Itemized Response to Reviewer's Comments

Ms. Ref. No.: egusphere-2024-4147

Title: Characteristics, main sources, health risks of $PM_{2.5}$-bound perfluoroalkyl acids in Zhengzhou, central China: From seasonal variation perspective

We sincerely apologize for our response so late. This is because we conducted the necessary experiments and consulted many papers to comprehensively solve the positive sampling artefacts. After experimental verification, the influence of positive sampling artefacts in this study can be ignored. We sincerely thank the editor and reviewer once again for their valuable and constructive comments on our manuscript. We have carefully addressed all the comments and believe that the quality of the manuscript has been further enhanced through this round of revisions. All modifications made in this revision are highlighted in red in the revised manuscript for ease of reference.

General comments:

Thank you for addressing my previous comments (Reviewer 2) in the revised manuscript. While I appreciate the efforts made, I believe there is still room for improvement in terms of the overall readability and clarity of the manuscript. Below, I provide further comments in response to the authors' answers to my earlier questions.

Response: Thank you again for your valuable and constructive comments on our manuscript. Detailed revisions have been listed below.

Specific comments:

Response to comment 2 - specific comments. The author's response to the comment on positive sampling artefacts is somewhat unclear. Specifically, I don't understand the link between positive sampling artefacts and practices like filter baking or the observation that PFAA levels were below MDL in process blanks, as this does not directly address the issue. As previously noted, certain PFAS compounds are known to partition between gas and particle phases. Given that several ionic PFAS are semi-volatile, they may exist in the gas phase and can adsorb onto quartz fiber filters during PM sampling. While the authors briefly mention the adsorption of gaseous PFAS in the revised manuscript, this discussion remains insufficient. It should be also noted that positive sampling artefacts such as adsorption of gaseous PFAS along with PFAS in particulate phase are not only due to increased flow rate but also could be due to the physicochemical properties of PFAS and filter material. I think the discussion on positive sampling artefacts is not adequate and a slightly better discussion should be given.

Response: We sincerely apologize for the delayed response to this comment. This was due to the implementation of additional experiments. Upon careful consideration of the reviewer's comment, we recognized that our study initially lacked an assessment of positive sampling artefacts. To address this gap, we conducted supplementary experiments to quantify the adsorption of gaseous-phase PFAAs onto quartz filters. We used the Teflon filter for particulate matter filtration and the quartz filter for the adsorption of gaseous-phase PFAAs. PFAA levels were below the MDL in the quartz filter sample. Furthermore, we have also discussed this comment in the

manuscript (Lines 184 – 189) in the new version.

Quartz filters are routinely employed for the collection of atmospheric organic carbon. Pre-combustion effectively eliminates interference from inherent organic background material within quartz filters (Kirchstetter et al., 2001), ensuring the accuracy of sample concentration measurements. Furthermore, baked quartz filters demonstrate low affinity for adsorption of organic compounds (Jung et al., 2011).

As the reviewer rightly points out, PFAAs may exist in both the gaseous and particulate phases. Positive sampling artefacts are a recognized phenomenon in such measurements (Turpin et al., 1994 and Chang et al., 2024), and it is acknowledged that the concentrations reported in this study have the potential to be overestimated due to this effect. To directly address this important comment, we implemented additional experiments, the details and results of which are presented below. To specifically isolate gaseous-phase PFAAs, we used a dual-filter sampling system: The Teflon filter was positioned upstream to remove particulate matter, followed by a quartz filter downstream to capture gas-phase PFAAs adsorbed onto the quartz filter (Turpin et al., 1994). The sampling period was from 10:00 to 9:00 the next day on June 10, 2025 (23 hours). Sample pretreatment, comprising ultrasonic extraction followed by solid-phase extraction, was performed prior to analysis. Two distinct samples were analyzed through UPLC-MS/MS: a 0.0001 $\mu g \cdot mL^{-1}$ PFAAs standard solution and the quartz filter sample. As shown in Fig. 1b, no detectable chromatographic peaks were observed in the quartz filter sample, indicating that PFAA levels were below the MDL. This result demonstrated that the impact of positive sampling artefacts on our findings could be ignored.

Lines 184 – 189 (New Version): This study used a dual-filter sampling system: The Teflon filter was positioned upstream to remove particulate matter, followed by a quartz filter downstream to capture gas-phase PFAAs adsorbed onto the quartz filter (Turpin et al., 1994). PFAA levels were below the MDL in the quartz filter sample. This result indicated that the impact of positive sampling artefacts in this study could be ignored.

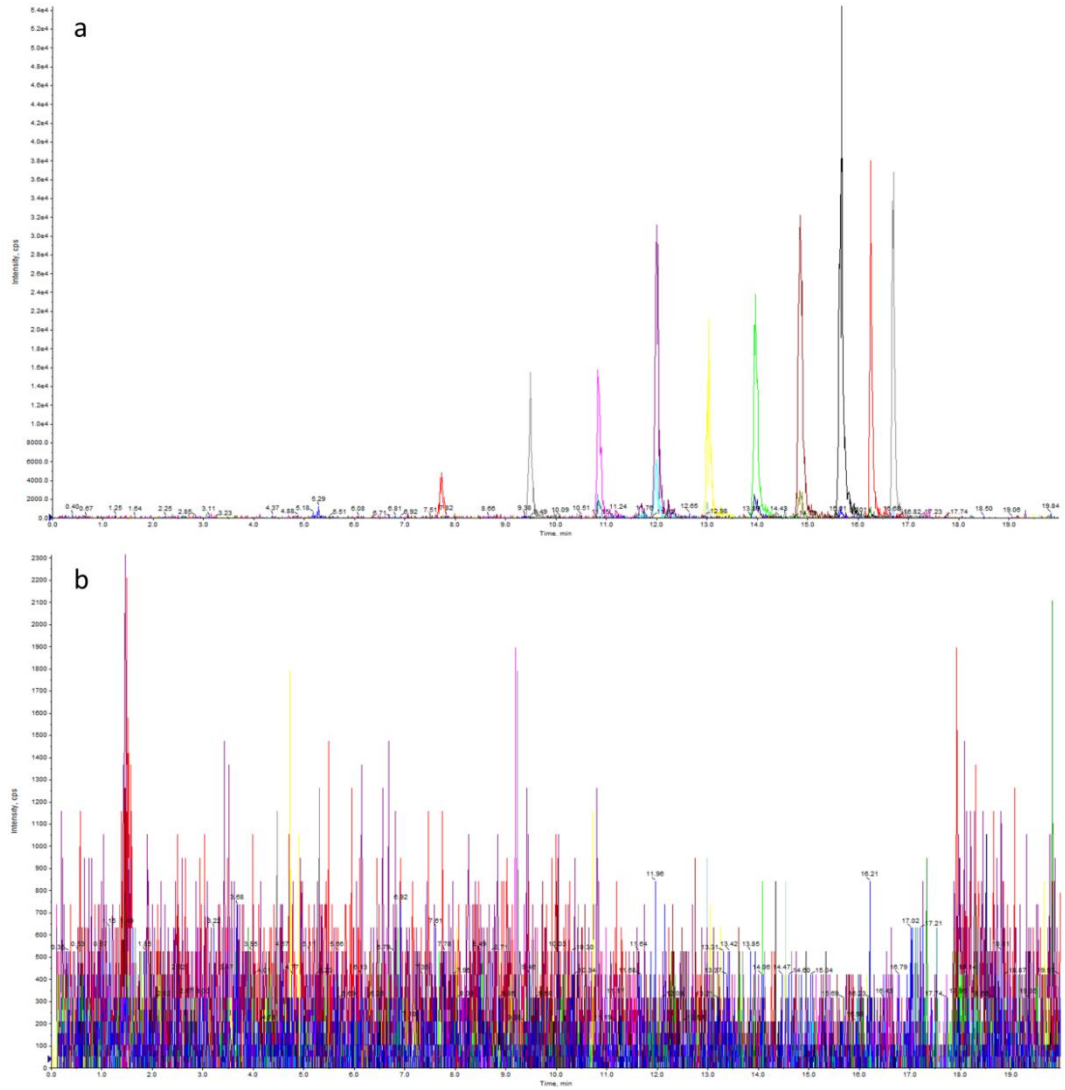

Fig.1 Chromatograms of 0.0001 μg·mL^{-1} PFAAs standard solution (a) and quartz filter sample (b)

Reference:

Chang, NY., Eichler, CMA., Amparo, DE., Zhou, JQ., Baumann, K., Hubal, EAC., et al., 2024. Indoor air concentrations of $PM_{2.5}$ quartz fiber filter-collected ionic PFAS and emissions to outdoor air: findings from the IPA campaign. Environ. Sci.-Process Impacts. 28, 3061-3071. https://dx.doi.org/10.1039/D4EM00359D

Jung, J., Kim, YJ., Lee, KY., Kawamura, K., Hu, M., Kondo, Y., 2001. The effects of accumulated refractory particles and the peak inert mode temperature on semi-continuous organic carbon and elemental carbon measurements during the CAREBeijing 2006 campaign. Atmos. Environ. 45, 7192-7200. https://dx.doi.org/10.1016/j.atmosenv.2011.09.003

Kirchstetter, TW., Corrigan, CE., Novakov, T., 2001. Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. Atmos. Environ. 35, 1663-1671. https://dx.doi.org/10.1016/S1352-2310(00)00448-9

Turpin, BJ., Huntzicker, JJ., Hering, SV., 1994. Investigation of organic aerosol sampling artifacts in the los angeles basin. Atmos. Environ. 28, 3061-3071. https://dx.doi.org/10.1016/1352-2310(94)00133-6

Response to comment 5 - specific comments

Matrix effects are about suppression/enhancement of ionisation of analytes due to the presence of matrix, which can still occur even if your blank is “clean”. A blank below MDL values could mean the matrix doesn’t contain detectable levels of your analyte, but it doesn’t confirm that the matrix won’t affect the analyte’s signal when it is present.

ESI is shown to be prone to matrix effects, leading to ion suppression or enhancement due to the interference of certain inorganic salts and compounds (Chekmeneva et al., 2017 – https://doi.org/10.1021/acs.jproteome.6b01003; Silva et al., 2016 - https://doi.org/10.5935/0103-5053.20150296). Atmospheric PM constituents such as sulfates, nitrates, and ammonium salts could cause ion suppression in ESI (Kourtchev et al., 2020 - https://doi.org/10.1021/acs.analchem.0c00971). Therefore, it is important to assess the matrix effect even if you have various blanks.

Response: As rightly noted, the determination is often subject to matrixeffect due to the presence of matrix components coeluting with the analyte of interest during LC-MS. The matrix effect-introduced MS signal suppression or enhancement may lead to erroneous results. (Smeraglia et al., 2002). To avoid the influence of matrix effects in this study, Solid Phase Extraction (SPE) was employed for sample pretreatment to enabled the selectively extract PFAAs from the sample (Cao et al., 2015 and de Navarro et al., 2024). Specifically, weak anion exchange (WAX) cartridges were utilized for the purification of PFAAs. The WAX cartridge, incorporating polar, reversed-phase, and ion-exchange functional groups, interacts effectively with the acidic functional groups characteristic of PFAAs, facilitating their retention (Hennrich et al., 2011 and Cao et al., 2024). The acidic functional groups present in PFAAs structures enable this specific interaction with the functional groups on the WAX sorbent, ensuring their capture on the extraction cartridge (Zou et al., 2024). The SPE procedure involved activation of the WAX cartridge, enrichment of PFAAs, washing to remove non-specific impurities (such as components like sulfate, nitrate, ammonium salt, etc), and elution of the target compounds. This

comprehensive process achieved both enrichment and purification of the PFAAs, thereby effectively eliminating the interference from sample matrix components.

Recovery has been widely used to evaluate the accuracy and reliability of analytical methods for PFAAs (Fang, 2019 and Han, 2019). Recovery refers to the ratio of the result obtained by LC-MS analysis to the theoretical value after adding a known amount of standard material to the sample. In this study, the recovery rates ranged from 71.27%–118.08%.

$$R = \frac{Q_1 - Q_2}{M} \times 100\%$$

Where：

R is the recovery rate,

Q_1 is the measured concentration in the methanol sample spiked with the standard,

Q_2 is the measured concentration in the blank methanol matrix,

M is the concentration of the added standard.

Reference:

Cao, FM., Wang, L., Sun, HW., Yang, J., Wang, RN., 2015. The optimization of sorbents and elution method for perfluorocarboxylic acids from the aquatic solution. J. Am. Fresenius Environ. Bull. 24, 2238-2244. https://orcid.org/0000-0002-8193-9954

Cao, WK., Chu, PY., Bruening, ML., Shi, RL., Hernandez-Barry, H., Tran, JC., 2024. Efficient, Low-Cost, and High-Throughput Sodium Dodecyl Sulfate (SDS) Removal from Protein Digests Using Weak-Anion Exchange. J. Am. Soc. Mass Spectrom. 36, 680-687. http://dx.doi.org/10.1021/jasms.4c00304

de Navarro, MG., Reyna, Y., Quinete, N., 2024. It's raining PFAS in South Florida: Occurrence of per- and polyfluoroalkyl substances (PFAS) in wet atmospheric deposition from Miami-Dade, South Florida. J. Am. Atmos. Pollut. Res. 15, 102302. http://dx.doi.org/10.1016/j.apr.2024.102302

Fang, S., Li, C., Zhu, L., Yin, H., Yang, Y., Ye, Z., et al., 2019. Spatiotemporal distribution and isomer profiles of perfluoroalkyl acids in airborne particulate matter in Chengdu City, China. Sci. Total. Environ. 689, 1235-1243. http://dx.doi.org/10.1016/j.scitotenv.2019.06.498

Han, D., Ma, Y., Huang, C., Zhang, X., Xu, H., Zhou, Y., et al., 2019. Occurrence and source apportionment of perfluoroalkyl acids (PFAAs) in the atmosphere in China. Atmos. Chem. Phys. 19, 14107-14117. http://dx.doi.org/10.5194/acp-19-14107-2019

Hennrich, ML., Groenewold, V., Kops, GJPL., Heck, AJR., Mohammed, S., 2011. Improving Depth in Phosphoproteomics by Using a Strong Cation Exchange-Weak Anion Exchange-Reversed Phase Multidimensional Separation Approach. Anal. Chem. 83, 7137-7143. http://dx.doi.org/10.1021/ac2015068

Smeraglia, J., Baldrey, SF., Watson, D., 2002. Matrix effects and selectivity issues in LC-MS-MS. Chromatographia. 55, S95-S99. http://dx.doi.org/10.1007/BF02493363

Zou, JM., Zhao, MZ., Chan, SA., Song, Y., Yan, SW., Song, WH., Song, et al., 2024. Rapid and simultaneous determination of ultrashort-, short- and long- chain perfluoroalkyl substances by a novel liquid chromatography mass spectrometry method. J. Chromatogr. A. 1734, 465324. http://dx.doi.org/10.1016/j.chroma.2024.465324

Response to comment 11 - specific comments

Thank you for clarifying that the concentrations (0.26–1.90 pg·m^{-3}) refer to PFAA levels in the Middle–Lower Yangtze River plains. Since these values are sourced from original studies, it would be more appropriate to cite the original research article rather than the critical review by Faust et al. (2023), as previously suggested.

Response: We have modified it to the critical review.

Lines 260 – 262 (New Version): The air mass originated from Middle-Lower Yangtze River plains (PFAA concentrations: 0.26–1.90 pg·m^{-3}) (Lu et al., 2018) and then entered the study region from Hubei Province.

Reference:

Lu, Z., Lu, R., Zheng, H., Yan, J., Song, L., Wang, J., et al., 2018. Risk exposure assessment of per- and polyfluoroalkyl substances (PFASs) in drinking water and atmosphere in central eastern China. Environ. Sci. Pollut. Res. 25, 9311-9320. http://dx.doi.org/10.1007/s11356-017-0950-x