Response to referees' comments on "Reduced volatility of aerosols from surface emission to the top of planetary boundary layer"

Reviewer 1:

General comment:

This study performs unique measurements in order to investigate the evolution of pollutants in the boundary layer (BL) over a polluted region, with particular focus on the lofted pollutants through the convective mixing when BL was well developed. The authors compared the characteristics between surface emissions and that on top of BL, finding a significantly reduced faction of more volatile substances, but enhanced lower-volatile species accordingly. This study provides a direct field evidence from reliable measurements about the evaporation process of condensed phase in the atmosphere. It is therefore necessary to consider this process during the vertical transport of aerosols or to any environment from higher to lower concentration of condensed phase. I recommend for its publication but there are a few places needing improvement.

[Response] We thank the referee for the positive comments and constructive suggestions, we have revised the manuscript according to the comments point by point.

1. It should be given at what layer the results observed here may or may not apply, such as in the lower BL, or in an upper free troposphere. I presume some variation of RH within the BL may introduce some variations on the comparison between both points. The phenomenon you present here may only apply for the dry layer, such as beyond the top of BL in the lower free troposphere. The way in which application should be applied needs to be more explicitly discussed.

[Response] Thanks for pointing this out. We agree with the reviewer that the variation of RH within the PBL will lead to different variations of aerosol chemical composition in vertical direction. The RH at both sites were lower than 40% at most of time during the whole observation period. Therefore, the phenomenon we observed in this study can only apply for the dry layer, and the applicable altitude range should be limited between the surface and the top of PBL. We added the suggestions as (Line 209-222):

"A previous study basing on aircraft measurements in this region showed that, aerosol chemical composition had a significant variation from surface to the top of the PBL under high RH conditions (surface RH>60%), which caused by secondary formation through the enhanced aqueous/heterogeneous processes in vertical direction (Liu et al., 2020). However, the RH was quite low at both sites (most of time RH<40%, Fig. S6b), below the deliquescence RH for most substances (Cruz and Pandis, 2000), water vapor may thus had not importantly participated in the phase transformation or chemical reactions during vertical transport. In addition, the bulk equilibrium between gas and condensed phase may be significantly hindered under conditions of lower temperature and lower RH due to the kinetically limited diffusion rate at the aerosol

surface (Koop et al., 2011). Therefore, the viscosity of aerosols may be enhanced and OA may be present as semi-solid or glassy state under these conditions. This means the evaporation process when aerosols are transported from lower and moister boundary layer to the upper level with lower temperature and moisture may be eventually depressed, hereby aerosols tend to be more solid-like and resistant to the evaporation. This evaporation-dominated variation on aerosol composition from the surface to the top of the PBL tend to only occur at the cold and dry condition."

2. A ratio of nitrate/BC, and org/BC etc. will be useful and more direct to demonstrate the lost of volatile species.

[Response] Thanks for your suggestion. We admit the difference of nitrate/BC or Org/BC between the two sites is director indicator for demonstrating the loss of semivolatile species during vertical transport process. Instead of that, we present a ratio of mountain to surface for each species during the daytime (11:00-14:00) in Fig. 4a, when the PBL was well developed. As it shown, the matched concentrations of inert species, such as BC and CO, indicating an efficient vertical transport from surface to the mountain site through the daytime convective mixing. Comparing with the surface, the significant reduction of semi-volatile species on the mountain indicated the net loss during upwards transport.

3. I would suggest expanding the discussions about the generic application on the dilution effect, such as a few previous studies pointed the dilution could be particularly important for biomass burning emissions. These high concentrations of condensed phase could importantly contribute to the gaseous precursors, and under certain conditions (after transport) could form secondary aerosol. In addition, these low-volatile aerosols transported to free troposphere may have longer lifetime and be transported to a longer distance.

[Response] We thank the reviewer to point this out. The related discussions are now added (Line 225-229).

"Previous studies pointed the dilution could be particularly important for biomass burning emissions (Li et al., 2021). The high concentrations of condensed phase could importantly contribute to the gaseous precursors, and under certain conditions, could form secondary aerosol. In addition, these low-volatile aerosols transported to the free troposphere may have longer lifetime and be transported to a longer distance (Liu et al., 2020a)."

4. There was also some westerly air mass besides your definition of regional advection, why these were not defined as the regional influence.

[Response] The period we defined as regional advection (RA) was characterized by continuously influencing on both sites from westerly air mass (4 days), which led to an accumulative increase for all aerosol species. For other westerly air mass periods besides the RA, the time of duration was relatively short and the concentrations of aerosol species on the mountain didn't exhibit a significant increase. Therefore, we didn't define these periods as the regional influence.

5. Fig. 5 has not been clearly presented, the data points are not shown, and it looks confusing merging both PMF and temporal results.

[Response] Thanks for pointing this out. The elemental ratio for each PMF factor at the two sites was also given in Fig. 6. To avoid confusing presentation, we removed the PMF results from Fig. 5.

6. It is necessary to state what is the surrounding environment of the mountain site, should be some biogenic SOA source?

[Response] Thanks for your suggestion. We rewrote the introduction of the mountain site as below (Line 93-98). In addition, there should be quite low biogenic emissions in winter due to low temperature, and the biogenic SOA source is barely resolved by the PMF analysis on AMS mass spectra.

"The mountain site (Haituo mountain, 40.52ºN, 115.78ºE, 1344 m a.s.l.) locates in the northwest Beijing area with a straight-line distance of ~85 km from Beijing downtown. The Haituo mountain belongs to Taihang mountains and connects to the continental plateau extended to the west. The surroundings of this site are covered with broad-leaf forest and without distinct anthropogenic emissions except for a few villages at the foot of the mountain. Thus, it can be considered an ideal receptor site for regional transport influenced and/or local influenced by vertical transport under certain conditions."

Technical corrections.

Line 28, "which subsequently interact with"

[Response] Revised.

Line 46, phase to phases.

[Response] Revised.

Line 66-67, replace one of the "yet to be".

[Response] Revised.

Line 68-70, you should really point out the advantage of your experimental setup.

[Response] Thanks for your suggestion. We rewrote the corresponding sentences as below, please see Line 72-80.

*"*In this study, by simultaneous and continuous measurements of detailed aerosol compositions were performed at both surface and surface-influenced mountain sites using advanced instrumentations, which provides an opportunity to realize the high time-resolution variations at different altitudes. Relative location of the mountain site to the top of the PBL varies with diurnal variation of PBL height (PBLH), which leave the mountain site in the free troposphere most time of the day and being influenced by PBL air masses around midday. Through comparing the difference of aerosol chemical compositions between the two sites, we aim to investigate the modification of compositions during the upward transport in the PBL and explore the generic mechanisms in driving the evolution of chemical composition.*"*

Line 88-97, the environment at both mountain and surface sites should be depicted.

[Response] Suggestion adopted. Please seen Line 89-98.

Line 82, which section.
[Response] This is revised.

Lin 85, COA is not resolved on the mountain, so it is not "four factors are resolved at both sites".
[Response] Suggestion adopted. We revised the presentation about the PMF-derived OA factors at the two sites. Please see Line111-116.

Line 92, could we show a temporal variation of PBLH.
[Response] Suggestion adopted. We added the temporal variation of PBLH in Fig. 1d.

Line 119, a redundant space.
[Response] Revised.

Line 121, have you defined what BC is.
[Response] Yes, we defined BC as black carbon in section 2.2 (Line 123).

Line 124, what accumulated? Needing rewrite.
[Response] Revised. We rewrote the sentence, please see Line 162-164.
"On the surface, the diurnal variation of BC concentration showed a minimum at the same hours due to the dilution effect of developed PBL, but had a sharp enhancement during nighttime due to accumulation in shallow nighttime PBL."

Line 146, the fractions of POA/SOA were quite similar, not "varied from.. to .. "
[Response] Revised.

Line 148, transporting pollutants upwards.
[Response] Revised.

Line 151, rewrite.
[Response] Revised.

Line 165-170, it is therefore important you stated the low concentration of gaseous precursors on the mountains before these discussions.
[Response] Suggestion adopted. We added the statements in Line 198-200.
"Due to few anthropogenic emissions on the mountain, the concentrations of gaseous precursors, such as ammonia and nitric acid vapor et al., should be significantly lower than that in urban environment."

Line 186, the additional input.
[Response] Revised.

Line 191, directly emitting into.

[Response] Revised.

Line 205, this sentence needs some breakups.
[Response] Revised. Please see Line 257-260.

Line 226 onwards, needing rewriting as two sentences.
[Response] This is revised.

Line 232-237, as mentioned in the main comment, the implication of this study should be expanded in terms of evolution after transporting into the free troposphere.
[Response] This is now added (302-303):
"These lower-volatile aerosols could be transported to a longer distance in the free troposphere hereby having longer lifetime."

Line 239, the font size needs to be adjusted.
[Response] Revised.

Reviewer 2:

General comment:

In the study by Liu et al. simultaneous gas and particle phase measurements at a surface and a mountain site in the Beijing area were performed and analyzed. The effects of the dilution of pollutants uplifted from the surface to the mountain site during periods with a well-mixed boundary layer was investigated. Difference in the characteristics of the semi volatile organic and inorganic fractions compared to the low volatile organic and inorganic fraction in the aerosols was observed. The results show a significant decrease in the more volatile fraction with a simultaneous increase in the low volatile fraction during period when convective mixing was strongest. The measurements provide direct field observations on an important aspect of the potential evaporation of semi-volatile compounds from the aerosol phase due to the dilution of the gas phase concentration. I recommend the study for publication after the following comments are addressed.

[Response] We thank the referee for the positive comments and constructive suggestions, we have revised the manuscript according to the comments point by point.

1. line 85: *"The instrument operation, calibration, and data analysis are detailed in the supplement information."* Actually, only information of the applied CE method (and not the result of the CE) and the treatment of the PMF analysis are giving in the SI. No information of calibration or operation are provided. Please add the typical information for the operation and results of the calibration for of both AMS at both sides (e.g. frequency of calibration, method, IE).

[Response] Thanks for pointing this out. We added the CE result in Fig. S1. The detailed instrument operation, calibration, and data analysis are now added in section 2.2 of the revised manuscript.

2. line 115ff and Figure 2: The classification and distinction of CM vs RA is not fully clear to me. While CM seemed to be based on the diurnal variation of the PBLH (e.g. as shown in Fig. 1b) the RA influence is based on a time period of several days with dominant contribution of regional (westerly) regions. Does the subsequent shown diurnal variation for CM in Fig. 2 includes the midday time periods of RM as well or are they excluded. Is CM diurnal variations only derived from the time periods which are not marked in grey as RA days? What about the midday time periods in the RA which seem to have a high local influence (up to 40 to 50% of local influence (by judging from Figure 2) during midday between Jan. 9th to 12th): are these midday local influences included in the RA diurnal variation or the CM diurnal in Fig. 2? Since CM seems to be defined by the time of the day and RA by a time period of days it is difficult to understand which data was used for Fig. 2. Please clarify.

[Response] Thanks for pointing this out. The whole RA period has been excluded for the diurnal analysis of CM in Fig. 2, and the diurnal analysis of CM is performed for the period without being marked as RA. We added a further illustration on the duration of statistical analysis for the CM and RA period respectively (Line 153-157).

"Note that the RA period was also influenced by the convective mixing of surface sources around midday, however being combined with additional sources from other regions besides the surface emission. In this study, the statistical results of the RA period include the whole period marked in the grey bar in Fig. 1d-h, and the rest period is used for the statistics of CM period."

3. line 124f: *"with elevated concentration by 82% from midday to early afternoon (Fig. 2a)."* Can you please be more precise in terms of what is the concentrations you use to derive the 82% increase, e.g. in brackets after the 82% the average concentration change in µg/m³ can be provided. Figure 2a) is too small that one has issues to reliably infer the values of the data from the axis label.

[Response] We added the related information as suggestion.

"…the 82% increase (from 0.19 to 0.34 µg m^{-3})"

We have also enlarged the labels in Fig. 2a.

4. line 125ff: *"This pattern was highly consistent with the development of PBLH and local air mass contribution. On the surface, lower BC concentration showed at the same hours due to the dilution effect of developed PBL, but accumulated towards the surface during nighttime inversion. Notably, BC concentration at 11:00-14:00 on the mountain almost matched with that on the surface, suggesting the well mix because of the daytime convective mixing."* Fig. 1b shows approx. a local air mass contribution of about 40% to the mountain site during the CM period (11:00 to 14:00). However, the mountain site has an average increase of about 82% in BC during the CM period and almost match the surface concentration while the local air mass on average only seem to contribute 40% to the mountain site. This seem to be confusing and it is not clear to me if the pattern observed is based on qualitative or quantitative comparison. Please elaborate in the discussion more about this comparison and potential discrepancy.

[Response] We thank the reviewer to point this out, which is an inspiring point. We have clarified this in the revision (Line 145-149).

"The local air mass faction as calculated from the dispersion model is only used to indicate the predominant local air mass influence in the midday. The aerosol concentration contained in the air mass depends on the transport efficiency, reaction and deposition rate of each aerosol type. The fraction of transported aerosols, even for the inert BC may not be quantitatively comparable with the air mass fraction."

5. line 128f: *"The inert gas CO was also efficiently transported without loss from surface to mountain (Fig. S5c)."* In the line of the precious comment can you please provide and explain this statement by giving the concentration changes in numbers and how this relates to the average local air mass contribution to the mountain site during the CM period. Just alone from the small graphs in Fig. S5c it is for me not possible to verify the statement that there are no losses of CO during transport.

[Response] We thank the reviewer to point this out.

The use of the inert gas CO is to emphasize the comparable concentration between both sites during the CM period, similar to BC. We have observed the efficient transport of BC and CO from surface to the mountain site. As the answer above, the air mass fraction is only broadly

estimated from the dispersion model, but may not directly refer this air mass fraction with the aerosol concentration fraction contained in air mass. We use the local air mass fraction to demonstrate the stronger influence of surface air mass to the top of boundary layer in the midday, but has not attempted to explicitly link this air mass fraction with the transport fraction of compositions. We have clarified this point in the revision.

6. line 157ff: It is pointed out that during the period of the measurement (wintertime) at both sites the conditions were dry (based on Fig. S6 RH<30% during CM periods) and relatively cold temperatures (-5.5 to 3.8 C). Both aspects are discussed in terms of being strong indications that no wet scavenging is taking place and most volatile species should be in the condensed phase. However these conditions also favor glass transition temperatures (Tg) for OA which could indicate that the aerosol might be in a semi-solid or "glassy" phase state (e.g. Koop et al., 2011) which might significantly hinder the evaporation of semi-volatile. Since the authors also mention the study by Koop et al., 2011 in the conclusion section and for the implication that an increase of the oxidation state of OA at the top of the BL might modify the viscosity of OA the possible effects on the relatively low humidity and low temperatures of a limited evaporation / equilibration time should be discussed and put into perspective in this section as well.
[Response] We thank the reviewer to point this out. We have now added related perspective discussions in the revision (Line 215-220).
"In addition, the bulk equilibrium between gas and condensed phase may be significantly hindered under conditions of lower temperature and lower RH due to the kinetically limited diffusion rate at the aerosol surface (Koop et al., 2011). Therefore, the viscosity of aerosols may be enhanced and OA may be present as semi-solid or glassy state under these conditions. This means the evaporation process may be eventually depressed, when aerosols are transported from lower and moister boundary layer to the upper level with lower temperature and moisture, hereby aerosols may be more solid-like and resistant to the evaporation."

7. Figure 1b): What does the color scale mean (particle concentration?) and what are the values and unit? Please add the information.
[Response] It is particle flux. We have revised this figure.

8. Figure 1c): What is the meaning of the dashed horizontal line? Please add explanation
[Response] Revised.

9. Fig. 4): Why was explicitly 0.8 chosen to be highlighted for the mountain/surface ratio for the species?
[Response] The 0.8 is the about transported fraction of BC mass and CO from surface to the mountain site. We have clarified this in the revised figure caption.
"Species with mountain/surface ratio above and below 0.8 (the transport efficiency for BC and CO) are marked in red and blue, respectively."

Technical comments
The readability of the English language in the manuscript varies significantly throughout the manuscript. Especially the English in the abstract and in the introduction needs to be improved

while the results and discussion section are well written. The beginning of the manuscript contains many phrases with missing or incorrect usage of articles, adjectives, adverbs, prepositions etc. which makes it unfortunately harder to read than necessary. In the following is a very incomplete list of examples for sentences which should be improved. I strongly suggest improving the English of the first sections.
[Response] We are thankful for the detailed comments and editing from the reviewer. We have gone through the manuscript with a native speaker for the improvement of language.

line 21: *"[...] subsequently interacting with clouds, serving important sources [...]"* should read [...] subsequently interacting with clouds, serving as important sources [...]
[Response] Revised.

line 24: *"[...] at both sits of urban Beijing [...]"* should likely mean "[...] at two sits, urban Beijing [...]"
[Response] Revised.

line 26: *"[...] top of PBL, [...]"* should read "top of the PBL"
[Response] Revised.

line 32: better would be "In combination [...]"
[Response] Revised.

line 37ff: *"The processes thermodynamically [..]"* The meaning of the sentence is not easy to understand and needs to be rephrased and should be split into more sentences and not enumerated using ";"
[Response] Suggestion accepted. The sentence was rewritten as below (Line 40-43):
*"*Gas-to-particle partition processes thermodynamically determine the production of secondary aerosol mass and the constituents of gases through condensation or evaporation process. The condensation process leads to gas molecular partitioning to the condensed phase, while the evaporation process occurs when aerosols were diluted in an environment with lower concentration (Donahue et al., 2006).*"*

line 77: *"[...] where represents the urban [...]"* should read "[...] which..."
[Response] Revised.

line 128: *"[...] suggesting the well mix [...]"* the phrase "the well mix" is odd. Do you mean "the well mixed layer"? please rephrase
[Response] Revised.

line 250: one "Acknowledgments" too many
[Response] Revised.

References

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