The paper by Zha et al. presents a study of the chemical composition of naturally charged molecular clusters present at the high altitude site of Chacaltaya, located in the Bolivian Andes. This analysis is mainly based on measurements performed with an APi-TOF during 5 months, in the framework of the SALTENA campaign (Jan-May 2018), and also includes results obtained from the simultaneous deployment of a nitrate CI-APi-TOF at the site. Concerning positive ions, the analysis focuses on the study of the diurnal cycle of the observed signal. For negative ions, on the other hand, the observations conducted over a period of 3 months belonging to distinct seasons (wet, wet to dry transition and dry) allow, in addition to the analysis of the diurnal cycles, the study of seasonal contrasts, in connection with the variability of the origin of the air masses sampled at the site; the involvement of the identified clusters in NPF, which is particularly frequent at the site during the dry season, is also rapidly explored.

This study provides observations of interest regarding the composition of the troposphere and the understanding of specific processes such as NPF; these data are all the more valuable as the process remains globally less well documented at high altitude than at low altitude. I also find the paper very clear and well written. I therefore recommend its publication in ACP. However, I have some questions and suggestions listed below.

P3, L94-95 : I would suggest adding here the review on high-altitude NPF by Sellegri et al. (2019), which includes a section that specifically discusses the role of ions in the process.

P4, L139: The paper by Collaud Coen et al. (2018) investigates the degree of influence of the boundary layer at different high altitude sites but does not specifically address/describe the variability of conditions at the sites in relation to the diurnal cycle of the boundary layer height. These aspects are instead specifically discussed for Chacaltaya in two previous publications: Rose et al. (2015) and Chauvigné et al. (2018).

P6, L167: “we only included the ion data from cloud-free days in this study”: I would find it useful to have more information on this filtering process:
- What measurement/method was used? Does the filter only concern clouds detected at the station's altitude, or also clouds that may be above?
- How much data was excluded? Is there a marked variability from month to month?

P6, L188-189: “The instrument can detect air ions with a diameter from 1.4 to 50 nm”: two size ranges (corresponding to the two operating modes of the instrument, i.e. naturally charged ions vs total particles) are usually reported (e.g. Manninen et al., 2010: 0.8 – 42 nm for naturally charged ions and ~2 -42 nm for particles), and the range reported here does not correspond to either of the traditionally reported ranges: is the observed difference explained by taking into account the (low) pressure at the site in the calculation of the mobility diameters from the electrical mobilities?

Also, without going into a detailed description of the instrument and its operation, I think it would be useful to say few words about the two measurement modes it allows (naturally charged particles vs. total particles), since the data from these two modes are discussed in the paper and they are in particular characterised by different cut-off diameters due to the presence of charger ions in the “total particles” mode.

P8, L243-244: “the representative periods cannot be directly identified via SRR[%]pathway values (e.g., using a certain threshold of the value) as in a previous study (Koenig et al., 2021).”: in order to clarify the explanation, I would suggest indicating briefly why the approach discarded here was possible in the study by Koenig et al. (2021) (longer dataset?).

P12, L328-334 : While both the abundance of the neutral parent species and its EA are discussed to explain the variations observed for $(HNO_3)_{0-1}\cdot NO_3^-$ and $(H_2SO_4)_{0-3}\cdot HSO_4^-$ (and indirectly $(NH_3)_{1-6}(H_2SO_4)_{3-7}\cdot HSO_4^-$) ion groups, only the EA is mentioned in the analysis of the MA-derived ion group. Does this mean that the abundance of malonic acid plays no role in the observed variations?

P12-13, L335-350 and P16, L445-462: Regarding the CHO/CHON·(HSO_4^-/NO_3^-) ion group. The authors highlight both diurnal and seasonal variability (Sect. 3.2.2) in the fraction of negative clusters made up by the CHO/CHON·NO_3^- and CHO/CHON·HSO_4^- groups. In Sect. 3.2.2 the variability in the composition of the OOM (i.e. CHO/CHON) is also discussed but while two figures are presented (Fig. 7.b and S6.b) to distinguish the day/night observations, the analysis is mainly focused on the influence of the different air mass origins, although there are also sometimes marked diurnal contrasts. In particular, a possible link to the day/night contrasted conditions related to the dynamics of the atmospheric boundary layer (as mentioned P4, L135-139) is not discussed, while the study by Beck et al. (2021) shows for example that the negative cluster ions observed in the different atmospheric layers above the boreal forest have different chemical composition. Can the authors comment on this point?

P14, L406: should be Fig. 6b instead of 7b.

P19, Sect. 3.4 :

- ➔ Yan et al. (2018) showed that there is a priori a link between the number of H_2SO_4 molecules present in H_2SO_4-NH_3 anion clusters and the occurrence of ion induced nucleation in the boreal forest. Did the authors observe, in addition to the link between the occurrence of NPF and the increase in the signal of the $(NH_3)_{1\text{-}6}(H_2SO_4)_{3\text{-}7}\cdot HSO_4^-$ clusters as a whole (Fig. 10.c), such kind of relationship at Chacaltaya? More broadly, in addition to the impact of the identified compounds on the occurrence of NPF, is there an impact on the type (occurrence of growth or only burst, continuous or interrupted growth) and/or intensity (particle formation and/or growth rates) of the events?
- ➔ As illustrated in Figure S7, and consistent with the previous results of Rose et al. (2015), the highest NPF frequencies are observed during the dry season. Figure 2 shows the frequent arrival of air masses from the Pacific Ocean at the site during this period, again consistent with the results of Rose et al. (2015) who also show a NPF probability close to 100% in these air masses. However, based on this previous work, the observed events seem to be triggered once the air masses arrive on the continent, suggesting that these air masses of marine origin may not directly contain the nucleating species but have a generally favourable character (e.g. low CS) allowing the nucleation of continental species. In Sect. 3.2.1 (P10, L289), the authors quickly mention the identification of IO_3^- but do not mention other compounds of marine origin: are they absent from the spectrum? In view of the results in Fig. S7 and 2, I believe that a more developed discussion of the presence or absence of these marine-derived compounds would be welcome in this study, and would in particular complement the analysis of Rose et al. (2015) regarding the understanding of the favourable character of marine origin air masses for NPF.

P21, L554-556: the comparison with the results obtained on non-event days seems necessary to evaluate the importance of the variability observed on event-days and the associated conclusions.

Fig. 1: I find it confusing that the marker representing Chacaltaya is so close to the “La Paz” indication on panel a. Since panel b is specifically intended to illustrate the positioning of La Paz in relation to the station, I would not include La Paz on panel a to avoid confusion.

Fig. 2: While I understand the general meaning of the results presented in Fig. 2b, I do not understand the unit used on the y axis.

References:

Beck, L. J., Schobesberger, S., Junninen, H., Lampilahti, J., Manninen, A., Dada, L., Leino, K., He, X.-C., Pullinen, I., Quéléver, L. L. J., Franck, A., Poutanen, P., Wimmer, D., Korhonen, F., Sipilä, M., Ehn, M., Worsnop, D. R., Kerminen, V.-M., Petäjä, T., Kulmala, M., and Duplissy, J.: Diurnal evolution of negative atmospheric ions above the boreal forest: from ground level to the free troposphere, Atmos. Chem. Phys., 22, 8547–8577, https://doi.org/10.5194/acp-22-8547-2022, 2022.

Chauvigné, A., Aliaga, D., Sellegri, K., Montoux, N., Krejci, R., Močnik, G., Moreno, I., Müller, T., Pandolfi, M., Velarde, F., Weinhold, K., Ginot, P., Wiedensohler, A., Andrade, M., and Laj, P.: Biomass burning and urban emission impacts in the Andes Cordillera region based on in situ measurements from the Chacaltaya observatory, Bolivia (5240 m a.s.l.), Atmos. Chem. Phys., 19, 14805–14824, https://doi.org/10.5194/acp-19-14805-2019, 2019.

Sellegri, K., Rose, C., Marinoni, A., Lupi, A., Wiedensohler, A., Andrade, M., Bonasoni, P. and Laj, P. : New particle formation : a review of ground-based observations at Mountain research stations, Atmosphere, 10(9), 493, https://doi.org/10.3390/atmos10090493, 2019.

Yan, C., Dada, L., Rose, C., Jokinen, T., Nie, W., Schobesberger, S., Junninen, H., Lehtipalo, K., Sarnela, N., Makkonen, U., Garmash, O., Wang, Y., Zha, Q., Paasonen, P., Bianchi, F., Sipilä, M., Ehn, M., Petäjä, T., Kerminen, V.-M., Worsnop, D. R., and Kulmala, M.: The role of H2SO4-NH3 anion clusters in ion-induced aerosol nucleation mechanisms in the boreal forest, Atmos. Chem. Phys., 18, 13231–13243, https://doi.org/10.5194/acp-18-13231-2018, 2018.