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Chemical analysis of the Asian Tropopause Aerosol Layer (ATAL) with emphasis on secondary aerosol particles using aircraft based in situ aerosol mass spectrometry

Appel et al.

Replies to the comments by Anonymous Referee #2

General Reply:
First of all, we would like to thank Referee #2 for the positive and constructive feedback. In the following, we will comment on the individual points.

The reviewer comments are written in black.

Our answers are written in blue.

Changes to the revised version of the manuscript are printed in red.

Review of "Chemical analysis of the Asian Tropopause Aerosol Layer (ATAL) with emphasis on secondary aerosol particles using aircraft based in situ aerosol mass spectrometry"

This paper discussed the unique aerosol and gas measurements aboard a high-altitude aircraft. It provided a promising dataset for atmospheric research, especially for understanding the aerosol particle composition within the Asian Tropopause Aerosol Layer (ATAL). The authors presented a very useful tool – ERICA-AMS for the atmospheric study and shared the exciting results from July and August 2017. The paper is well written. The topic is well aligned with the journal scope and should be considered for publication after minor revision.

Specific comments:

Page 9, lines 256-262. The discussion about Fig 2 in this section can not support this statement. "Consequently, the ATAL chemical composition is largely determined by the relative contributions of new particle formation and secondary particle growth at altitude compared to the upward transport of already nucleated secondary or of primary particles from below." Maybe include the gas phase measurements to indicate the new particle formation trend?

We agree. We removed this sentence.

Figure 2 showed the sulfate concentration increased from 0.5 – 1 .5 ug/m^3 above 19 km. However, Figure 3 showed that the particle number concentrations from COPAS or UHSAS were less than 90 #/cc. What does the size distribution above 19 km? Are those particles all

sulfuric acid? Even if we assume they were ammonium sulfate and larger than 110 nm, the integrated mass seemed still lower than the AMS data.

Yes, all these particles are sulfuric acid, or at least contain a coating of sulfuric acid. Our first analyses of the single particle data show that practically all negative ion spectra contain lines with sulfur fragments. (Pure sulfuric acid can not be detected by our 266 nm laser ablation system.) Thus, the single particle analysis and the acidity analysis show, that the particles above 19 km are mainly sulfuric acid containing particles. A juxtaposition of the AMS with the UHSAS data here is quite difficult, because: (1.) The detected size ranges of both instruments are not the same, especially for the large sizes. Also, the sampling inlets are quite different. (2.) The particle diameter definition of the UHSAS is optical diameter, calibrated with the refractive index of PSL. Thus the sizing of the UHSAS can deviate from particles with a different index, which is difficult to estimate because of the inclusions of primary material components in the particles. (3.) As mentioned by Mahnke et al. (2022), a custom-made pump system had to be integrated in order to operate at low pressures. There might be yet unquantified losses inherent in the inlet system. In order to resolve these issues dedicated laboratory experiments are planned for the future application of the UHSAS and ERICA during the ACCLIP campaign with HIAPER (2022) and the PHILEAS campaign (2023) with HALO.

Figure 5: are those data points are from the averaged data? If so, what is the uncertainty?

The data are the median values in individual altitude bins. We have included percentiles for nitrate and uncertainties for NO in the graph and added the following text to the caption:

The horizontal bars reflect the 25th to 75th percentile range for nitrate and the vertical bars present an uncertainty of 30 % for NO.

Section 3.3 provided essential information about the mixing state of the aerosol particles. The abstract also mentioned, "…the majority of the particles encountered in the ATAL consisted solely of secondary substances, namely an internal mixture of nitrate, ammonium, sulfate, and organic matter. These particles are externally mixed with particles containing primary components as well." Does the mixing state remain the same at different aerosol particle sizes? Do you see a spatial variance in the mixing state?

Figure 10 shows the size distributions of purely secondary particles (type 1 represents mainly ATAL particles) as well as the primary/mixed type, restricted to particles in the ATAL. While the secondary particles show the highest fraction at a vacuum aerodynamic diameter between 200 and 300 nm, particles containing primary material show a much wider distribution. Thus, the mixing state significantly changes with size, smaller particles being mainly secondary type, whereas larger particles often contain primary material.
A spatial variance was not observed in our analysis up to now. The results are being prepared for a forthcoming new manuscript. There we will pick up and address the reviewer's question/suggestion regarding a potential spatial inhomogeneity.

Figure 10, It is not clear to me what the particle fractions for each particle type are. For example, at 300 nm, primary was 15%, type 1 – 65% or 40%, type2 68% or 5%? Should they add up to 1?

The particle fractions are cumulative, thus in the example of 300 nm: ~15% primary inside the ATAL, ~45% type 1 and ~5% type 2. The fractions do not add up to one, because primary particles found outside the ATAL, as well as unidentified particles are not included. To clarify this we have included the following into the caption:

The distribution of primary particles is limited to particles in the ATAL, thus the fractions do not add up to one.

Figure 14, why is there no data above 19 km?

R44_43 includes a fraction of data for organics, org44 and org43. We only show data points, where all three values are above the calculated detection limit for the corresponding vertical bin. Due to the low values for organics concentration and thus org44 and org43, this is not the case for data above 19 km. In response the reviewer's question, we changed the caption to:

Only data points are shown where values of organic mass concentration as well as org44 and org43 signals are above the detection limit of the corresponding vertical bins. This condition is not fulfilled above 19 km and 440 K.

Line 528: 'The ERICA mass spectrometry data will be available in the Edmond database (Edm, 2017) and the Halo database (Hal,2017).' Should data be available by now?

After addressing technical issues, the data are available at the EDMOND database since 10.03.2022. The data are also uploaded to the HALO database. The mission PI will make the data on the HALO database publicly accessible at some point in the future. The citations of the databases have been re-worded.

The ERICA mass spectrometry data are available from the Edmond database (Edmond, 2022) and will be additionally available from the HALO database (HALO-DB) (HALO-DB, 2017) in the near future.

In addition to the changes in reply to the referees comments:

Line 136: 20.5 km instead of 20.0 km. 20.0 km was the maximum pressure altitude reached, 20.5 km for GPS altitude.

Line 541: FP7/ instead of FP/

Fig.2: Caption has been changed from organic to organics and scale reduced to 2 µg/m^3 to improve the visibility of the enhancement in the ATAL.

We added to the caption of Fig. 2: Concentrations in the boundary layer can exceed the displayed range.

Supplementary figures S2-S9: Caption has been changed from organic to organics.

In the introduction, one sentence is added introducing the new paper by Wang et al., 2022, which appeared on May 18, 2022. (Wang et al., Synergistic HNO3–H2SO4–NH3 upper tropospheric particle formation, https://doi.org/10.1038/s41586-022-04605-4, Nature, 2022)

According to the reviewers suggestions, we looked into the GLORIA measurements of acetylene on July 31 (Johansson et al., 2020). For this reason, we re-worded the sentence in lines 438-439 as follows:

The mixing ratios of acetylene measured with the GLORIA instrument feature increased values in the upper troposphere and even in the lower stratosphere (Johansson et al., 2020).