands.

and perfluoroalkyl carboxylic acids (PFCAs) [46]. In contrast, short chain perfluorinated alkyl acids (PFAAs) are more easily translocated due to their smaller molecular size and lower lipophilicity.

The translocation dynamics of PFAS are not only influenced by the physicochemical properties of the contaminants, but also by external factors, including temperature, salinity, and pH. Zhao et al. (2016) demonstrated that elevated temperatures increase transpiration rates, promoting contaminant uptake, while higher salinity enhances PFAS partitioning into root organic matter through a 'salting-out' effect [47]. The pH also plays a critical role, with maximum PFOS uptake observed in wheat at pH 6–8, whereas uptake decreases significantly at pH 4 and 10 [48]. All these parameters collectively influence PFAS mobility and bioavailability within plants, with implications for root-to-shoot translocation. Furthermore, the elevated Fe^{3+} concentrations in wetland sediments, as a consequence of the chemical dosing, further reduce PFOS and PFOA bioavailability by strongly sequestering these compounds in the sediment. As previously discussed in Section 3.2, this effect is more pronounced for PFOS, whose sulfonate group has a greater affinity for Fe^{3+} , confining it to the root zone and limiting its movement through plant vascular tissues (Fig. 5b and d). Additionally, Fe dosing may indirectly influence rhizosphere microbial communities, potentially facilitating microbial degradation or transformation of PFAS within the root zone [29].

3.5. Opportunities and challenges

The findings of this study provided insights into using surface flow TWs to effectively retain PFAS 'forever chemicals'. The removal efficiencies were observed in the range of 29%–38% for PFOS and 15%–34% for PFOA, with an annual retention capacity in water of 0.61–0.90 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOS and 0.18–0.29 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOA during wastewater treatment. These performances are comparable to the removal capabilities of surface flow TWs for other chemical micro-pollutants, including pharmaceuticals, pesticides, and heavy metals [19,49]. Importantly, the effluent from both TWs consistently met most regulatory thresholds for PFAS in drinking water, including the UK's current guideline [10]. Considering other multiple co-benefits TWs could offer as a nature-based solution, TWs can be considered an eco-friendly and cost-effective approach for water utilities and other stakeholders.

Although plant uptake contributes to PFAS removal, it plays a secondary role compared to sediment adsorption. In this study, PFAS uptake and accumulation in plant biomass ranged from 0.11–0.12 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOS and 0.04–0.07 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOA in both TWs (Table 1). The values were significantly lower than the PFAS retained in the sediment, which achieved 1.34–2.80 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOS and 0.07–0.09 $\text{mg m}^{-2} \text{y}^{-1}$ for PFOA in both TWs. The results suggest that while plant harvest could marginally enhance long-chain PFAS removal, long-term management of sediment remains essential to prevent the remobilisation of accumulated PFAS. Therefore, future opportunities for improving PFAS removal in TWs include optimising wetland designs with advanced substrate materials. Incorporating iron amendments or other adsorptive media could improve sediment sorption capacity,

Table 1
PFAS mass distributions in Ingoldisthorpe and Langham's surface flow treatment wetlands treating the effluent of domestic WWTPs.

Site	Water inlet ($\text{mg m}^{-2} \text{y}^{-1}$)	Water outlet ($\text{mg m}^{-2} \text{y}^{-1}$)	Sediment + rooting media ($\text{mg m}^{-2} \text{y}^{-1}$)	Plants ($\text{mg m}^{-2} \text{y}^{-1}$)
PFOS				
Ingoldisthorpe	0.27	0.21	2.80	0.12
Langham	0.16	0.07	1.34	0.11
PFOA				
Ingoldisthorpe	0.16	0.14	0.09	0.07
Langham	0.07	0.04	0.07	0.04

addressing the primary retention mechanism for PFAS. Additionally, advancing research into the microbial degradation of PFAS within wetland systems could unlock new possibilities for PFAS removal after the sediment adsorption.

Challenges persist, particularly regarding the multiple sources of PFAS, including urban and agricultural runoff, which can introduce additional PFA loads into receiving waters. Comprehensive monitoring and mitigation approaches are crucial to tackling PFAS concentrations both upstream and downstream of wetland discharge points. A conventional mass balance calculation was conducted (Table 1) to provide further insight into the removal processes and to guide system design and operations. However, an apparent imbalance was observed for both PFOS and PFOA, with retention in sediment and rooting media exceeding the mass difference between inlet and outlet concentrations in water samples. One potential explanation for this imbalance may be found in the generation of PFOS and PFOA from the degradation of PFAS precursors present in the system. Prior research in wastewater treatment systems has demonstrated the formation of PFOA from the degradation of fluorotelomer alcohols (e.g., 8:2 FTOH) and fluorotelomer acrylates [50]. Similarly, PFOS has been shown to originate from the breakdown of perfluoroalkane sulfonamides (FASAs) and sulfonamidoethanols (FASEs). The degradation of these precursors into their stable terminal products presents a challenge to mass balance calculations and contributes to the increased concentrations of PFOS and PFOA in stored sediments. Additionally, the complex dynamics of flow and sediment distribution, especially in relatively new tertiary systems, may also contribute to this discrepancy. Together, these scientific and technical factors highlight the complexity of PFAS mass balance calculations and highlight the need for more comprehensive monitoring efforts to account for precursor transformation and sediment dynamics.

4. Conclusions

This study offers valuable insights into the behaviour of PFAS within water, sediment, and plant compartments in two large-scale, multi-cells surface flow TWs for domestic wastewater treatment. The level of PFOS and PFOA in water samples showed in the low ng L^{-1} range, with a moderate decrease after each cell, leading to final effluent concentrations in line with stringent international regulation proposed for drinking water quality. A significant finding is the impact of upstream treatment with ferric sulphate dosing on the enhancement of PFAS retention. The introduction of ferric ions created positively charged sites that facilitate the adsorption of PFOS and PFOA to sediments, with a stronger affinity for the sulfonate groups of PFOS. Consequently, PFOS concentrations in sediments were higher than those of PFOA and displayed a decrease from the inlet to the outlet zone of the first cell. The positive correlations with Fe content, sediment depth, and bulk density, thereby support the hypothesis that sediment characteristics and accumulation may significantly influence the sequestration and mobility of PFAS within the wetland. In plant samples, PFOS and PFOA were predominantly retained in the roots, with minimal translocation to above-ground tissues, consistently with the hydrophobic characteristics of these compounds. This tendency is likely further accentuated by the considerable presence of Fe ions, which enhance the adsorption of PFAS to sediments, thereby reducing their bioavailability in pore water accessed by plant roots. In conclusion, these findings highlight the potential of ferric dosing in large-scale CW as a viable approach for PFAS mitigation and provide insights to optimise the design of CWs as scalable strategy for reducing the mobility and release of PFAS in natural treatment systems, thereby safeguarding the ecosystems of receiving water bodies.

CRedit authorship contribution statement

Chiara Sarti: Writing – original draft, Validation, Investigation, Formal analysis, Conceptualization. **Ayisha Affo Souleymane:** Writing

– original draft, Investigation. **Gabriela Dotro**: Writing – review & editing, Supervision, Funding acquisition. **Alessandra Cincinelli**: Writing – review & editing. **Tao Lyu**: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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.jwpe.2025.107236>.

Data availability

Data available within the article and its supplementary materials

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