



1 **Measurement report: Per- and polyfluoroalkyl substances (PFAS) in** 2 **particulate matter (PM₁₀) from activated sludge aeration**

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8 **Abstract.** Environmental pollution with per- and polyfluoroalkyl substances (PFAS), commonly referred to as “forever
9 chemicals”, received significant attention due to their environmental persistence and bioaccumulation tendencies. Effluents
10 from wastewater treatment plants (WWTPs) have been reported to contain significant levels of PFAS. Wastewater treatment
11 processes such as aeration have the potential to transfer PFAS into the atmosphere. However, understanding their fate during
12 sewage treatment remains challenging. This study aims to assess aerosolisation of PFAS during WWTP process. Special
13 emphasis is given to new generation and legacy PFAS (e.g., perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid
14 (PFOA)) as they are still observed in sewage after years of restrictions. Particulate matter with aerodynamic size $\leq 10 \mu\text{m}$
15 (PM₁₀) collected above a scaled-down activated sludge tank treating domestic sewage for a population $>10,000$ people in the
16 UK were analysed for a range of short-, medium- and long-chain PFAS. Eight PFAS including perfluorobutanoic acid (PFBA),
17 perfluorobutanesulfonic acid (PFBS), perfluoroheptanoic acid (PFHpA), perfluorohexanesulfonic acid (PFHxS), PFOA,
18 perfluorononanoic acid (PFNA), PFOS and perfluorodecanoic acid (PFDA) were detected in the PM₁₀. The presence of legacy
19 PFOA and PFOS in the PM₁₀ samples, despite being restricted for over a decade, raises concerns about their movement through
20 domestic and industrial sewage cycles. The total PFAS concentrations in PM₁₀ were 15.49 pg m^{-3} and 4.25 pg m^{-3} during
21 Autumn and Spring campaigns, respectively. PFBA was the most abundant PFAS, suggesting a shift towards short chain PFAS
22 use. Our results suggest that WWT processes such as activated sludge aeration could aerosolise PFAS into airborne PM.

23 **1. Introduction**

24 Particulate matter (PM) is a critical component of air pollution and has significant implications for environment (Boucher et
25 al., 2013; Chen et al., 2021; Taylor and Penner, 1994; Zhang et al., 2023) and human health (Pope III et al., 2020; Vohra et
26 al., 2021; Zhou et al., 2024). PM with aerodynamic diameter $\leq 10 \mu\text{m}$ (PM₁₀) is of particular concern because they are known
27 to penetrate into the human respiratory system and cause severe health effects (Abbey et al., 1995; Pope III et al., 1992). The
28 chemical composition of PM is very complex, and it can contain thousands of organic compounds (Goldstein and Galbally,



29 2007) including persistent organic pollutants (POPs) and new and emerging pollutants (NEPs) such as per- and polyfluoroalkyl
30 substances (PFAS) (Kourtchev et al., 2022; Zhou et al., 2021; Zhou et al., 2022).

31 PFAS, commonly referred to as “forever chemicals”, are a large group of synthetic organic compounds. PFAS are thermally
32 and chemically inert due to the strong carbon-fluorine bonds (Buck et al., 2011) and therefore they are widely used in the
33 production of numerous consumer goods such as water and thermal-resistant apparel, engine oil, cooking wares, etc (Glüge et
34 al., 2020). PFAS are known for their environmental persistence and bioaccumulation potential (Buck et al., 2011; Lesmeister
35 et al., 2021). Many PFAS are shown to have negative health effects e.g., endocrine disruption, cancer, and liver disease (Fenton
36 et al., 2021; Sunderland et al., 2019).

37 Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the most scrutinised PFAS due to their
38 environmental persistence and human health effects (Beach et al., 2006; Saikat et al., 2013; US EPA, 2024b; Zareitalabad et
39 al., 2013). In 2009, the Stockholm Convention on POPs included PFOS and its salts in Annex B of restricted compounds.
40 Further, in 2019 and 2022, PFOA and perfluorohexanesulfonic acid (PFHxS) were added to Annex A of compounds for
41 elimination. Despite being restricted for more than a decade, these compounds are still observed in various environmental
42 matrices (Li et al., 2022; Nguyen et al., 2017; Xiao et al., 2015; Zhou et al., 2022). Shortly after the introduction of restrictions
43 for several PFAS, they were replaced with short-chain and other new-generation PFAS that are thought to be less hazardous
44 (Brendel et al., 2018; Wang et al., 2013, 2015). These include perfluorobutanesulfonic acid (PFBS), fluorotelomer sulfonates
45 (FTS), and hexafluoropropylene dimer acid (HFPO-DA, more commonly known as GenX) (Wang et al., 2013, 2015). Recent
46 studies indicated that numerous replacement PFAS could potentially have similar health effects to those of the legacy ones
47 (Gomis et al., 2018; Liu et al., 2020; Solan and Lavado, 2022).

48 The majority of reports on PFAS pollution have predominantly focused on drinking water (Domingo and Nadal, 2019), surface
49 water (Podder et al., 2021), sewage (Lenka et al., 2021), and soil matrices (Brusseu et al., 2020). Therefore, most of the
50 current regulations on PFAS are focused on water matrices (Directive (EU) 2020/2184, 2020; US EPA, 2024a). There is
51 growing evidence that PFAS can transfer from contaminated waters via aerosolisation/volatilisation into atmosphere (Ahrens
52 et al., 2011; Johansson et al., 2019; Shoeib et al., 2016; Qiao et al., 2024).

53 Laboratory simulation experiments have shown that the aeration of PFAS-contaminated water leads to formation of aerosolised
54 PFAS (Nguyen et al., 2024; Pandamkulangara Kizhakkethil et al., 2024). The extent of PFAS aerosolisation has a clear
55 dependence on the PFAS carbon chain length and functional groups (Johansson et al., 2019; Pandamkulangara Kizhakkethil
56 et al., 2024; Reth et al., 2011).

57 Wastewater treatment techniques such as activated sludge (AS) and secondary extended aeration which involve vigorous
58 aeration/mechanical turbulence, could lead to the aerosolisation/volatilisation of PFAS from contaminated wastewater
59 effluents (Ahrens et al., 2011; Shoeib et al., 2016). PFAS were detected in gas phase and total suspended particles (TSP) near
60 the aeration tanks and secondary clarifier in a WWTP in Canada (Vierke et al., 2011). Airborne PFAS were also observed at
61 WWTPs that employ treatment techniques such as AS, secondary extended aeration, and facultative lagoons in Canada (Shoeib
62 et al., 2016). PFAS, including restricted PFOS, were identified in the TSP and gas phase above aeration tanks in a WWTP in



63 northern Germany (Weinberg et al., 2011). A more recent study by Qiao et al. (2024) identified PFAS in both gas and particle
64 phases above the influent and aeration tanks at a WWTP in China.

65 Limited studies have assessed the PFAS emission associated with inhalable PM fraction (e.g., PM₁₀) during WWT processes.
66 For example, a recent study identified PFAS in the 11 PM size fractions between 0.1 μm to 18 μm, collected from three
67 WWTPs in Hong Kong, China (Lin et al., 2022). These WWTPs (largest in Hong Kong) utilised treatment techniques such as
68 AS and chemically enhanced primary treatment (CEPT) to treat sewage from industrialised areas. The study reported that
69 atmospheric PFAS in WWTPs (e.g., PFOS, PFOA, PFBS and perfluorobutanoic acid (PFBA)) are primarily distributed in
70 aerosol particles with aerodynamic diameter ≤10 μm. Additionally, the distribution of PFAS depend on the type of WWT
71 process, nature of sewage, and aerosol properties (e.g., organic content, presence of microbes, etc.) (Lin et al., 2022). This
72 suggests that PFAS levels in inhalable PM, and thus the associated health risks, will vary based on the location and the type of
73 sewage being treated. European countries have restricted the production and use of several PFAS such as PFOS, PFOA,
74 PFHxS, and C9–C14 perfluorocarboxylic acids (PFCA) (Directive (EU) 2020/2184, 2020; ECHA, 2022a; ECHA, 2022b).
75 Nevertheless, the restricted PFOA and PFOS are still observed in wastewater effluents (Eriksson et al., 2017; Gobelius et al.,
76 2023; Moneta et al., 2023; Müller et al., 2023; Semerád et al., 2020) raising a question whether these chemicals could be
77 aerosolised during open air aeration WWT processes. To the best of our knowledge, there are no studies assessing the PFAS
78 levels in PM₁₀ at European WWTPs. Furthermore, PM₁₀ associated emission of PFAS from WWTPs have been assessed only
79 for a limited number of PFAS.

80 As highlighted in the reviews by Phong Vo et al. (2020) and O'Connor et al. (2022), domestic wastewater has been reported
81 to contain significant levels of PFAS, albeit at concentrations lower than those typically found in industrial effluents. Despite
82 this, studies on PFAS atmospheric emissions from sewage have primarily focused on WWTPs processing industrial effluents
83 or a mix of industrial and domestic sources. Consequently, a knowledge gap exists regarding the atmospheric fate of PFAS,
84 particularly their association with PM₁₀ aerosols, during the treatment of domestic wastewater, especially under conditions of
85 vigorous aeration.

86 The aim of the current study is to assess the aerosolisation potential of PFAS during WWTP process that involves vigorous
87 aeration steps. Special emphasis is given to (a) legacy PFAS, such as PFOS and PFOA, as they are still observed in sewage
88 after 15 and 5 years of restrictions, respectively, and (b) new generation and replacement PFAS such as FTS. To achieve this,
89 PM₁₀ samples collected from a scaled-down AS tank processing domestic wastewater (from a population of > 10,000 people)
90 in the United Kingdom (UK) were screened for 15 PFAS (C4–C11) including legacy and new-generation replacement
91 compounds such as FTS.



92 2. Method

93 2.1 Materials and chemicals

94 The materials and chemicals include: 10 mL headspace glass vials (Chromacol 10-HSV, Thermo Scientific); metal screw caps
95 (Chromacol 18-MS, Thermo Scientific); polytetrafluoroethylene (PTFE) septa (Chromacol 18-ST101 Thermo Scientific);
96 PTFE membrane filter (Iso-Disc PTFE-13-4, 13 mm × 0.45 μm); glass fiber filters (GFF) (47 mm, Advantec®, Model No.
97 GB-100R); EPA 533 PAR mix containing 25 PFAS i.e., PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUDA,
98 PFDoA, HFPO-DA, PFMPA, PFMBA, 3,6-OPFHpA, L-PFBS, L-PFPeS, PFHxS, L-PFHpS, PFOS, 4:2 FTS, 6:2 FTS, 8:2
99 FTS, NaDONA, 9Cl-PF3ONS, 11Cl-PF3OudS, PFEESA each having a concentration of 0.5 ng μL⁻¹ (Wellington laboratories
100 Inc, Canada); EPA533ES isotope dilution standard mixture containing 16 mass labelled (¹³C) PFAS i.e., M3PFBS, M5PFHxA,
101 M6PFDA, M3PFHxS, M8PFOS, MPFBA, M5PFPeA, M4PFHpA, M8PFOA, M9PFNA, M7PFUDA, MPFDoA, M2-4:2 FTS,
102 M2-6:2 FTS, M2-8:2 FTS and M3HFPO with the concentrations of 0.5–2.0 ng μL⁻¹; liquid chromatography (LC)-mass
103 spectrometry (MS) grade water (Optima™, Fisher Scientific); methanol, LC-MS grade (Optima™, Fisher Scientific); formic
104 acid, LC-MS grade (Optima™, Fisher Chemicals); ammonium acetate, LC-MS grade (Optima™, Fisher chemicals). The full
105 names of the listed chemicals are given in the Table S1 and S2 of supplement.

106 2.2 Sampling site

107 The PM₁₀ samples were collected above a scaled-down AS tank processing municipal wastewater equivalent to that of a
108 population > 10,000 people (the location of the facility is anonymised due to a non-disclosure agreement). The AS tank,
109 constructed from high-density polyethylene (HDPE), contains an aeration basin of volume 3.06 m³. The aeration basin of the
110 AS tank is connected to a secondary clarifier (of volume 0.86 m³) where sewage, after aeration, is allowed to settle. The AS
111 tank continuously receives and processes primary treated sewage (with a solid retention time (SRT) of 10 days) from the parent
112 large-scale WWTP using pumps.

113 2.3 PM₁₀ sample collection

114 The MiniVol™ tactical air sampler (Air Metrics, United States of America) used for PM₁₀ sampling was installed near the
115 aeration tank with the sampling head slightly above the rim of the tank. The PM₁₀ samples were collected on GFF at 10 L min⁻¹.
116 Prior to sampling, GFF were baked at 450 °C for 24 h to eliminate potential organic contaminants. The samples were
117 collected during two sampling periods: between (1) 2 October 2023–6 October 2023 and (2) 4 March 2024–8 March 2024.
118 PM₁₀ samples were collected separately during day and night. Sampling dates and duration are given in Table 1.
119 GFF with PM₁₀ were rolled using prewashed stainless-steel tweezers, keeping aerosol content inside, and placed into a
120 prewashed 10 mL headspace glass vial. 5 mL methanol (LC-MS grade) was added to the vial to disinfect the filters from
121 potential pathogenic microorganisms and extract the organic compounds including PFAS. The samples were then stored at 5



122 °C until the day of analysis. The vials, PTFE septa, and metal screw caps were prewashed with LC-MS grade methanol and
123 dried before use to remove potential PFAS contamination. PFAS leaching from the vials, PTFE septa, and metal screw caps
124 was assessed in another study which reported minimal PFAS leachables from these consumables (Kourtchev et al., 2022).
125 Various types of blanks were prepared to evaluate possible PFAS contamination from handling the filters. These include: 1)
126 baked filters and 2) baked filters placed in MiniVol® air sampler and collecting air above the AS tank at 10 L min⁻¹ for 2 min.
127 It is important to note that the use of GFF and quartz fiber filters (QFF) during PM sampling has been reported to cause positive
128 sampling artefacts, such as the adsorption of gas-phase organic compounds (Turpin et al., 1994). Previous studies have shown
129 that certain PFAS, such as PFOS and PFOA, can transition from aqueous aerosols to the gas phase (Ahrens et al., 2012;
130 McMurdo et al., 2008). As a result, the GFF used in our study may also include a small fraction of gas-phase PFAS.
131 Consequently, the reported PM₁₀ concentrations of PFAS in our study might be slightly overestimated.

132

133 **Table 1** PM₁₀ sample collection dates and duration

Sampling date	Sample type	Sampling duration (h)
2 October 2023	Day sample	3.3
	Night sample	9.2
3 October 2023	Day sample	5.7
	Night sample	17.9
4 October 2023	Day sample	5.7
	Night sample	18
5 October 2023	Day sample	5.7
	Night sample	18
4 March 2024	Day sample	1.4
	Night sample	19.1
5 March 2024	Day sample	4.5
	Night sample	18.8
6 March 2024	Day sample	4.8
	Night sample	18.5
7 March 2024	Day sample	4
	Night sample	19



134 **2.4 Extraction and analysis of PM₁₀ GFF samples**

135 The GFF samples stored in methanol were spiked with internal standards (IS), a mixture of 16 ¹³C PFAS labelled compounds
136 (EPA533 ES, Wellington laboratories Inc, Canada) at concentrations 20 ng L⁻¹ for M2-4:2 FTS, M2-6:2 FTS, and M2-8:2FTS
137 and 5 ng L⁻¹ for the remaining compounds and extracted using the procedure published in Kourtchev et al. (2022).

138 Briefly, the vial content was subjected to ultrasonic agitation for 40 min. The methanol extracts were then filtered through a
139 prewashed 0.45 µm PTFE syringe filter. The PTFE filters used in our study were assessed for PFAS leaching potential in
140 Kourtchev et al. (2022). Minimal leaching of PFAS was observed from the PTFE filters after purging them with 5 mL LC-MS
141 grade methanol three times (total volume of 15 mL) (Kourtchev et al., 2022). The extracts were then reduced by volume to 1
142 mL under gentle nitrogen flow.

143 The methanolic extract was then topped up with 4 mL of LC-MS grade water providing the 80:20 (v/v) water: methanol ratio
144 required for the online solid phase extraction (SPE) (Kourtchev et al., 2022). The vial content was homogenised by vortex
145 mixing and analysed using online SPE LC-high resolution mass spectrometry (HRMS) using the method published elsewhere
146 (Kourtchev et al., 2022).

147 The online SPE and chromatographic separation was carried out using EQuan MAX Plus Thermo Scientific™ Vanquish™
148 UHPLC system using a Thermo Scientific™ TriPlus™ RSH autosampler. Online SPE was performed using a Thermo
149 Scientific™ Hypersil GOLD aQ Column, 20 × 2.1 mm, 12 µm column. 0.1 % formic acid in water was used as the loading
150 phase for the online SPE. Following online SPE, the chromatographic separation was achieved using Waters® CORTECS
151 C18 Column, 90 Å, 100 × 2.1 mm, 2.7 µm analytical column. The eluents used for chromatographic separation were A) 2 mM
152 ammonium acetate in 10 % methanol and B) 100 % methanol. A Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ Mass
153 Spectrometer (Thermo Fisher, Bremen, Germany) fitted with electrospray ionisation (ESI) (Ion Max™) source was employed
154 for the mass spectrometric analysis. The mass spectrometric analysis was performed in single ion monitoring (SIM) negative
155 ionisation mode. The mass spectrometer was calibrated prior to analysis to have a mass accuracy of ≤ 5 ppm. The limit of
156 detection (LOD) values for the analytes in this study were similar to those reported by Kourtchev et al. (2022), with the
157 exception for PFBA. The LOD for PFBA was 1.47 ng L⁻¹, which is higher than the value reported by Kourtchev et al. (2022)
158 and could potentially be due to higher background levels of the analyte in the system blanks.

159 **2.5 Quality assurance (QA) and quality control (QC)**

160 Several steps were taken to ensure the QA and QC during the sampling and analysis. PFAS-containing consumables were
161 avoided as much as possible during the sampling, extraction, and LC-HRMS analysis. To prevent accumulation of PFAS in
162 the LC-HRMS system, prior to the analysis, the system was flushed with the mobile at composition of 60:40 A: B (A: 2 mM
163 ammonium acetate in 10 % methanol and B: 100 % methanol) and 0.3 mL min⁻¹ flow rate, overnight (Kourtchev et al., 2022).
164 System suitability tests (SST) were performed before the analysis of each batch to ensure the adequate performance of the LC-
165 HRMS system. Pass criteria were evaluated based on chromatographic peak area and height, retention times, mass accuracy,

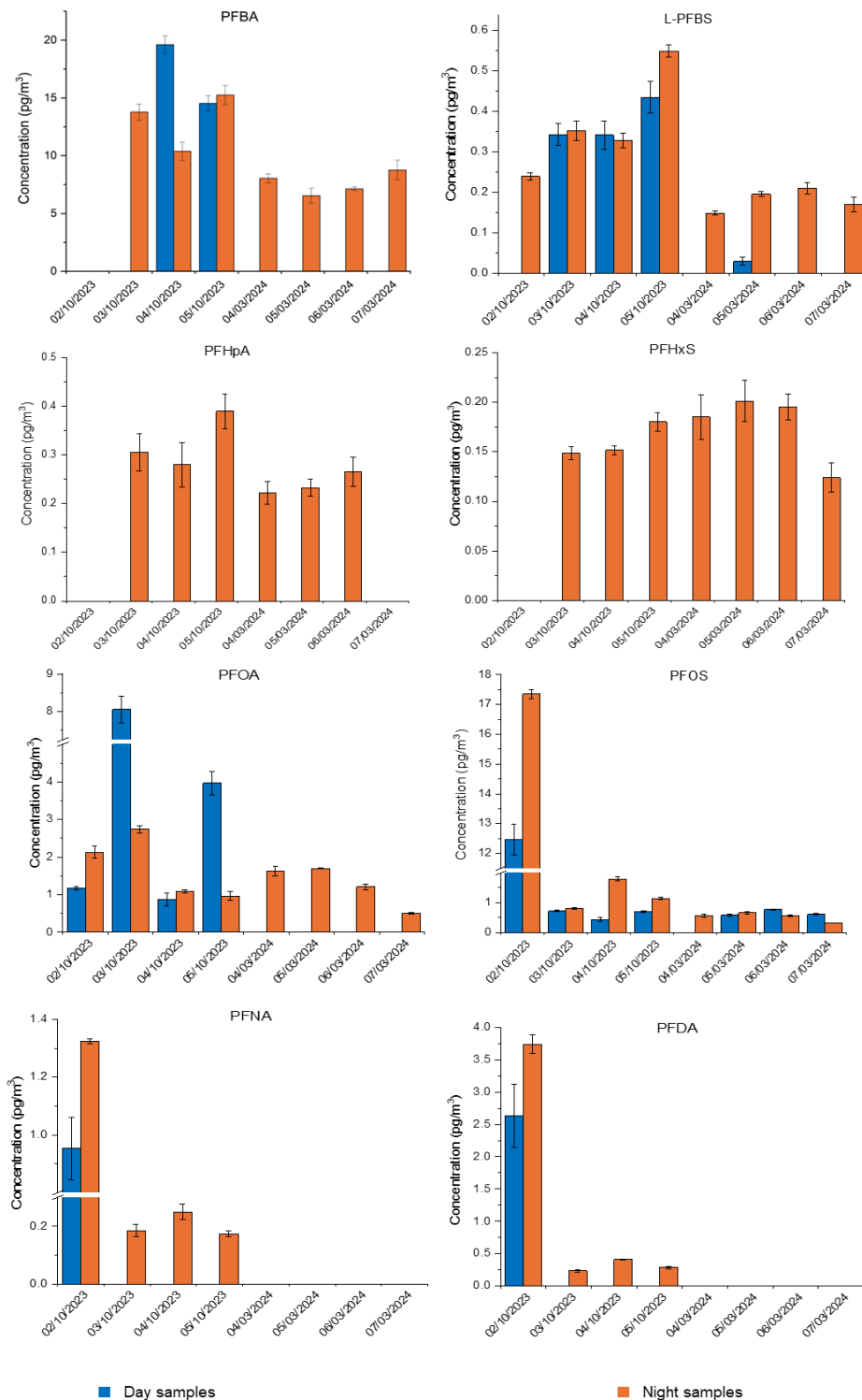


166 and peak tailing factors. System blanks (“zero volume”) and 80:20 water: methanol (v/v) blanks were injected at the start of
167 the batch, in between the samples, and at the end of the batch to monitor a potential PFAS carry over. The zero volume blanks
168 and 80:20 water: methanol blanks reported PFAS concentrations less than the method LOD values.

169 **3. Results and discussion**

170 **3.1 PFAS composition of PM₁₀ above the AS tank**

171 Figure 1 shows the concentrations of PFAS detected in PM₁₀ samples collected above the AS tank during the two sampling
172 periods. Out of the 15 target PFAS, eight compounds were detected across the collected samples.





174 **Figure 1** Concentrations of PFBA, PFBS, PFHpA, PFHxS, PFOA, PFOS, PFNA, and PFDA in the PM₁₀ samples collected
175 from the AS tank in October 2023 and March 2024. The absence of data points on certain sampling days indicates that the
176 compound was either not detected or below the method LOD. The error bars represent the standard deviation of the value from
177 three replicate injections. The data of Figure 1 are shown in Tables S3 and S4.

178

179 The detected PFAS include short-chain PFBA and PFBS, medium-chain PFHpA, PFHxS, PFOA, PFNA, and PFOS, and long-
180 chain PFDA. The most abundant PFAS detected in the PM₁₀ from both sampling campaigns was a short-chain PFBA with a
181 maximum concentration of 19.6±0.8 pg m⁻³ in October 2023 and 8.8±0.9 pg m⁻³ in March 2024. The concentration of PFAS
182 detected in the samples from October 2023 followed the order PFBA>PFOS>PFOA>PFDA, with maximum concentrations
183 recorded at 17.4±0.2 pg m⁻³ for PFOS, 8.1±0.4 pg m⁻³ for PFOA, and 3.7±0.1 pg m⁻³ for PFDA. The samples collected during
184 March 2024 showed a different pattern, with PFOA (1.70±0.01 pg m⁻³) having the highest concentration after PFBA, followed
185 by PFOS at 0.76±0.02 pg m⁻³. It has been reported that aerosolisation of PFAS from contaminated water depends on carbon
186 chain length and functional groups, with higher aerosol enrichment for long chain PFAS and perfluorosulfonic acids (PFSA)
187 compared to PFCA (Johansson et al., 2019; Pandamkulangara Kizhakkethil et al., 2024; Reth et al., 2011). However, it is
188 interesting to note that the PFAS levels in the PM₁₀ in our study followed a reverse order with short chain PFBA detected at
189 higher values.

190 The detected PFAS have been associated with different sources. For example, PFOS, PFNA, and PFOA have historically been
191 produced and used in the manufacturing of numerous products, such as firefighting foam, fluoropolymers, textiles, leather,
192 paper, and lubricants (ATSDR, 2015; Buck et al., 2011; de Alba-Gonzalez et al., 2024; Wang et al., 2014). PFHxS and its
193 salts/related compounds have been used in applications such as firefighting foam, coatings, electronics and semiconductors,
194 and polishing agents (in many of these applications PFHxS has been introduced as a replacement for PFOS)
195 (UNEP/POPS/POPRC.15/7/Add.1, 2019). PFBA and PFBS, have been used as replacements for legacy and longer chain PFAS
196 (Ateia et al., 2019; Christian, 2024; Wang et al., 2013). PFBA is used in the manufacturing of food packaging materials,
197 carpets, and fluorosurfactants (Christian 2024; US EPA, 2022). PFBS and PFBS based compounds are used in applications
198 such as metal plating, as flame retardant, and surfactant (Wang et al., 2013). PFDA, a long chain PFAS identified in the PM
199 in this study, have been reported as a breakdown product of stain- and grease-proof coatings on food packaging, furniture, and
200 carpets (Christian, 2024).

201 Clear differences were observed in the concentrations of PFAS in PM₁₀ samples from the two sampling campaigns. In general,
202 concentrations of all detected PFAS except PFHxS were higher in the samples collected in October 2023 compared to the
203 March 2024 samples. For example, highest concentration of PFBA reported during the March 2024 period was less than half
204 of that reported in the October 2023 period. PFNA and PFDA were absent in the samples from March 2024, but they were
205 detected in the October 2023 samples. The concentrations of PFHxS and PFHpA reported during both sampling periods were
206 higher than the method LOD but slightly lower than the method limit of quantification (LOQ) values. There are several
207 potential reasons for the observed seasonal differences in the concentrations of PFAS which include the pH value, density, and



208 composition of the wastewater. The pH value of the contaminated water has been found to affect the water to atmospheric
209 transfer behaviour of PFAS (Ahrens et al., 2012; Barton et al., 2007; Pandamkulanagra Kizhakkethil et al., 2024; Vierke et al.,
210 2013). For example, the average pH of the wastewater in October 2023 was 7.5, whereas the average pH was 9.3 during the
211 March 2024 sampling campaign. Additionally, the sewage density and potentially the composition were different during the
212 two sampling periods (the pH and density data are not shown in the manuscript due to the non-disclosure agreement). PFAS
213 are well known for their sorption to biosolids in sewage (Ebrahimi et al., 2021; Link et al., 2024). During the March 2024
214 sampling period, the sewage was thicker compared to October 2023, potentially leading to higher sorption of PFAS in the
215 biosolids and consequently lesser PM₁₀ associated emissions. It should be noted that the sewage composition was not static
216 during the sampling periods. The SRT of the AS tank was 10 days, and the chamber received and processed primary treated
217 wastewater from the parent WWTP continuously. Therefore, the variation in the sewage composition could potentially explain
218 the differences in the airborne PFAS concentration. Moreover, the surface runoff, linked to rainfall, could also be a factor
219 influencing the overall PFAS levels, as it may introduce additional contaminants to the wastewater system.

220 Since the sampling campaigns were conducted at two different seasons, the atmospheric conditions e.g., temperature, relative
221 humidity (See Fig. S1–S4 of a supplement for the average temperature and relative humidity at the sampling periods) could
222 also influence the PFAS partitioning to aerosols from the contaminated water (Ahrens et al., 2012). It should be noted that the
223 absence of PFNA and PFDA in the March 2024 samples could be attributed to lower concentration of these analytes in the
224 sewage resulting in PFAS PM₁₀ bound concentrations below the method LOD.

225 Several PFAS exhibited day and night variations in PM₁₀ samples. For example, the PFBA concentration was higher during
226 the day compared to the night in specific sampling days of October 2023. On the other hand, PFBA concentration during the
227 day was close to the background levels during the March 2024 campaign. PFHpA and PFHxS were not detected in the day
228 samples during both sampling campaigns. Legacy PFOS and PFOA showed higher concentrations during the day on specific
229 sampling days. The difference in the diurnal concentrations could potentially be due to variability in the composition of the
230 wastewater at the respective sampling time. The diurnal variations in the environmental conditions such as temperature and
231 relative humidity could also contribute to the observed higher PFAS concentrations observed in the specific day samples
232 compared to the night samples.

233 3.2 Comparison to previous studies

234 The observation of high levels of PFBA in our study is consistent with the results of Weinberg et al. (2011), who identified
235 PFBA (up to 8.4 pg m⁻³) as the most abundant PFAS in the PM samples (TSP) collected above the aeration tanks of two
236 WWTPs processing a mixture of domestic and industrial wastewater in Northern Germany. PFBA was also identified as the
237 dominant ionic PFAS in the atmosphere of WWTPs in other studies (Shoeib et al., 2016; Lin et al., 2022). For example, air
238 samples collected using sorbent-impregnated polyurethane foam (SIP) passive air samplers at WWTPs employing AS
239 (processing mixed wastewater), secondary extended aeration (one processing domestic and the other two processing mixed



240 wastewater), and facultative seasonal discharge lagoons (processing domestic wastewater) in Canada detected PFBA up to
241 60 ± 21 % of the total PFCA detected (Shoeib et al. 2016). Similarly, Lin et al. (2022) reported PFBA at considerable levels in
242 the atmosphere near the aeration tanks of two WWTPs and above a WWTP using CEPT (processing wastewater from urban
243 areas) in Hong Kong, China. The concentrations of PFBA in TSP reported by Lin et al. (2022), with maximum values of 9.17
244 pg m^{-3} and 15.6 pg m^{-3} near the aeration tanks, which are comparable to the values reported in our study.

245 The high PM_{10} -associated concentration of PFBA in our study could potentially be explained by the recent increase in the use
246 of short-chain PFAS as a replacement for legacy PFOS and PFOA (Ateia et al., 2019; Wang et al., 2013). PFBA is one of the
247 most volatile PFAS observed in our study. Further, short chain PFAS such as PFBA and PFBS are reported to have lower
248 aerosolisation tendencies compared to long chain compounds (e.g., PFOS and PFOA) (Johansson et al., 2019;
249 Pandamkulangara Kizhakkethil et al., 2024). Despite being volatile and having low aerosolisation tendency, the presence of
250 PFBA in the PM_{10} aerosols at considerable concentrations in our study could potentially be due to the presence of high levels
251 of PFBA in the sewage during the sampling period.

252 The concentrations of PFAS in PM_{10} reported in our study, except for PFHxS, were higher than those estimated by Weinberg
253 et al. (2011) in the particulate phase (TSP) above the aeration tanks of a WWTP that processed a mix of domestic and industrial
254 waste in Northern Germany. For example, during the October 2023 sampling period, legacy PFAS such as PFOS and PFOA
255 were detected in our study at levels up to $17.4 \pm 0.2 \text{ pg m}^{-3}$ and $8.1 \pm 0.4 \text{ pg m}^{-3}$, respectively. In contrast, the maximum
256 concentrations of PFOS and PFOA during March 2024 were $0.76 \pm 0.02 \text{ pg m}^{-3}$ and $1.70 \pm 0.01 \text{ pg m}^{-3}$, respectively. Weinberg
257 et al. (2011) estimated PFOS and PFOA concentrations in the TSP to be up to 0.9 pg m^{-3} and 1.3 pg m^{-3} , respectively. The
258 difference in the PFAS emission levels could be potentially due to the difference in PFAS composition in the wastewater.
259 PFAS composition in wastewater across European Union (EU) have been reported to differ depending on the region (Lenka
260 et al., 2021)

261 The PFDA concentrations of (up to 1.31 pg m^{-3}) in the TSP samples reported by Lin et al. (2022) above the aeration tanks of
262 WWTPs in Hong Kong, China were lower than the PFDA levels observed in our study during the October 2023 period ($3.7 \pm$
263 0.1 pg m^{-3}). However, for other PFAS compounds such as PFBS, PFHxS, PFHpA, PFOA, PFOS, and PFNA, Lin et al. (2022)
264 reported considerably higher values in the TSP samples than those observed in our study. Lin et al. (2022) investigated the
265 distribution of PFAS across 11 PM size fractions (ranging from $0.1 \mu\text{m}$ to $>18 \mu\text{m}$) collected from three WWTPs (two using
266 aeration and one using CEPT), as well as a landfill and two reference sites. PFOS in PM from all studied WWTPs (treating
267 urban wastewater) showed major distribution around the PM fractions with aerodynamic size between 0.1 and $10 \mu\text{m}$.
268 Similarly, PFBA and PFBS were also found to be primarily associated with particles of aerodynamic size less than $10 \mu\text{m}$,
269 indicating that the PM_{10} collected in our study could have potentially captured a majority of the PFAS bound particles. The
270 reported values in our study therefore provide insights into the total aerosol bound emissions of studied PFAS during the WWT
271 process.

272 The PFAS reported in our study were significantly lower than the PM (TSP) values reported by Vierke et al. (2011) (processing
273 wastewater from Ontario, an urban area in Canada). For example, the average PM concentrations of PFOS and PFOA above



274 the aeration tank of a WWTP in Canada study were 3900 pg m^{-3} and 71 pg m^{-3} , respectively (Vierke et al., 2011). Similarly,
275 Qiao et al. (2024) also reported considerably higher values for legacy PFOS ($1.7\text{--}65.1 \text{ pg m}^{-3}$) and PFOA ($3.1\text{--}101 \text{ pg m}^{-3}$) in
276 the TSP samples above the influent and aeration tanks of two WWTPs (one processing domestic wastewater and the other one
277 processing industrial wastewater) in China.

278 It is interesting to note that the PFAS levels in PM_{10} reported in our study are comparable to those reported by Weinberg et al.
279 (2011) in the TSP samples, which is the only study that investigated atmospheric PFAS levels in European WWTPs. The
280 similarity in the TSP and PM_{10} concentrations could be due to PFAS being associated mainly with aerosols having aerodynamic
281 size less than $10 \mu\text{m}$ as shown for several type of sewage in Lin et al. (2022). In contrast, higher PFAS levels in TSP samples
282 were reported in all other studies conducted at WWTPs in Canada and China (Lin et al., 2022; Vierke et al., 2011; Qiao et al.,
283 2024). The differences of PFAS levels in PM could potentially be due to variations in wastewater composition in these regions.
284 For example, the WWTP studied by Vierke et al. (2011) is situated in Ontario, a heavily industrialised city in Canada. Similarly,
285 the WWTPs investigated by Lin et al. (2022) and Qiao et al. (2024) are located in China, one of the most heavily industrialised
286 countries in the world. The facility in our study processes sewage mainly from households (for approximately 30,000 people)
287 rather than industries, which may contain lower PFAS levels in the sewage and thus in aerosol. The total PFAS concentrations
288 associated with PM_{10} fractions in our study were 15.49 pg m^{-3} in October 2023 and 4.25 pg m^{-3} in March 2024 (see Table S3
289 and S4 of supplement), which is comparable ($2\text{--}13 \text{ pg m}^{-3}$) to that in the TSP from mixed wastewater in Northern Germany
290 reported by Weinberg et al. (2011).

291 **4. Conclusion**

292 In this study, we investigated, for the first time, the PFAS concentrations associated with the health-relevant PM_{10} fraction of
293 airborne aerosols emitted during the AS aeration process at a WWTP processing domestic wastewater. PM_{10} samples were
294 collected over two sampling campaigns at two different seasons (i.e., October 2023 and March 2024) above a scaled-down AS
295 tank consisting of an aeration basin of volume $\sim 3 \text{ m}^3$, treating wastewater equivalent to $> 10,000$ people. Eight PFAS were
296 observed across the collected PM_{10} samples. These include legacy PFOS and PFOA, which were detected up to concentrations
297 of $17.4 \pm 0.2 \text{ pg m}^{-3}$ and $8.1 \pm 0.4 \text{ pg m}^{-3}$, respectively in the samples from October 2023.

298 The presence of legacy PFOS and PFOA in the PM even after a decade-long restriction raises concern and suggests that PFOS
299 and PFOA-containing products are still in use or in the recirculation cycle. More studies are needed to understand if these
300 legacy compounds could have been formed in the wastewater during the treatment process from the degradation of precursor
301 compounds such as fluorotelomer alcohols (FTOH) perfluorooctane sulfonamides (FOSA), perfluorooctane
302 sulfonamidoethanols (FOSE) as suggested by Dauchy et al. (2017) and Xiao (2022).

303 Presence of PFBA at high concentrations in the collected samples potentially suggests the increased shift towards the use of
304 short-chain PFAS as a replacement for legacy PFAS.



305 Our results indicate that WWT processes involving aeration could aerosolise and transfer PFAS into the atmosphere.
306 Considering the sheer number of different PFAS that are in the production and used today, the estimated total PFAS
307 concentrations could potentially represent only a fraction of the actual emissions during the aeration process.
308 To the best knowledge, this is the first study to investigate the presence of PFAS in the PM₁₀ fraction of the airborne aerosols
309 from the AS aeration process in a WWTP in the UK and Europe.

310 **Data availability**

311 The data are not publicly accessible due to a non-disclosure agreement with a wastewater treatment company, which is also
312 anonymised. The data of Figure 1 are shown in Tables S3 and S4.

313 **Competing interests**

314 Some authors are members of the editorial board of journal ACP. The authors have no other competing interests to declare.

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319 **Author contributions**

320 JPK conceived the study and performed field measurements, sampling, sample analysis, data processing and interpretation.
321 AB supervised the project. ZS supervised the project and provided resources. IK conceived and led the study, supervised the
322 project, obtained funding, provided the resources, performed field measurements, sampling, data interpretation. JPK and IK
323 prepared the original draft of the paper. All authors contributed to reviewing and editing the manuscript.

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