

List of changes made followed by replies to the comments by the referees

Changes made:

Table 1: No changes made

Fig. 1: Similar to old version, but now based on mixing ratio

Fig. 2: Removed but replaced by another fig that explains the methodology

Fig. 3: The same as before except for that the change in methodology affected the details

Fig. 4: A new fig that better explain the connection between the 2nd regression step and the measurement data

Fig. 5: (old Fig. 4) The same as before except for that the change in methodology affected the details

Fig. 6: (old Fig. 5) The same as before except for that the change in methodology affected the details

Fig. 7: (old Fig. 6) The same as before except for that the change in methodology affected the details

Fig. 8: New fig used to explore the ATAL

Abstract

- Added mention of CALIPSO, which is used in the new version
- Language improvements
- Adjusted the final 3 – 4 lines to comply with changes made to the manuscript

1. Introduction

- Added 4 lines about the ATAL
- Removed one sentence that repeats information given in the Discussion section
- Added 2.5 lines to further explain the need of chemical measurements to complement lidar measurements

Methods 2.1

- Added a line on aircrafts used and sampling time periods
- Exchanged 2 lines with 5 lines due to change from volume concentration to a mixing ratio.

Methods 2.2

- Changed two R^2 values due to change from volume conc. to mixing ratio
- Added half a line to further explain the altitude parameter.
- Minor language adjustments

Methods 2.3

- Re-written the explanation of how the seasons overlap.

- Reduced number of data groups from 60 to 52 in order to avoid data groups containing few measurements.
- Moved the description of the data exclusions made (handling of outliers)
- Added approximately 1 page that illustrates and explains the choice of forced linear regression in the first regression step (between particulate sulfur concentration and altitude above the tropopause).
- Replaced old Fig. 2 with a new that shows the regression results based on different methods
- Simplified the regression by eliminating the use of ordinary linear regression (now only used for illustration purposes).
- Replaced approximately half a page describing the old methodology with approximately equally long text describing the new, including a clearer explanation of the error handling.
- Minor language adjustments

Methods 2.4

- New section. We make use of satellite data (CALIPSO) in the revised version of the manuscript in order to further explain the results obtained. This section gives the experimental details.

3. Results

- Made some minor changes in the first section due to the changes in methodology
- Added ¼ page to comment a new (added) Fig. 4 that shows the connection between the two regression steps used.
- Old equation 9, now 7, was changed to accommodate the change from volume concentration to mixing ratio in the regressions, and ¼ page was added to explain how the column concentration can be obtained from a mixing ratio.
- Minor language adjustments

4. Discussion

- The change in the regression methodology did somewhat change the seasonal dependence of the tropospheric source of UT particulate sulfur (Fig. 5b; old Fig 4b) that induced some small changes to the wording in the two first sub-sections.
- Descriptions of extratropical transport of boundary layer air to the UT has been reduced from ½ to ¼ and moved approximately 1 page up.
- The discussion of the seasonal dependence of the tropospheric source of the UT particulate sulfur has been changed by simplifying the descriptions of relations to other species.
- The new look of the seasonal dependence of the tropospheric source of the UT particulate sulfur with a very clear peak in the fall (Fig. 5b in the new version) prompted further analysis where we found that the Asian monsoon, which forms an aerosol layer at 14 – 18 km altitude (ATAL) was the most likely cause. Approximately 1 page was added and a Fig. (8) was added containing 10 images obtained from the CALIOP sensor of CALIPSO.

5. Conclusions

- 4 lines of text was replaced by 10 lines to accommodate the new findings, mainly on the ATAL.

Reply to referees

Referees#2 and #3 made comments on the review of referee#1. We therefore include all answers in this file (referee comments in blue). We would also like to apologize to Referees#2 and #3 for making frequent references to the answer to Referee#1, because we first answered the comments of the latter.

Summary:

We thank the three referees for the comments. In response we have adjusted the data handling by using mixing ratios which are converted to volume concentrations in a late stage of the evaluation. We also have simplified and clearer motivated the choice of regression methodology in a new Fig. 2 (b and c), as well as clearer explained the weighting used in the second regression step. We have re-written section 2 accordingly. The changes did of course affect all Figs., and in particular the tropospheric source of particulate sulfur where a clear fall maximum was obtained. In order to explain this feature, further analyses were undertaken based on lidar data from the CALIPSO satellite. We found that the aerosol layer ATAL, formed from the Asian monsoon at 14 – 18 km altitude, is the likely cause. This added one fig (Fig. 8). We have also improved the presentation of the original data by adding a cumulative frequency distribution of the coefficient of determination (Fig. 2a), as well as adding a new fig (Fig 4) that clearer shows the first step regression and hopefully increase the understanding of the relations between the two regression steps used. We have also changed the description of the seasons used, and in general tried to improve the legibility.

Answers to Referee#1

[Interactive comment on “Particulate sulfur in the upper troposphere and lowermost stratosphere – sources and climate forcing” by Bengt G. Martinsson et al. Anonymous Referee #1 Received and published: 24 February 2017](#)

[This manuscript analyzes measurements of particulate sulfur taken from commercial aircraft altitudes in the IAGOS and CARIBIC programs. It attempts to derive the fraction of upper tropospheric sulfate that is from the stratosphere. This is an excellent data set but I find the analysis inadequate for several reasons. A previous paper by many of the same authors on a subset of these data \(Friberg et al., 2014 but it only uses data through 2008\) is a much better analysis. I would recommend resubmission with completely new analysis based on extending the Friberg et al. techniques to include the newer data and more emphasis than the Friberg paper on non-volcanic periods.](#)

We appreciate the kind words about Friberg et al. (2014). The entire author group is well acquainted with the usefulness of O3 in interpreting particulate sulfur in the LMS. More than 10 years ago we developed an O3-based model to study particulate sulfur in the volcanically quiescent period at the turn of the

millennium (Martinsson et al., JGR 2005). Following the Kasatochi eruption we introduced the ratio of particulate sulfur to O3 in order to express volcanic influence on the concentration of the former species (Martinsson et al., GRL 2009), which make samples that were variably impacted by mixing across the tropopause more comparable. In the present study we seek a standalone methodology to be able to express concentration gradients and to integrate to obtain radiative impact. This is important because this data allow us to identify the volcanic component also close to the tropopause in contrast to lidar measurements that are biased by tropospheric sources (dust, condensed water and other species). This is altogether different in the goals compared to our previous studies, and to our knowledge the first such study. Therefore, a different methodology is required.

1) The manuscript (line 135) states that the analysis is based on concentrations per unit volume rather than mixing ratio. This is a mistake; straightforward analysis of fits of concentration versus a parameter like distance from the tropopause requires the use of mixing ratio. For an idealized example, suppose the aircraft ascends 1 km as it goes through a perfectly uniform air mass. That ascent would change both the x-coordinate (distance from the tropopause) and the y-coordinate (concentration not corrected to mixing ratio). This coupling of the independent and dependent variables makes it impossible to interpret the slopes in a simple fashion. The stated reason for using a volume concentration (integration over an altitude range) can always be done later in the analysis.

This problem was considered already before the analysis of the data, but was deemed insignificant due to the relatively narrow altitude range of the measurements, which, in principle, was a mistake. In response to this criticism we did make a change in the analysis to undertake the regression analyses based on STP-normalized concentrations ($C_{STP} = aZ + b$), which is a mixing ratio. This means that the regression results need to be converted to volume concentration in the final integration ($C_{STP}/C_V = Q_V/Q_{STP}$, where C and Q are concentrations and molar volumes). We used ECMWF data to estimate the slope of the molar volume from pressure and temperature profiles in the LMS. Based on the average slope of all our samples we describe the molar volume with an exponential function:

$Q(Z) = Q_{TP} e^{wZ}$, where Z is the height above the TP and $w = 0.0001535 \text{ m}^{-1}$ (from ECMWF).

For each measurement we have a molar volume Q_m obtained at height Z_m above the TP. For this measurement the TP molar volume is obtained by $Q_{TP} = Q_m e^{-wZ_m}$. We integrate to obtain the column concentration for the first 3000 m of the LMS:

$$C_{col} = \int_0^{3000} \frac{Q_{STP}}{Q_V(Z)} C_{STP}(Z) dZ = \int_0^{3000} \frac{Q_{STP}}{Q_{TP}} e^{-wZ} (aZ + b) dZ$$

2) The distance from a tropopause defined by potential vorticity (PV) is not a very good choice for the independent variable (Figures 1 and 2 and subsequent analysis). First, the PV values come from a meteorological analysis with substantial uncertainty. A colleague I spoke to estimated +/- 500 meters. There are also ambiguities with multiple tropopauses. Consider what Figure 2a would look like with uncertainties of +/- 500 m in the horizontal for most points, and more for a few points in the neighborhood of multiple tropopauses. Note that using an independent variable with significant uncertainty not only introduces noise into line fits but also biases the results to smaller slopes and, for positive data, larger intercepts. (This is worse than uncertainty in the dependent variable, which introduces noise but not bias.) Second, there is no reason why the gradient in PV has to be uniform with distance above the tropopause,

so deeply stratospheric air could be close to or far above the tropopause. No tracer is perfect, but ozone, as used in Friberg et al., would be a far better choice than distance from a PV tropopause.

Locally there can be large uncertainties in the model tropopause. However, a sample was taken over typically 1500 km or more in flight range, meaning that the distance to the tropopause is based on typically 100 ECMWF positions along the flight track. Therefore, these samples become less sensitive to local errors of the model. The referee need to acknowledge the different purpose here compared to other studies of the ExTL. The objection “there is no reason why the gradient in PV has to be uniform with distance above the tropopause” is difficult to interpret. We do not use the PV as a tracer, and hence we do not need to make any assumptions concerning PV uniformity. Instead we use the dynamical TP at 1.5 PVU as the lower boundary of the stratosphere, which is generally recognized as the lower boundary of the stratosphere in view of chemical composition. Then we use the linear distance to this TP in the regression analyses, which tests the uniformity. The coefficient of determination (R^2) exceeds 0.6 in 72% of the 52 ordinary linear regressions undertaken. The deviations from the linear models consists of scatter without any trends. We do not force an erroneous shape of the gradient.

We considered using an O₃-based distance according to Sprung and Zahn (JGR 2010) which is available in the IAGOS-CARIBIC dataset. However, we decided against that for two reasons:

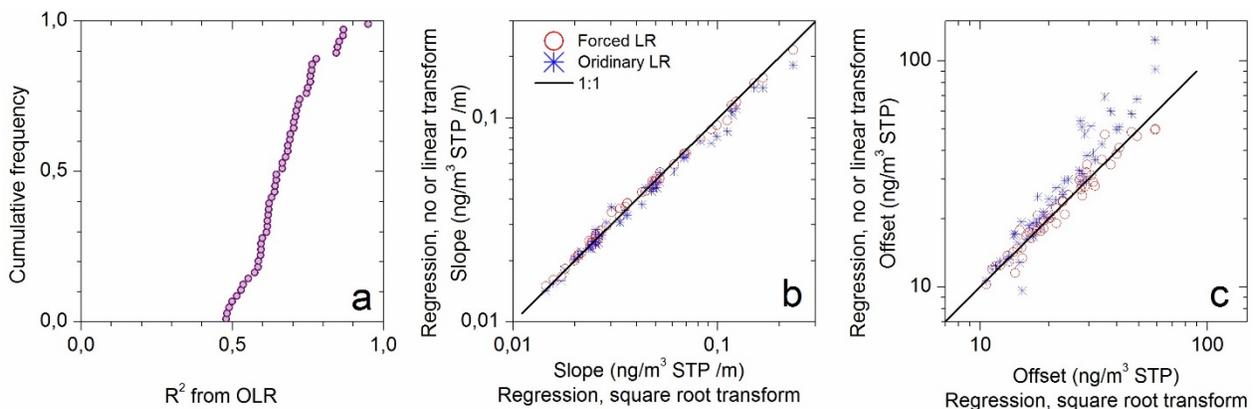
- A) That parameter refers to a static tropopause implying that approximately 1000 m of the LMS falls below.
- B) The use of a tracer would potentially introduce non-linearity in the vertical parameter that could introduce a bias in the results

3) The analysis of the stratospheric influence fraction is very convoluted with no propagation of uncertainty shown. There are three successive line fits to data, as shown in Figure 2a to 2c. After reading through the manuscript several times, and having worked extensively with similar data, I still do not understand how the measurement uncertainties and atmospheric noise propagate into the results.

Due to the good detection capacity for particulate sulfur, the total measurement errors are 12% (Martinsson et al., AMT 2014), which is small compared with atmospheric variation of this species. In the analysis we use a method of forcing the linear regression to comply with the observations close to the TP, as a way to deal with the heteroscedastic nature of the data. In response to this comment we have simplified the analysis. We skipped the ordinary linear regression (now only used for illustration purpose) and used only forced linear regression, where the regression was forced to the average concentration C_0 and distance Z_0 of the measurements closest to the tropopause. With a simple linear variable transformation (forming $C - C_0$ and $Z - Z_0$) this becomes equivalent to forcing the regression through the origin. Thus, first a forced linear regression, and then a weighted regression between the obtained slopes and offsets of each month. The uncertainty in the slopes of the first step regression is propagated. The error estimates used in Fig 3 are based on the student t distribution (t70% and t95%, two-sided) because the number of measurements available to estimate C_0 in some cases is small. The error in b (at $Z = 0$) is based on the uncertainties in C_0 (at Z_0) and the slope, and is computed using the weakest slope at the upper error limit of C_0 and strongest slope to the lower limit.

To further advocate this method, we undertook a small study of the scedastic nature of our data using variable transformations. The most common transforms, square root and logarithm of the dependent variable, were investigated. Like most natural science data set our is heteroscedastic, showing increasing

variance with distance from the TP. The log transformation changed the data in a way that the variance became smallest at large distance from the TP, whereas the square root transformation resulted in a rather constant variance in the dependent variable along the independent variable axis. This transform is thus more suitable for regression. After transformation the relation between the dependent ($y' = \sqrt{y}$) and the independent (x) variable is not linear (y and x has a linear relation). Thus the following expression should be minimized with respect to a and b : $(y' - \sqrt{ax + b})^2$. This resulted in rather tedious expressions that we had to solve numerically. In the Fig (Fig. 2 in a revised manuscript) you can see a comparison of slope (Fig b) and offset (Fig c) between the sqrt-transformed regression and ordinary linear regression (OLR) and forced LR. As can be seen, the OLR deviates sometimes strongly, in particular the offset, from the sqrt-transformed due to the heteroscedastic data. The forced LR, on the other hand, shows only small differences from the analysis based on sqrt-transformation. Due to more direct determination of the offset as well as the simpler analysis we chose to use forced LR.



4) Putting aside the choice of independent and dependent variables and the propagation of uncertainty, there is a conceptual problem with defining the stratospheric influence from a corrected intercept derived from the line fits, as is done in this manuscript. Such an analysis of the slope and intercept of two variables in the lowermost midlatitude stratosphere generally assumes that both variables are conserved quantities controlled largely by transport and mixing (e.g. Plumb 1996 JGR tropical pipe paper). But sulfate mass in the lowermost stratosphere is mostly controlled by sedimentation (Wilson et al., Steady state aerosol distributions. . ., ACP, 2008). In the presence of sedimentation, it is not obvious what the slope and intercept of a correlation plot mean. Indeed, it is clear from Figure 5 in Wilson et al. that a line fit over an altitude range that goes deep into the stratosphere could easily produce an intercept unrelated to the tropopause value.

Yes, there is sedimentation going on in the stratosphere, which, through the Cunningham slip correction factor describing the viscous contact between a particle and the surrounding air, is strongly dependent on altitude. In the LMS, with typical size distributions (background or moderately volcanically influenced), the sedimentation velocity is typically less than 0.15 km/month, implying that the particulate sulfur mainly is removed from the LMS by air transport (Martinsson et al., JGR 2005). Considering the recommendation above by the referee to use a tracer to improve the analysis, this comment is somewhat surprising. Whereas this effect in principle could affect the relation to a tracer, the observed gradient in our present study carries no such assumptions.

Lesser concerns are: (a) Distance from the tropopause is strongly correlated with latitude, since commercial flights generally only get well above the tropopause at high latitudes. This makes it difficult to separate latitude and altitude as causes of a correlation. (b) The introduction is too broad.

The referee is right in the assumption that observations deep into the LMS could be more frequent at higher latitudes. Ideally we would want to have enough observations to also study the latitude dependence. However, the salient features of the LMS with its ExTL are caught by the broad latitude band.

[Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1142, 2017.](https://doi.org/10.5194/acp-2016-1142)

Answer to referee#2 follows

Answers to Referee#2

Interactive comment on “Particulate sulfur in the upper troposphere and lowermost stratosphere – sources and climate forcing” by Bengt G. Martinsson et al. Anonymous Referee #2 Received and published: 22 March 2017

This manuscript reports on measurements of aerosol sulfur in aerosol samples collected from the IAGOS-CARIBIC platform over a 16 year period. Analysis focuses on a new regression technique that the authors suggest can be used to infer both the gradient of sulfur concentration and the integrated burden in the lowermost stratosphere (LMS), starting at the dynamical tropopause and extending to 3 km above it. It is also suggested that this analysis provides an estimate of the relative contribution of stratospheric sulfate mixed downward and tropospheric sources on the sulfur concentration in the upper troposphere (UT), and how these contributions vary seasonally.

My biggest problem with the paper is that the authors do not show and discuss enough raw data to demonstrate that the regression approach is reasonable. Figure 1 does C1 give the reader a useful impression of both the range and seasonality of sulfur observed in the UT, and supports the authors impression that there is little correlation with distance below the tropopause. However, the LMS concentration data are never shown so the reader has no idea if fitting linear regressions is a remotely logical approach.

The reason we have not included figs of the first step linear regressions is that they are so many. In Fig 3 you in principle can see them all, but we agree that it is difficult to get the impression of the data from that Fig. However, a useful compromise could be to, instead of making 52 graphs, present the R^2 of the 52 ordinary linear regressions (OLR). Fig. 2a (the new version) shows the cumulative frequency of R^2 . As can be seen, R^2 of the 52 OLRs span 0.48 to 0.95 and 50% of the OLRs have R^2 exceeding 0.66. We have also added a new fig (Fig 4) that together with Fig 3 better explain how the actual measurements are connected with the regression in the second step, which in Fig. 5 becomes the seasonal dependences of $k(s)$ and $C_{S,UTtrop}(s)$, which in turn are used to obtain a_i and b_i in Figs. 6a and b.

This is compounded by the fact that the analysis apparently required multiple steps which are not well explained in section 2.3.

As explained in the answer to Referee#1 we have simplified the data evaluation, please see above for details.

I realize that this group has written a number of previous papers on this data set, and perhaps some of these have already presented spatial and seasonal distributions of sulfur in the LMS in ways that set the stage for this new analysis. However, I did not, and readers in general should not have to, read these earlier works to understand this one. I could provide a fairly long list of specific sentences and paragraphs that I found to be confusing or misleading.

That would have been helpful.

However, I just noticed that reviewer 1 has suggested major revision, starting with fundamentally changing the approach to analysis, which will clearly require rewriting most of the text.

Based on the comments from all the referees the revision should mainly concern the methods section. The revision of the methods has, however, induced changes in other places, mainly the discussion section.

Therefore it seems that specific editorial suggestions to improve clarity are premature I agree with the concerns reviewer 1 raised regarding the use of concentrations rather than mixing ratios, and relying on distance from the tropopause as the independent indicator of degree of stratospheric character captured by a given sample. (I also note that simply defining this distance for sample intervals approaching 2 hours in length would often seem ambiguous, even without double tropopauses or crossings of the tropopause.). I cannot comment on the suggestion to extend the analysis used by Friberg et al., 2014, since, as noted above, I am not familiar with this paper.

We have made a new analysis based on mixing ratios, and extensively answered the comments by referee#1, please see above.

[Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1142, 2017](https://doi.org/10.5194/acp-2016-1142)

Answer to referee#3 follows

Answers to Referee#3

Interactive comment on “Particulate sulfur in the upper troposphere and lowermost stratosphere – sources and climate forcing” by Bengt G. Martinsson et al. Anonymous Referee #3 Received and published: 28 March 2017

The paper describes the use of measurements of sulphur collected onto filters on board CARIBIC commercial aircraft over the past decade. The filters were analysed by PIXE. The data analysis develops a relationship between the concentration measurements and vertical distance to the tropopause derived from a PV analysis of re-analysis data. This is used to build a seasonal profile by combining data from multiple flights in each 3 monthly period. The analysis is used to show the amount of sulphur in the lower stratospheric column and derive an aerosol optical depth resulting from it.

I found the description of how the analysis was done to be less than clear. Some of the sentences were long and not transparent and on a number of occasions the sentence did not scan well or had typos in it e.g. “This was undertaken for 4 up to 7 groups of data for each season, and a total of 60 regression groups distributed over 12 overlapping seasons were used. This overlapping places each month in the center of a three-month season thus adjusting to smooth seasonal changes in the UTLS.” I would recommend this whole section and how this relates to the further description of the approach in the results section need re-writing and clarifying.

We have looked carefully on the formulations. We have also simplified the analysis (see answer to referee#1), which hopefully will further help to improve legibility.

Further, it is not clear what is meant by “overlapping”, does this mean that the some of the same data are used in multiple regressions? I assume this is a 3 month average centred on a particular month from the legend in figure 3. Please clarify.

Your interpretation is correct. We have clarified this in the revised manuscript.

A previous referee is critical of the use of concentration rather than mixing ratio and I can see why in principle. Equally I can understand the authors’ use of concentration since the column abundance of sulphur can be retrieved from the regressions and hence the AOD which would not be the case if the mixing ratio was used. This is also true of the use of altitude deriving from a PV definition of the tropopause rather than ozone. However, as far as I can see this only works if the pressure changes over the altitude range of the samples are sufficiently small that the regression derived results from the relative position to the tropopause and not the absolute altitude, this needs to be clarified before the analysis can be verified. We have changed the analysis in this respect to follow the recommendation of Referee#1 of using mixing ratios, and complemented with the use of a transformation to volume concentrations in the integration of the column concentrations.

The weighting of the regression isn’t described in sufficient detail for a reader to follow and replicate. This needs clarification.

The weighting is undertaken based on the error estimated of each forced LR (in step 1), where the inverted, squared linear error (t70%; see answer to Referee#1) of each first step regression is used as weights in the second step regression. This is clarified in the revised manuscript.

[Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1142, 2017.](https://doi.org/10.5194/acp-2016-1142)

Particulate sulfur in the upper troposphere and lowermost stratosphere - sources and climate forcing

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Formatted: English (U.S.)

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Abstract. This study is based on fine mode aerosol samples collected in the upper troposphere (UT) and the lowermost stratosphere (LMS) of the northern hemisphere extratropics during monthly intercontinental flights of the IAGOS-CARIBIC platform in the time period 1999 – 2014. The samples were analyzed for a large number of chemical elements using the accelerator-based methods PIXE (particle-induced X-ray emission) and PESA (particle elastic scattering analysis). Here the particulate sulfur concentrations, obtained by PIXE analysis, are investigated. In addition, the satellite-borne lidar aboard CALIPSO is used to study the stratospheric aerosol load. A steep gradient in particulate sulfur concentration extends several kilometers into the LMS, ~~affected by~~ as a result of increasing dilution towards the tropopause of stratospheric, particulate sulfur-rich air by ~~strato~~ tropospheric air forming the extratropical transition layer (ExTL) towards the tropopause. Observed concentrations are related to the distance to the dynamical tropopause. A linear regression methodology ~~revealing~~ handled seasonal variation and impact from volcanism, ~~is~~ This was used to convert each data point to standalone estimates of a concentration profile and column concentration of particulate sulfur in a 3 km altitude band above the tropopause. We find distinct responses to volcanic eruptions, and that this layer in the LMS has a significant contribution to the stratospheric aerosol optical depth and thus to its radiative forcing ~~of this lowest part of the LMS~~. Further, the origin of UT particulate sulfur shows a strong seasonal variation. We find that tropospheric sources dominate during ~~summer and the~~ fall as a result of downward transport of the Asian tropopause aerosol layer (ATAL) formed in the Asian monsoon, whereas ~~these sources make a small contribution during winter and spring~~ transport down from the Junge layer is the main source of UT particulate sulfur in the first half of the year. In ~~this~~ these latter ~~seasons~~ part of the year, the stratosphere is the clearly dominating source of particulate sulfur in the UT during times of moderate volcanic influence as well as background conditions.

30 1 Introduction

The global mean surface temperature has increased considerably in the two last years (NOAA, Dec. 5, 2016), which followed on a 15-year period with slow temperature evolution. CMIP5 (coupled model intercomparison project) models predict stronger than observed temperature increase in this period (Fyfe et al., 2013; Fyfe et al., 2016). Reasons for these differences were sought, and the Interdecadal Pacific Oscillation connected with increased subduction and upwelling (England et al., 2014; Meehl and Teng, 2014), variations in volcanic aerosol (Solomon et

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al., 2011; Santer et al., 2014) and solar (Myhre et al., 2013) forcings were identified as main causes of the discrepancies. These phenomena are all elements of natural climate variability, thus highlighting the importance of these influences for assessing the human impact on the climate (Ramanathan and Feng, 2008).

Air from the tropical troposphere containing aerosol precursor gases is lifted into the tropical stratosphere in the Brewer-Dobson circulation. Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in the atmosphere. When lofted into the stratosphere, OCS is converted to sulfur dioxide (SO₂) at approximately 25 km altitude aided by UV radiation (Crutzen, 1976) and in a next step to sulfuric acid, giving rise to the background stratospheric aerosol layer. The upward tropical flow is connected with a downward flow in the extratropics, where stratospheric air flows back to the troposphere.

The stratospheric aerosol concentration varies strongly due to volcanic influence, from events like the strong 1991 Mt. Pinatubo eruption, inducing negative radiative forcing in excess of 1 W/m² (McCormick et al., 2005), to close to background conditions at around the turn of the millennium (Bauman et al., 2003; Martinsson et al., 2005). Overall, anthropogenic influence on stratospheric aerosol is small compared to that from volcanism (Neely et al., 2013). Recent volcanic eruptions, such as in 2008 and 2009 of the Kasatochi and Sarychev in the extratropics and in 2011 of the Nabro in the tropics, significantly altered the stratospheric aerosol (Vernier et al., 2011a; Bourassa et al., 2012). These eruptions also had a profound impact on the northern hemispheric lowermost stratosphere (LMS) (Martinsson et al., 2009) and the global aerosol optical depth (AOD) of the stratosphere (Andersson et al., 2015). After reaching the LMS, the stratospheric aerosol is transported to the upper troposphere (UT). A recent study indicates that volcanic aerosol also has an indirect climate effect by affecting the reflectance of cirrus clouds in the UT (Friberg et al., 2015).

The UT particulate sulfur, in addition, has tropospheric sources. In the tropics, convection lofts aerosol and aerosol precursor gases from low altitudes into the UT (Hess, 2005). During the monsoon season, primarily the Asian monsoon, appreciable amounts of aerosol and gaseous aerosol precursors are lifted to the tropopause region, extending from the UT to approximately 420 K potential temperature in the stratosphere forming the Asian tropopause aerosol layer (ATAL) (Vernier et al., 2011b). The ATAL is a seasonal and regional phenomenon, which according to atmospheric modelling is strongly connected with Asian pollution sources (Neely et al., 2014). ~~whereas in the extratropics both warm conveyor belts (WCB) (Stohl, 2001) and deep convection are the main lofting channels, the latter especially in the summer season. Large amounts of pollutants are long-range transported across the Pacific and Atlantic oceans, where sources are affecting the background concentrations of various species over remote continents. This transport is most efficient above the boundary layer in the pressure interval 700 – 900 hPa (Luan and Jaeglé, 2013). WCBs reaching the UT have their maximum frequency in the winter (Eckhardt et al., 2004) and transport of boundary layer air into the LMS maximizes in the winter and spring (Skerlak et al., 2014), whereas deep convection dominates in the summer (Kiley and Fuelberg, 2006). The time required for vertical transport in WCBs is considerably longer than in deep convective systems, which could be of importance for the vertical transport of short-lived species like SO₂ (TF-HTAP 2010).~~

Aerosol particles in the UT and LMS contain a large fraction of sulfur compounds, mostly sulfates (Dibb et al., 2000, Martinsson et al., 2001, Xu et al., 2001; Kojima et al., 2004). These particles also contain a considerable fraction of carbonaceous aerosol (Murphy et al., 1998; Nguyen et al., 2008; Martinsson et al., 2009), whereof a minor fraction is black carbon (Schwarz et al., 2010; Friberg et al., 2014). In some periods, particularly during spring, crustal particles also are found in this part of the atmosphere (Papasiropoulos et al., 2002).

In this study the concentration of particulate sulfur in the UT and LMS is investigated based on aerosol samples collected from the IAGOS-CARIBIC platform in the time period 1999 – 2014. In this period the UT and LMS aerosol was affected by volcanism from several eruptions as demonstrated in our previous studies based on this data set (Martinsson et al., 2009; Andersson et al., 2013; Friberg et al., 2014; Martinsson et al., 2014; Friberg et al., 2015; Andersson et al., 2015). The IAGOS-CARIBIC aerosol elemental concentration measurements from the LMS are taken in strong concentration gradients that are affected by mixing tropospheric air into the lowest part of the LMS. Each measurement flight results in a small number of samples, being insufficient to reconstruct the gradient. Therefore, we have frequently relied on concurrent IAGOS-CARIBIC measurements, mostly by relating the particulate sulfur measurements to ozone concentrations to express e.g. volcanic influence on the aerosol concentration (Martinsson et al., 2009). Satellite-based measurements do usually not provide specific chemical information about aerosol particles. This lack of chemical information in e.g. lidar measurements can cause a bias in LMS particle concentrations close to the extratropical tropopause from non-volcanic species such as crust and particle-bound water. Here we present standalone estimates of the stratospheric sulfur aerosol—in terms of mass concentration profiles and column concentrations based on a new method, which is then used to study the AOD of the lowest part of northern hemispheric LMS and its radiative forcing. This study also comprises a discussion on the relative importance of stratospheric and the tropospheric sources to the UT of particulate sulfur, seasonal dependences, and different modes of tropospheric transport involved.

2 Methods

2.1 Sampling, analysis and classification

This study is based on measurements of particulate sulfur taken from the IAGOS-CARIBIC platform (Brenninkmeijer et al., 2007; www.caribic-atmospheric.com/), where the atmosphere is studied using ~~a~~-modified passenger aircrafts (March 1999 – April 2002: Boeing 767-300 ER from LTU International Airways, and May 2005 – present: Airbus 340-600 from Lufthansa) ~~from Lufthansa~~ during monthly sets of usually four intercontinental flights. A large number of trace gases and aerosol parameters are measured from that platform during flights in the altitude range 9 – 12 km, including gaseous and condensed water, O_3 , CO, NO/NO_x, VOCs, greenhouse gases, halo-carbons, mercury, particle number concentrations, size distributions and elemental concentrations (Brenninkmeijer et al., 2007, Hermann et al., 2003; Schuck et al., 2009; Baker et al., 2010; Oram et al., 2012; Zahn et al., 2012; Martinsson et al., 2014; Dyroff et al., 2015; Slemr et al., 2016; Hermann et al., 2016).

Aerosol sampling from the IAGOS-CARIBIC platform in the time period 1999 – 2014 has resulted in 1198 samples analyzed for aerosol elemental concentrations. The measurements were mainly taken in the northern hemisphere

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(NH) extratropics and the tropics, while only a small fraction of the samples were taken in the southern hemisphere.

Here the focus is on the extratropical LMS and UT of the NH. Aerosol particles with aerodynamic diameter in the size-range 0.08 – 2 μm were collected with a multi-channel impactor with a collection efficiency of $97\% \pm 4\%$ (Nguyen et al., 2006). The typical time required to collect one sample is 100 minutes. Accelerator-based methods were used to analyze the collected samples with respect to elemental concentrations, using Particle-induced X-ray emission (PIXE) ~~was used~~ to analyze the concentration of elements with atomic number larger than 15 (Martinsson et al., 2001). Concentrations of hydrogen, carbon, nitrogen and oxygen were investigated by particle elastic scattering analysis (PESA; Nguyen and Martinsson, 2007). Here the particulate sulfur concentrations are used. The accuracy of the analyses is estimated to 10% and the combined uncertainty in sampling and analysis is estimated to 12%. Further analytical details are found in Martinsson et al. (2014). Finally, the concentration of particulate sulfur is mostly given as a mixing ratio by normalization to STP (standard temperature (273.15 K) and pressure (101300 Pa)). When computing column concentration and AOD of the lowest 3 km of the LMS, the STP concentrations are converted to volume concentrations using the pressure and temperature of the measurement, and the altitude dependence in the LMS of the molar volume obtained from ECMWF (European centre for medium-range weather forecasts). in previous publications based on these data the concentrations are given normalized to standard temperature and pressure, which to its nature is a mixing ratio. Here volume concentrations are used in order to facilitate integration over the aerosol column.

The dynamical tropopause (Gettelman et al, 2011) at the potential vorticity (PV) of 1.5 PVU (potential vorticity units; $1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$) was used to classify samples with respect to tropospheric and stratospheric air. The PV along the flight track was obtained from archived analyses from ECMWF (~~European centre for medium range weather forecasts~~) with a resolution of 1×1 degree in the horizontal and 91 vertical hybrid sigma-pressure model levels. The PV was interpolated linearly in latitude, longitude, log pressure and time to the position of the IAGOS-CARIBIC aircraft.

2.2 Altitude

The UT usually holds significantly lower particulate sulfur concentration than the LMS. Combined with bi-directional exchange of tropospheric and stratospheric air across the tropopause, this leads to a gradient of increasing concentration in the LMS from the tropopause. In addition, the concentration of particulate sulfur in the LMS varies due to the influence from volcanism (Martinsson et al., 2009), which has been shown to cause significant radiative forcing (Andersson et al., 2015). In order to study the particulate sulfur gradient in the LMS, fine aerosol elemental concentration measurements from the IAGOS-CARIBIC platform were used in relation to the distance between measurement position and the tropopause (Z):

$$Z = Z_a - Z_{tp} \quad (1)$$

where Z_a and Z_{tp} are the altitudes of the aircraft and the tropopause. Z_{tp} refer to the dynamical tropopause of 1.5 PVU, which is a low limit to ensure that very little LMS air will be considered as tropospheric. The Z_{tp} was obtained from the ERA-Interim data of ECMWF, whereas the altitude of the aircraft was obtained from pressure measurement which was converted to altitude using the ECMWF data. The position of the tropopause was obtained using the

aircraft as the starting position. If that position is in the UT, i.e. has a potential vorticity lower than 1.5 PVU, the tropopause is found by searching upwards in the potential vorticity field. ~~When the aircraft is located in the stratosphere-~~Tropopause folds in a small number of cases induce multiple tropopauses in the vertical direction, ~~complicating the analysis of the stratospheric samples.~~ In order to handle that problem, searches were undertaken both upwards and downwards to find the tropopause closest to the aircraft. That distance is assigned a positive value irrespective of ~~whether~~ the tropopause is below or above the aircraft, because positive sign indicates stratospheric air.

The study of the aerosol concentration gradient deals primarily with the LMS. The dataset, however, contains observations both in the LMS and the UT and one sample sometimes contains particles from both regions. These concentrations are connected by the exchange across the tropopause. Figure 1 shows the samples that were taken in the UT during the entire sampling time. It is clear that the dependence on the distance from the tropopause is ~~weak or~~ non-existent ($R^2 = 0.02$). Further evaluation (not shown) by normalization to seasonal average concentrations ($R^2 = 0.0108$) or to individual groups of concentration data that will be explained below ($R^2 = 0.0024$) did not reveal a ~~UT particulate sulfur concentration~~ dependence ~~of the UT particulate sulfur concentration~~ on the distance from the tropopause, ~~either~~. It should be pointed out that the variability in distance to the tropopause is mainly caused by variability in the altitude of the tropopause, because the altitude of the measurement aircraft is fairly constant. This implies that the distance from the tropopause in Fig. 1 does not reflect the ~~measurement-sampling~~ altitude, and hence not temperature decrease in relation to the surface of the earth or the degree of cloud processing. The distance to the tropopause for some summer measurements was very large, due to the seasonality of the position of the tropics. Approximately one third of all stratospheric air masses transported across the extratropical tropopause reach the 500 hPa level of the atmosphere, corresponding to approximately 5000 m transport, in 4 – 5 days (Skerlak et al., 2014). This illustrates that the exchange from the stratosphere goes deep in a rather short time. Based on these observations and arguments, the UT particulate sulfur concentration is considered independent of the distance from the tropopause under presented conditions, and thus indicative of the particulate sulfur concentrations of the air mixed into the LMS.

The time required to collect one sample was subdivided into ten time intervals ~~of equal length~~, where Z was computed along the flight route. For samples taken in the LMS, the sample was represented by the average distance to the tropopause of the ten time intervals. Those time intervals when the sampling was undertaken in the UT, i.e. with $Z < 0$, Z was set to zero, ~~since no Z dependence of the UT particulate sulfur concentration could be identified~~. This implies that samples collected entirely in the UT are found at $Z = 0$ ~~in forthcoming graphs~~. Some of the samples were collected both in the LMS and in the UT. In these cases, the average Z over the ten time intervals of each sample was computed with all UT parts of a sample ~~was~~ set to $Z = 0$. That way all samples could be utilized to study the particulate sulfur concentration in the LMS.

2.3 Methodology to evaluate the S gradient around the tropopause

The particulate sulfur concentration in the LMS ~~will be~~ investigated by linear regression in ~~three-two~~ steps. To that end we need to consider that the LMS shows a seasonal dependence induced by variability in stratospheric circulation and exchange across the tropopause over the year. Within one season differences between years can be large, mainly due to varying influence from volcanism. Further, the onset of volcanic influence on the particulate

sulfur concentration can cause large variability within the season in the same year, and patchiness of young volcanic clouds can further affect the data analysis.

180 This study was limited to ~~the extratropics of the NH, because the data set contains few measurements taken in the southern hemisphere. Samples taken north of 30° N were used in this study, where in total 765 samples are available.~~ The highest latitude of sampling was 77° N, and 90% ~~of the samples~~ (5% removed each side) ~~were of the samples~~ taken in the range 32 - 64° N. ~~Almost all~~ Most of the LMS samples (95%) were taken within 3000 m from the tropopause. In terms of altitude, the results of this study therefore can be considered representative of the range 0
185 - 3000 m above the tropopause.

~~In order to obtain statistical significance a~~ large number of measurements is needed ~~to obtain high statistical significance. To obtain~~ For that, ~~seasons data averaged over~~ three months were used. ~~However, to allow for exchange of data in the analyses in order to test the stability of the results, as well as catch smooth seasonal variations in the UTLS, a seasonal overlapping technique is used. In doing so three-months-seasons shifting by one month are used, e.g. the season MAM is followed by a season AMJ where data from April and May are used in both~~ “seasons”. Data from one season were grouped with respect to concentration levels of the different years, ~~resulting in 4 to 5 groups of data for each season, and in total 52 groups of data from the 12 seasons to be analyzed. Some data were excluded from these regressions~~ analyses, which reduced the amount of data from 765 to 694. ~~Of the excluded 71 samples, 60 pertained to periods when fresh volcanism induced strong patchiness in the particulate sulfur concentration. Eleven samples were considered outliers for other reasons, e.g. single samples affected by volcanism during a season or recent up-transport from strongly polluted regions. This means that way~~ groups with varying degrees of volcanic ~~activity-influence~~ were formed. Groups typical of “background” conditions were primarily based on data obtained during the 1999 – 2002 period characterized by low volcanic influence on the stratospheric aerosol (Bauman et al., 2003; Deshler et al., 2008) and data from mid-2013 to mid-2014 when the LMS is back to near-background conditions in the NH extratropics, see Table 1 for relevant volcanic eruptions. Another period that we will return to later is mid-2005 to mid-2008 when the stratosphere was affected by ~~the three tropical eruptions in 2005 – 2006: in 2005—2006 of~~ Manam, Soufriere Hills and Rabaul (Vernier et al., 2009), which also affected the NH LMS (Friberg et al., 2014). There was some variability during these years, implying that not always all of the years were grouped together. They could be grouped with other years, e.g. 2011 and 2013 often had similar concentrations and gradients during the winter and spring seasons. These groups were handled individually in the regression procedures described next, but in a context of the discussion section these groups of “moderate ~~influence from tropical volcanism~~ ~~influence~~” were averaged to describe the UT aerosol along with the “background” group described above.
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210 ~~The groups were modeled by an initial unweighted linear regression between the particulate sulfur concentration (C_s) and the altitude above the tropopause (Z). This was undertaken for 4 up to 7 groups of data for each season, and a total of 60 regression groups distributed over 12 overlapping seasons were used. This overlapping places each month in the center of a three-month season thus adjusting to smooth seasonal changes in the UTLS. The overlapping also serves the purpose of exchanging data in the regression, which further tests the stability of the results. Some data~~

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215 ~~were excluded from these regressions, which reduced the amount of data from 765 to 694. Of the excluded 71 samples, 60 pertained to periods when fresh volcanism induced strong patchiness in the particulate sulfur concentration. Eleven samples were considered outliers for other reasons, e.g. single samples affected by volcanism during a season or recent up transport from strongly polluted regions.~~

220 First linear vertical concentration gradients of particulate sulfur in the lower LMS was calculated. Ordinary linear regression (OLR) was undertaken for the 52 groups of data mentioned above of particulate sulfur concentration as a function of the altitude above the tropopause. Figure 2a shows the cumulative frequency of the coefficient of determination (R^2) of the 52 OLRs undertaken. R^2 spans 0.48 to 0.95, 72% of the groups having R^2 exceeding 0.6 and 50% exceeding 0.66. The deviations from the OLR models consists of scatter that does not show any trends.

225 When investigating the variance of the dependent variable (the particulate sulfur concentration, C_s) along the independent variable (altitude above the tropopause, Z) it is clear that the variance of C_s increases with increasing Z . This heteroscedastic nature of the data, which is shared by most natural science data sets, could unfavorably affect in particular the offset of the OLR. In order to further investigate the effects of this problem two variable transformations of the dependent variable were tested: logarithmic and square root transformations. The logarithmic transformation turned the problem around to the other side, i.e. the logarithm of C_s has large variance for small Z and small variance for large Z . The square root transformation of C_s , on the other hand, shows rather constant variance along the Z axis, thus making this transformation more suitable for regression. The transformation $C'_s = \sqrt{C_s}$ was applied to the data. As already pointed out, C_s and Z has a linear relation implying that the following expression should be minimized with respect to slope (a) and offset (b): $(C'_s - \sqrt{aZ + b})^2$. This results in rather tedious expressions that we solved numerically for all the 52 data groups. Figures 2b and c show comparisons between the slopes and the offsets obtained by the square root transformed regression results and the OLRs. It is clear that the heteroscedastic nature of the data causes large deviations, especially in the offset.

235 Yet another transformation, based on forcing the regression to comply with the data for small Z , was investigated. To that end, the average concentration ($C_{s,0}$) of the data points closest to the tropopause at the average distance Z_0 from the tropopause was formed. $C_{s,0}$ of the 52 data groups is on average based on 13 measurements, and the minimum was 5, and the average Z_0 is 88 m and the largest is 273 m. The data were transformed linearly to place $C_{s,0}$ and Z_0 in the origin by forming $C'_s = C_s - C_{s,0}$ and $Z' = Z - Z_0$, followed by linear regression forced through the origin, i.e. $C'_s = aZ'$. Finally, the regression results are transformed back to the form $C_s = aZ + b$, where the slope a is not changed by the translation, and the offset is obtained by $b = C_{s,0} - aZ_0$. These results of the forced linear regressions are compared with the square root transformed regressions in Figures 2b and c. As can be seen, the forced linear regressions, in contrast to the OLRs, show only small deviations from the square root transformed data. Due to the more direct determination of the offset as well as the simplicity of forced linear regression compared with square root transformation, the forced linear regression method is chosen for the analyses. Thus, for each season (s) and year (y) in total ~~5260~~ forced linear regressions were undertaken:

$$C_s(y, s, Z) = a(y, s)Z + b(y, s) \quad (2)$$

where a and b varies with season and the strength of the volcanic influence.

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250 An example of such a regression is shown in Fig. 2a. Sometimes the regression failed to reflect the tropopause concentrations because of influence from measurements taken at higher altitudes. In order to well represent the tropopause concentration, a method of forcing the offset towards observed concentrations was used. Due to problems with few observations in the UT, the average of observations up to 300 m above the tropopause ($\langle C_{s,z < 300m} \rangle$) were utilized to obtain a first estimate of the concentration at the tropopause. These averages were related to $b(y,s)$ from the regression according to equation 2 in a weighted regression involving all the data groups of a season, with the inverse of the variance in $\langle C_{s,z < 300m} \rangle$ used as weights (see Fig. 2b):

$$b' = c_1 b(y,s) + c_2 \quad (3a)$$

and the corresponding slope of each data group of the season becomes

$$a' = (\langle C_{s,w} \rangle - b') / \langle Z_w \rangle \quad (3b)$$

260 where index w indicates weighted quantities. This estimate of the offset b' is thus somewhat affected by stratospheric air since measurements up to 300 m above the tropopause were included. To correct the estimate of the offset, in a third step, the average altitude above the tropopause of these samples ($\langle Z \rangle_{z < 300m}$) was used:

$$b'' = b' - a' \langle Z \rangle_{z < 300m} \quad (4)$$

and the corresponding, corrected slope (a'') was computed in the same way as a' , but based on b'' (eq. 3b).

265 The S concentration at the tropopause and in the UT, expressed by b in eq. 2, which, by eq. 3 and 4 transforms to b'' , is dependent on the stratospheric concentration which is affected by volcanism (Friberg et al., 2015). This means that the offset of the regressions is affected. This is expressed here by:

$$b(y,s) = C_{s,UT}(y,s) = a(y,s)k(s) + C_{s,UTtrop}(s) \quad (3)$$

270 where the first term expresses the contribution from stratospheric sources and the second that of tropospheric sources. This $b''(y,s) = C_{s,UT}(y,s) = a''(y,s)k(s) + C_{s,UTtrop}(s)$

$$(5)$$

resulting in the combined equation:

$$C_s(y,s,Z) = a(y,s)Z + a(y,s)k(s) + C_{s,UTtrop}(s) \quad (4)$$

$$C_s(y,s,Z) = a''(y,s)Z + a''(y,s)k(s) + C_{s,UTtrop}(s) \quad (6)$$

275 where $k(s)$ reflects stratospheric influence on the UT particulate sulfur concentration and $C_{s,UTtrop}(s)$ is the particulate sulfur concentration of tropospheric origin.

280 The In order to obtain estimates of k and $C_{s,UTtrop}$ a second regression for each season is undertaken where the offsets (b) are related to the slopes (a), see Fig. 3. The groups of data of a season differ in a and b mainly due to volcanic influence. A zero slope ($a = 0$) would be obtained, should the stratospheric concentration become as low as the UT concentration. The UT aerosol of tropospheric origin ($C_{s,UTtrop}$) thus can be estimated as the offset of the $b - a$ regression. The slope of that regression shows how the offset b changes with increased slope a , hence expressing the sensitivity (k) of the UT concentration to changes in stratospheric concentration. With access to these two parameters, $C_{s,UTtrop}(s)$ and $k(s)$, the LMS concentration gradient and tropopause concentration can be estimated based on a single measurement of the particulate sulfur concentration. results of a season are obtained in a weighted

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285 ~~linear regression of the offset b'' against the slope a'' (from eq. 6) for all the groups of data available from that season.~~

The uncertainties of the forced regression results of a given season vary among the data groups. In order to account for this variability, weights are used in the regression between the offsets and slopes of a season. The weights are based on 70% double-sided student t distribution ($t_{70\%}$) estimates because some of the estimated $C_{S,0}$ and Z_0 rely on few observations. The $t_{70\%}$ estimate of b ($b = C_{S,0} - aZ_0$, see above) is obtained by combining the upper $t_{70\%}$ limit of $C_{S,0}$ with the weakest $t_{70\%}$ slope (a) and the strongest $t_{70\%}$ slope at the lower limit multiplied with Z_0 . The inverse variances of b'' of the squared $t_{70\%}$ estimates of b obtained in this way are then used as weights in the second step regressions.

295 Figure 2c shows an example of this regression step for the months September to November (SON). The groups of data have different slopes (a'') and offsets (b'') caused mainly by volcanism. Should the stratospheric concentration become as low as the UT concentration, a zero slope a'' would be obtained. Therefore we can estimate the fraction of the UT aerosol of tropospheric origin ($C_{S,UTtrop}$) as the offset of the $b'' - a''$ regression (Fig. 2c). The slope of that regression shows how the offset b'' changes with increased slope a'' , hence expressing the sensitivity (k) of the UT concentration to changes in stratospheric concentration. With access to these two parameters, $C_{S,UTtrop}(s)$ and $k(s)$, the LMS concentration gradient and tropopause concentration can be estimated based on a single measurement of the particulate sulfur concentration.

2.4 Lidar data from the CALIPSO satellite

305 The evaluation of the particulate sulfur concentrations from the IAGOS-CARIBIC aircraft was aided by the use of lidar data from the CALIOP sensor aboard the CALIPSO (Cloud-aerosol lidar and infrared pathfinder satellite observation) satellite from NASA (Winker et al., 2010), performing 15 orbits per day covering the globe from 82° S to 82° N with a repeat cycle of 16 days during nights and days. The data evaluation was based on the methodology developed by Vernier et al., (2009). Here only the night-time data of the 532 nm wavelength lidar signals were used. The level 1 data of version 4-10 (averaged in a grid of 180 m vertically and 1x1 horizontally) were used to obtain scattering ratios, i.e. the ratio of the measured, combined air and aerosol scattering to the modeled air scattering based on molecule and ozone number concentrations from the GMAO (global modelling and assimilation office). Cloud pixels were removed by rejecting pixels of a depolarization ratio greater than 5%. This cloud mask was extended 360 m upwards to remove faint cloud residues, and pixels from underneath clouds were removed to avoid bias from cloud absorption, see Andersson et al., (2015) for further details. Removal of cloud pixels as well as periods of instrument failure, sometimes resulted in few observations in these pixels. In order to avoid statistical noise at least 20% of the maximum possible observation data was required for any given pixel (latitude, altitude). The pixels were generated by averaging in the longitude interval 60° E to 120° E, the main longitude region of the ATAL (Vernier et al., 2015).

3. Results

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320 The linear regression methodology described in the previous section was applied to particulate sulfur concentrations (C_S) as a function of distance from the tropopause (Z) for seasons comprising three months. Data from different years of one season were grouped according to their concentrations, resulting in ~~several four or five~~ groups differing with respect to the $C_S - Z$ relation. The resulting groups of data from each season were modeled by forced linear regression. These model ~~results were, are after some further considerations described in section 2,~~ used in a second regression step to model seasonal influences from transport, which in turn are used ~~dependence and to obtain~~ the response of the LMS and UT particulate sulfur concentrations to changes induced mainly by volcanic eruptions. ~~An example of the steps in the methodology is shown in Fig. 2.~~

330 This methodology was applied to all seasons, having a duration of three months. The final product of the regression methodology, i.e. the second regression step, of all twelve overlapping seasons is shown in Fig. 3. It is clear that slopes and offsets of the season groups obtained in the first step of forced linear regression, differing in particulate sulfur concentration related to distance from the tropopause, can readily be described by linear regressions for all twelve three-month seasons. The relation between slopes and offsets has a very strong seasonal dependence. In some seasons small changes in the LMS sulfur concentration slope is connected with a strong change in tropopause sulfur concentration. This is most pronounced for the seasons centered in February, March and April. At the other end, ~~i.e. where changes in the LMS sulfur concentration is connected with small changes in the tropopause concentration,~~ we find the seasons centered in September, July to October and November, where a change in the slope of the first regression step due to varying influence from volcanism has little effect on the tropopause concentration. To further illustrate the connection to the measurements, Fig. 4 shows the four data groups of the seasons most (Fig. 3: FMA) and least (Fig. 3: OND) susceptible to change in the tropopause concentration due to changed stratospheric concentration. In Fig. 4 the data group of least volcanic influence includes years 1999 – 2002 and 2014, and the most influenced years are 2009 and 2012 which are the springs after the Kasatochi (August 7, 2008) and Nabro (June 12, 2011) eruptions (we have no late winter/spring data after the most powerful eruption of the period studied (Sarychev, June 12, 2009) due to maintenance of the measurement aircraft). The season centered in November have the weakest volcanic influence years 1999 – 2001, 2012 and 2013 (Fig. 4), whereas the group with strongest slope includes the three strongest eruptions of the period studied (Kasatochi, Sarychev and Nabro) a few months after respective eruption. Despite the very strong volcanic influence of the latter group, the tropopause concentration ($Z = 0$) remains close to that of the closely distributed tropopause concentrations of the other groups of that season.

340 The sensitivity of the tropopause and UT concentration to changes in LMS concentration slope is denoted k in equations 5 – 63 and 4, which thus is obtained for each regression depicted in Fig. 3. These results are collected in Fig. 54a. The salient features of the seasonal dependence can be described by ~~a two~~ Gaussian distributions added to a low, constant background level (Fig. 54a). The maximum sensitivity appears in the late winter and early spring when the seasonal variation in tropopause altitude has its maximum in rate of upward motion of the tropopause maximizes (Appenzeller et al., 1996). The maximum in rate of downward motion of the tropopause stratosphere is growing appears in the fall, ~~i.e. the extratropical tropopause is moving downwards~~. This delays transport from the stratosphere to the troposphere, which is reflected by a low sensitivity k . This sensitivity can, in addition, be affected by the residence time of particulate sulfur in the UT. Interestingly, the downward transport in association with the

Brewer-Dobson circulation from deeper, aerosol-rich stratospheric layers through the LMS takes place in the same season as the maximum in k, thus further enhancing the stratospheric influence on the UT by the term $a''(y,s) \times k(s)$ in eq. 64.

360 The offsets of the regression lines shown in Fig. 3 (when $a''(y,s) = 0$) expresses the case when the stratospheric and tropospheric concentrations are equal, implying that this offset expresses the particulate sulfur concentration of tropospheric origin ($C_{S,UTrop}$) that is mixed into the LMS, see Fig. 54b. Two Gaussian distributions were used as fits to the seasonal variation of $C_{S,UTrop}$. As for k, the seasonal variation of $C_{S,UTrop}$ is strong. The seasonal variation of $C_{S,UTrop}$ will be elaborated in the discussion section.

365 After obtaining $C_{S,UTrop}$ and k, the data that are needed for conversion of every measurement of the concentration to an estimate of the slope and offset of the LMS concentration are available. Thus, for each individual measurement (i) in the LMS, consisting of the particulate sulfur concentration ($C_{S,i}$) and the altitude Z_i above the tropopause (Z_t), the slope and offset of equations 5-3 and 6-4 are obtained from:

$$a_i'' = \frac{C_{S,i} - C_{S,UTrop}(s)}{Z_i + k(s)} \quad (75)$$

$$b_i'' = a_i'' k(s) + C_{S,UTrop}(s) \quad (86)$$

370 The estimated slopes and offsets are shown in Figs. 5a-6a and b, where the dots are individual measurements and the histogram monthly averages. Here measurements taken at an altitude of less than 50 m above the tropopause are not shown, because they were judged to have too small stratospheric character for an estimate of the concentration slope in the LMS. Both the slope and the tropopause concentration are affected by volcanism (Table 1), but the relative response of the slope is much stronger than that of the tropopause concentration, see e.g. the falls of 2008 and 2009 affected by the Kasatochi and Sarychev eruptions.

380 Observations at various altitudes above the tropopause are difficult to compare, due to the concentration gradient in the LMS. With the estimates of the tropopause concentration and the slope in the particulate sulfur LMS concentration, each measurement becomes an estimate of the total amount of particulate sulfur in the altitude interval investigated by integration of eq. 64. However, first the STP concentrations ($C_{S,STP} = C_S = aZ + b$) need to be converted to volume concentrations ($C_{S,V}$), which are related by $C_{S,V} = C_{S,STP} Q_{STP} / Q_V(Z)$, where Q are molar volumes. For that purpose, the altitude dependence of the molar volume from the tropopause up to 5 km above the tropopause was extracted from temperatures and pressures obtained from ECMWF for each sample. The molar volume can be expressed as $Q_V(Z) = Q_V(0) e^{wZ}$, where the tropopause is at $Z = 0$ and $w = 0.0001535 \text{ m}^{-1}$ obtained as the average of all samples. For a measurement the molar volume is Q_m obtained at distance Z_m from the tropopause, and the tropopause molar volume is computed by $Q_V(0) = Q_m e^{-wZ_m}$. Finally, the column concentration of particulate sulfur for the first 3 km above the dynamical tropopause of 1.5 PVU is obtained by integration of the volume concentration:

$$C_{S,col} = \int_0^{3000} \frac{Q_{STP}}{Q_V(Z)} C_{S,STP}(Z) dZ = \int_0^{3000} \frac{Q_{STP}}{Q_V(0)} e^{-wZ} (aZ + b) dZ \quad (7)$$

$$C_{S,col} = \int_0^{3000} (a''(y,s)Z + a''(y,s)k(s) + C_{S,UTrop}(s)) dZ \quad (9)$$

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The particulate sulfur column is calculated for altitudes above the tropopause (Z) in the range 0 to 3000 m, the upper limit because too few measurements (5%) were taken above that level. After integrating the column, it is also interesting to estimate the total amount of sulfur-connected aerosol. To that end, it was assumed that the aerosol consists of 75% sulfuric acid and 25% water, which is a commonly used stratospheric composition (Rosen, 1971; Arnold et al., 1998). This means that the total sulfur column was multiplied by a stoichiometric factor of $h = 4.084$ to obtain the column of the sulfuric acid – water aerosol:

$$C_{A,col} = hC_{S,col} \quad \text{_____} \quad (498)$$

The measurements were taken in the northern hemispheric latitudes higher than 30° with the highest latitude of 77° , with 90% of the data in the latitude range ~~34–32~~ - ~~65~~~~64~~⁶⁴° N and 70% of the data between ~~44–37~~ and ~~57~~~~6~~⁶° N. The northern mid-latitudes sulfur aerosol columns are shown in Fig. 65c as monthly averages with standard errors (the few months with only one measurement available are shown without an error bar). The sulfur aerosol column of the LMS shows large variability primarily caused by volcanism. The lowest columns are found in the period 1999 – 2002, when the volcanic influence on the stratospheric aerosol was small, see Table 1 ~~over-for~~ relevant volcanic eruptions. The time period mid-2005 to mid-2008 was affected by tropical volcanism (Vernier et al., 2011a), which also caused elevated concentrations in the NH LMS (Friberg et al., 2014). The eruptions of the extratropical volcano Kasatochi in August 2008 placed two volcanic clouds in the stratosphere (Andersson et al., 2015), one in the LMS causing strongly elevated aerosol column of the LMS that ceased by November the same year, and the other above the LMS. The latter cloud was transported downward, causing a rise of the lower LMS aerosol column in December 2008. After some influence from several eruptions of the extratropical volcano Redoubt in the spring of 2009, the eruption of Sarychev strongly affected the northern hemispheric stratosphere from ~~the summer of June of~~ 2009. The eruption of the Icelandic volcano Grimsvötn in May 2011 had a strong and short impact on the northern LMS, which is reflected by a peak in June to July 2011 (Fig. 65c), before the tropical volcano Nabro reached the northern LMS in the early fall of the same year. After that eruption a gradual decrease of the aerosol load can be seen. The concentrations after mid-2013 approaches those of the period 1999 – 2002, which was close to stratospheric background conditions.

The LMS aerosol contains a significant fraction of carbonaceous ~~aerosol-material~~ (Martinsson et al., 2009), mainly organic in nature (Friberg et al., 2014), which will add to the aerosol columns of Fig. 65c and affect the refractive index of the particles. However, this work is dealing with the sulfurous fraction, the main fraction of the stratospheric aerosol. To put the results presented in Fig. 65c into perspective, the AOD ~~will be~~ estimated using a simplified aerosol ~~(which thus likely is an underestimation of the AOD)~~. Thus, the “standard” stratospheric 75% sulfuric acid – 25% water composition, the particle density 1.669 g/cm^3 and the refractive index 1.44 will be used. Furthermore, particle size distribution measurements from IAGOS-CARIBIC have been taken since 2010 (Hermann et al., 2016). The changes of the size distribution induced by the moderate 2011 eruptions of Grimsvötn and Nabro were small (Martinsson et al., 2014), and agree well with previous measurements (Andersson et al., 2015) of the stratospheric background particle size distribution by Jäger and Deshler (2002). Thus, for the estimation of the AOD the latter particle size distribution was used for the entire time period studied. For fixed composition and particle size distribution the AOD is obtained as a fixed relation to aerosol column: $AOD = fC_{A,col}$, where f contains the relations

between mass and area/extinction, in this case $f = 3.29 \cdot 10^6 \text{ m}^2/\mu\text{g}$. Finally, converting the AOD to radiative forcing (RF) using the global average relation (Hansen et al., 2005; Solomon et al., 2011) of:

$$430 \quad RF = -25 \times AOD; \quad \text{in } Wm^{-2} \quad (94)$$

to obtain an estimate of the climate influence of the sulfate aerosol of the lower LMS. The peak AOD of the Kasatochi and Sarychev eruptions is approximately 0.0067, corresponding to -0.158 W/m² in regional radiative forcing of the lowest 3000 meters of the northern hemisphere LMS. Although no detailed comparisons will be made here, we find that the AOD and radiative forcing obtained from the particulate sulfur measurements show similar tendencies as satellite-based measurements (Andersson et al., 2015). The findings presented here also corroborates the findings of Andersson et al. (2015) on the importance of the LMS for the total stratospheric AOD and radiative impact.

4 Discussion

440 The results presented here are based on measurements in the extratropical UT and the LMS of the NH, where the latter includes the extratropical transition layer (ExTL). Bi-directional exchange across the tropopause affects strong gradients in the ExTL for species having clearly different stratospheric and tropospheric concentrations (Hoor et al., 2002), such as particulate sulfur (Martinsson et al., 2005). In the previous section, ~~the gradient, the~~ UT concentration, ~~the gradient in the LMS~~ and column amount of particulate sulfur in the ExTL ~~were investigated~~, with its seasonal dependence (Fig. 5) and the influence from volcanism (Fig. 65) ~~were investigated~~. In the processing of the data to obtain these results, in particular one feature stands out: the seasonal dependence of the particulate sulfur concentration from tropospheric sources that is mixed into the ExTL (Fig. 54b). It shows a broad maximum from ~~June-August~~ to ~~November-December~~, ~~peaking in September to November~~, and a deep minimum in the late winter and early spring (February ~~to April~~ and March).

450 Let us now compare these concentrations in the UT of tropospheric origin ($C_{S,UTrop}$) with average concentrations of particulate sulfur in the UT for two cases: “background conditions” dominated by data from mid-1999 to mid-2002 and “moderate ~~influence from tropical~~ volcanism ~~influence~~” dominated by data from mid-2005 to mid-2008, see section 2.3 for details. The seasonal dependence of these two categories are shown in Fig. 76a together with $C_{S,UTrop}$. It is clear that, in line with the findings of Friberg et al. (2015), the UT particulate sulfur concentration is affected by volcanism. In Fig. 76a we see that the main differences in UT concentrations of the two cases appears from ~~December-January~~ to ~~July~~, coinciding with the ~~main~~ season of transport ~~down~~ from ~~aloft the Junge layer~~ into to the LMS and the shrinkage of the LMS due to tropopause upward motion (Appenzeller et al., 1996; Gettelman et al., 2011). In the period ~~July-September~~ to November ~~the influence we see a small influence~~ from volcanism on the UT particulate sulfur concentrations ~~is small, by comparing~~ the background and moderate volcanism cases (Fig. 76a). Comparing these cases to the concentration of particulate sulfur found to be of tropospheric origin it is clear that 460 there is a strong agreement between all three categories in ~~the late summer and~~ the fall months, whereas differences are large during the remainder of the year. The UT particulate sulfur concentration of stratospheric origin can be estimated by subtracting $C_{S,UTrop}$ from the two cases of UT concentrations. The results are shown in Fig. 76b, where

465 peak stratospheric influences of ~~just above 619~~ and ~~almost 1236~~ ng/m³ STP are found in the spring, and minimum contributions of ~~less than~~ approximately 1 ng/m³ STP in the fall for the “background” and “moderate volcanism” cases. Summing the observations up (Fig. 76c), a clear seasonal dependence in the fraction of the UT particulate sulfur concentration originating in the stratosphere was found, from close to 100% in late winter/spring to approximately 10% in ~~late summer and the~~ fall. On a yearly average the fraction of the UT particulate sulfur that originates in the stratosphere is approximately 50% during background conditions and 70% during moderate influence from tropical volcanism influence.

470 The tropospheric source of UT particulate sulfur could be transported from the planetary boundary layer either in the form of particulate sulfur or precursor gases, in the latter case primarily sulfur dioxide (SO₂). In fall, winter and spring, with maximum in the winter, vertical transport by WCBs from the boundary layer to the UT is strong (Eckhardt et al., 2004), whereas in the summer deep convection is the most important mode (Hess, 2005; Kiley and Fuelberg, 2006) in the extratropics. For sulfate, the most common chemical form of particulate sulfur, the concentration usually shows a rapid decline with altitude in the troposphere (Heald et al., 2011) associated with formation of precipitation. Cloud processing also tends to strongly reduce SO₂ concentrations with altitude, where the relative availability of SO₂ and hydrogen peroxide (H₂O₂) is important for the SO₂ lifetime in the cloud.

480 We have found some very distinctive characteristics of the particulate sulfur concentration in the UT, with low concentrations in February and March, increasing concentrations during the summer and maximum in the sources of tropospheric origin in the ~~summer and~~ fall. Carbon monoxide (CO) is often used as a tracer of air pollution. Zbinden et al. (2013) found winter/spring maximum in the CO concentration in the UT of the NH in contrast to the tropospheric component of the UT particulate sulfur. This contrast can, at least in part, be explained by the oxidizing capacity in the UT, ~~where t~~ the summer abundance of the hydroxyl (OH) radical (Bahm and Khalil, 2004) induces a decline in CO (Bergamaschi et al., 2000; Osman et al., 2016). High abundance of this radical, on the other hand, and availability of SO₂ can lead to production of particulate sulfur. SO₂ measurements by the satellite-based instrument MIPAS indicate a UT seasonal variation in the NH midlatitudes with low concentrations in December to March and the highest concentrations in June to September (Höpfner et al., 2015). Deep convection provides a rapid route upwards in the atmosphere, favoring transport of short-lived species like SO₂ (TF-HTAP-2010; Dickerson et al., 2007). Low abundance of both SO₂ and OH in the NH UT thus could explain the weak tropospheric contribution to the UT particulate sulfur during late winter and early spring. The increase in C_{S,UTrop} during the spring and summer months coincides with increases in the concentration of both SO₂ and OH, thus offering a plausible explanation. Still, we need to consider the late maximum in the fall of the tropospheric source of UT particulate sulfur.

495 The Asian monsoon is an important feature of the global circulation in June to September, which has been found to reach deep into the lower stratosphere. This intrusion of tropospheric air into the tropical transition layer (Sunilkumar et al., 2017) has been manifested by gas phase components including water and ozone (Gettelman et al., 2004; Randel and Park 2006) and hydrogen cyanide (Randel et al., 2010). Later an aerosol layer extending from the UT to the potential temperature of 420 K in the lower stratosphere was found at 14 to 18 km altitude (Vernier et al., 2011b;

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500 Thomason and Vernier, 2013; Vernier et al., 2015). Figs. 8a-e show monthly means of the scattering ratio obtained from the CALIPSO sensor CALIOP for the months June to October 2013, when the volcanic influence was low. Formation of the ATAL can be identified in July (Fig. 8b) with maximum intensity in August (Fig. 8c). In September still a weakened ATAL can be identified (Fig. 8d), whereas in June and October the scattering in the ATAL region at 14 – 18 km altitude is very weak (Figs. 8a and e).

505 The altitude range of the ATAL is above the measurement altitudes of IAGOS-CARIBIC (9 – 12 km). However, the stratospheric circulation is directed downwards in the extratropics, but the ATAL is too weak to be traced by CALIOP in the downward transport (Figs. 8 a-e). We therefore illustrate the subsidence using the eruption of the tropical volcano Nabro in the summer 2011 (Table 1). The effluents of this eruption were rapidly transported to the north in the TTL. Figs 8f-j actually includes two volcanic eruptions, besides the tropical volcano Nabro, the Icelandic volcano Grimsvötn injected a volcanic cloud to the tropopause region at midlatitudes which is visible in June and
510 July 2011. The time series of the Nabro volcanic cloud in Figs. 8f-j unambiguously demonstrates the transport down to the IAGOS-CARIBIC flight altitudes in the season of the ATAL. In Fig. 6c we see a clear increase in the particulate sulfur column in September 2011, following the decline of the June-July 2011 short peak from the of Grimsvötn eruption in May 2011, thus demonstrating agreement between CALIOP and IAGOS-CARIBIC measurements of particulate sulfur. The volcanic cloud from Nabro initially resided at somewhat higher altitude than the ATAL, implying that the ATAL can be expected to reach IAGOS-CARIBIC flight altitudes somewhat earlier in the year. The transport in this season contains little particulate sulfur during periods without fresh volcanic aerosol, compare in Fig. 7 “tropical volcanism” (this category of Fig. 7 does not include the Nabro eruption, see section 2.3) with “background” and the particulate sulfur of tropospheric origin.

515 The downward transport allows delayed detection of the ATAL in the fall from altitudes above the measurement altitude range of IAGOS-CARIBIC in the same way as the spring detection of aerosol transported from the Junge layer, with or without volcanic influence, as shown in Fig. 7. A difference between these two seasons is that in the spring the strong source of particulate sulfur is stratospheric, whereas in the fall the source is tropospheric extending from the UT into the stratosphere. We therefore conclude that the UT particulate sulfur concentration of tropospheric origin that starts to increase rapidly in August, peaking in September to November, and is back at low concentration in January (Fig. 5b) most likely is caused by the ATAL formation from the Asian monsoon.

525 Model studies find similar UT – stratosphere distribution of the ATAL as the experimental studies, as well as that Asian pollution sources strongly contribute to the ATAL, and that sulfate is an important component of that aerosol layer (Neely et al., 2014). Besides this component, primary and secondary organic aerosol constituents are predicted to be important components of the ATAL (Yu et al., 2015). The present study is, as far as we know, the first observation of a chemical component of the ATAL. In agreement with modeling results we find that particulate sulfur is a component of the Asian tropopause aerosol layer. This component affects the tropopause region from July to September at 14 to 18 km altitude (Fig. 8) and the extratropical tropopause region from August to December (Fig. 5b). The tropospheric source of UT particulate sulfur could be transported from surface sources of either particulate sulfur or precursor gases, in the latter case primarily sulfur dioxide (SO₂). Warm conveyor belts (WCB) are

530 Model studies find similar UT – stratosphere distribution of the ATAL as the experimental studies, as well as that Asian pollution sources strongly contribute to the ATAL, and that sulfate is an important component of that aerosol layer (Neely et al., 2014). Besides this component, primary and secondary organic aerosol constituents are predicted to be important components of the ATAL (Yu et al., 2015). The present study is, as far as we know, the first observation of a chemical component of the ATAL. In agreement with modeling results we find that particulate sulfur is a component of the Asian tropopause aerosol layer. This component affects the tropopause region from July to September at 14 to 18 km altitude (Fig. 8) and the extratropical tropopause region from August to December (Fig. 5b). The tropospheric source of UT particulate sulfur could be transported from surface sources of either particulate sulfur or precursor gases, in the latter case primarily sulfur dioxide (SO₂). Warm conveyor belts (WCB) are

535 transporting large amounts of particles and trace gases from East Asia to North America and from the east coast of
North America to Europe (Luan and Jaeglé, 2013). For sulfate, the most common chemical form of particulate sulfur,
the concentration usually shows a rapid decline with altitude in the troposphere (Heald et al., 2011) associated with
formation of precipitation. Cloud processing also tends to strongly reduce SO_2 concentrations with altitude, where
540 the relative availability of SO_2 and hydrogen peroxide (H_2O_2) is important for the SO_2 lifetime in the cloud. This
seems to suggest that transport of SO_2 to the UT could be especially strong in the winter when the H_2O_2
concentrations are low. However, SO_2 measurements by the satellite based instrument MIPAS indicate, consistent
with $C_{\text{S,UTtop}}$ described above, a clear UT seasonal variation with low concentrations in December to March and the
highest concentrations in June to September (Höpfner et al., 2015). This seemingly contradictory result could
possibly be connected with modes of vertical transport. In fall, winter and spring, with maximum in the winter,
545 vertical transport by WCBs from the boundary layer to the UT is strong (Eckhardt et al., 2004), whereas in the
summer deep convection is the most important mode (Hess, 2005; Kiley and Fielberg, 2006). Deep convection
provides a rapid route upwards in the atmosphere, favoring transport of short lived species like SO_2 (TF HTAP
2010; Dickerson et al., 2007).

550 Fast summertime transport in deep convection provides high concentrations of SO_2 in the UT (Höpfner et al., 2015),
which together with a rich abundance of radicals (Bahm and Khalil, 2004) for SO_2 conversion to sulfuric acid, forms
a plausible explanation for the dominance of tropospheric sources in the UT in the summer and fall, whereas
tropospheric sources have only a weak impact on the UT particulate sulfur concentration in the winter and spring. In
contrast, the stratosphere was found to be a strong source of the UT particulate sulfur in the latter seasons, and the
strength of that source is strongly dependent on the degree of volcanic impact on the stratosphere.

555 5 Conclusions

Particulate sulfur (usually sulfate) in the upper troposphere (UT) and the lowermost stratosphere (LMS) obtained
from the IAGOS-CARIBIC platform was investigated at northern midlatitudes in the time period 1999 – 2014, which
covers several tropical and extratropical volcanic eruptions. The study is based on the use of linear regression
models, where individual measurements in the strong gradient of the extratropical transition layer (ExTL) can be
560 converted to an estimate of the column of particulate sulfur in a 3000 m layer above the dynamical tropopause (here
defined at 1.5 potential vorticity units). The obtained time series in particulate sulfur column concentration shows
distinct response to extratropical volcanism and delayed elevation of the column concentration following tropical
eruptions. Assuming the stratospheric background particle size distribution and composition (75% sulfuric acid and
25% water) the AOD and radiative forcing were estimated, e.g. the peak value following the 2009 Sarychev
565 eruptions were estimated to 0.0067 and -0.158 W/m^2 , respectively. These estimates refer mainly to the ExTL, i.e.
lowest part of the LMS, thus highlighting the importance of the lowest part of the stratosphere for the overall climate
impact of volcanism.

As a part of this investigation the sources of UT particulate sulfur were explored. A distinct pattern emerges where
tropospheric sulfur sources dominate the supply of particulate sulfur to the UT in the summer and fall, whereas

570 stratospheric sources dominate in January to July, the main season of transport from the Junge layer into the LMS.
The smallest contributions from the troposphere are found in February and March in conjunction with low sulfur
dioxide (SO₂) and oxidant concentrations. As the concentrations of these species increase, the UT particulate sulfur
concentration of tropospheric origin increases somewhat in April to July. The particulate sulfur concentration shows
575 a threefold increase during the fall, with maximum concentration in September to November. Making use of lidar
data from the CALIPSO satellite together with the in situ measurements we find that the Asian tropopause aerosol
layer (ATAL) resulting from the Asian monsoon is the cause of the increase. The ATAL is formed at 14 – 18 km
altitude and extends from the UT to approximately 420 K potential temperature in the stratosphere, with main
extension in July to September. The ATAL is transported downwards, and affects the extratropical tropopause region
580 in August to December. As far as we know, this is the first measurement of a chemical species in particles connected
with the ATAL. This coincides with the highest concentrations of sulfur dioxide and radicals in the UT and the deep
convection season, where the rapid vertical transport provides a pool of UT sulfur dioxide which assisted by high
radical concentrations form particulate sulfur. In contrast, during winter and spring the tropospheric sources are very
weak. Instead, the seasonal transport down from the stratosphere is a strong source of particulate sulfur. Thus, the
585 stratospheric and tropospheric contributions to the UT particulate sulfur concentrations thus have strong and opposite
seasonal dependences. On annual average the stratospheric contribution to the UT particulate sulfur is estimated to
50% during stratospheric background conditions. During influence from moderate tropical volcanism the
stratospheric fraction rises to 70%. The particulate sulfur concentration in the UT is thus to a large degree governed
by the stratosphere and volcanism.

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Data availability

590 Data are available upon request to the corresponding author.

Competing interests

The authors declare that they have no conflict of interest.

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820 **Tables****Table 1.** Most significant volcanic eruptions for the aerosol concentration in the northern hemisphere LMS in the time period studied.

Volcano	Date	Lat./Long.	SO₂ (Tg)
Manam	27 Jan 2005	4° S / 145° E	0.1 ^a
Soufriere Hills	20 May 2006	17° N / 62° W	0.2 ^b
Rabaul	7 Oct 2006	4° S / 152° E	0.2 ^a
Jebel at Tair	30 Sep 2007	16° N / 42° E	0.1 ^c
Okmok	12 Jul 2008	53° N / 168° W	0.1 ^c
Kasatochi	7 Aug 2008	52° N / 176° W	1.7 ^c
Redoubt	23 Mar 2009	60° N / 153° W	0.1 ^d
Sarychev	12 Jun 2009	48° N / 153° E	1.2 ^c
Grimsvötn	21 May 2011	64° N / 17° W	0.4 ^f
Nabro	12 Jun 2011	13° N / 42° E	1.5 ^f

^aPrata and Bernardo, 2007^bCarn and Prata, 2010825 ^cThomas et al., 2011^dBrühl et al., 2015^eHaywood et al., 2010^fClarisse et al., 2012

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Figures

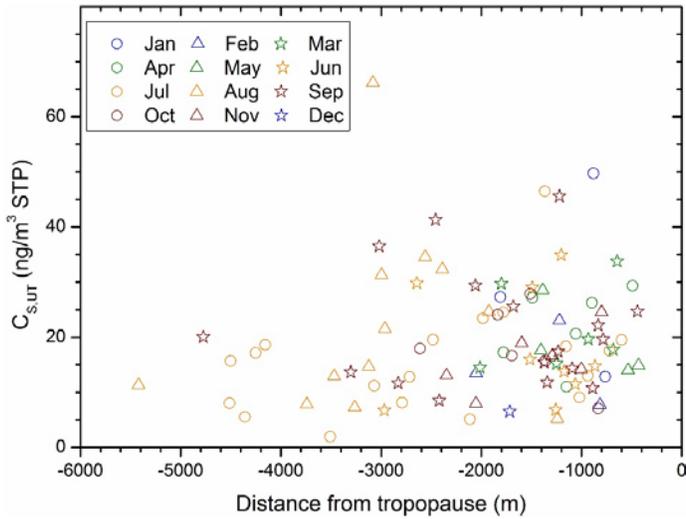


Figure 1: Upper tropospheric particulate sulfur concentration related to distance from the tropopause, where the symbols indicate sampling month.

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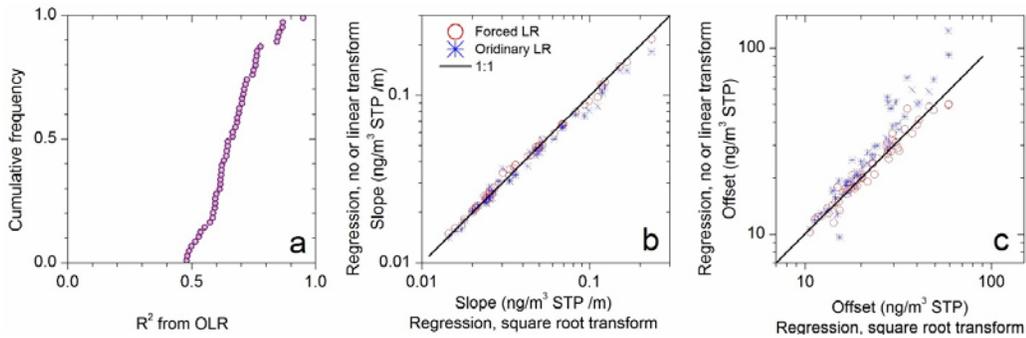
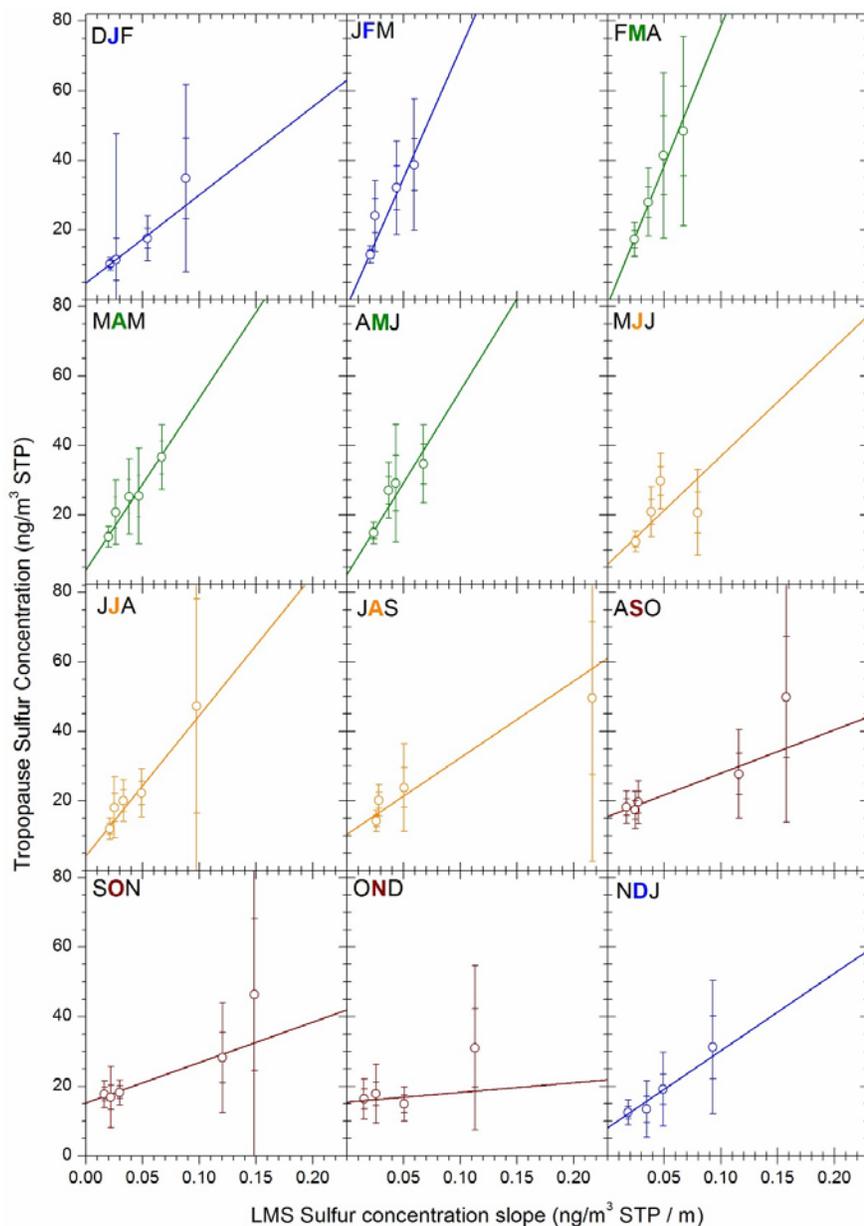
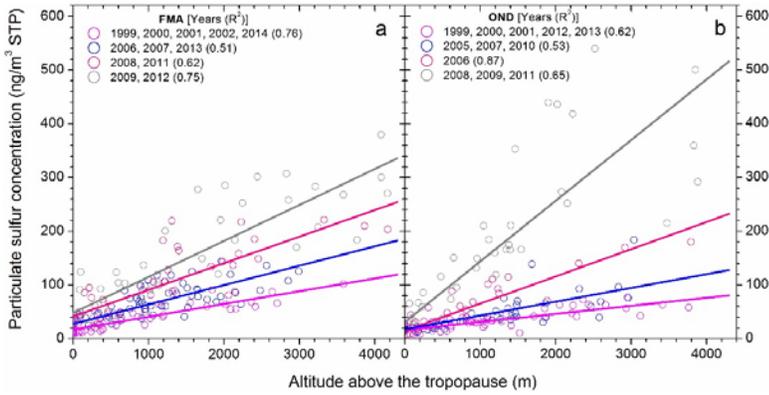


Figure 2: [a\) Cumulative frequency of the coefficient of determination \(\$R^2\$ \) of ordinary linear regression \(OLR\) between particulate sulfur concentration and distance from the tropopause of the 52 data groups used in this study.](#) [b\) and c\) Comparison of slope \(Fig. 2b\) and offset \(c\) between a square root transformed dependent variable and both OLR and forced linear regression.](#)



840 Figure 3: Weighted regression between slopes and offsets of all groups of each season (as in Fig. 2c). The offset indicates the tropopause (and UT) concentration of tropospheric origin ($C_{S,UTrop}$) and the slope of the fit (k) expresses the sensitivity of the UT concentration to changes in the stratospheric concentration slope (a''). The error bars show standard deviation and student-t 70% and 95% confidence interval, respectively.



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Figure 4: Examples of first step forced linear regression between the particulate sulfur concentration and the altitude above the tropopause for the data groups of two seasons: a) FMA (February, March and April) and b) OND (October, November and December). The legend shows which years are included in the respective data groups followed by the coefficient of determination in paranthesis.

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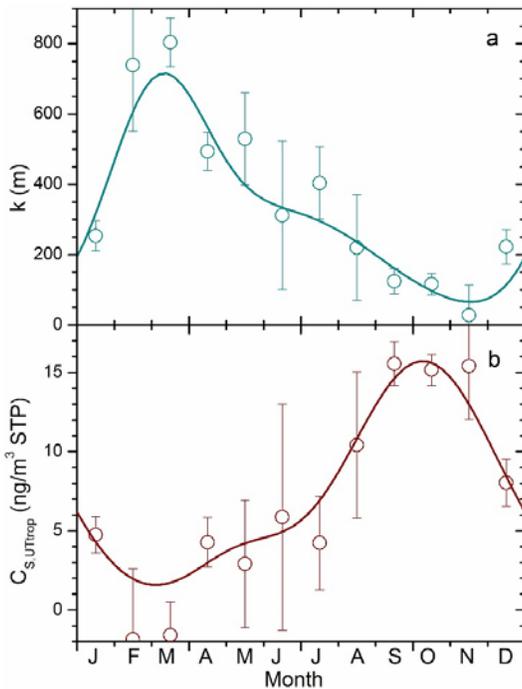
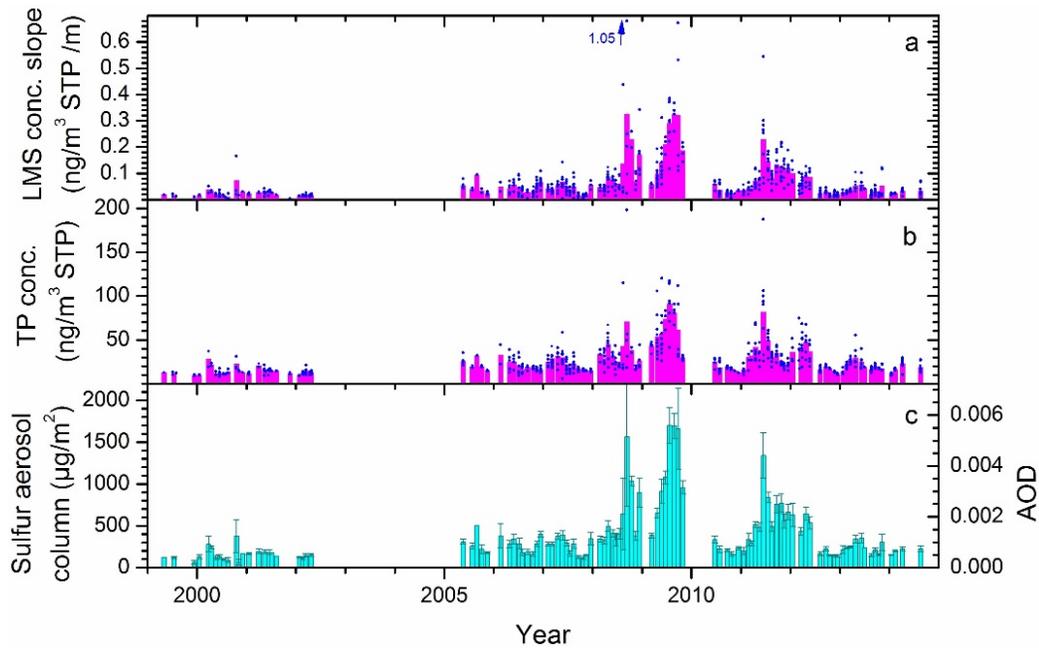
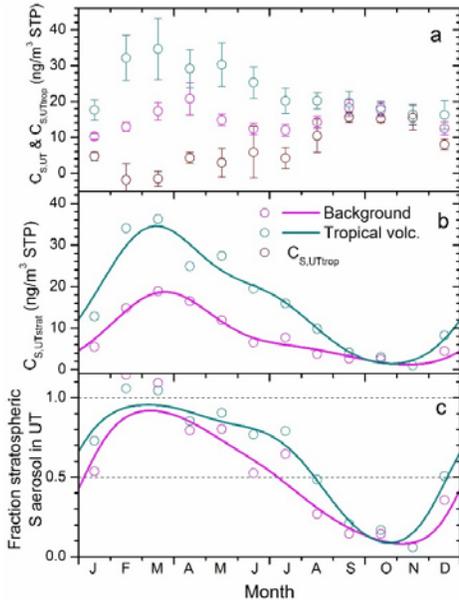


Figure 54: Seasonal variation of (a) the sensitivity of the UT aerosol-particulate sulfur concentration to the concentration slope in the LMS (k), and (b) the UT particulate sulfur concentration of tropospheric origin ($C_{s,UTrop}$).



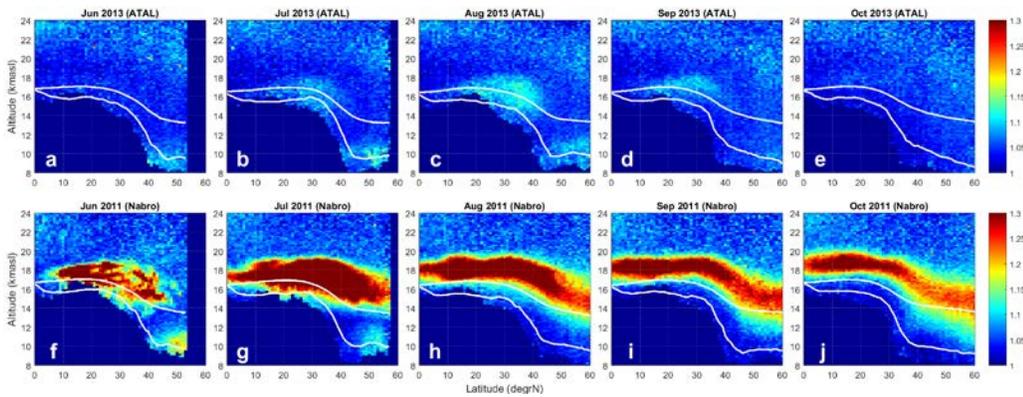
855 | Figure 65. Estimated (a) slopes and (b) offsets based on individual measurements (dots) and monthly averages (magenta bars). (c) Sulfur aerosol column of the lowest 3000 m of the LMS with standard errors, assuming particles of 75% sulfuric acid and 25% water, and AOD (right y axis) assuming stratospheric background aerosol particle size distribution.



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Figure 76. Seasonal variation of (a) the UT particulate sulfur concentration during LMS background conditions and moderate volcanic influence, together with the estimated UT particulate sulfur concentration of tropospheric origin ($C_{S,UTtrop}$), (b) UT particulate sulfur concentration of stratospheric origin ($C_{S,UTstrat}$) obtained by subtracting the $C_{S,UTtrop}$ from the two UT concentration cases in Fig. 76a, and (c) the ratio $C_{S,UTstrat}/C_{S,UT}$ for the two cases.

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Figure 8. Latitude and altitude distribution of scattering from aerosol in the stratosphere and the UT. Two series, from 2013 (upper row, a - e) and 2011 (lower row, f - j), show the monthly mean 532 nm wavelength scattering ratio from June to October without respectively with fresh volcanic influence. The former series allows identification of the comparably weak ATAL in July to September. The lower series includes two volcanic eruptions: the high altitude cloud from the tropical volcano Nabro (eruption in June 12, 2011) and the low altitude and midlatitude faint volcanic cloud from Grimsvötn (May 21, 2011). The two white lines in every graph show the monthly averaged positions of 380 K potential temperature (upper line) and the 1.5 PVU dynamical tropopause.