

Dear ACP editor:

After reading the comments from you and the reviewers, we have carefully revised our manuscript. Our responses to the comments are itemized below.

Anything for our paper, please feel free to contact Prof. Gehui Wang via ghwang@geo.ecnu.edu.cn.

All the best

Can Wu

On behalf of Prof. Gehui Wang

September 30, 2022

Reviewer(s)' Comments to Author:

Reviewer 3

Comments:

This work investigated PM_{2.5} and nitrogen isotope composition at a high-elevation site of Mt. Hua and a nearby surface site. By comparing the analysis results of the two sites, the authors proposed a conceptual model to illustrate the different behaviors of nitrate and ammonium during vertical transport. NH₄NO₃ decomposes into gaseous NH₃ and HNO₃ during the transport, followed by heterogeneous reactions of HNO₃ and dust, leading to a shift of nitrate from fine to coarse particles. This chemical process has already been well documented in many previous studies. Additionally, the partitioning of ammonia toward the particle phase during vertical transport neutralized HSO₄⁻ from the surface and reduced the aerosol acidity. Due to the lack of direct evidence, synchronous PM characterizations at two sampling sites at different elevations can hardly explain chemical-dynamic processes. Here are my major comments.

Reply: Thanks for reviewer's valuable comments on improving our work. It is generally believed in prior work that the aerosol acidity would be enhanced during the transport from the polluted to cleaner/remote regions (Nault et al., 2021; Liu et al., 1996). Whereas, our finding revealed that the aerosol acidity can also be weakened in aging process, which was mainly due to the different physicochemical behaviors of the nitrate and ammonium. Currently, numerous chemical transport models cannot well commendably the profile of nitrate and ammonium. One of the reasons is poor understanding of aerosol-related processes of above two semi-volatile salts. Our work provides more insight into physicochemical behaviors above salts. To further substantiate our finding, we have added some evidences, e.g., organic tracer and meteorological field of the sampling site. See details below.

Comments:

This study assumes that the vertical transport of surface aerosols is the primary source of aerosols at the high-elevation site (MS site).

Besides the vertical transport, aerosols at the mountain top might also come from the subsidence of air parcel and horizontal transport, which is a possible cause for the difference in aerosol compositions and size distributions between mountaintop and ground surfaces.

As no atmospheric modeling was conducted to simulate the transport of air parcels, at least the meteorological field of the sampling location, we might not assure that the NH_4NO_3 observed at the MS area is coming from the air parcels from the MF area.

Maybe the difference in PM composition is also caused by source variations, not only by the difference in physicochemical behaviors. Could the authors rule out the possibility of source variation?

Reply: According to reviewer's advice, the WRF-Chem model was applied here to simulate wind field and the divergence that represents the expansion-rate of the air mass in unit time. As shown in the vertical distribution of divergence from the near surface up to 500 hPa (Figure 1(a)), the values of divergence at MF area were greater than zero and decreased with enhanced elevation, which would drive the upward motion of the surface air parcel. And the southerly winds that would blow the pollutants into the valley prevailed at mountain foot area during the whole campaign (Figure 1(b)). These favourable meteorological conditions manifest that the surface pollutants can be transported to the upper layer by the updrafts. In addition, a westerly dominates the upper layer (above 800

hpa), of which speeds increase with enhanced elevation, indicating the significant horizontal motion of air mass in these areas. Whereas, the MS site is far below these layers, and is blocked by mountains in both east and west directions. Thus, we think that the horizontal transport may be not the major sources for the pollutants at MS site when it's inside the boundary layer.

To rule out the change of emission sources during the vertical transport, we further analyzed the organic compounds in PM_{2.5} samples, e.g., levoglucosan, BkF and IP+BghiP, which are major tracers for the emissions from biomass burning, coal combustion and vehicle exhausts, respectively (Wu et al., 2020; Wang et al., 2009; Wang et al., 2007). From Figure 2, indistinctive divergences of diagnostic ratios and proportion of these organic tracers were found among both sampling sites, suggesting an insignificant change of the corresponding emission sources. Given all this, the new evidences can strongly endorse our conclusions. Above discussions have been added in the manuscript. See page 15, line 320-333.

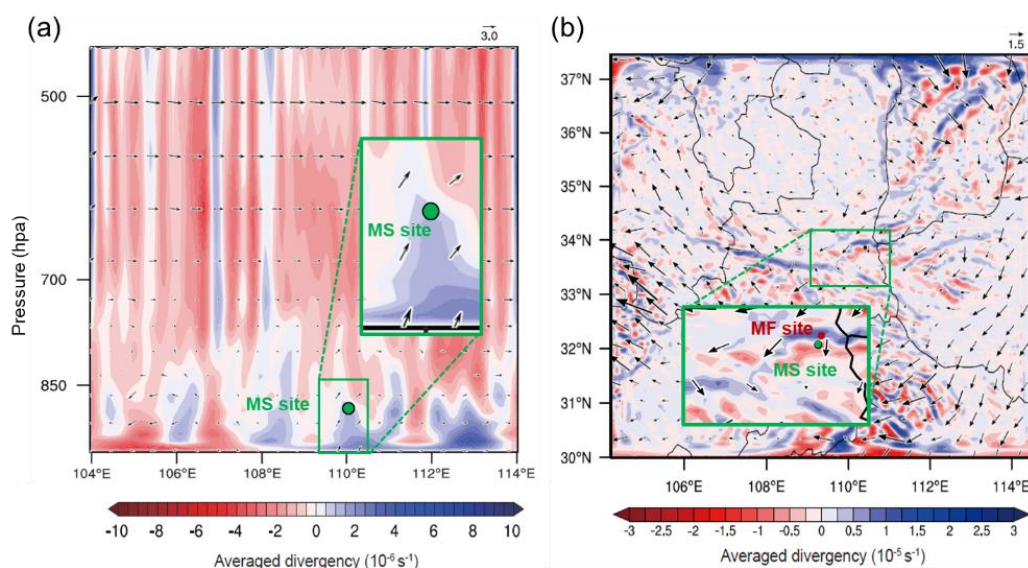


Figure 1 The distribution of averaged diurnal divergence over the whole campaign, with corresponding wind filed. (a) Longitude-pressure cross-sections at 34°29'N. (b) Horizontal distribution at surface. Wind speeds were represented by arrows sizes, and the W component of wind vectors was magnified 10 times.

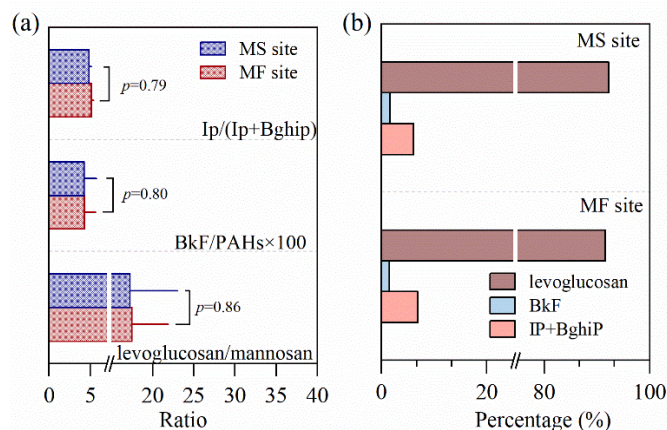


Figure 2 The mass ratio and proportion of organic tracers at two sampling sites.

Comments:

Have the authors considered the time scales of vertical transport and atmospheric reactions mentioned in this work? Maybe the transport time between the two sites is shorter than the chemical-dynamic processes proposed in this work.

Reply: As depicted in Figure 1(a), the vertical wind speed was really low with averaged value $< \sim 0.12$ m/s at the layer blow 850 hpa, indicating that the vertical motion of air mass was not as fast as expected. We simply evaluated transport time by using above speed, and found that it would take about 1.7 hours for the air parcel to move up MS site from MF site. However, as revealed by the laboratory smog chamber simulations (Liu and Abbatt, 2021; Zhang et al., 2022), the secondary ions can be rapidly generated on the initial seeds when the corresponding precursor gases were introduced in the chamber for a few minutes (Figure 3). The semblable phenomenon was also discovered in the filed observation (Wang et al., 2016). Thus, we think the chemical-dynamic processes proposed could be complete within the transport time between two sampling sites.

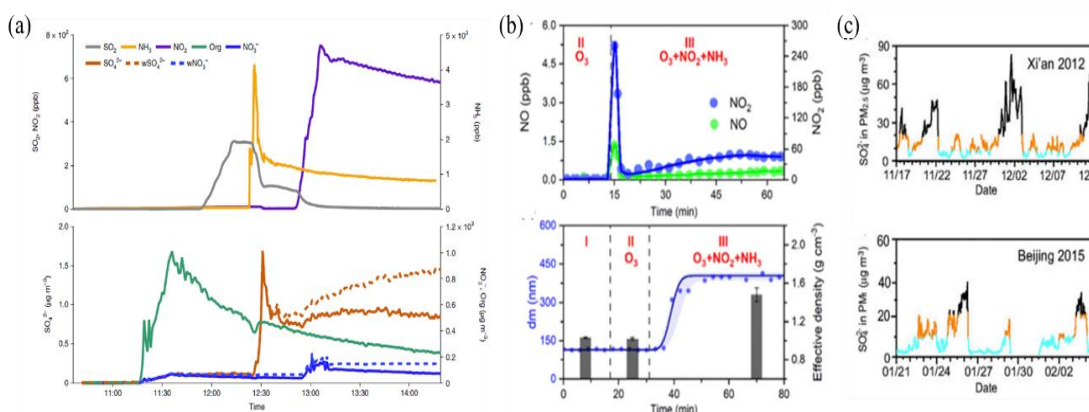


Figure 3 Smog chamber simulation experiments for secondary ions (a and b) (Liu and Abbatt, 2021; Zhang et al., 2022). The variation of sulfate concentration during pollution episodes in Xi'an and Beijing, China (c) (Wang et al., 2016).

Comments:

Lines 124-125. Are there any studies investigating chemical-dynamic processes that drive haze episodes in the lower troposphere using observations at high-elevation mountain sites? Please provide examples.

Such observations might only reflect the difference in aerosol chemical composition and properties between ground and high-elevation sites, but not the chemical-dynamic process.

Reply: Sorry for our inaccurate expression. It was indeed scarce of the study to investigate above chemical-dynamic processes by using field observation only. To avoid ambiguity, we rewrote the sentences. See page 6, line 125-127.

Comments:

Lines 330-334. Why does the similarity in mass concentrations of sulfate and ammonium at the two sites indicate further formation during the transport? Couldn't these two ions be formed at the MS site?

Reply: Based on the statistical analysis, the averaged concentration of sulfate was $9.2 \pm 7.1 \mu\text{g}/\text{m}^3$. Whereas, more than 75% data had the SO_2 concentration below $8.0 \mu\text{g}/\text{m}^3$ (Figure 4). Similar phenomenon was also found in the ammonia. Thus, we think that the precursor masses were insufficient to form so much sulfate and ammonium only at MS site.

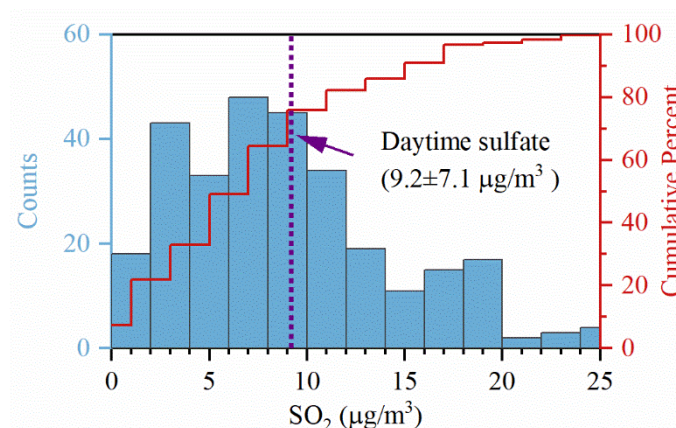


Figure 4 The statistical analysis of SO_2 concentrations measured at MS site over 8:00-19:00.

Comments:

Lines 335-336, many components show increased concentrations with elevation, like Na^+ and K^+ . Except for NO_3^- , only Ca^+ , OC, and PM showed decreasing trends.

Reply: Thank you for reminding. Due to the different filter manufacturers, the filters for

the mountainside samples collected during 8/27-8/29 have a higher background level of Na^+ than that of the remaining ones (Figure 5). But we inadvertently used a lower background value (i.e., the Na^+ concentration in blank filter for the sample collected during 8/29-9/17) to deduct the background interference for the samples in above three days. This led an overestimation of the sodium concentration, and a higher sodium concentration at MS site. In the revised manuscript, the Na^+ concentrations have been modified by using the correct background values, which exhibited a higher value at MF site after correction. As depicted in Figure 5, worth noting that background levels of other ions in the filters using over these three days were extremely low, and there's almost no change in their concentration especially for SNA. Furthermore, in the previous version, the rounding of the data results in the same values in Cl^- and Mg^{2+} concentrations at two sites.

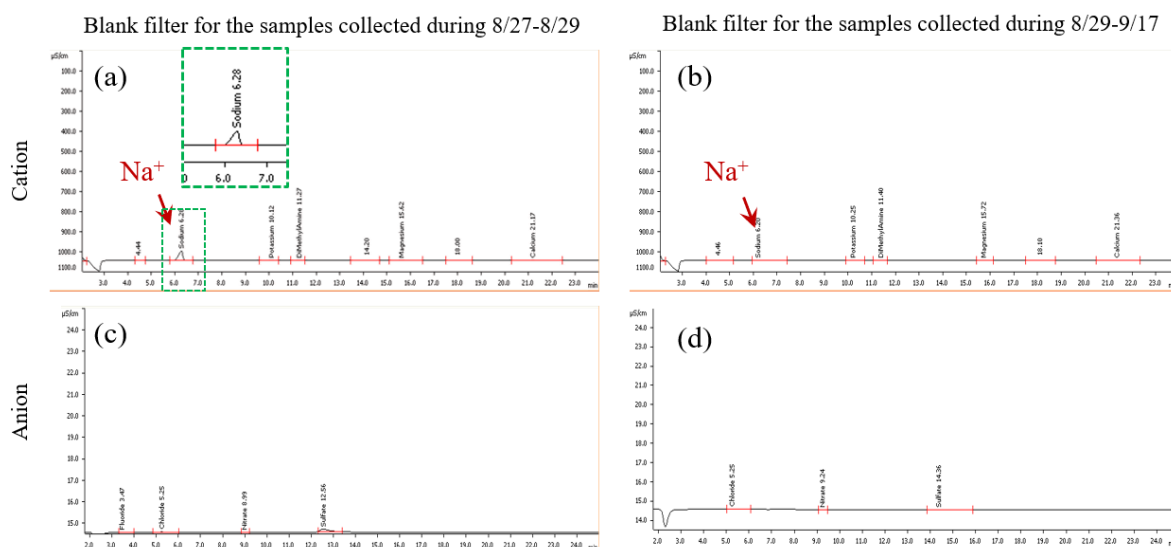


Figure 5 The chromatograms of ions extracted from different blank filters.

Comments:

Lines 351-357, the shift of fine mode nitrate toward the coarse mode was well documented in previous work. Did the temperature increase with elevation? Since the dissociation of NH_4NO_3 tends to happen in warmer periods or areas, why high-elevation nitrate exhibited a bimodal pattern, but not the surface nitrate? Are the size distribution data of PM at the two sites available? The size distribution of nitrate might be closely related to the PM size distribution.

Reply: The temperatures recorded at both sampling exhibited a decreasing trend with elevation. As shown in Figure S6(a), the surface nitrate was also distributed in the coarse mode that only accounts for very small fraction of the total nitrate. This feature conformed

to other surface field observations in the summertime (e.g., Beijing, Yangtze River Delta) (Wang et al., 2015; Yang et al., 2017). At MF site with high temperature, the NH_4NO_3 did have a relatively high volatilization rate, even so it still needs sufficient time to achieve the volatilization amount that may change the particle size distribution. Whereas, NH_4NO_3 particles aloft were derived from aerosol at ground, which would be undergo volatilization and heterogeneous reaction (e.g., $\text{HNO}_3(\text{g}) + \text{fugitive dust}$) during whole transport process. This finally results in the accumulation of nitrate on the coarse-mode particles at high elevation. Furthermore, such a bimodal mode of nitrate was also found on mountaintop of Mt. Hua as revealed in our previous study (Wang et al., 2011). Thereby, we think that above size distribution may be common at high-elevation of Mt. Hua.

Comments:

Lines 367-373, could the decrease in nitrate concentration at the MS site be partly caused by dilution during the transport? As shown in Figure S1, NO_2 concentrations at the MS site are way lower than the MF site, and no information on NH_3 and SO_2 concentrations was available.

Reply: The boundary-layer growth at daytime did lead to the nitrate concentration decrease to some extent. To eliminate the dilution effect caused by the enhanced by boundary-layer, we further discussed the proportion of nitrate in $\text{PM}_{2.5}$, which also exhibited a decreasing trend with enhanced elevation as depicted in Figure 5. Thus, we think that the decreasing nitrate mass concentration was not mainly driven by the boundary-layer growth at daytime.

Comments:

Lines 405-408. Why was the MS site an ammonia-poor environment? NH_3 was not measured in this study, and sulfate and nitrate were almost fully neutralized by NH_3 .

Reply: Sorry for our inappropriate expression. We just want to express that the ammonia level at MS site was relatively low compared to that at MF site, according the observational data collected during 2020 summertime. The sentence has been rewritten in the revised manuscript, see page 20, line 432-437.

Comments:

Lines 409-423. The authors provided a possible explanation for the change in the chemical forms of sulfate and bulk $\text{PM}_{2.5}$ pH from MF to the MS site. However, have the authors considered the change in aerosol water content from the MF to the MS site? Would the

changes in chemical forms of sulfate and pH be caused by variations in aerosol water content?

Reply: Based on the statistical analysis, the aerosol liquid water contents (ALWC) at MS site and MF site were $26.9 \pm 71.4 \mu\text{g}/\text{m}^3$ and $27.6 \pm 63.9 \mu\text{g}/\text{m}^3$, respectively, indicating an indistinctive change among two sites (Table 1). Furthermore, we artificially enhanced the ALWC by 50%, and recalculated the aerosol pH at both sampling sites. As shown in the Figure 6, ~7% of pH was changed when the ALWC increased by 50%, which indicated that the aerosol pH in this study was insensitive to the ALWC change. Thus, we think that the change in chemical composition was the major reason for the different acidity among two sampling sites. Above discussions have been added in the revised manuscript. See page 21, line 448-453.

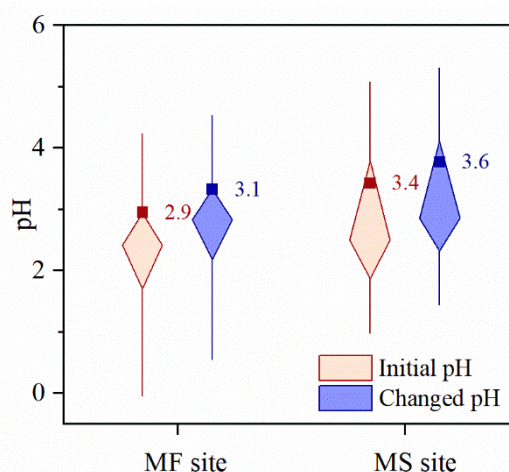


Figure 6 The comparison of pH by changing the ALWC at both sampling sites.

Comments:

Lines 425-436. The authors mentioned that the temperature decreased from MF to the MS site (line 433), why is volatile NH_4NO_3 easily converted to gaseous NH_3 and HNO_3 during the transport? Theoretically, more NH_4NO_3 should be formed through gaseous reactions at the MS site with lower temperatures.

Reply: As revealed by previous studies (Arthur et al., 1982; Bergin et al., 1997), dissociation constant of NH_4NO_3 (K_p) is related not only to temperature but also to relative humidity. As the RH decrease, the K_p enhances, indicating a higher evaporation rate of NH_4NO_3 from the particles. However, the RH at MS site was lower than that at MF site, which would promote NH_4NO_3 volatilization at MS site. As depicted in the next question, the lower value of $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p$ at MS (Figure 7) also conforms to above conclusion,

implying that NH_4NO_3 at MS site tend to remain in gaseous phase.

Comments:

Lines 453 – 455, would the authors explain the inconsistent calculation compared to Lindaas et al. (2021)? Could it be attributed to the large uncertainties in the empirical calculations of $P_{\text{HNO}_3} \times P_{\text{NH}_3}$ and K_p ?

Reply: Thank you for reminding. There are indeed some uncertainties in the empirical calculations of $P_{\text{HNO}_3} \times P_{\text{NH}_3}$ and K_p as indicated by a wide range of $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p$ ratios. To minimize the uncertainty caused by data dispersion, we only choose the 15th ~ 85th percentiles of the data points ($P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p < 1$) to further verify the result, which is same as that described in the manuscript (Figure 7). Therefore, we think that the phenomenon about a lower $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p$ ratio at high-elevation did exist during the campaign. The aircraft observations conducted by Lindaas et al. (2021) were mainly focused on the wildfire smoke plumes aloft, which usually contains abundant NH_3 and NO_x . This would lead to a higher NH_3 and HNO_3 mixing ratio compared to that at lower elevation, and drive a higher $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p$ ratio at the upper layers.

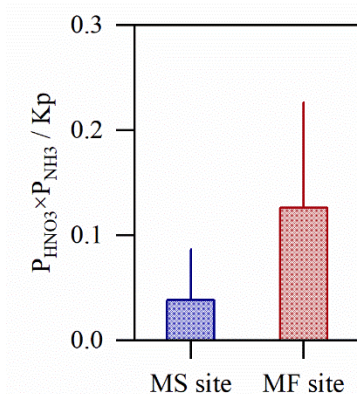


Figure 7 Comparison of $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p$ ratio among both sampling site. (15th ~ 85th percentiles of the data points with $P_{\text{HNO}_3} \times P_{\text{NH}_3} / K_p < 1$)

Comments:

In this work, the authors always assumed that NH_4NO_3 was in an aqueous state. But K_p is the dissociation constant of dry salts. Will aerosol water content impact the dissociation of NH_4NO_3 ?

Reply: As previously mentioned, the aerosol liquid water contents (ALWC) show an indistinctive change between MS site ($26.9 \pm 71.4 \mu\text{g}/\text{m}^3$) and MF site ($27.6 \pm 63.9 \mu\text{g}/\text{m}^3$) (*t*-

test, $p=0.83$). This a little discrepancy of ALWC among both sites indicated that the ALWC may be not the major driving factor for NH_4NO_3 dissociation or evaporation. Furthermore, the experimental discovery by Harrison et al. (1990) also demonstrated a little difference in the evaporation rates of dry NH_4NO_3 aerosol (-0.45 \AA/s) and aqueous ones (-0.49 \AA/s) at $20 \text{ }^\circ\text{C}$. Thus, we think that the ALWC may have a slight effect on the dissociation of NH_4NO_3 in our study.

Comments:

Lines 460-494. The sources of NH_4^+ and NO_3^- at the high-elevation site are probably not the same as those collected at the MF site, and this might lead to the difference in $\delta^{15}\text{N-NH}_4^+$ and $\delta^{15}\text{N-NH}_4^+$ values at the two sampling sites.

Reply: As we answered to the first question of the reviewer, the mass ratio and proportion of organic tracers exhibited an indistinctive divergence among both sampling site, indicating an insignificant change in pollutant sources. Thus, we think that the difference in $\delta^{15}\text{N-NH}_4^+$ and $\delta^{15}\text{N-NO}_3^-$ values at the two sampling sites was mainly driven by physicochemical processes rather than the change in emission sources.

Minor corrections

Lines 60-61, abstract. Define MS and MF where they first appear.

Reply: Suggestion taken.

Minor corrections

Lines 165-167, what type of aerosols was sampled? $\text{PM}_{2.5}$, PM_{10} , or TSP.

Reply: Sorry for our inaccurate description. We have changed the expression as “the $\text{PM}_{2.5}$ aerosol samples with a 4-hr interval” in the revised manuscript. See page 8, line 168.

Minor corrections

Line 342, typo, “so much”, not “so such”.

Reply: Suggestion taken.

Minor corrections

Line 453, typo, Change “that” to “than”.

Reply: Suggestion taken.

Reference

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