Responses to the **Reviewer 2** comments

Comment: In this article, the authors measure the concentrations of 15 legacy and emerging PFAS in PM10 collected from a scaled down activated sludge aeration tank. This study was conducted at two different time points, Oct 2023 and March 2024 using domestic sludge from a wastewater treatment plant in the UK. This manuscript is well written and fills a knowledge gap regarding PFAS aerosolization from domestic sludge wastewater treatment processes. I recommend this paper for publication following revision.

Response: We would like to sincerely thank Reviewer 2 for recognising importance of our work in bridging the knowledge gap on the aerosolisation of PFAS from domestic wastewater treatment processes. We also appreciate his/her recommendation of our work for publication following the revision, as well as his/her insightful comments that have helped strengthen our work. Our detailed responses to the reviewer's comments are provided below in blue. The new text added to the revised manuscript is shown below in italics.

General Comments:

I strongly recommend including both the LOD and LOQ values in the SI. I also recommend reporting the lab, field, and system blanks as well.

Response: We thank the reviewer for this comment. The LOD, LOQ, and values for different types of blanks (i.e., filter blanks, field blanks, and system blanks) have been now reported in SI in tables S5-S7.

In line 90, the authors mention screening from 15 PFAS but then in line 97 state that the EPA 533 PAR mix, which contains 25 PFAS, was used. Please list which PFAS were targeted and provide justification for why some were targeted, and others were not.

Response: The analysis of the PM_{10} samples was done using the analytical method published elsewhere (Kourtchev et al., 2022). This analytical method is fully validated for analysis of 15 out of the 25 compounds present in the EPA 533 PAR mixture. To ensure the accuracy, reliability, and reproducibility of analytical results we only focused on those fully validated analytes. This has now been addressed in Section 2.4 of the main text: "*The analytical method is validated for screening and quantifying 15 PFAS including PFBA, PFPeA, PFBS, 4:2 FTS, PFHxA, PFPeS, PFHxS, PFHpA, PFOA, PFHpS, PFNA, PFOS, 8:2 FTS, PFDA, and PFUdA. Therefore, to ensure the accuracy, reliability, and reproducibility of analytical results, the current study focused only on those fully validated analytes.*" (lines 148-151, page 6 of the revised main text).

Please provide further clarity regarding the scaled-down AS tank as well as the sample collection. How much smaller was the scaled-down tank compared to the large-scale WWTP? How far from the tank and how high above the rim of the tank was the MiniVol placed?

Response: Thank you for this comment. Due to our strict non-disclosure agreement (NDA) with the wastewater treatment company, we cannot provide additional details on the scale-down AS tank. However, we strongly believe that even without this information, our results still provide critical information on PFAS emissions, particularly for legacy PFAS that remain in wastewater streams despite their ban, highlighting their persistence in sewage processing and the challenges of their removal. Moreover, our results highlight their distribution beyond expected environments, including partitioning between water and aerosol phases in sewage processing.

The position of the air sampler relative to the AS tank has been now included in Section 2.3 of the main text: "*The MiniVol™ tactical air sampler (Air Metrics, United States of America) used for* PM_{10} *sampling was installed near the aeration tank (<0.2 m from the aeration tank) with the sampling head slightly above the rim of the tank (10 cm above)*." (lines 114-115, page 4 of the revised main text).

Why is there such a difference in the sampling time for day and night samples? Would the short day sampling periods (1.4 h to 5.7 h) account for the low detection frequency for day samples, especially as compared to the night?

Response: We thank the reviewer for this important comment. The day period sampling started after 10.00 AM and finished before 3.00 PM while the night period sampling started after 3.00 PM and finished before 10.00 AM the next morning. This is because the working time of the staff in the facility is between 9.30 AM and 3.30 PM. Moreover, the MiniVol™ tactical air sampler does not allow automatic filter change requiring us to manually replace filters within the facility's access hours. Due to these restrictions, the day samples are lower in sampling duration than the night time samples. As the reviewer pointed out, the low detection frequency of PFAS in the day samples could be indeed attributed to lower aerosol mass load on the filters caused by the shorter sampling duration. This has been now included in Section 3.1 of the main text: "*The shorter sampling duration of day samples compared to the night samples likely led to a lower aerosol mass load on the filters, resulting in several PFAS mass loads below the LODs, which could explain the observed diurnal differences in PFAS concentrations*." (lines 248-250, page 10 and 11 of the revised main text).

Line 135: Were the filters spiked with IS and then the 5mL of methanol added? Or were the filters sitting in methanol and then, when ready for extraction, the solution of methanol with a filter was spiked with IS?

Response: After sampling, the filters were stored in 10 mL headspace vials and 5 mL of methanol was added immediately to decontaminate the filters from potentially pathogenic microorganisms present in sewage. The samples were then stored at 5 °C until the day of extraction. At the time of extraction, the internal standard was spiked into the vial containing the filter soaked in 5 mL of methanol. This was discussed in lines 119-122 of Section 2.3 in the main text of the original submission.

Section 2.5 – What were the recoveries/extraction efficiencies for the targeted PFAS? Please report these in the SI.

Response: Thank you for this comment. The extraction efficiencies of the targeted PFAS have now been included in SI as Table S8.

Line 225: This section seems incomplete and highly speculative. PFBA was detected during the day, twice, in the October sampling period and only once was it higher than the night concentration. I don't know that it can be claimed that the differences are attributable to diurnal variations when the sampling periods for day and night are so different. For PFHpA and PFHxS, the measured concentrations during the night sampling are so low (how close to the LOD/LOQ?) that it might simply be that the sampling time during the day was not long enough to collect sufficient mass to be quantified.

Response: We thank the reviewer for this comment. We agree that PFHpA and PFHxS were not detected in the day samples potentially due to the low mass load in the day time samples associated with the shorter sampling duration. PFHpA and PFHxS were detected above LOD but below LOQ values in the nighttime samples. However, in the case of PFBA, the concentrations detected in the samples were higher than the LOD/LOQ values. This suggests that the differences in the PFBA concentrations during the day and night reported in our study could potentially be attributed to the diurnal variations in the environmental conditions. To clarify this, we have now added the following text: "*The shorter sampling duration of day samples compared to the night samples likely led to a lower aerosol mass load on the filters, resulting in several PFAS mass loads below the LODs, which could explain the observed diurnal differences in PFAS concentrations*." (line 248-250, page 10 and 11 of the revised main text).

I recommend adding a limitations section or at least paragraph on the limitations of the study. It may be beneficial to include the following: wastewater was not analyzed for PFAS, targeted PFAS was limited to 15 out of thousands, and collection of both gas- and particle-phase PFAS. Studies (see Ao et al., 2024 - 10.1016/j.jhazmat.2023.133018) have also detected polyfluoroalkyl phosphate esters (PAPs) at high concentrations in household dust as well as in food-contact materials, cosmetics, and other consumer products. They've also be shown to biodegrade into PFOA (8:2 diPAP) and to other PFCAs (see Lee et al., 2010 - https://doi.org/10.1021/es9028183 and Liu and Liu 2016 - 10.1016/j.envpol.2016.01.069).

Response: A limitation section has been now included in the main text: "*Future research should consider simultaneous characterisation of wastewater PFAS levels alongside PM measurements to improve understanding of the relationship between airborne PFAS emissions. Expanding the range of monitored PFAS beyond the 15 fully validated targets in our study, particularly including neutral PFAS such as FTOHs and FOSEs, would enhance understanding their role in the WWTP aerosolisation. Additionally, incorporating gas-phase sampling would be valuable in assessing the potential partitioning of PFAS into the gaseous phase, further refining our understanding of their atmospheric behaviour.*" (lines 326-331 page 13 of the revised main text).

Additionally, while the authors note that anonymity of the WWTP limits the environmental data they can share, can the authors provide any comment on possible nearby sources of ambient PFAS (e.g., other fluorochemical manufacturing plants or point sources). Wind direction and wind speed data could have also been informative.

Response: We thank the reviewer for recognising the challenges caused by the NDA in revealing the environmental data. As detailed in the manuscript, the major source of sewage to the WWTP is from households. Unfortunately, we are unable to share the wind direction/wind speed data as this would require revealing the WWTP location, which is restricted by the NDA. As mentioned above, even without this information our results provide critical insights into PFAS, particularly for legacy PFOA and PFOS, emissions from the process despite their ban, highlighting their persistence, the challenges of their removal, and their distribution beyond water into other environmental media.

The authors may also find it useful to expand their discussion to include the implications of detecting PFAS in PM10 from aerosolized domestic waste. What does this mean for long-range transport and human exposure? As more stringent regulations are placed on emissions of PFAS from major fluorochemical plants, domestic-related emissions are likely to become more important.

Response: We appreciate the reviewer's suggestion. Due to NDA restrictions, we are limited in how much we can elaborate on this aspect. The potential contribution of WWTPs to PFAS pollution remains an open question that warrants further investigation. While we cannot draw definitive conclusions at this stage, we have acknowledged this limitation in the manuscript. It must be noted that for the limitations outlined above, the article was submitted as a Measurement Report rather than a full research article. The following text has been added to the manuscript: "*Future research should consider simultaneous characterisation of wastewater PFAS levels alongside PM measurements to improve understanding of the relationship between airborne PFAS emissions. Expanding the range of monitored PFAS beyond the 15 fully validated targets in our study, particularly including neutral PFAS such as FTOHs and FOSEs, would enhance understanding their role in the WWTP aerosolisation. Additionally, incorporating gas-phase sampling would be valuable in assessing the potential partitioning of PFAS into the gaseous phase, further refining our understanding of their atmospheric behaviour*." (lines 326-331 page 13 of the revised main text).

Specific Comments:

Line 35: Specify types of cancer associated with exposure to PFAS.

Response: The examples of the type of cancer associated with PFAS exposure have been included in Section 1 of the main text: "Several PFAS are shown to have negative health effects e.g., endocrine disruption, cancer including *kidney and testicular cancer,* and liver disease (Fenton et al., 2021; Sunderland et al., 2019)" (line 35-36, page 2 of the revised main text).

Lines 185 – 187: Does the composition of the contaminated water (particularly the organic content of wastewater) also influence the degree of aerosolization?

Response: We thank the reviewer for this comment. A recent study on PFAS sea spray aerosol (SSA) simulation experiments by Sha et al., (2024) reported enhanced PFAS enrichment in the generated SSA when organic matter was introduced to artificial sea water. However, it should be noted that the aerosol generation mechanism from WWTPs could be different from that of SSA. This information have been now updated in Section 3.1 of the main text: "It has been reported that aerosolisation of PFAS from contaminated water depends on carbon chain length, functional groups *and organic content,* with higher aerosol enrichment for long chain PFAS and perfluorosulfonic acids (PFSA) compared to PFCA (Johansson et al., 2019; Pandamkulangara Kizhakkethil et al., 2024; Reth et al., 2011; *Sha et al., 2024*)." (lines 197-200, page 9 of the revised main text).

Line 201: I think it's interesting that PFOA was detected in all day samples during the October period but not in the March samples. The authors comment on differences in sewage composition affecting the measured concentrations in PM10, but what about domestic activities that occur in the Fall vs the Spring that may contribute to this? Are the authors able to provide insight into this seasonal difference beyond the sewage differences? I recognize this is probably quite difficult as there are many different sources of PFAS, but this line of thinking could yield interesting theories and questions. However, it may be that the authors simply state (if they agree) that this suggests that there are seasonal variations in household activities that may affect sewage concentrations.

Response: We agree with the reviewer that differences in household activities during different seasons could potentially influence the sewage concentrations of the PFAS and thereby the PFAS levels in the PM. This has now been included in Section 3.1 of the main text: "*Seasonal variations in PFAS* PM_{10} *levels could also be due to changes in household activities throughout the year and thus concentrations in domestic wastewater entering the WWTP*." (lines 234-235, page 10 of the revised main text).

Line 249: Is it possible that PFBA and PFBS, which are volatile, are present in the gas-phase and sorbed to the GFF? Or is this unlikely. Can the authors provide insight into this?

Response: PFBA has a vapor pressure of 2.92 mm Hg at 25°C (Zhang and Suuberg, 2023), whereas PFBS has a vapor pressure of 0.0268 mm Hg at 25°C (Pubchem, 2025) suggesting that they are semi-volatile.

Nevertheless, as the reviewer pointed out, a fraction of PFBA or PFBS volatilised during the WWTP process could be adsorbed onto the glass fiber filters (GFF). This was acknowledged in the initial submission i.e. "It is important to note that the use of GFF and quartz fiber filters (QFF) during PM sampling has been reported to cause positive sampling artefacts, such as the adsorption of gas-phase organic compounds (Turpin et al., 1994). Previous studies have shown that certain PFAS, such as PFOS and PFOA, can transition from aqueous aerosols to the gas phase (Ahrens et al., 2012; McMurdo et al., 2008). As a result, the GFF used in our study may also include a small fraction of gas-phase PFAS. Consequently, the reported PM_{10} concentrations of PFAS in our study might be slightly overestimated." (lines 127-131, section 2.3).

Line 252 and Line 257: Are the values estimated or measured by Weinberg et al. (2011)?

Response: The values reported by Weinberg et al. (2011) are measured values, not the estimated ones. This word 'estimated' is now replaced with '*measured*' in Section 3.2 of the main text.

Line 285: Specify the two cities where Lin et al., (2022) and Qiao et al. (2024) sampled. It seems a bit like apples and oranges to specify Ontario, Canada and then all of China.

Response: This has been now addressed in Section 3.2 of the main text: "Similarly, the WWTPs investigated by Lin et al. (2022) and Qiao et al. (2024) are located in China (*Hong Kong and Tianjin, respectively*), one of the most heavily industrialised countries in the world." (lines 298-299, page 12 of the revised main text).

Line 287 – 290: Is this a useful comparison? Are the two studies comparing the same number and types of PFAS? Perhaps it would be more comparable to sum report the total PFAS concentrations for only the matched PFAS. Also, are the LOD/LOQs for this study and Weinberg et al. (2011) comparable?

Response: The authors thank the reviewer for this comment. The ionic PFAS in TSP detected by Weinberg et al. (2011) include PFBS, PFHxS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, and perfluorosulfonamide (PFOSA). Our method is able to detect and thus quantify all the ionic PFAS (except PFDoA and PFOSA) detected by Weinberg et al., (2011). By removing the concentrations reported for PFDoA and PFOSA, the ∑PFAS concentrations in TSP are in the range of 1-10.8 pg m^{-3}, which is comparable with already reported 2-13 pg m^{-3}. The LOD and LOQ values reported by Weinberg et al. (2011) are higher than our LOD and LOQ values. For example, the LOD and LOQ for PFOS reported by Weinberg et al. (2011) are 1.0 pg μL^{-1} and 10 pg μL^{-1}, respectively. While the LOD and LOQ values for PFOS in our study are 0.23 pg mL^{-1} and 0.71 pg mL^{-1}, respectively.

To clarify this, we have added the following text to the Section 3.2 of the main text: "*It is important to note that the later study considered the same set of ionic PFAS as our study but included two additional analytes i.e. PFDoA and perfluorosulfonamide (PFOSA), which were not targeted by our method.*" (lines 303, page 12 of the revised main text).

Lines 301 – 302 – add in the polyfluoralkylphosphate esters – See Ao et al., 2024 (DOI provided in previous comment).

Response: We thank the reviewer for this comment. The *polyfluoralkylphosphate esters* are now mentioned in the text. (lines 315, page 13 of the revised main text).

SI Tables S3 and S4 – list the CAS number for each compound

Response: The CAS number of each compound listed in Tables S3 and S4 has been now included in Tables S1.

SI Tables S4 and S5 – I assume the reported SD is the SD for replicate injections? Please state in this tables. I also recommend replacing CSB with the measured value as this is more informative, especially if the authors include the blank concentrations, LOD, and LOQ values in the SI.

Response: Thank you for this comment. This has now been addressed in the captions of Tables S4 and S5 of SI: "*The reported standard deviation of the concentrations is from three replicate injections*." (line 58 and 70, page 4 and 5 of the revised SI).

The system blank values are now included in the SI in Tables S6 and S7.

Technical Corrections:

Line 43: …"PFAS that are thought to be less…" – change are to were; considering lines 45 – 47 states that studies have shown that replacement PFAS have similar adverse health effects as long chain counterparts.

Response: "Are" was replaced with "*were*".

Line 60: WWTP – define at first use in main text

Response: This has now been addressed in Section 1 of the main text.

Line 62: TSP – define at first use

Response: The acronym 'TSP' has been defined on its first use in line 59 of the main text in the original submission.

Line 70: change depend to depends -> "the distribution of PFAS depend[s] on the type…"

Response: "Depend" was replaced by "*depends*".

Line 129: change transition to partition

Response: "Transition" was replaced by "*partition*".

Line 281: change size to diameter

Response: "Size" was replaced by a "*diameter*".

References

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