A point-by-point response to editor

Dear Editor,

We are very pleased to submit a revised manuscript entitled with "Characterizing the volatility and mixing state of ambient fine particles in summer and winter of urban Beijing" for possible publication in journal of Atmospheric Chemistry and Physics.

We greatly appreciate your effort and time on handling this paper. We also thank you for the further comments, which help us greatly improve this paper.

Yours sincerely,

Fang Zhang

On behalf of all authors

Comments from the editor:

Thank you for the next version of the manuscript! Based on the referee reports, Referee #2 was satisfied with your answers and edits already earlier. After assessing your latest version, I think you have addressed also the concerns of the Referee #1. I have marked some of my own comments in the attached pdf. Some of my suggestions are editorial to improve clarity, some related to terminology and methods while many are related to the role of oxidized organics and their role in aerosol formation, growth and their influences on aerosol volatility.

Line 15: insert the studied sizes here.
Re: Revised.

Line 15: that there are two persistent aerosol volatility modes (high-volatile and one less or non-volatile mode) present both in the summer and winter.
Re: Revised.

Line 17: This and the next sentence seem to be in contradiction. Figure 6 shows that the summer aerosol in all sizes are more volatile with a lower VSF at smaller sizes. However, the same figure also shows that there is a clear non-volatile mode at 40 nm during the summer. This has actually even higher contribution in the summer than in the winter in the size range pertinent to NPF. The overall process of NPF requires low-volatile vapors to form, cluster and nucleate. It is not feasible that they would be easily evaporated from the particle phase. This is in line with your next sentence.

Re: This sentence has been revised, as follows:

"Although the new particle formation (NPF) process requires low-volatile vapors to form molecular clusters and nuclei, the significant high-volatile mode around noontime on NPF days indicates volatile substances could be produced during the growth stage of newly formed particles in the summer."

Line 21: On the other hand.
Re: Revised.

Line 70: sources and chemical composition of aerosol particles.
Re: Revised.

Line 75: There are also other non-volatile components in addition to BC.
Re: This sentence has been revised to "…leaving refractory materials such as BC and other non-volatile components…"

Line 89: there.
Re: Revised.

Line 113: was.
Re: Revised.

Line 117: How? Please explain. Assuming no evaporation at low temperature and dissociation at a high enough temperature?
Re: During the measurement, ambient aerosols were first sampled by a $PM_{2.5}$ inlet and subsequently passed through a Nafion dryer that reduced the sample flow RH to below 30%. "The RH was calibrated periodically with ammonium sulfate during the measurement period" means the accuracy of RH was verified by comparing the delirium point of ammonium sulfate measured by HTDMA with the theoretical delirium point. An explanation has been included in lines 122-124, as follows:

"The accuracy of humidity can be verified by comparing the deliquescence point of ammonium sulfate measured by HTDMA with the theoretical deliquescence point."

Line 123: how?
Re: The calibration of VTDMA can be found in lines 116-118: "The VSF-PDF was retrieved based on the $TDMA_{inv}$ algorithm developed by Gysel et al. (2009). The scans in which the temperature between the two DMAs was not increased were used to define the width of the transfer function". The calibration of other instruments (AE-33 and SMPS) can be found Wu et al (2020). A supplementary explanation has been included in line 129: "Detailed calibration process of these auxiliary instruments can be found in Wu et al (2020)".

Line 136: Did you account for the cubic shape factor of NaCl?
Re: $\eta_{D_p,T}$ is the transportation efficiency of the sampled particles, which represents

particle losses between DMA_1 and DMA_2 due to diffusion and thermophoretic forces (Philippin et al., 2004), and always determined at each particle diameter and heating temperature with NaCl particles in laboratory calibrations for that they do not evaporate even at high temperatures (Philippin et al., 2004; Cheung et al., 2016). Thus in this study, $\eta_{D_p,T}$ at each particle size is determined from the number concentration of NaCl particles before and after heating at 300 °C (i.e. $\eta_{D_p,T} = N_r(NaCl)/N_{D_p}(NaCl)$). An explanation has been included in lines 140-142, as follows:

> "…and always determined at each particle diameter and heating temperature with sodium chloride (NaCl) particles in laboratory calibrations for that they do not evaporate even at high temperatures (Philippin et al., 2004; Cheung et al., 2016)…"

Line 163: split this section into 2-3 paragraphs for clarity and to improve readability.
Re: Revised.

Line 202: add the year. is the date MM/DD or DD/MM?
Re: Revised.

Line 226: Please make the figure larger to reduce overlap between the labels and to improve clarity.
Re: Revised.

Line 245: See my comment in the abstract. Furthermore, organic condensation is highly size dependent. See e.g. Riipinen et al. (2012). For different sized aerosol particles, their growth is governed by organics of different volatility. For example, the semi-volatile organics only condense onto the largest particle sizes whereas the extremely low volatile organics can condense even below 10 nm in size. The prominent HV mode in summer could be due to condensation of semi-volatile material, but this does not have anything to do with new particle formation.
Re: This sentence has been revised to "…while the prominent HV mode in the summer especially for large particle size could be due to condensation of semi-volatile materials on nucleated particles (Riipinen et al., 2012)."

Line 266: see my earlier comment regarding organic condensation.
Re: This sentence has been revised to "…Obviously, the seasonal differences in VSF_{mean} are more significant than that of among different clusters especially for larger size particles."

Line 272: There is a considerable tail of BC from traffic that can contribute to the non-volatile fraction in urban environments also at 40 nm size range. Therefore the comparison between 40 nm and 150 nm sizes is far from trivial.
Re: Thanks for this comment. It's true that part of the 40 nm particles could be pre-existing particles. The statements have been revised, as follows:

> "…Although the local primary emission sources (e.g. vehicles, cooking) can contribute to the pre-existing background small particles in urban environments, the fraction was probably lower during the new particle formation (NPF) events. It was

reported that the ultrafine particles during clear days (e.g. NPF days) in urban Beijing were primarily from secondary formation (Wang et al., 2018), and the pre-existing particles are predominant in accumulated mode."

Line 275: for which size?
Re: The size information has been included in this sentence, see line 287, or as follows:

"During the summer, low VSF during the daytime (08:00–18:00 LT) and high VSF during the nighttime were observed for 40 nm and 150 nm particles (Fig. 8a)."

Lines 283-288: see the previous comment.
Re: The editor is right about the explanations of decreased VSFs during the NPF events. The discussions have been revised, as follows:

"…Although the NPF process requires low-volatile vapors to form molecular clusters and nuclei (Ehn et al., 2007), the significant high-volatile mode around noontime on NPF days indicates volatile substances could be formed during the growth stage of newly formed particles in the summer. Previous study also showed that the growth process of the nucleated particles primarily formed non-refractory sulfate and organics in Beijing (Wehner et al., 2009)..."

Line 308: Please clarify. Biogenic precursor concentrations are expected to be higher, anthropogenic precursors could be lower. The boundary layer and mixing / dilution can be different.
Re: Revised. Here we meant that the anthropogenic precursors could be lower.

Line 339: Pyrolysis can transform the organic aerosol into non-volatile, but this is only after treatment in 300 degC. The "charred" organics probably do not contribute to the growth in ambient conditions.
Re: Revised.

Line 354: Please split this section into 2-2 paragraphs to improve readability and clarity.
Re: Revised.

Line 412: Please check the conclusions after considering my comments in the earlier sections.
Re: Thanks for the editor's constructive comments and suggestions. A revised conclusion has been included in the new version.