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 have carefully addressed your comments on our manuscript and made necessary revisions of the previous manuscript. We sincerely thank you for valuable and constructive inputs. We believe that we have adequately addressed all of your comments and thus the current version has been greatly improved with those valuable comments and further English editing. 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 carefully. I understand the authors tested for gaseous-phase PFAS adsorption using a Teflon–Quartz double filter system, following Turpin et al. (1994). The authors reported that PFAS were below MDL level in the second (quartz) filter and thus suggest that adsorption artefacts from gaseous PFAS are negligible. While I appreciate these efforts, I have some follow-up questions and suggestions that I believe should be addressed before final acceptance.

Comment 1: Where was the double filter system experiment conducted? Was it carried out at the same location and under similar environmental conditions as the main PM sampling campaign? The modified manuscript text does not provide this important contextual information.

Response: We apologize for the insufficient explanation in our previous response, which has led to this question of yours. The double filter system experiment was conducted at the same location as the main $PM_{2.5}$ sampling campaign, which was on the rooftop of the Collaborative Innovation Building at Zhengzhou University (34°48′N, 113°31′E), with a height of 14 meters. This location is approximately 500 meters east of the West Fourth Ring Road and 2 kilometers south of the Lianhuo Expressway.

The experiment was carried out under the same environmental conditions as the main sampling campaign. The sampling conditions, such as the use of quartz filters (pretreated by baking and conditioning in a super clean room), the sampler flow rate (100 $L \cdot min^{-1}$), and the avoidance of adverse weather conditions (rain, snow, power outages) that would invalidate samples, were consistent for both the main $PM_{2.5}$ sampling and the double filter system experiment. Additionally, strict quality control measures (e.g., avoiding fluorinated plastic materials) were applied uniformly across all sampling and analytical processes, ensuring that the double filter system experiment was integrated into the main campaign's contextual and environmental setup.

We have also supplemented this background information in the original manuscript; please refer to Lines 187 – 190 for details.

Lines 187 – 190 (New Version): The dual-filter sampling system was used for supplementary experiments. The sampling location and conditions were consistent with the main $PM_{2.5}$ sampling work, and the sampling time was from 10:00 on June 10, 2025 to 9:00 on the following day.

Comment 2: The added text (Lines 184–189) could be misinterpreted. It gives the impression that the double filter system was employed throughout the study, rather than being used in a one-time supplementary experiment.

Response: Thank you for pointing out this issue. We have supplemented this information in the manuscript, which can be found in Lines 187-190.

Lines 187 – 190 (New Version): The dual-filter sampling system was used for supplementary experiments. The sampling location and conditions were consistent with the main $PM_{2.5}$ sampling work, and the sampling time was from 10:00 on June 10, 2025 to 9:00 on the following day.

Comment 3: From the response, it appears that only a single experiment with the double filter setup was performed. Could the detection of PFAS in the quartz filter below MDL levels simply be due to low atmospheric PFAS levels on that specific day?

Response: After comprehensive consideration, we conclude that it cannot be attributed to the low level of PFAAs in the atmosphere on that specific day. The reasons are as follows:

(1): Due to the relatively high temperatures in summer, elevated temperatures can promote the diffusion of PFAAs from the particulate phase to the gas phase, which may result in higher gaseous PFAA concentrations in summer. (Liu et al., 2018 and Li et al., 2024).

(2): After the filters were baked (450°C, 5h), their adsorption capacity for gaseous PFAAs was significantly reduced (Jung et al., 2011). Each sample had a sampling duration of 23 hours (sampling volume: 3.25 m^3), and this process should represent a balance between the adsorption and desorption of gaseous PFAAs.

(3): The emission sources of PFAAs remained relatively stable over a certain period. The main factor affecting PFAA concentrations is meteorological conditions,

among which temperature plays a key role in regulating the gas-particle partitioning of PFAAs (Han et al., 2019 and Li et al., 2024).

(4): Each sample was collected over a 23-hour period (from 10:00 on the first day to 09:00 on the next day), which was sufficient to represent the average atmospheric conditions over a period of time rather than transient daily fluctuations.

In summary, we believe the results of the supplementary dual-filter experiment conducted in summer are reliable. The detection of PFAAs below the MDL on the quartz filter indicated that the amount of PFAAs adsorbed by the quartz filter was negligible.

Reference:

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

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

Li, X., Wang, Y., Cui, J., Shi, Y., Cai, Y., 2024. Occurrence and Fate of Per- and Polyfluoroalkyl Substances (PFAS) in Atmosphere: Size-Dependent Gas-Particle Partitioning, Precipitation Scavenging, and Amplification. Envion. Sci. Technol. 58, 9283-9291. http://dx.doi.org/10.1021/acs.est.4c00569

Liu, W., He, W., Wu, J., Wu, W., Xu, F., 2018. Distribution, partitioning and inhalation exposure of perfluoroalkyl acids (PFAAs) in urban and rural air near Lake Chaohu, China. Environ. Pollut. 243, 143−151. http://dx.doi.org/10.1016/j.envpol.2018.08.052

Comment 4: Since the double filter system was not employed during the main sampling campaign, the potential for gaseous PFAS adsorption onto quartz fiber filters remains a valid concern. While your additional test is useful, it does not fully rule out the occurrence of positive sampling artefacts throughout the study period."

Response: Regarding your concern about the adsorption of gaseous PFAAs by quartz filters, we conducted a supplementary dual-filter experiment in summer. There

may be relatively high content of gaseous PFAAs in summer (Liu et al., 2018 and Li et al., 2024). The result indicated that the PFAA concentrations in the quartz filter were below the MDL.

Several factors support the conclusion that the PFAAs adsorbed by the quartz filter are negligible: first, the high temperatures in summer may lead to relatively high gaseous PFAA levels (Liu et al., 2018 and Li et al., 2024); second, the adsorption capacity of the filter for gaseous PFAAs is significantly reduced after calcination (Jung et al., 2011); third, the emission sources of PFAAs remain relatively stable over a certain period, and meteorological conditions are the main factors affecting the gas-particle partitioning of PFAAs (Han et al., 2019 and Li et al., 2024). Against this background, the detection of PFAAs below the MDL on the quartz filter confirmed that the adsorbed PFAAs were negligible.

The dual-filter experiment provided direct evidence that gas-phase adsorption was not a major issue under the tested conditions (June 2025). However, as you worried, it could not fully rule out the possibility of positive sampling artefacts occurring throughout the entire study period. Therefore, we have added the following limitation of this study in the manuscript (Lines 192 – 194): "Since the dual-filter experiment was not conducted throughout the entire sampling phase, the possibility of positive sampling artefacts could not be completely excluded."

Lines 192 – 194 (New Version): Since the dual-filter experiment was not conducted throughout the entire sampling phase, the possibility of positive sampling artefacts could not be completely excluded.

Reference:

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

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

Li, X., Wang, Y., Cui, J., Shi, Y., Cai, Y., 2024. Occurrence and Fate of Per- and Polyfluoroalkyl Substances (PFAS) in Atmosphere: Size-Dependent Gas-Particle Partitioning, Precipitation Scavenging, and Amplification. Envion. Sci. Technol. 58, 9283-9291. http://dx.doi.org/10.1021/acs.est.4c00569

Liu, W., He, W., Wu, J., Wu, W., Xu, F., 2018. Distribution, partitioning and inhalation exposure of perfluoroalkyl acids (PFAAs) in urban and rural air near Lake Chaohu, China. Environ. Pollut. 243, 143−151. http://dx.doi.org/10.1016/j.envpol.2018.08.052