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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Occurrence and source apportionment of perfluoroalkyl acids (PFAAs) in the atmosphere in China" *by* Deming Han et al.

Deming Han et al.

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A list of responses for comments from editors and reviewers

Dear Editors and Reviewers:

Thank you for your letter and for the reviewers' comments concerning our manuscript entitled "Occurrence and source apportionment of perfluoroalkyl acids (PFAAs) in the atmosphere in China" (Ref: acp–2019–676). These comments are valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied comments carefully and have made correction, the correction in the manuscript was marked–up with blue colour and underline (e.g. Revised Manuscript) which we hope meet with approval. The main corrections in

the paper and the responds to the reviewer's comments are as flowing: Responds to the editors' and reviewers' comments:

Interactive comment on "Occurrence and source apportionment of perfluoroalkyl acids (PFAAs) in the atmosphere in China" by Deming Han et al.

Anonymous Referee #1 Received and published: 12 August 2019

Major comment: Query 1. It is very unlikely that PFSAs occur in the gas phase. Recent studies have shown that PFSAs have been measured in passive samplers since passive samplers are also collecting particles. It is really important to clarify in this manuscript that PFSAs are typically particle–bound and the measured concentrations of PFSAs are most likely due to the collection of particles using the passive samplers. Make also clear that the measured concentration is NOT the gas phase but rather "air concentrations" with mainly gas phase and partly particulate phase. This has to be clarified at all places in the manuscript, figures and SI before a publication can be considered. Response: Thanks for the reviewer's hard work on reviewing our manuscript. We respect the reviewer's opinion and made the corresponding revision in the revised manuscript, however we didn't agree that PFSAs can not occur in the gas phase. PFSAs maybe could occur in the gas phase. Due to the lower acid dissociation coefficient (pKA), 0–3.8 for PFCAs and –3.3 for PFSAs, PFAAs are expected to be mainly associated with aerosols in the non–volatile anionic form (Lai et al., 2018;Pavlína et al., 2018). Additionally, in one research of particle–size distribution of airborne PFASs, PFOA was predominantly (>70%) observed in small size fraction (<0.14 μm), PFOS mass fractions were preferred to exist in the coarser size fractions (1.38–3.81 μm) (Dreyer et al., 2015). However, the occurrence of ionic PFAAs is not clear, more recent field studies have confirmed their occurrence in gaseous phase. For example, Fang et al., (2018) found that C2, C4–C10 PFCAs and C6 and C8 PFSAs were detected in the gas phase in the air above the Bohai and Yellow Seas, China, with total gaseous concentrations of 0.076–4.0 (0.77$\pm$0.97) pg/m3. Karásková et al., (2018) conducted an investigation via a active air sampler with quartz fiber filter and XAD impregnated sorbent based

PAS to capture particulate and gaseous PFAAs, found PFASs were primarily in the gas phase, with gaseous associated fractions of PFASs of 93%±96%; while PFCAs distribute between both particles and gas phase, with gaseous associated fraction values of 6%–98%. However, just as proposed by the reviewer that the XAD–PAS may collect particle bound PFAAs in this study. Despite several research suggest the collecting efficiency of particle PFAAs sample to be similar to gaseous samples, it is still difficult to distinguish them. According to reviewer's suggestion, it has clarified in this revised manuscript that PFSAs concentration are a combine of gaseous and particulate phases, at all places. Additionally, the description of "We should keep in mind that the unimpeded movement of particle bound PFAAs would be captured during sampling using XAD–PAS, which cannot differentiate PFAAs between gas and particle phases. Despite some research suggest the sampling efficiency of gas and particle phase PFAAs were similar (Karásková et al., 2018). In the present study, the two phases PFAAs sampled by XAD–PAS were treated as the whole atmosphere PFAAs concentration." in lines 100–104 in the revised manuscript.

General comments: Query 2. Use two significant numbers; Response: The number format has revised according to reviewer's suggestion.

Query 3. Table 1: It should be "HV–AAS" for Toronto, Canada; Response: Both HV–AAS and XAD impregnated sorbent based SIP–PAS samplers were used in the cited reference for Toronto, Canada. The PFASs concentrations sampled for these two samplers were different for their different sampling volume. The "XAD–PAS 0.7–20 pg/m3" has revised to "SIP–PAS 11.24±7.95 pg/m3" in Table 1 in the revised manuscript.

Query 4. Figure 3: Change to "Northwest"; Response: This mistake has been revised in Figure 3 in the new version of manuscript.

Figure R1. The revised Fig. 3

Query 5. Figure 4: Describe the four factors in the figure caption; Response: According to reviewer's suggestion, all the factor names were added in Figure 4 caption in the

revised manuscript.

Figure R2. The revised Fig. 4 (The right figure is the revised figure with the corresponding figure caption)

Specific comments: Query 6. Line 13: Add total number of samples, number of sampling locations and which sampling method was used; Response: Thanks for reviewer's good suggestion. It has been revised in the new version manuscript in lines 17–20 in the revised manuscript, detailed description as "A nationwide geographical investigation considering atmospheric PFAAs via XAD–Passive Air Sampler was conducted in 23 different provinces/municipalities/autonomous regions in China, which provides an excellent chance to investigate their occurences, spatial trends, and potential sources. The total atmospheric concentrations of thirteen PFAAs (n=268) were 6.19–292.6 pg/m3,"

Query 7. Line 13: indicate if PFAAs were measured in the gas or particulate phase; Response: Just as discussed above, the PFAAs samples gathered via XAD–PAS should be a combine of gaseous and particulate phases. Hence, it was revised as "The total atmospheric concentrations of thirteen PFAAs (n=268) were 6.19–292.6 pg/m3," in lines 13–14 in the revised manuscript.

Query 8. Line 18: Specify which location are these "areas"; Response: According to reviewer's suggestion, "Spatially, the content of PFAAs displayed a declining gradient trend of central ares> eastern areas> western areas," has been changed to "Spatially, the content of PFAAs displayed a declining gradient trend of central of China> northern of China> eastern of China> northeast of China> southwest of China> northwest of China> southern of China areas, " in lines 18–20 in the revised manuscript.

Query 9. Line 24: Change to "ionizable"; Response: This mistake has been revised in line 26 in the revised manuscript.

Query 10. Lines 187–189: Clarify that this is the average of x numbers of sampling

locations in China; Response: According to reviewer's suggestion, it was changed to "In general, an increasing seasonal mean of PFAAs concentrations from 23 sampling sites existed for summer (31.4 pg/m3) < autumn (35.6 pg/m3) < spring (42.4 pg/m3) < winter (52.8 pg/m3). " in lines 199–201 in the revised manuscript.

Query 11. Lines 216–218: Indicate, how many sites were included from each area "(n = : : :); Response: According to reviewer's suggestion, the description of "Overall, the predominant declining gradient of PFAAs' contents was CC> NC> EC> NE> SW> NW> SC areas in China,", was changed to "Overall, the predominant declining gradient of PFAAs' contents was CC (3 sites)> NC (3 sites)> EC (7 sites)> NE (2 sites)> SW (3 sites)> NW (3 sites)> SC (2 sites) areas in China, " in lines 228–229 in the revised manuscript.

Special thanks to you for your careful reading and good comments!

Reference Dreyer, A., Kirchgeorg, T., Weinberg, I., Matthias, V. Particle-size distribution of airborne poly- and perfluorinated alkyl substances. ChemosphereÂă129, 142-149, 2015. Fang, X., Wang, Q., Zhao, Z., Tang, J., Tian, C., Yao, Y., Yu, J., and Sun, H.: Distribution and dry deposition of alternative and legacy perfluoroalkyl and polyfluoroalkyl substances in the air above the Bohai and Yellow Seas, China, Atmos Environ, Karásková, P., Codling, G., Melymuk, L., and Klánová, J.: A critical assessment of passive air samplers for per- and polyfluoroalkyl substances, Atmos Environ, 185, 186-195, 2018. Lai, F. Y., Rauert, C., Gobelius, L., and Ahrens, L.: A critical review on passive sampling in air and water for per- and polyfluoroalkyl substances (PFASs), TrAC Trends in Analytical Chemistry, Available online 23 Nov. 2018. Pavlína, K., Garry, C., Lisa, M., and Jana, K.: A critical assessment of passive air samplers for per- and polyfluoroalkyl substances, Atmos Environ, 185, 186-195, 2018.

We tried our best to improve the manuscript and made some changes in the manuscript. These changes will not influence the content and framework of the paper. We appreciate for Editors/ Reviewers' warm work earnestly, and hope that the

correction will meet with approval. Once again, thanks very much for your comments and suggestions.

Yours sincerely,

Best regards!

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-676/acp-2019-676-AC1-supplement.pdf

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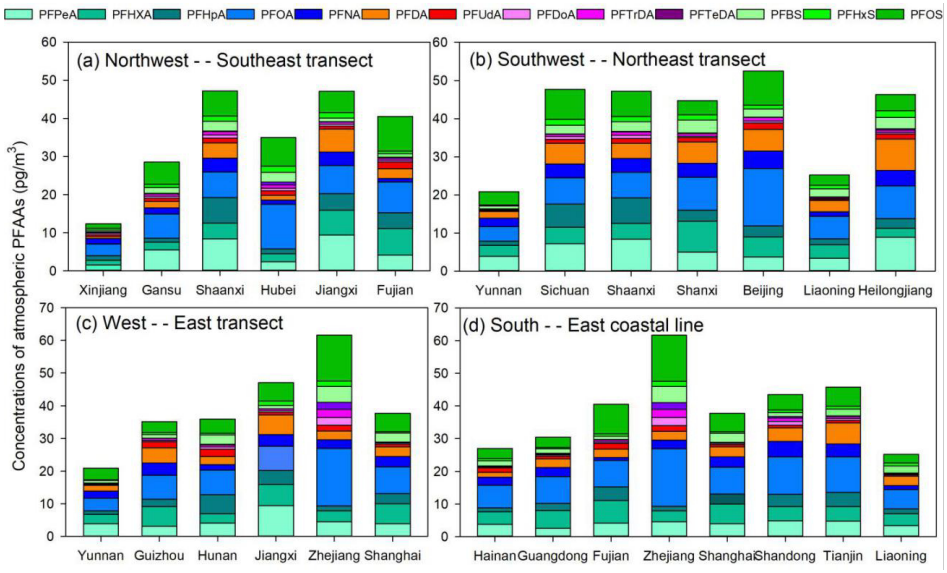
PFPeA PFHXA PFHpA PFOA PFNA PFDA PFUdA PFDoA PFTrDA PFTeDA PFBS PFHxS PFOS
(a) Northwest - - Southeast transect
(b) Southwest - - Northeast transect
(c) West - - East transect
(d) South - - East coastal line
Concentrations of atmospheric PFAAs (pg/m3)
Xinjiang Gansu Shaanxi Hubei Jiangxi Fujian
Yunnan Sichuan Shaanxi Shanxi Beijing Liaoning Heilongjiang
Yunnan Guizhou Hunan Jiangxi Zhejiang Shanghai
Hainan Guangdong Fujian Zhejiang Shanghai Shandong Tianjin Liaoning

Fig. 1.

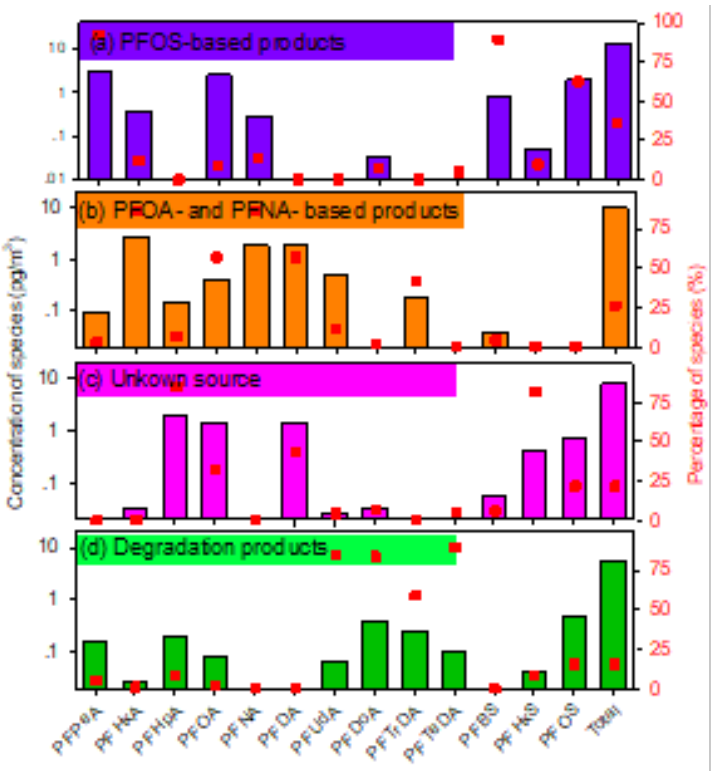
(a) PFOS-based products
(b) PFOA- and PFNA- based products
(c) Unkown source
(d) Degradation products
Concentration of species (pg/m3)
Percentage of species (%)
PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUdA PFDoA PFTrDA PFTeDA PFBS PFHxS PFOS Total

Fig. 2.