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

RESPONSE TO REVIEWERS

Reviewers Comments:

RESPONSE: We sincerely thank the valuable and constructive inputs of the reviewers on our manuscript. We believe that we have adequately addressed all comments and thus the current version has been greatly improved with those valuable comments. In the revised manuscript, all the modifications were highlighted in red.

Itemized Response to Review#1's Comments

General Comments:

While the data presented represent a tremendous undertaking in terms of samples collected, quality assurance, and depth of analysis, the manuscript readability could greatly benefit from an in-depth editorial review. There are numerous instances where it is either unclear or ambiguous what the authors are trying to convey (ex. lines 48 – 49 "PFAAs levels in the atmosphere have attracted adequate attention due to people breathe second by second." the phrase "systemative investigation" in line 109, and "The polypropylene tubes were used." in lines 168 – 169.) Analytically speaking, it is evident that the authors have taken careful consideration in their sampling and data analysis, with numerous blanks, quality assurance checks, and data validation methods. It is also appreciated that methods for calculating MDLs were provided, and gives evidence that the researchers were thorough in their investigation.

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

Specific Comments:

Comment 1: In Figure 1, it is unclear whether the reported data is averaged across all seasons or is for a single season. Line 192 suggests the highest average concentration was 181.63 pg m^{-3}, but PFBA, PFOA, and PFOS all appear to have concentrations above 200 pg m^{-3} in the figure. Please clarify.

Response: The data in the manuscript (46.68 – 181.63 pg·m^{-3}) refers to the average PFAA concentrations for each season and the data in Figure 1 refers to the PFAA concentrations for the four seasons. These sentences have been rephrased in this manuscript.

Lines 193 – 201 (New Version): The PFAA average concentrations ranged from 46.68 to 181.63 pg·m^{-3} in Fig. 1 across four seasons. However, the increased airflow during pump operation enhanced the adsorption of gaseous PFAA on quartz filters (Turpin et al., 1994; McMurdo et al., 2008; Ahrens et al., 2012; Chang et al., 2024), which may lead to a slight overestimated of PFAA values in this study. The PFAA average concentrations were comparable to levels observed in Chengdu (150 pg·m^{-3}) (Fang et al., 2019), but significantly higher than those recorded in Shenzhen (8.80 pg·m^{-3}) (Liu et al., 2015a) and the average concentration in China (39.84 pg·m^{-3}) (Han et al., 2019).

Line 215 (New Version): Fig. 1. Box diagram of 17 PFAA concentrations in $PM_{2.5}$ across four seasons.

Reference:

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

Liu, B., Zhang, H., Yao, D., Li, J., Xie, L., Wang, X., et al., 2015a. Perfluorinated compounds (PFCs) in the atmosphere of Shenzhen, China: Spatial distribution, sources and health risk assessment. Chemos. 138, 511-518. http://dx.doi.org/10.1016/j.chemosphere.2015.07.012

Comment 2: In Figure 2, it may be appropriate to increase the spacing between the text and the markers in the legend, if possible, to increase the readability of the figure.

Response: The spacing between the text and the markers in the legend has been increased to improve readability.

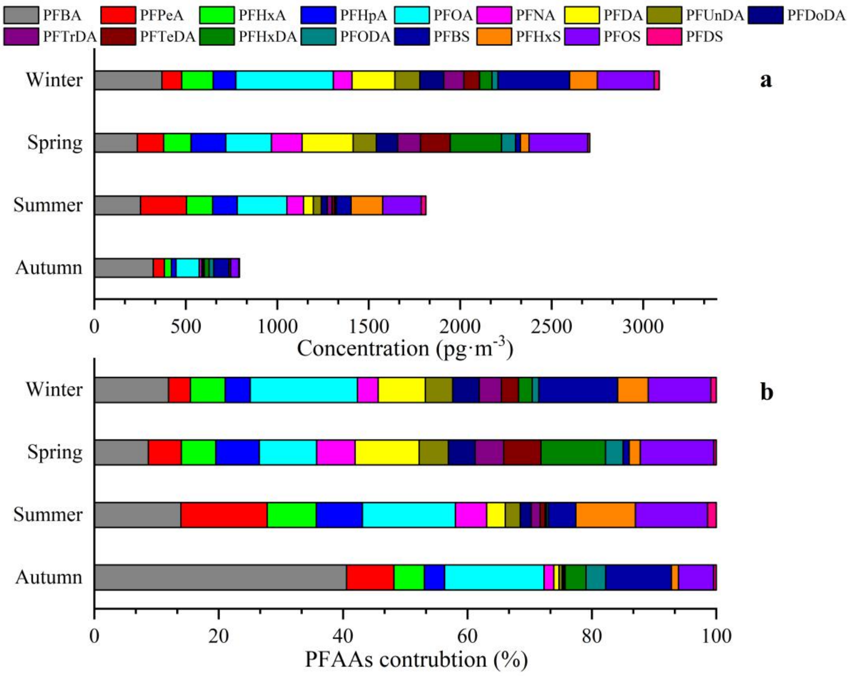

Fig. 2. PFAA concentrations characteristics across four seasons

Comment 3: While there are several mentions that this information can be used to better shape policy to control PFAA levels in $PM_{2.5}$, it is unclear what such policies could entail. Lines 298 – 303 suggest that management of local emissions is one way to control PFAAs, but it would be helpful to provide potential methods for emission reductions in industrial applications.

Response: In this manuscript suggestions for reducing PFAA pollution levels have been added, with the perspectives of PFAA proportion and air mass transport pathways.

Lines 242 – 245 (New Version): Long-chain PFAAs (e.g., PFOA and PFOS) were major pollutants and require replacement with short-chain alternatives (e.g., PFBS and PFPeA) or non-fluorinated substitutes such as silicon-based emulsifiers.

Lines 309 – 314 (New Version): For example, regulate PFAA emissions from textile and electroplating industries along southern urban in spring, collaborate with northwestern provinces to curb coal combustion in key transport cities in winter, establish pollution-blocking monitoring networks at northwestern entry points (e.g., Jiaozuo city and Jiyuan city) and leveraging the Taihang Mountains and Loess Plateau to intercept pollutants, in summer and autumn.

Comment 4: In line 159 of the supplement, "ED" is referred to as the burst time. It may be more appropriate to refer to this as the "exposure duration". I am assuming the authors use 72 as a general value for life expectancy. Also in line 159, the EF, exposure frequency is 350 days/year. Is this to suggest a two-week annual vacation? If so, perhaps it would be beneficial to more explicitly list the assumptions made, and why.

Response: The "ED" has been amended and more detailed information of EF has been added in this supplement.

Lines 158 – 160 (New Version): EF is the annual exposure frequency (350 days·year^{-1}, without the time of two-week annual vacation), ED is exposure duration (72 a).

Comment 5: In line 226, “the researches have identified PFHxDA as…” is unclear. Perhaps “Previous studies have identified PFHxDA as…” would be better-suited here.

Response: This sentence has been rephrased.

Lines 232 – 234 (New Version): Previous studies have identified PFHxDA as a degradation byproduct of substances based on FTOHs (Ellis et al., 2004; Loewen et al., 2005).

Reference:

Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Andersen, M.P.S., et al., 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. Envion. Sci. Technol. 38, 3316-3321. http://dx.doi.org/10.1021/es049860w

Loewen, M., Halldorson, T., Wang, F.Y., Tomy, G., 2005. Fluorotelomer carboxylic acids and PFOS in rainwater from an urban center in Canada. Envion. Sci. Technol. 39, 2944-2951. http://dx.doi.org/10.1021/es048635b

Comment 6: In line 323, “The research indicated hat” should be “the research indicated that”

Response: This sentence has been revised.

Lines 336 – 339 (New Version): The research indicated that three primary kinds of chemicals related to PFOS-namely perfluorooctane sulfonates, substances containing these compounds and polymers were widely useded in industrial production (Xie et al., 2013).

Reference:

Xie, S., Wang, T., Liu, S., Jones, K.C., Sweetman, A.J., Lu, Y., 2013. Industrial source identification and emission estimation of perfluorooctane sulfonate n hina. Environ. Int. 52, 1-8. http://dx.doi.org/10.1016/j.envint.2012.11.004

Itemized Response to Review#2's Comments

General comments:

The manuscript presents a study on $PM_{2.5}$-bound perfluoroalkyl acids (PFAAs) in Zhengzhou, China, focusing on seasonal variations, source apportionment using positive matrix factorization (PMF), and health risk assessment. The study is relevant and contributes to understanding PFAS contamination in urban air. The manuscript is well-structured and logically organised. However, it contains several typographical and grammatical errors. While some of these have been highlighted in the 'technical corrections' section, the list is not exhaustive. A thorough proofreading is recommended to enhance clarity and readability.

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

Specific comments:

Comment 1: L.38 – Please change the expansion of PFAS to per- and polyfluoroalkyl substances from perfluoroalkyl substances.

Response: This sentence has been rephrased.

Lines 37 – 41 (New Version): Perfluoroalkyl Acids (PFAAs), a subset of per- and polyfluoroalkyl substances (PFASs), can form smooth surfaces that are waterproof, oil-resistant, and stain-resistant, hence their widespread application in various industrial productions, such as paints, surfactants, coatings, emulsifiers, and fire retardants (Lindstrom et al., 2011).

Reference:

Lindstrom, A.B., Strynar, M.J., Libelo, E.L., 2011. Polyfluorinated Compounds: Past, Present, and Future. Envion. Sci. Technol. 45, 7954-7961. http://dx.doi.org/10.1021/es2011622

Comment 2: Section 2.1 – The use of quartz fiber filters during PM sampling is known to produce positive sampling artefacts such as the adsorption of gas phase compounds onto the filter. For further details on such artefacts, refer to Turpin et al. (1994) (https://doi.org/10.1016/1352-2310(94)00133-6) and Chang et al. (2024) (https://doi.org/10.1039/D4EM00359D). PFAS such as PFOA are known to partition out into gas phase from the aerosols (please see studies by Ahrens et al. 2012 (https://doi.org/10.1021/es300898s) and McMurdo et al. 2008 (https://doi.org/10.1021/es7032026). Additionally, short-chain PFAS, including PFBA and PFBS, are semi-volatile and may exist in both the gaseous and particulate phases. As a result, the PFAA concentrations measured in this study may be slightly overestimated due to the potential inclusion of gaseous PFAA. Consider addressing these sampling artifacts in the methodology section.

Response: We sincerely appreciate the reviewer for highlighting this comment. It should be noted that the positive sampling artefacts raised by reviewer is existent. However, there is still a lack of effective methods for PFAA sampling in particulate matter and the quartz fiber filters were also widely to sample particulate matter in previous researches (Fang et al., 2019; Wu et al., 2019 and Li et al., 2024). Before sampling, quartz filters could be baked to remove disturb from organic matter. In process blanks of this study, PFAA levels were below the method detection limits (MDLs). Considering that the increased airflow during pump operation enhances the adsorption of gaseous PFAA on quartz filters, this study illustrated in the Results and Discussion section that the adsorption effect of quartz filters may lead to a slight overestimated of PFAA concentrations.

Lines 194 – 197 (New Version): However, the increased airflow during pump operation enhanced the adsorption of gaseous PFAA on quartz filters (Turpin et al., 1994; McMurdo et al., 2008; Ahrens et al., 2012; Chang et al., 2024), which may lead to a slight overestimated of PFAA values in this study.

Reference:

Ahrens, L., Harner, T., Shoeib, M., Lane, D.A., Murphy, J.G., 2012. Improved Characterization of Gas-Particle Partitioning for Per- and Polyfluoroalkyl Substances in the Atmosphere Using Annular Diffusion Denuder Samplers. Envion. Sci. Technol. 46, 7199-7206. http://dx.doi.org/10.1021/es300898s

Chang, N.Y., Eichler, C.M.A., Amparo, D.E., Zhou, J., Baumann, K., Hubal, E.A.C., 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. http://dx.doi.org/10.1039/d4em00359d

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

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

McMurdo, C.J., Ellis, D.A., Webster, E., Butler, J., Christensen, R.D., Reid, L.K., 2008. Aerosol enrichment of the surfactant PFO and mediation of the water - Air transport of gaseous PFOA. Envion. Sci. Technol. 42, 3969-3974. http://dx.doi.org/10.1021/es7032026

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

Wu, J., Jin, H., Li, L., Zhai, Z., Martin, W., Hu, J., et al., 2019. Atmospheric perfluoroalkyl acid occurrence and isomer profiles in Beijing, China. Environ. Pollut. 225. http://dx.doi.org/10.1016/j.envpol.2019.113129

Comment 3: L.126-130 – The sentences are not clear. Please rephrase.

Response: The sentences have been rephrased.

Lines 124 – 133 (New Version): Before sampling, quartz filters were wrapped in aluminum foil and baked in a muffle furnace at 450°C for 5 hours to eliminate organic components. They were then placed in a super clean room (temperature of 20 ± 5℃; relative humidity of 50 ± 5%) for 48 hours. Clean the instrument with alcohol cotton before and after each sampling and record the standard state volume of the sampler. Quartz filters were weighed twice before and after sampling respectively, and the error between the two weighing was not more than 10 mg. After weighing the quartz filter, the quartz filter was wrapped in aluminum foil and stored at –18 ° C. The above experimental processes were carried out in the ultra-clean room.

Comment 4: Section 2.2 – Please provide more information on the product details of the PFAA and mass labelled PFAA mix.

Response: More information of the PFAA and mass labelled PFAA mix has been supplemented in Supplementary Table. S1 and S2.

Table. S1. PFAAs CAS and corresponding internal standard substance

Compound	CAS	Internal Standard	Relative Molecular Mass	Retention time (min)
PFBA	375-22-4	$^{13}C_4$PFBA	214.04	2.7
PFPeA	2706-90-3	$^{13}C_4$PFBA	264.05	3.9
PFHxA	307-24-4	$^{13}C_4$PFHxA	314.06	5.1

PFHpA	375-85-9	$^{13}C_4$PFHxA	364.07	5.4

Continued Table. S1

Compound	CAS	Internal Standard	Relative Molecular Mass	Retention time (min)
PFOA	335-67-1	$^{13}C_4$PFOA	414.08	6.1
PFNA	375-95-1	$^{13}C_4$PFNA	464.09	6.9
PFDA	335-76-2	$^{13}C_4$PFDA	514.10	7.5
PFUnDA	2058-94-8	$^{13}C_4$PFUnDA	564.11	7.8
PFDoDA	307-55-1	$^{13}C_2$PFDoDA	614.12	8.6
PFTrDA	72629-94-8	$^{13}C_2$PFDoDA	664.13	9.2
PFTeDA	376-06-7	$^{13}C_2$PFDoDA	714.14	9.4
PFHxDA	67905-19-5	$^{13}C_2$PFDoDA	814.16	10.2
PFODA	16517-11-6	$^{13}C_2$PFDoDA	914.18	10.8
PFBS	375-73-5	$^{18}O_2$PFHxS	300.11	11.0
PFHxS	355-46-4	$^{18}O_2$PFHxS	400.14	11.8
PFOS	1763-23-1	$^{13}C_4$PFOS	500.16	13.2
PFDS	335-77-3	$^{13}C_4$PFOS	600.18	14.4
$^{13}C_4$PFBA			226.04	2.7
$^{13}C_4$PFHxA			326.04	5.1
$^{13}C_4$PFOA			426.05	6.9
$^{13}C_4$PFNA			476.06	7.5
$^{13}C_4$PFDA			526.07	7.8
$^{13}C_4$PFUnDA			576.08	8.6
$^{13}C_2$PFDoDA			626.09	9.2
$^{18}O_2$PFHxS			402.10	9.4
$^{13}C_4$PFOS			526.08	10.2

Table. S2. PFAAs standard and corresponding internal standard substances and test information

Compound	Internal Standard	Standard (internal standard) Precursor Ion（m/z）	Standard (internal standard) Product Ion（m/z）	Standard (internal standard) DP（V）	Standard (internal standard) CE（V）	Mark recovery（%）	MDL（$ng \cdot L^{-1}$）
PFBA	$^{13}C_4$PFBA	213（217）	169（172）	–40（–50）	–13（–12）	97.49–112.02	0.3
PFPeA	$^{13}C_4$PFBA	263（217）	219/69（172）	–40（–50）	–10/–50（–12）	73.61–112.98	0.2
PFHxA	$^{13}C_4$PFHxA	313（315）	269/119（270）	–45（–55）	–13/–27（–14）	94.84–115.89	0.2
PFHpA	$^{13}C_4$PFHxA	363（315）	319/169（270）	–30（–55）	–14/–24（–14）	71.74–111.84	0.2
PFOA	$^{13}C_4$PFOA	413（417）	369/169（372）	–40（–70）	–14/–24（–20）	91.04–117.75	0.3
PFNA	$^{13}C_4$PFNA	463（468）	419/169（423）	–35（–70）	–16/–24（–22）	92.55–112.96	0.2
PFDA	$^{13}C_4$PFDA	513（515）	469/219（470）	–40（–75）	–18/–26（–17）	96.81–115.60	0.2
PFUnDA	$^{13}C_4$PFUnDA	563（565）	519/319（520）	–70（–60）	–16/–28（–15）	96.81–115.24	0.2
PFDoDA	$^{13}C_2$PFDoDA	613（615）	569/169（570）	–70（–60）	–18/–36（–15）	97.46–116.71	0.2
PFTrDA	$^{13}C_2$PFDoDA	663（615）	619/169（570）	–65（–60）	–20/–38（–15）	96.88–110.99	0.3
PFTeDA	$^{13}C_2$PFDoDA	713（615）	669/169（570）	–85（–60）	–20/–38（–15）	98.10–113.01	0.2
PFHxDA	$^{13}C_2$PFDoDA	813（615）	769/169（570）	–90（–60）	–18/–30（–15）	99.38–118.08	0.3
PFODA	$^{13}C_2$PFDoDA	913（615）	869/169（570）	–40（–60）	–25/–45（–15）	85.64–104.97	0.2
PFBS	$^{18}O_2$PFHxS	299（403）	80/99（103）	–90（–90）	–70/–38（–75）	71.27–106.25	0.3
PFHxS	$^{18}O_2$PFHxS	399（403）	80/99（103）	–90（–90）	–90/–72（–75）	89.91–102.78	0.3
PFOS	$^{13}C_4$PFOS	499（503）	80/99（80）	–105（–90）	–110/–98（–95）	96.42–111.07	0.3
PFDS	$^{13}C_4$PFOS	599（503）	80/99（80）	–120（–90）	–124/–110（–95）	97.56–109.07	0.2

Comment 5: Section 2.4 – Were matrix effects evaluated?

Response: We sincerely appreciate the reviewer for raising this critical point. In this study, two field blanks and procedure blanks were included during each sampling period. Notably, the PFAA concentrations detected in both field and procedure blanks were below the MDLs. These results indicated that the influence of matrix effects exerted on experimental results was negligible, thereby proving the reliability of the experimental data.

Comment 6: L.174 – I suggest reporting procedure blank values of the targeted PFAS in the SI.

Response: As addressed in response to **Comment 5**, PFAA concentrations in procedure blanks were below the MDLs, and the information has been added in line 177 in this manuscript.

Line 178: PFAAs were not detected in field blanks and program blanks.

Comment 7: L.192 – The authors report a maximum average seasonal PFAA concentration of 181.63 pg/m³. However, in Fig. 1, the average concentrations of PFBA, PFOA, and PFOS exceed 200 pg/m³. Could the authors clarify this discrepancy?

Response: The data in the manuscript (46.68 – 181.63 pg·m–3) refers to the average PFAA concentrations for each season and the data in Figure 1 refers to the PFAA concentrations for the four seasons. These sentences have been rephrased in this manuscript.

Lines 193 – 201 (New Version): The PFAA average concentrations ranged from 46.68 to 181.63 pg·m^{-3} in Fig. 1 across four seasons. However, the increased airflow during pump operation enhanced the adsorption of gaseous PFAA on quartz filters (Turpin et al., 1994; McMurdo et al., 2008; Ahrens et al., 2012; Chang et al., 2024), which may lead to a slight overestimated of PFAA values in this study. The PFAA average concentrations were comparable to levels observed in Chengdu (150 pg·m^{-3}) (Fang et al., 2019), but significantly higher than those recorded in Shenzhen (8.80 pg·m^{-3}) (Liu et al., 2015a) and the average concentration in China (39.84 pg·m^{-3}) (Han et al., 2019).

Line 215 (New Version): Fig. 1. Box diagram of 17 PFAA concentrations in $PM_{2.5}$ across four seasons.

Reference:

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

Liu, B., Zhang, H., Yao, D., Li, J., Xie, L., Wang, X., et al., 2015a. Perfluorinated compounds (PFCs) in the atmosphere of Shenzhen, China: Spatial distribution, sources and health risk assessment. Chemos. 138, 511-518. http://dx.doi.org/10.1016/j.chemosphere.2015.07.012

Comment 8: L.206, 210, and 221 – I assume the primary substitutes of PFOA and PFOS are the compounds mentioned in lines 204 and 205. However, this is difficult to understand. Please clearly mention which compounds are the substitutes for PFOA and PFOS.

Response: The substitutes of PFOA and PFOS have been added in this manuscript.

Lines 210 – 214 (New Version): During the study period, PFOA and PFOS along with its primary substitutes (PFOA primary substitutes: PFBA and PFHxA. PFOS primary substitutes: PFPeA and PFBS.) accounted for 23%–34% and 18.1%–29.9% of total PFAAs, consistent with the research (Liu et al., 2017).

Reference:

Liu, Z., Lu, Y., Wang, P., Wang, T., Liu, S., Johnson, A.C., et al., 2017. Pollution pathways and release estimation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in central and eastern China. Sci. Total. Environ. 580, 1247-1256. http://dx.doi.org/10.1016/j.scitotenv.2016.12.085

Comment 9: Fig. 2- Please provide the unit in the x-axis of the second plot. Also, label the plots as ‘a’ and ‘b’.

Response: The x-axis unit has been explicitly labeled in Fig. 2, with plots clearly labelled using ‘a’ and ‘b’.

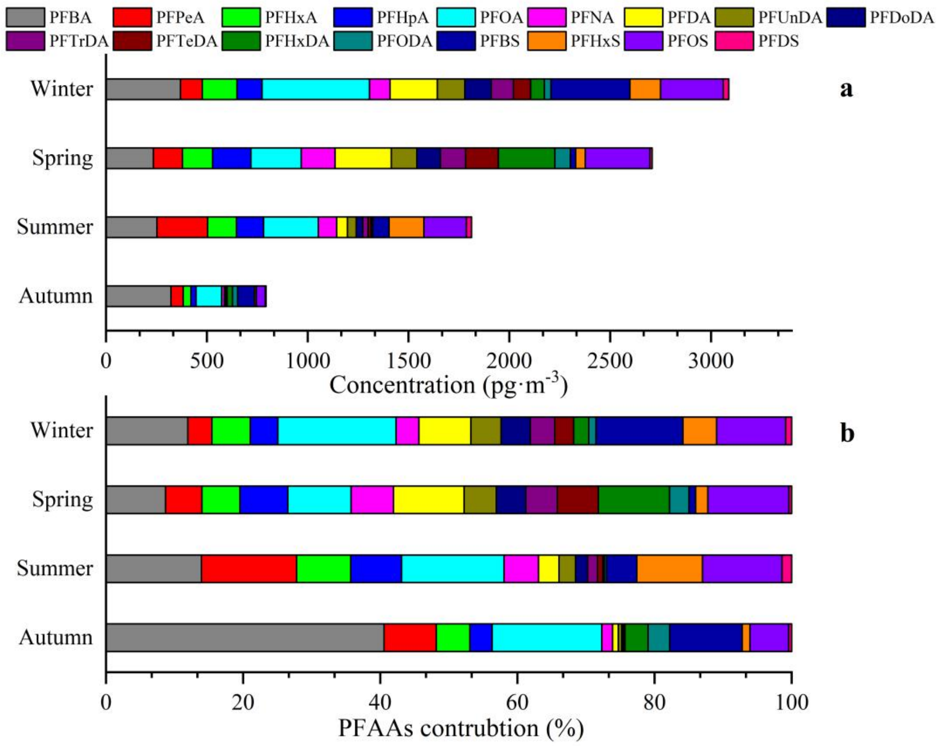

Fig. 2. PFAA concentrations characteristics across four seasons

Comment 10: L.237-239 – What were the different types of chemical industries near the sampling region? Were any fluorochemical manufacturing plants present within the vicinity of the sampling region?

Response: The chemical industrial profile of the study area primarily encompasses rubber manufacturing, fine chemicals production, pharmaceutical intermediates synthesis, and advanced materials development. These industries are also associated with emissions of fluorinated products. For example, Alchemist-pharm Chemical Technology Co., Ltd. (http://www.alchemist-pharm.com/En), situated 2.8 km distance from the study area, can produce fluorine-containing chemicals, and is a representative presence in the region's fluorine chemical manufacturing.

Comment 11: L.247-249 – This sentence is unclear. What do the concentrations (0.26–1.90 pg/m³) in parentheses represent? Do they indicate the range of total $PM_{2.5}$ PFAA concentrations in the Middle-Lower Yangtze River plains? Were these values measured in this study, or are they sourced from the literature? If they are from the literature, please cite the original source instead of referencing the critical review by

Faust (2023).

Response: The concentrations (0.26–1.90 pg·m^{-3}) in parentheses represented PFAA concentrations in the Middle-Lower Yangtze River plains. The values sourced from the literature. The reference format has been modified.

Lines 255 – 257 (New Version): The air mass originated from Hubei Province, passed through Middle-Lower Yangtze River plains (PFAA concentrations: 0.26–1.90 pg·m^{-3}) (Faust et al., 2023), and then entered the study region.

Reference:

Faust, J.A., 2023. PFAS on atmospheric aerosol particles: a review. Environ. Sci.-Process Impacts 25, 133-150. http://dx.doi.org/10.1039/d2em00002d

Comment 12: L.281-290 – Were there any wastewater treatment plants (WWTPs) in the vicinity of the study region? WWTPs are also reported to introduce PFAS into the atmosphere through aerosolisation and volatilisation during treatment processes such as aeration (please refer to the studies by Qiao et al. 2024 (https://doi.org/10.1016/j.jhazmat.2024.134879), Lin et al. 2022 (https://doi.org/10.1016/j.envint.2022.107434)).

Response: The WWTP of near the study area is Zhongyuan Environmental Protection Wulongkou Water Affairs Branch Company (distance: 7.8 km, total designed daily treatment capacity: 200,000 m^{-3}day^{-1}, http://www.cpepgc.com/20180626/77.html). Other WWTPs are located farther away, such as Chen Sanqiao WWTP (distance: 7.8 km, total designed daily treatment capacity: 150,000 m^{-3}day^{-1}, https://public.zhengzhou.gov.cn/D250406X/196731.jhtml).

Comment 13: 291- Please provide the correct reference.

Response: The references have been revised.

Lines 298 – 299 (New Version): This result was consistent with conclusions drawn by Chen et al. (2021) and Han et al. (2019).

Reference:

Chen, M., Wang, C., Gao, K., Wang, X., Fu, J., Gong, P., et al., 2021. Perfluoroalkyl substances in precipitation from the Tibetan Plateau during monsoon season: Concentrations, source regions and mass fluxes. Chemos. 282. http://dx.doi.org/10.1016/j.chemosphere.2021.131105

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

Comment 14: L.312 – Could other precursor compounds such as polyfluoroalkyl phosphate esters (PAP) or perfluorooctane sulfonamides (FOSA) degrade into these compounds?

Response: PAP are a class of PFAS. These substances typically exhibit a telomer-based chemical structure (denoted as n:2 PAP, such as 6:2 and 8:2 PAP), with their primary degradation products being short-chain perfluorocarboxylic acids (PFCAs). Theoretically, PAP with longer telomeric chains (e.g., 11:2 and 12:2 PAP) could degrade into long-chain PFAAs. However, in practical applications, the industrial use of long-chain PAP (⩾C11) remains limited, and environmental studies on their behavior and fate are sparse. Current scientific literature predominantly focuses on telomer-based PAPswithin the C6 – C10 chain-length range. FOSA features a fixed C8 carbon chain structure and its principal degradation end-product is PFOS.

Lines 324 – 326 (New Version): Long-chain PFAAs (C11–C14) were known degradation products of Long-chain FTOHs (Liu et al., 2017; Thackray and Selin, 2017; Wang et al., 2014).

Reference:

Liu, Z., Lu, Y., Wang, P., Wang, T., Liu, S., Johnson, A.C., et al., 2017. Pollution pathways and release estimation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in central and eastern China. Sci. Total. Environ. 580, 1247-1256. http://dx.doi.org/10.1016/j.scitotenv.2016.12.085

Thackray, C.P., Selin, N.E., 2017. Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors. Atmos. Chem. Phys. 17, 4585-4597. http://dx.doi.org/10.5194/acp-17-4585-2017

Wang, Y. Q., 2014. Meteolnfo: GIS software for meteorological data visualization and analysis. Meteorol. Appl. 21, 360-368. https://doi.org/10.1002/met.1345

Comment 15: Fig. 5 – the caption for Figure 5(C) is missing, please include this.

Response: The caption for Figure 5(C) have been added.

Line 332 – 333 (New Version): Fig. 5. The source distribution spectrum of PFAAs in PMF (a), the annual source proportion diagram (b) and the winter source proportion diagram (c)

Technical corrections:

Comment 1: L.48-49 – The phrasing of the sentence is a bit awkward. Please rephrase.

Response: The sentence has been rephrased.

Lines 47 – 49 (New Version): PFAAs levels in the atmosphere have attracted adequate attention due to the bioaccumulation and potential toxicity of PFAAs.

Comment 2: L.77 and 79 – please provide the in-text citation in the correct format.

Response: The format has been revised.

Lines 77 – 82 (New Version): Han et al. (2022) employed positive matrix factorization (PMF) to identify four sources of PFAAs within the atmosphere. Meanwhile, Chen et al. (2021) and Wang et al. (2022b) combined principal component analysis with back-trajectory model to assess air mass influence PFAA concentrations in precipitation from the Tibetan Plateau and airborne particulate matter in Chengdu, China.

Reference:

Chen, M., Wang, C., Gao, K., Wang, X., Fu, J., Gong, P., et al., 2021. Perfluoroalkyl substances in precipitation from the Tibetan Plateau during monsoon season: Concentrations, source regions and mass fluxes. Chemos. 282. http://dx.doi.org/10.1016/j.chemosphere.2021.131105

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

Wang, S., Lin, X., Li, Q., Liu, C., Li, Y., Wang, X., 2022b. Neutral and ionizable per-and polyfluoroalkyl substances in the urban atmosphere: Occurrence, sources and transport. Sci. Total. Environ. 823. http://dx.doi.org/10.1016/j.scitotenv.2022.153794

Comment 3: L.150 – Change the word 'extracts were' to 'extraction was'.

Response: The sentence has been revised.

Lines 151 – 153 (New Version): After the addition of methanol, the extraction was performed 3 times by sonication. Following the centrifugation (4500 r/min, 15 min), the extracts were diluted with ultrapure water.

Comment 4: L.156 and 163 – Supplementary section 1.2 details the source apportionment analysis. The instrument analysis is detailed in section 1.1 of the SI. Please change this.

Response: The ‘Supplementary 1.2’ in section 2.3 have been changed.

Lines 156 – 157 (New Version): Detailed steps for sample pretreatment are documented in Supplementary 1.1.1.

Lines 163 – 164 (New Version): Comprehensive details regarding the instrumental analysis can be found in Supplementary 1.1.2.

Comment 5: L.41 of SI – The ‘Evaporationoff’ seems to be a typo. Please correct this.

Response: The word has been revised in this supplementary.

Lines 40 – 42 (New Version): Nitrogen Evaporation was performed using a nitrogen evaporator to completely dry the eluate (the nitrogen blow temperature should not exceed 40°C, and no bubbles should be present on the liquid surface).