Reply on RC2
Quan Liu et al.

Author comment on "Reduced volatility of aerosols from surface emission to the top of planetary boundary layer" by Quan Liu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-362-AC2, 2021

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.

- 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.
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."

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 suggestions.

"...the 82% increase (from 0.19 to 0.34 µg m⁻³)"

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

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 fraction 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.”

- 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.

- 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.”

- 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.

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

- 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.