Reply on RC1
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-AC1, 2021

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.

- 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
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.

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.

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).”
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.

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.

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”.
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.

“Suggestion adopted. Please seen Line 89-98.

Line 82, which section.

This is revised.

Lin 85, COA is not resolved on the mountain, so it is not “four factors are resolved at both sites”.

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.

Suggestion adopted. We added the temporal variation of PBLH in Fig. 1d.

Line 119, a redundant space.

Revised.
Line 121, have you defined what BC is.

[Response] Yes, we defined BC as black carbon in section 2.2 (Line 123).


[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.


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.