

EGUsphere-2024-7

The influence of extratropical cross-tropopause mixing on the correlation between ozone and sulfate aerosol in the lowermost stratosphere

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Author comments to Reviewer #1

The reviewer comments are written in this font style and color.

Our answers are written in this font style and color.

Changes in the revised version of the manuscript are written in red.

In this work the authors suggest an alternative tracer-tracer metric for exploring the ‘Extra-tropical Transition Layer’ using the correlation between sulfate aerosol and ozone. The work is based on aircraft measurements of aerosol sulfate using an Aerosol Mass Spectrometer aboard the DLR HALO aircraft and trace gas measurements from the HALO and DLR-Falcon from 2020 over central Europe. In part 1 the authors show a robust relationship between sulfate and ozone near the tropopause, and seek to use the variability in this relationship to identify atmospheric processes, of particular interest is the persistent minima in sulfate mixing ratio near the tropopause. In part 2, the authors identify a specific case of enhanced sulfate from one ascent in one flight and then perform an analysis to conclude that this enhancement is the result of mixing through the ExTL followed by gas to sulphate aerosol conversion from a distant volcanic eruption.

We thank the reviewer for reading our paper carefully and providing comments to improve the manuscript.

Major comments:

- 1. The correlation between aerosol sulfate and ozone is interesting, and establishing a background ratio is useful to identify perturbations in sulfate aerosol on top of the steeply sloped vertical aerosol gradient. However, the analysis of aerosol sulfate seems to be performed in isolation from the other aerosol properties that must surely have been made on the same measurement platform, or even by the same instrument (the C-ToF-AMS). In terms of the analysis in part 2 of the enhanced sulfate plume observed in RF01, a discussion of the aerosol size distribution and the variation of other chemical constituents (particularly organics and nitrates) would provide both context and a much more convincing argument that this particular enhancement is volcanic in origin. Furthermore, including the size distribution of the observed sulfate would reassure the reader the analysis of the C-ToF-AMS is actually capturing the bulk of the sulfate aerosol within the somewhat limited size range.*

It may seem that the performed analysis was done isolated from the other properties that were measured by the C-ToF-AMS (e.g., organics, nitrate and ammonium mass concentration as well as the particle size distribution measured by the SkyOPC), but we also looked carefully at the whole set of available data. The results are not shown here explicitly, because we did not observe the same unexpected results in the data as we did for the sulfate concentration. However, we added the time series and vertical profiles of all species measured by the C-ToF-AMS as well as the size distribution measured by the OPC to the supplement information (Fig, E1- E4) to complete the picture.

- 2. The authors make a convincing argument that the enhancement observed on RF01 is in fact anomalous and possibly of tropospheric origin (figures 5, 6 and 8). However, the argument that this enhancement is of volcanic origin and is due to gas to particle conversion in the ExTL is less convincing. The authors seem to start with the conclusion that this is in fact a volcanic event, then search for a candidate volcano and use a combination of forward and backward trajectory models to try and link the observation to the event, which is convoluted and unconvincing. A more convincing argument to show this event is volcanic in origin (and not anthropogenic for example) would be to present the total aerosol composition and size distribution, as discussed above. It is also interesting that RF01 only observed this enhancement on one or maybe two climbs of the flight, despite reaching higher altitude and theta on the subsequent climb. Is this enhancement limited in geographic scope? Without a broader analysis and a more convincing identification of the source of gas phase sulfur, part 2 of the paper is of less scientific relevance than part 1.*

We agree with the reviewer that Figs. 5, 6 and 8 are the main figures which show the anomalous observation of enhanced sulfate in the lowermost stratosphere. We want to point out that Fig. 9 is also (very) important for the argument of gas-to-particle conversion. It clearly shows enhanced sulfur dioxide in the UTLS region (as described by Tomsche et al. (2022)) which decreased along one mixing line in the correlation framework. To emphasize the volcanic origin, we added the size distribution and the vertical profiles of the complete AMS species to the supplement as mentioned above. These show that only the particulate sulfate is enhanced within the anomaly. Furthermore, this enhancement of sulfate aerosols correlates with an increase in the total aerosol number concentration along the observed mixing line which shows that no tropospheric compounds are directly mixed into the LMS. Additionally, the size distribution shows that during the measurement period of the anomaly up to a factor of two more particles with diameters below one μm were observed. Further, we want to state that models show that the Shiveluch volcano had an impact on the measurement region, but these results are preliminary and planned to be published later this year.

Regarding the geographic scope of the anomaly, we have to admit that the flight planning during the campaign was focused on the PBL and the troposphere and not on the UTLS region, so the results might be biased by the flight pattern with only short times in the UTLS region. In addition, in the planned publication mentioned above, we will analyze the geographic extent of the volcanic plume in model simulations.

Minor Comments:

The figures are not well aligned with the text that references them, making it difficult to reference while reading the text.

We reorganized the figures in the revised version with fixed positions to simplify reading and referencing.

Line 28: I am not sure what you mean by 'photochemical dissolving'?

We rephrased the sentence to describe the origin of OCS as follows:

OCS is the main sulfur containing trace gas in the atmosphere with direct emissions by the oceans or biomass burning as well as photochemical production by oceanic emissions like DMS or CS₂.

Line 71 / Section 2.1: It may be important to note the limitation of the HALO aircraft measurement with respect to altitude – it appears to be limited to a peak altitude of around 12km, which may not really reach the top of the ExTL in May at latitudes below about 45N leading to a bias to higher latitude measurements.

We agree with the reviewer that it is important to note the limitation of covering the complete vertical structure of the ExTL in May. However, peak altitudes, also during RF01, were around 14 km. HALO's ceiling altitude is above 15 km, but during this campaign the scientific questions focused on vertical profiles close to urban areas and the tropospheric chemistry during COVID-19 lockdown. We added the following sentences:

... This point leads to flight planning during the campaign with focus on urban areas and low altitude profiles and less on studying processes in the UTLS region. Therefore, it was not possible to conduct measurements over the complete vertical extent of the ExTL during May 2020. Nevertheless, we were able to obtain measurement data up to 14 km altitude. During the campaign period...

Line 163 and Figure 3: The persistent minima in sulfate at the 'ozone tropopause' of 90 – 120 ppb is surprisingly consistent and robust. This may be worth more than a passing mention.

We agree with the reviewer that this observation very robust for the dataset, but our current status of research does not allow any conclusion about a climatology of particulate sulfate at the chemical ozone tropopause, or especially one about climatology of the sulfate-ozone correlation in the LMS. We added the following sentence:

This observation of low particulate sulfate aerosol amounts at the chemical tropopause is very robust over the whole campaign period, such that it might be controlled by atmospheric processes that need more investigation.

Line 186: It is not clear what you mean by 'not connected to the stratosphere' when the airmass meets both the $PV > 2$ and ozone > 120 ppb criteria by a large margin.

The connection to the stratosphere in this case refers to a connection to the bins with a potential temperature above 370 K and sulfate mixing ratios around 0.3 ppbv which represent the lower boundary of the stratospheric aerosol layer.

We reformulated the sentence as follows:

The observed sulfate anomaly occurs in Fig. 5b between 40° N and 45° N at potential temperatures between 345 K and 350 K and is not connected to the observed stratospheric aerosol layer that starts at higher altitudes, above the 370 K isentrope (see Fig. 5).

Line 219: Won't dilution equally impact all tracers and not just CO?

That is correct. In contrast, sulfate is formed during its transport into the stratosphere, resulting in an increasing ratio of sulfate to other tracers such as CO. We reformulated:

In contrast to sulfate, CO will decrease during the transport into the stratosphere, both by dilution and photochemical destruction, with an atmospheric lifetime of one to three months (Seinfeld and Pandis, 2016).

Line 225: The stratospheric water vapor background is closer to 5 ppm, why would you expect it to be 10 – 15 ppm, and doesn't Fig 8e show that the water vapor us is in the range of 10 – 20 ppm?

We agree with the reviewer that the stratospheric water vapor background is around 5 ppm and it was misleadingly written. We reformulated the line to the following:

If the air masses were stratospheric origin, we would expect O₃ mixing ratios higher than 400 ppbv and a water vapor mixing ratio around 5 ppmv. Instead, we observe lower O₃ mixing ratios and water vapor mixing ratios around 10 – 20 ppmv.

Figure 7: Is there an easy way to show latitude on this figure? It may help understand the geographic extent of the anomalous layer and why it is only observed on some of the climbs?

We added the timeseries of the latitude to Fig. 7 to compare the same measurement regions easily. The anomaly with the highest mixing ratios of particulate sulfate is observed on the highest level around 12:00 UTC. Moreover, we observe the same air mass characteristics with weaker signals between 10:30 and 11:00 UTC within the same measurement region. In contrast to these two observations over Northern Germany, we measured another air mass in the same altitude with a different composition over Southern Germany between 13:00 and 14:00 UTC.

Figure 8: The caption does not agree with the figure labels, and the color bar labels for theta are incorrect.

We are sorry for this mistake and corrected the figure including the caption.

Figure A1: The y-axis label is incorrect.

We are sorry for this mistake and corrected the figure (y-axis label).