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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of volcanic aerosol on stratospheric NO_2 and N_2O_5 from 2002–2014 as measured by Odin-OSIRIS and Envisat-MIPAS" *by* Cristen Adams et al.

Cristen Adams et al.

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Response to Referee 1

We thank you for your comments, which have helped to improve our manuscript. Below we address the recommended changes point-by-point.

The manuscript presents interesting and novel results, but important issues should be addressed before publication. The main one, in my opinion, is that the analysis relies on averages calculated into monthly 10° latitude bins. Using such large intervals in time and space to study quite short-lived and local events such as volcanic plumes can lead to important biases in the results.

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Discussion paper

See response to General Comment B in response to Referee 3.

Specific comments:

p.2, l.9: "NOx" should be defined.

We have added a definition for NOx.

p.4, l.18: Please give more details on the climatological profiles used for ozone and temperature, and explain your choice of using these profiles rather than using directly MIPAS and OSIRIS measurements of O_3 and T.

This has been addressed in response to Reviewer 3 under Sect. 2.3.

p.4, 19-20: Please clarify the sentence "All remaining species are calculated to be in a 24-hour steady-state by integrating the model over 30 days, but fixed to a specified Julian day".

This has been addressed in response to Reviewer 3.

p.4, l.22: The effects of polar stratospheric clouds are not considered here. However, these could play a role in the altitude range under consideration, especially in summer, which is the season on which this study is focused. This should be discussed while interpreting the results.

The lack of PSCs should not be a large factor here since only latitudes north of 55S are considered in the updated analysis (see Response to Reviewer 3, General Comment A). Moreover, the intent of the model is to demonstrate that the 'average' relationship seen in the OSIRIS NO_2 and aerosol extinction observations can be captured by the model, thereby demonstrating that the two are consistent with our current understanding of the impact of aerosol on NOy partitioning. It is possible that one or more OSIRIS monthly/zonal means might be contain some PSC signal, and this would lead to some departure from the non-PSC expected relationship, but there is no evidence of this in the observations at 70° or 80°N and at the high end of the AOD scale (the last two

panels in Figure 5).

p.5, l.9-10: How the factors 3 and 1/3, used to account for potential errors in your background aerosol surface area, have been chosen?

The relationship between surface area and extinction, for Mie theory, is through the scattering efficiency, which depends on several factors. The most important of is the aerosol size distribution. As there is some uncertainty in the parameters than define this, such as the effective radius and the variance of the distribution, we considered a range of different values. The end results was the scattering efficiency was found to vary by a factor of 2 (1/2), and so we used a factor of 3 (1/3) to be conservative in our uncertainty estimates

p.5, l.21: Place clarify "for the five measurement layers from 3-7 km above the NCEP thermal tropopause..." I do not clearly understand which measurement layers you are using.

We are adding the partial column using the layers 3, 4, 5, 6, and 7 km above the tropopause. We have clarified this throughout the text by instead referring to the partial column over "the 5-km layer starting 3 km above the mean tropopause at the given latitude"

Section 3: The analysis is based on monthly means calculated in 10° latitude bins. The choice of such large intervals in time and space does not seem to be the most appropriate to study volcanic plumes, which are quite short-lived and local events. A different distribution of the observations from OSIRIS and MIPAS in a given bin might lead to very different results. The same comment is also relevant for the photochemical model, which covers the whole bin in a uniform way, while this is probably not the case for the observations. Was it not possible to perform the analysis using more appropriate bins? In this case, the authors should find a way to estimate the sensitivity of their results to this problem, and this should be thoroughly discussed in the paper. Have the authors try to use only the modelled data in collocation in time and space with the

observations?

For OSIRIS and the photochemical model, there should not be great sensitivity to this. OSIRIS NO_2 and extinction measurements are sampled approximately the same. For the photochemical model, we are interpolating NO_2 to the mean extinction as measured by OSIRIS.

MIPAS sampling is not identical to OSIRIS, but covers the selected bins fairly evenly. This has been discussed in Response to Reviewer 3, General Comment B.

p.8, l.13-17 and Fig.3: Please comment the high AOD levels at southern high latitudes, which are obviously not due to volcanic eruptions. We can read, p.9 l. 5-6, that these are "perhaps due to polar stratospheric clouds". This should be discussed already in the description of Fig.3, and this statement should be explained, or at least associated with a reference.

We have removed southern hemisphere high latitudes from analysis, as discussed in General Comment A in response to Referee 3.

p.9, l8: Is the second interval considered to calculate the correlation coefficients 40° N-80° N or 40° S-80° N? The information given in the figure is inconsistent with what is said in the text. Same remark p.9, l.22.

Thank you for noticing these typos. We have corrected the text to 40°N-80°N.

p.9, l.16-18: This could be checked by applying MIPAS averaging kernels to the OSIRIS data. This has already been done in several studies comparing MIPAS data to other data sets characterised by a better vertical resolution.

This has now been tested. See response to General Comment C in response to Referee 3.

p.10, l.15-16: Was the vertical resolution of the MIPAS N_2O_5 profiles also not good enough to look at the effect of volcanic aerosol on this species as a function of altitude?

The vertical resolution of N_2O_5 is 6-8 km for much of the lower stratosphere (see Fig. 3 of Mengistu Tsidu et al 2004) and therefore is not sufficient to look at the effect of volcanic aerosol. We have clarified this in the text in Sect. 4.2:

"The MIPAS NO_2 and N_2O_5 profiles were not considered because of limitations in the vertical resolution in the lower stratosphere."

Technical corrections:

p.1, l.24: Remove "of"

This has been removed

p.1, l.25: Please change "relationship" to "anti-correlation"

This has been replaced

p.3, l.22, p.4, l.1, p.4, l.14 for example: Please write "lower than" or "greater than" instead of "<" or ">".

We have replaced the ">" and "<" throughout the document.

p.5, l.19: For the sake of clarity, please add "number densities" after "SO_2, NO_2, N_2O_5 and HO_3".

This has been added

p.6, l.13: "on the same order of magnitude AS the variation..."

This has been corrected

p.6, l.27: "...periods that WERE not affected by volcanic aerosol."

This has been corrected

p.10, l.17: Please add "percent difference" in "OSIRIS and modelled NO_2 percent difference profiles".

This has been corrected

p.10, l.20-23: For the sake of clarity, the given percent different values should be negative (same remark p.11, l.2)

We have specified all the percent differences as negative, as recommended

Fig. 3, 6, 7 and 8: These figures would be clearer if there was a limited number of colours in the colour bar, so that it corresponds to the colour levels shown in the plots.

We have changed the figures as recommended.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-242, 2016.

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Discussion paper

Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-242-AC2, 2017

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of volcanic aerosol on stratospheric NO_2 and N_2O_5 from 2002–2014 as measured by Odin-OSIRIS and Envisat-MIPAS" *by* Cristen Adams et al.

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Received and published: 11 April 2017

Response to Referee 2

We thank you for your comments, which have helped to improve our manuscript. Below we address the recommended changes point-by-point.

1 General Comments

A big problem with the paper is that it totally relies on monthly zonal means which is not appropriate for the rather local and short lived volcanic plumes. Because of this, MIPAS SO_2 data are provided as 5-day means (Höpfner et al., 2015). Regarding the monthly zonal mean binning of AOD, smaller bins have been tested and found to have minimal

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Discussion paper

impact for the OSIRIS measurements. Please see response to General Comment B in response to Reviewer 3 for further details. We have elected to remove MIPAS SO_2 from the analysis, as described in more detail in responses below. Several important volcanic events listed there are missing or placed at the wrong latitude (Figure 3).

Volcanic events are missing because we have only listed events that were observed in the OSIRIS stratospheric aerosol measurements. We have clarified this in the figure caption:

"The yellow triangles indicate the volcanic eruptions that were followed by significant increases in OSIRIS aerosol extinction, as listed in Table 2."

We have also clarified how volcanic eruptions are identified in other parts of the text, as noted in the details of this reviewer response below.

Thank you for noticing the problem with the latitudes of the volcanic eruptions in Fig. 3. The latitude of Sarychev Peak has been corrected in the revised figure.

There is also no need to use inconsistent climatological ozone for the photochemistry, from both instruments, OSIRIS and MIPAS, are selfconsistent data available.

Uncertainties due to the use of these climatologies have been estimated and are described in the text (Sect. 2.3), as well as in Figure 8 of response to Reviewer 3.

2 Specific comments

Abstract: Do the authors mean a 4 km thick layer above the tropopause, in tropics and midlatitudes, and against what conditions is the change?

We have re-worded this part of the abstract as follows:

"OSIRIS profile measurements indicate that the strongest correlations between NO_2 and volcanic aerosol extinction were for the 5-km layer starting 3 km above the mean tropopause at the given latitude. OSIRIS stratospheric NO_2 partial columns in this layer were found to be smaller than baseline NO_2 levels during these aerosol enhancements

by up to 60

Please define NOx in line 9 of page 2.

We have added the definition.

Please improve wording in line 13 of page 3, it contains contradictions.

We have reworded this to

"OSIRIS measures limb-scattered radiances from 82°S to 82°N, with nearly full coverage in the summer hemisphere."

From the data version number, it looks like that Höpfner et al (2015) is used (line 9ff,page 4), here also the SO_2data prior to 2005 are OK. In these data, especially if the 5-day means are used, all important volcanic events should be identified with significance (see also lines 15 and 25, page 8). This is not the case for the older dataset presented in Höpfner et al (2013) which had the focus on the middle and upper stratosphere.

MIPAS SO_2 played a very minor role in this paper. We included it because it was interesting to see how the SO_2 VCDs varied in the context of the OSIRIS AOD time-series. Since we are using monthly averages for the other species in this study, we presented SO_2 in a consistent way. However, we don't want misrepresent the resolution/capabilities of MIPAS SO_2. Therefore, we have elected to remove MIPAS SO_2 from the paper. This means that panel b of Fig. 3 has been removed and that we have deleted the paragraph describing the MIPAS SO_2 and replaced it with a reference to Hopfner et al. 2015. This has not affected any of the major conclusions/results of this paper.

For the crude assumptions on the Mie scattering efficiency the wavelength should be repeated (line 2, page 5). The statements on particle size (line 5, page 5) are confusing, more details please, give at least a range for the effective particle size. If you model particle size from aerosol formation from injected SO_2, you get in increase in effective

particle size for both volcanoes. What is the basis for the crude error assumptions (factor 3)?

The basis for the large uncertainty we prescribe is two-fold: (1) We can only make an educated guess at the particles sizes and (2) since average particle sizes can increase or decrease following and eruption, depending on the relative amounts of new (smaller) particles formed vs. growth of existing particles. For a handful of eruptions there are some observations available, but most of those considered here this is not the case. This leads to uncertainty as to how to adjust the scattering efficiency. For (1) we conservatively estimated a factor of 3 based on sensitivity studies using different size parameters and distributions, and for (2) we estimated uncertainty based on Thomason et al. (1997). It is worth noting these uncertainties (presumably towards an upper limit) still do not have that large an impact on the model results, showing that the simulations are quite robust.

In response to the comment above we have fleshed this out with some additional detail/explanation.

"A scattering efficiency of 0.40 was calculated using Mie theory for background spherical sulfate particles (based on a log-normal distribution with size parameters of r_g=0.08 μm and σ_g=1.6). However, volcanic eruptions alter the size distribution, as SO_2 rapidly forms sulfuric acid, which can condense to form new small particles or increase the size of existing ones. This change in size distribution will affect the scattering efficiency, but the sign of this change is unknown. For example, two months after the Kasatochi eruption, there was a shift in the ambient size distribution toward smaller particles (Sioris et al., 2010) whereas Sarychev led to a shift toward larger particles (O'Neill et al., 2012)."

And

"To account for potential errors and variability over 2002-2015 in our background SA, we scaled 10000 by factors of 3 and 1/3. The large factor is based on the sensitivity of scattering efficiency to the aerosol size parameters for the particles sizes and

wavelengths considered here. For example, a change in effective radius by a factor of 2 leads to a change in scattering efficiency by a factor of 3 (see Hansen and Travis [1974] Figure 8)."

Isn't there also an averaging kernel for OSIRIS (line 19ff, page 5)?

There are not averaging kernels for OSIRIS retrievals. The resolution of OSIRIS is 2 km at the altitudes considered here, which is sufficient to retrieve partial column VCDs for the 5-km altitude range.

In Fig. 1 an additional panel with the zonal wind at 20 km (?) might be useful (line 21, page 6).

We have not included the zonal wind at 20 km since the QBO principal components are derived directly from the zonal winds.

Why are different partial columns given in section 3.3 (line 23, page 7) and earlier in the text (including abstract)?

The same partial column ranges are given in all section. The partial columns are calculated for the 5 measurement layers between 3-7 km above the mean thermal tropopause (e.g., over a 5-km range). We have clarified this in the text in Sect. 3.1.

". . . a 5-km altitude range starting at 3 km above the mean NCEP thermal tropopause at each latitude"

In Table 2 at least the eruption of Rabaul in Oct. 2006 is missing.

There was not a significant increase in OSIRIS aerosol extinction following the Rabaul eruption and therefore it, and likely other volcanoes, are not included in this table. We have added the following to the table caption to make sure this is clear:

"Note that this table only include eruptions that were followed by significant increases in OSIRIS aerosol extinction. Therefore it does not include all volcanoes known to have affected the stratosphere during this time-period."

There appear to be contradictions between Fig. 3 and 4.

I cannot find these apparent contradictions. The data presented in these figures come from the same data vectors, etc. We have revised the colorbar of Fig. 3 in order to make it easier to compare.

Improve Fig. 3 concerning $SO_2$with the Höpfner (2015) 5-day dataset. We have removed MIPAS SO_2 from the figure and the paper, as described above.

Fig. 3: Place the symbols for the volcanoes at the correct latitude.

The latitude for Sarychev Peak has been corrected.

It might be better to use volume mixing ratios at 19 km (or 3 km above the tropopause) instead of the partial columns to reduce data gaps.

In earlier iterations of this analysis, we did consider VMRs at fixed altitude levels above the tropopause, but elected to present the results as partial columns. We have added the following text to the first paragraph of Sect 3.1 in order to explain this:

"Partial columns were used, instead of, e.g., volume mixing ratios at a fixed altitude, because the largest observed aerosol extinction ratios related to volcanic aerosol were observed at different altitude layers for different latitudes and times. The partial column altitude range was selected to include most of these large extinction ratios. Furthermore, MIPAS NO_2 measurements have low resolution at the altitudes affected by volcanic aerosol and therefore are better presented as partial columns."

The results are also sensitive to the treatment of negatives in the individual data.

We did not remove negative values in the individual profiles before averaging because we did not want to create a high bias in the datasets when averaging values that are close to zero.

I don't understand the statement on tropospheric water vapor (line 22, page 8). The current understanding is that for explosive eruptions SO_2 is directly injected into the

stratosphere, in the plume only water from the volcano might matter, but the satellite sees only what comes out of the plume.

Since we have removed SO_2 from the paper, this has been deleted.

Section 4.2: In Figs. 1, 6 and 7 appear often extinction ratios < 1. Please explain or correct, from definition this should not happen. Please adjust color bars to reasonable range,

The extinction ratio is defined as (Aerosol Extinction / Raleigh Extinction), in which case if the aerosol extinction is greater than the Rayleigh extinction, the ratio will be greater than 1.

We are also unsure what the reviewer means by "reasonable range". Therefore, we have adapted the color bars on various figures using the recommendations of Reviewer 1.

Don't use formulations like 'somewhat linear' (line 4, page 10; line 3, page 12).

This has been corrected, as per response to Reviewer 3.

3 Technical corrections

Line 20ff, page 1: Better 'anticorrelation' instead of 'relationship'.

This has been changed

Line 6, page 5: typo and bad wording.

We have reworded this paragraph, with the text starting with "In order to remove the seasonal variation from the NO_2 time series, the NO_2 anomaly (dNO_2) was calculated for each bin of the monthly mean NO_2 VCDs. . ."

Figure 3, caption line 4: Do you mean a 4 km thick layer 3 km above the tropopause? Please improve text.

This has been changed to "5–km layer starting 3 km above the thermal tropopause"

Truncate Figs. 6 and 7 at 12 km, the data below are not relyable. Say 'aerosol extinction ratio' also in captions. The black contours are superfluous. The colorbars should have the same steps as the colors in the figures (less is more!).

We have changed "extinction" to "extinction ratio" in the captions and the figure color bars and contours have been changed.

Fig.8: Caption: Say 'correlation coefficient' instead of 'R'. The colorbar should have the same steps as the colors in the figure.

The caption and figure have been changed as recommended.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-242, 2016.

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Discussion paper

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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of volcanic aerosol on stratospheric NO_2 and N_2O_5 from 2002–2014 as measured by Odin-OSIRIS and Envisat-MIPAS" *by* Cristen Adams et al.

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Response to Referee 3

We thank you for your comments, which have helped to improve our manuscript. Below we address the recommended changes point-by-point.

General comments:

Since these general comments have been repeated/clarified in the specific comments below and by other reviewers, we have labelled them A, B, C (as listed below), so that the responses could be more easily cross-referenced.

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Discussion paper

A. NO_2 anomalies in presence of polar stratospheric clouds, a case for which discussion is avoided in the paper, seems not to reflect the denitrification expected in this case.

The reasons for the variations in AOD at the Southern Hemisphere high latitudes are unknown. In order to remove profiles potentially affected by PSCs from the analysis, layers of extinction profiles that were measured at temperatures < 195 K, the temperature for PSC formation, were removed from the analysis. The high monthly mean AODs at these latitudes were not removed with this new filter. Since the reasons for these fluctuations are unknown, we have decided to remove 60°S to 90°S from the analysis. We have adjusted the figures accordingly and have added the following text to the first paragraph of Sect. 3.1

"Latitudes south of 50°S were excluded from the analysis because there is no evidence of volcanic aerosol at these southern hemisphere high latitudes and OSIRIS AODs are dominated by seasonal variation."

Overall, the paper provides interesting observations, but I think that two aspects have not been considered appropriately and might explain the inconsistencies found between MIPAS and OSIRIS measurements.

B. First, the authors consider monthly zonal means, with 10° latitude bins. This is a very coarse grid to study volcanic plume such as the ones considered in this study. The effects the authors want to study are largely diluted in the bin averaging and the mean values obtained from the binning are likely to be biased depending on the coverage of the instrument. Obviously, the effect of the bias is expected to increase if the comparison concerns data from two different instrument (with different coverage). Another similar source of bias could be the use of climatological data for ozone, neglecting the effects of local chemistry

The 10° monthly latitude bins were selected for two reasons:

1. Bins of this size are often used in studies of long-term variations and trends. Therefore, the results of this work is more directly applicable when understanding, e.g., long-term trends in NO_2 timeseries.

2. This allowed a large amount of data to be averaged in most bins (typically ~100 measurements for both OSIRIS and MIPAS), which helped to decrease noise and smear out short-term natural variation. This is particularly useful when fitting contributions from QBO and estimating baseline NO_2, which varies seasonally and with latitude.

In order to test the effect of the bin sizes on our ability to assess processes around volcanic aerosol, we recalculated OSIRIS AODs in 5° latitude bins at a sampling of four times per month (approximately weekly). Based on the OSIRIS sampling, these are the smallest bins that would yield reasonable results. The observed AODs are shown in Figure 1 for latitude bins centered around 60°N, a latitude at which there were several episodes of enhanced volcanic aerosol. The maximum AODs for both bin sizes are very similar, suggesting that the smaller bin sizes do not give additional information on the volcanic events. Similar results were observed at other latitudes. The maximum observed AOD for all latitude/time bins was 0.0086 for the 10° monthly bins and was 0.0088 for the 5°, $\frac{1}{4}$ month latitude bins.

The 10° monthly bins are suitable for this analysis because the lifetime and transport of sulfate is slow compared with SO_2 and ash. Furthermore, individual OSIRIS profiles with very large extinctions (>2x10^{-3} km^{-1}), which could be associated with ash or very fresh plumes (~1-2 weeks) were removed from this analysis, which allowed for the direct focus on sulphate/NO_2 chemistry.

An example of the MIPAS sampling relative to OSIRIS AOD sampling is given in Figure 2 and Figure 3 for the 50°N latitude bin. This latitude was chosen to explore sampling because this latitude had valid MIPAS measurements for larger OSIRIS AODs (see Fig. 4a of the paper). Both OSIRIS AODs and MIPAS NO_2 measurements are sampled fairly consistently in latitude and time, with no obvious biases that would skew

the relationship between MIPAS NO_2 anomalies and OSIRIS partial column AODs, nor that would lead to large biases in ozone between the MIPAS and OSIRIS sampling. Furthermore, comprehensive tests on MIPAS and OSIRIS sampling have been performed for ozone by Toohey et al. (J. Geophys. Res., 118 (11), pp847–11,862, doi:10.1002/jgrd.50874, 2013) and found that MIPAS and OSIRIS have sampling biases of < 2% and < 5% for most latitudes/altitudes.

We have added the following text to the paper to address these comments:

- Sect. 3.1, second paragraph "Bins were tested for smaller latitude and time ranges, but yielded similar ranges of AODs, suggesting that smaller bin sizes did not capture more detailed processes in the volcanic plume."

- Sect. 4.1, fifth paragraph "These discrepancies could not be attributed to differences in sampling between OSIRIS and MIPAS, since MIPAS and OSIRIS both sample throughout the monthly 10° latitude bins. MIPAS measurements are not clustered in parts of the bin where smaller OSIRIS AODs were observed."

C. The second weakness of the paper, in my opinion, concerns the discussion of the comparison between OSIRIS and MIPAS data, where arguments based on the limited degrees of freedom provided by MIPAS are used to justify the disagreement between results obtained from both instruments. Before drawing definitive conclusions from this hypothesis, the authors should check their interpretation by degrading both datasets to similar resolutions. These issues should be addressed before publication of the manuscript.

In order to test the effect of the MIPAS resolution on the data, representative MIPAS NO_2 averaging kernels, A, were considered for the 50°N and 0° latitude bins and applied to the OSIRIS NO_2 profiles. The representative profiles had averaging kernel diagonal elements (AKD) closest to the mean averaging kernel diagonal elements ($\overline{AKD}$) within the vertical range of interest that the VCDs were calculated over. E.g., the representative MIPAS averaging kernels minimized

$\sum_j \left(AKD(z_j) - \overline{AKD}(z_j) \right)^2$,

where z_j are altitude layers in the 5-km altitude range used to calculate the VCDs. The representative averaging kernels, in Figure 4, show reduced resolution over the altitude ranges used to calculate the partial columns in this paper, indicated by the dashed lines.

Since MIPAS NO_2 retrievals are logarithmic, smoothed OSIRIS NO_2 profiles, x_s, could be calculated using from original OSIRIS profiles, x, using

$x_s = e^{A \cdot ln(x) + (1-A) \cdot ln(x_a)}$,

where x_a is the MIPAS a priori. It then follows that the OSIRIS percent difference profiles, PD, can be interpolated to the MIPAS grid smoothed using

$PD_s = e^{A \cdot ln(PD+1)} - 1$.

Figure 5 and Figure 6 show the unsmoothed and smoothed OSIRIS profiles for 0° latitude and 50°N latitude, respectively. The dashed lines indicate the altitudes over which the partial columns were calculated. The unsmoothed OSIRIS profiles are what is shown in Fig 6 and Fig 7 of the paper respectively, but are presented here as a line plot so that the values of the NO_2 percent differences can be compared more closely. For both latitude ranges, the magnitude of negative NO_2 percent differences is reduced after applying the MIPAS averaging kernels. For example, at 50°N, NO_2 percent differences of approximately -45% to -50% are smoothed to approximately -30% after the MIPAS averaging kernel is applied. Therefore these tests demonstrate that the resolution of MIPAS decreases the observed NO_2 anomalies under the presence of volcanic aerosol.

These tests could not be applied quantitatively to the entire analysis because the MIPAS averaging kernels vary for each profile and are correlated with the amount of NO_2 present. Individual MIPAS averaging kernels could not be applied directly to the OSIRIS data because MIPAS averaging kernels are only available for the measure-

ment times and locations of MIPAS, which are not coincident with OSIRIS measurement times and locations. This is why representative averaging kernels were used to assess this problem. The mean DOFS of the MIPAS VCDs tended to be lower during periods with enhanced OSIRIS partial column AODs, described in the text of the paper and shown in Figure 7. This decreased resolution would further smooth out the MIPAS measured NO_2 anomalies.

The following text has been added to Sect. 4.1, 5th paragraph:

"In order to test this, representative MIPAS averaging kernels were applied to the OSIRIS NO_2 percent difference profiles at 50°N and 0° latitudes. Representative averaging kernels were used because MIPAS NO_2 is retrieved in the logarithmic domain and the averaging kernel thus refers to the logarithm of the mixing ratio. By applying the averaging kernel directly to the percent difference profile, the MIPAS a priori profile does not need to be included in the calculations. The magnitude of the largest percent differences in the NO_2 percent difference profiles decreased from approximately -45% in the original OSIRIS profiles to approximately -30% in the smoothed OSIRIS profiles, demonstrating this damping effect. These tests did not account for variation of MIPAS DOFS with partial column AOD. The smaller DOFS observed for larger OSIRIS partial column AOD would lead to further damping of the MIPAS NO_2 percent differences. "

Specific comments:

Abstract

L. 23: The authors mention percent difference of up to ~25%. They should mention with respect to what (to OSIRIS? To quiescent periods?)

We have clarified this by adding "relative to baseline levels" to the text.

1. Introduction

L. 8, p.1: The authors should define NOx like they defined NOy. Possibly at the same place to lighten the text, see technical comment on L. 4.

A definition of NOx has been added

L. 16, p.2: For the sake of clarity: "NOx/NOy decreased with increasing aerosol surface area".

This has been edited as recommended

2. Satellite and model datasets

2.3 Photochemical modelling

All three reviewers had comments regarding the inputs to the photochemical model. In order to address these comments, we have changed the input ozone climatology and have revised our model errorbars using a series of perturbation tests. These tests are described in Sect. 2.3 and summarized in Table 1, and included in Fig. 5 of the revised paper. The break-down of the major contributions to the uncertainty estimates is given in Figure 8. These tests are described in Sect. 2.3 and summarized in Table 1, and included in Fig. 5 of the revised paper. The break-down of the major contributions to the uncertainty estimates is given in Figure 8. Aerosol (black) are for the two error terms related to extinction to surface area conversions. Ozone (blue), temperature (red), albedo (cyan), and NOy (green) refer are for year-to-year variability in these inputs. Systematic errors in ozone, temperature, albedo, NOy, NO_2 cross-section, and NO-O_3 reaction rates are mostly 1-2

L. 16, p.4: Which type of climatological data are used for ozone and temperature? And why don't they use MIPAS ozone data which would be fully consistent with the used data for SO_2, N_2O_5, HNO_3 and NO_2 ? Perliski et al. (1989), cited in Randeniya et al. (op. cit., 1997), indicate that the ozone behaviour at high latitudes is expected to be dominated by local chemistry during summer, which is the time and region of interest for the present study, and where Eq. (2) is expected to have the greatest impact on ozone. Hence, using climatological data for the ozone field in this specific study focussing on the effect of volcanic eruptions might bias the results of the analysis.

We initially used a standard O_3 climatology (from McPeters et al., JGR, 1999). However, we have since switched to an OSIRIS zonal, monthly-mean climatology for the revised version. (From previous experience we knew OSIRIS agreed very well with other ozone climatologies and so we simply used our model default inputs.) For temperature we use a climatology from Nagatani and Rosenfield (1993). OSIRIS does not measure temperature. We could have used MIPAS temperatures, and it has a small (2 K) bias in the lower stratosphere (Stiller et al., Atmos. Meas. Tech., 5, 289–320, 2012), but as demonstrated in the sensitivity study, systematic errors in temperature, make very little difference. The uncertainties associated with interannual variability in ozone were estimated and included in the errorbars in Fig. 5 of the revised paper. The contributions to these error estimates from ozone are shown in Figure 8, and are ~3-10% for most of the data points, except in the tropics (see Figure 8 of this reviewer response).

Nagatani, R. M., and J. E. Rosenfield (1993), Temperature, net heating and circulation, in The Atmospheric Effects of Stratospheric Aircraft: Report of the 1992 Models and Measurements Workshop, NASA Ref. Publ. 1292, edited by M. J. Prather and E. E. Remsberg, pp. A1–A47, NASA, Washington, D. C.

L. 18, p.4: I don't understand what the authors mean with "but fixed to a specified Julian day". Please clarify.

The model is integrated forward in time but instead of moving from JD to JD+1, where there would be differences in solar illumination, it again repeats JD. It continues to loop over this same day, up to 30 times, until the model converges. That is, concentrations at the end of the day match the beginning ("in a 24-hour steady-state").

The text has been modified to read "All remaining species are calculated to be in a 24-hour steady-state by integrating the model for as many as 30 days, but where the model remains fixed on the original, specified Julian day".

L. 20, p.4: Since Thomason's climatology covers the whole period 1979-1995, it would

be useful to explain in a few words which data are used in the present study (specific year and/or region?). If they only use the approximated expressions (5) of Thomason's work as discussed in the following of the section, the authors could already announce that here (e.g.: "(...) using the aerosol surface area climatology of Thomason et al (1997) as explained later, (...)"). Actually, I don't know why the authors want to consider heterogeneous chemistry on background stratospheric aerosols, since they aim at studying typically volcanic situations. Besides, they mention further that they match the extinction coefficient with OSIRIS values, which should normally reflect this volcanic feature. All these points should be clarified.

The sentence in question is an artifact of a much earlier draft of this paper that was not properly adjusted to reflect the methodology used herein. We did not use the Thomason et al. climatology at all, as the reviewer questions. Further, the use of the word "background" is also not correct in this context, also caught by the reviewer. The sentence now reads "Heterogeneous chemistry on stratospheric sulfate aerosols is included, but polar stratospheric clouds are not included."

L. 24, p.4 to L. 10, p.5: The estimation of the SA in function of the extinction seems particularly crude, with a succession of approximations with choices which are not always clear nor convincing. The authors use the fact that in the case of Kasatochi, the mean particle size (see also next comment) decreases and that in the case of Sarychev, it increases, to choose a dependence between SA and the extinction which reflect none of these cases. This is a questionable way to approach this investigation focussing on a selection of recent volcanic eruptions (including those two ones). It is also worth to mention that Thomason et al (1997, op. cit.) uses such linear expression to describe cases where the extinction is higher than 2. 10^{-2} km^{-1}*, which is a really high value rarely encountered in the period considered here. The wavelength used to characterize the extinction in the equation in L. 26, p.4 is not mentioned, making it meaningless and preventing to compare this value with Thomason's coefficient (equal to 2000 to characterize the extinction at 1020 nm). They also "test" a non-linear SA*

dependence mentioning Thomason's work, but their choices are quite different form what Thomason proposes. The choice of p=0.7 is quite similar to Thomason's one in the case of the weakest extinction values, but the choice p=1.3 is much higher than the value of 1 used with the highest extinction values. The final scaling "to account for potential errors" gets rid for good of any reference to real cases, making the reader definitively lost in the accumulation of assumptions.

While it is true that in the case of Kasatochi and Sarychev one can attempt to model them in more detail based on the size distribution findings from the cases studies referenced (Sioris et al. and O'Neill et al.), this additional level of information is not available for most of the eruptions considered in this paper. But even this would be limited since the size distributions constantly evolved following the eruption (e.g., Kasatochi shifted the distribution towards smaller particles, and then later on, towards larger particles). Our goal was to use a consistent approach for all eruptions, and hence our "middle of the road" decision to use a linear k→SA relationship. While some of our choices for the sensitivity study are debatable, we opted to err on the conservative side (e.g., to consider a p=0.7 value which is more extreme than in Thomason et al.). This reflects the fact that not all values in the literature are directly applicable (as pointed out above) to our case, and that even these larger perturbations did not have a serious impact our modeled change-in-NO_2 – AOD relationships.

L. 5, p.5: Sioris et al. (2010) don't claim that the stratospheric particle size decreases in the case of Kasatochi. They consider statistical values (through median radius and Angström exponent) which show a decrease of the averaged particle size. This is not the same thing. A particle size decrease supposes the occurrence of some evaporation process, while what happens here is the addition of a significant amount of very thin particles. The authors should change their formulation to avoid the confusion.

We agree with the reviewer, and were simply sloppy with our wording here. We have adjusted this to read "For example, two months after the Kasatochi eruption, there was a shift in the ambient size distribution toward smaller particles (Sioris et al., 2010)

whereas Sarychev led to a shift towards larger particles (O'Neill et al., 2012)".

L. 1, p. 5: The reference by Hansen and Travis, 1974 is a very interesting general reference on light scattering, but I don't see anything in this reference able to clarify the choices and formulation of the equation in L. 26, p.4. Hence, I am not sure it is really useful here.

We assume you are referring to equation (3), on the bottom of page 4. The Hansen and Travis reference does not have this equation literally, although all the 'pieces' are there and it would have been left up to the reader to pull our equation out of this. In light of this, we explicitly derive our equation (3) in a short Appendix that was added to the manuscript and we reference it instead of Hansen and Travis.

3. Calculation of monthly averages, anomalies, and baseline levels

3.1 OSIRIS and MIPAS

L. 13-20, p. 5: The use of monthly zonal means over latitude intervals as large as 10° might really bias the data and limit the quality of the correlative study of quantities derived from two different experiments such as OSIRIS and MIPAS in the present case. If as few as 5 measurements are possible for one bin, it could be possible, for instance, that one instrument covers only regions with low aerosol background while the other one catches the plume of an eruption. Or that one instrument covers a large region of the bin and returns average values of a quantity while the other one only catches some very local spot with specific (low or high) volcanic load. Did the authors prevent this kind of situation in some way?

See response to General Comment B at the beginning of this reviewer response.

L. 1 p. 7: Concerning the NO_2 response to the QBO, do the authors mean the fitted response as illustrated by the cyan curve in Figure 1b?

Yes, we mean this and have replaced "the NO_2 response to the QBO" with "the fitted response to the QBO, as illustrated by the red dashed line in Fig. 1b" in the text to

clarify this.

L. 11-15, p. 7: same remark as for L. 13-20, p. 5: I suppose that the model covers the whole 10° latitude monthly bin, while corresponding measurements might cover a reduced region of the bin, introducing potentially a bias in the analysis.

The sampling of the OSIRIS measurements is fairly uniform across the bins, as demonstrated in the response to General Comment B, shown above in this document. Furthermore, the model data is calculated for a range of partial column AODs and then interpolated to the mean partial column AOD, as measured by OSIRIS. Therefore, the modelled NO_2 anomalies are for the mean partial column AODs as sampled by OSIRIS.

3.3 Conversions between partial column AODs, aerosol extinction, and extinction at various wavelengths

L. 21-24, p. 7 (or L. 15-18, p. 5): I guess that profiles for which valid data don't cover the whole interval 3-7 km above the tropopause are rejected. This could be mentioned for the sake of completeness.

We have clarified this in Sect. 3.1 with the following: "If a profile does not have valid data over all five measurement layers, it is not included in the analysis."

4. Results

4.1 NO_2, N_2O_5, and HNO_3 VCDs

L. 26, p.8 and Figure 3: Overall, there is indeed a very clear correlation between the AOD enhancement and the NO_2 anomalies found by OSIRIS in the Northern latitudes. On the contrary, in the Southern polar latitudes, most of the time, no significant NO_2 decrease is found by OSIRIS and even more, strong local enhancements are observed each year. In the case of the Sounthern polar latitudes, the high AOD is most probably due to PSC, for which one would expect a denitrification, thus a decrease in NO_2. MIPAS NO_2 seems rather to behave in the opposite way, although the very limited coverage of the "volcanic regions" defined by the cyan curves would impose to be

cautious in any conclusion.

See response to General Comment A, above.

L. 2, p.9: I don't understand the reason given by the authors why the AOD should be excluded from the correlation before of its large variability. Large volcanic eruptions are able to produce an even larger variability.

This text was not written very clearly. Data were not removed due to large variability in AODs, but because the large variability in AOD was not related to stratospheric aerosol. We have removed this statement from the text, as have removed data for 60°S to 80°S throughout the analysis, as described in the response to General Comment A, above.

L. 6-7, p.9: Again, the authors consider monthly zonal bins with 10° latitude intervals for their analysis. This might be the reason for the apparently inconsistant behaviour (MIPAS vs OSIRIS, Northern latitudes vs. Southern latitudes) shown in Figure 3 (see comment on L.26, p.8 and Figure 3). Although the use of monthly zonal means is widely used in the community, as mentioned above, such large intervals are not well suited to study atmospheric processes at the level of a volcanic plume for such kind of eruptions, because the spatial extend and the temporal duration of the volcanic perturbation is relatively limited with respect to the spread of the bins. Hence, biases are potentially important and make any conclusion uncertain, especially if different instruments with different coverage and data rates are compared. The authors should remake their analysis by considering much shorter time and latitude intervals to see if the inconsistencies persist.

See response to General Comment B, above.

L. 9-15, p.9: The validity of the explanation given by the authors could be easily checked by degrading the OSIRIS using the MIPAS' averaging kernels (and possibly vice-versa). This way would allow comparing like with like. Did the authors make such check?

See response to General Comment C, above.

L. 29, p.9-L. 1, p. 10: The concept "somewhat linear" is strange. Overall, the interpretation of the shape of the curve is highly subjective, and the superposition of the modelled values on the plots biases our perception. As an example, the OSIRIS plots at 20° N show a behaviour which is neither linear at low AOD, nor saturated at the highest AOD values. The authors should remove these dubious interpretations.

We have deleted the following "For smaller AODs (< ~3x10^{3}), this relationship appears to be somewhat linear. For larger AODs, however, this relationship displays greater curvature with additional aerosol having an increasingly smaller impact, which is consistent with the saturation at higher aerosol levels (e.g., Fahey et al., 1993)."

L. 4-5, p.10: In the same way, the agreement in shape and in quantity between modelled and observed data is very relative, and in some case, quite bad. Hence, the authors should qualify their affirmation.

We have replaced this sentence "The modelled data agrees well quantitatively with the OSIRIS measurements across latitudes and AOD ranges and reproduces the shape of the curve approaching saturation." with the following text:

"The modelled data agree well with the OSIRIS measurements and are within the estimated model errors for most OSIRIS data points."

We have also changed the abstract and conclusion to reflect this.

4.2 OSIRIS NO_2 profiles

L. 25, p.10: The authors should remove the sentence "At this latitude, decreases in NO_2 are observed between ~10-20 km". This sentence is confusing, since in some cases (e.g. in 2002), an increase is observed in NO_2 instead of a decrease, and anyway, the next sentence expresses appropriately and in more detail what the authors mean.

This has been deleted

5. Conclusions

L. 20-21, P. 11: I think the conclusion concerning the influence of the DOFS on the disagreement between MIPAS and OSIRIS is premature, and should be verified as proposed above, before it is claimed.

This has now been confirmed – see response to General Comment C.

L. 22, p. 11: This line, with the qualification of "somewhat linear", should definitely be removed. The characterization of this relationship using the correlation coefficient is more than sufficient. In the same way, the expression "perfect linearity" on the next line should also be removed. As long as observations are concerned, there cannot be any perfect linearity.

We have replaced "relationships. . . are somewhat linear" with "relationships. . . are observed".

We have removed the reference to "perfect linearity" and have replaced this with the following: "Heterogeneous chemistry becomes saturated toward larger aerosol concentrations (e.g.,Fahey et al., 1993) and can vary throughout the timeseries with other factors, such as temperature and available sunlight (e.g., Coffey, 1996), all of which can affect the linearity of the correlation."

L. 27-28, p.11: The last sentence should be qualified according to the comment in L. 4-5, p.10.

We have change this to "The modelled data agree well with the OSIRIS measurements and are within the estimated model errors for most OSIRIS data points."

Technical corrections:

L.19, p.1: The authors could consider using "relationship" in the singular, or more precise, the word "correlation"?

This has been changed

L.23, p1: "periods affected by volcanic aerosol"

This has been corrected

L. 4, p.2: reformat the parenthese after $BrONO_2$ (no subscript). Writing "NOy species (where NOy = NOx +HNO_3+etc.+$BrONO_2$, and NOx=etc.; e.g. Coffey 1996)" might be more fluent. See also specific comment on L. 9.

This has been changed as recommended

L. 13, p.4: I suggest to write 10:00 LT to be consistent with the previous mention of time, and for the sake of clarity.

This has been changed

L. 6, p.5: "to keep the scattering efficiency constant".

This has been corrected

L. 15, p.8: It seems there is a problem of cross reference for Table 2.

This has been corrected

L. 13, p.10: "time [blanco] series"

"timeseries" has been replaced with "time series" throughout

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-242, 2016.

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Discussion paper

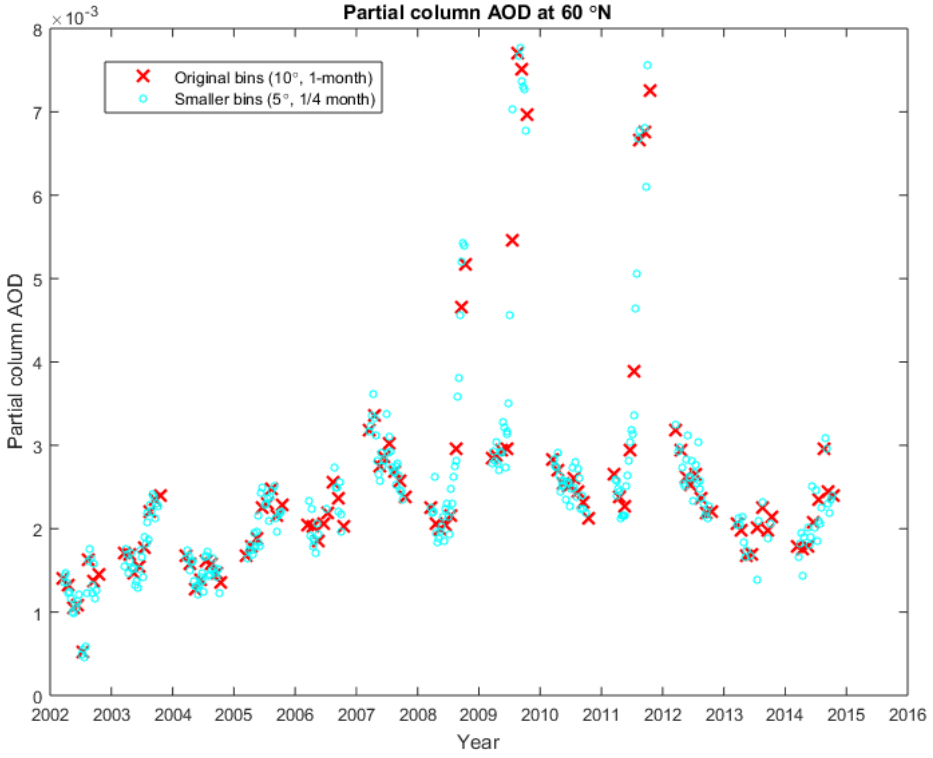

Fig. 1. OSIRIS partial column AOD at 60°N for the 10° monthly bins used in this paper and for smaller bins of 5° and $\frac{1}{4}$ of a month.

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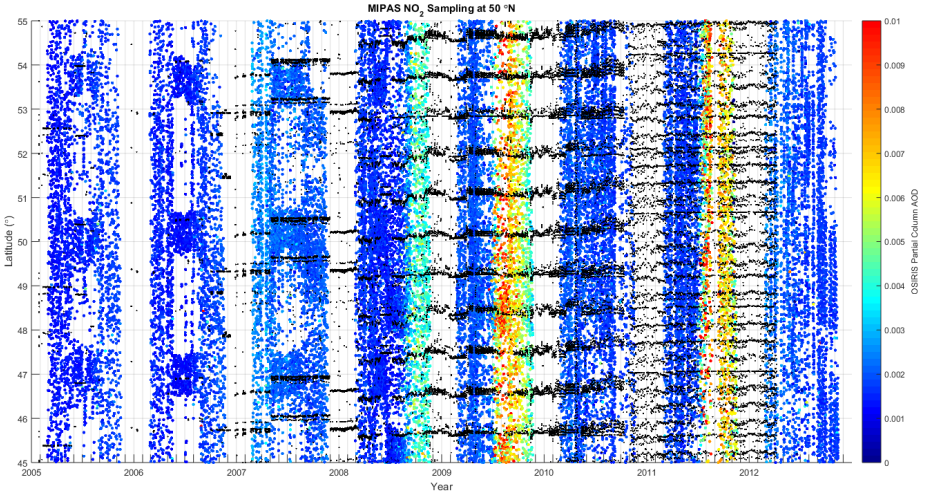

Fig. 2. OSIRIS partial column AOD (color-scale) and MIPAS NO2 measurement locations (black dots) versus time and latitude for data included in the 50°N latitude bin.

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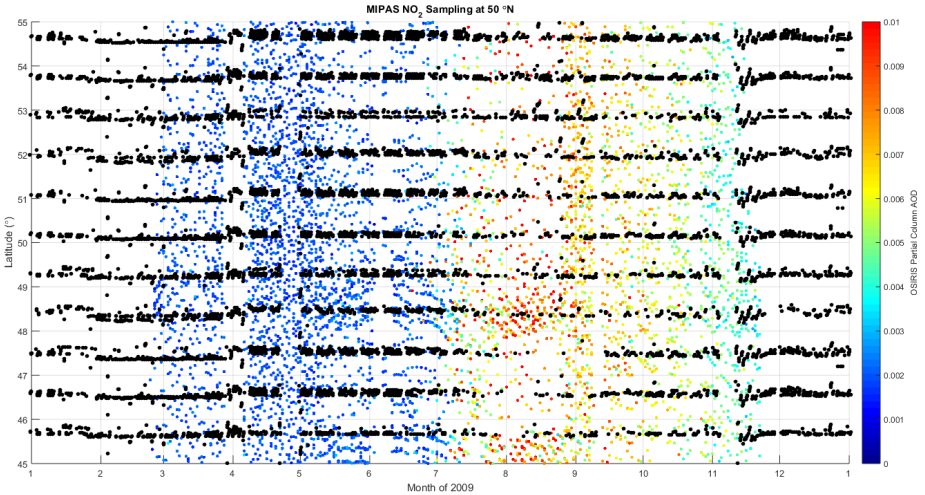

Fig. 3. As for Figure 2, for 2009 only.

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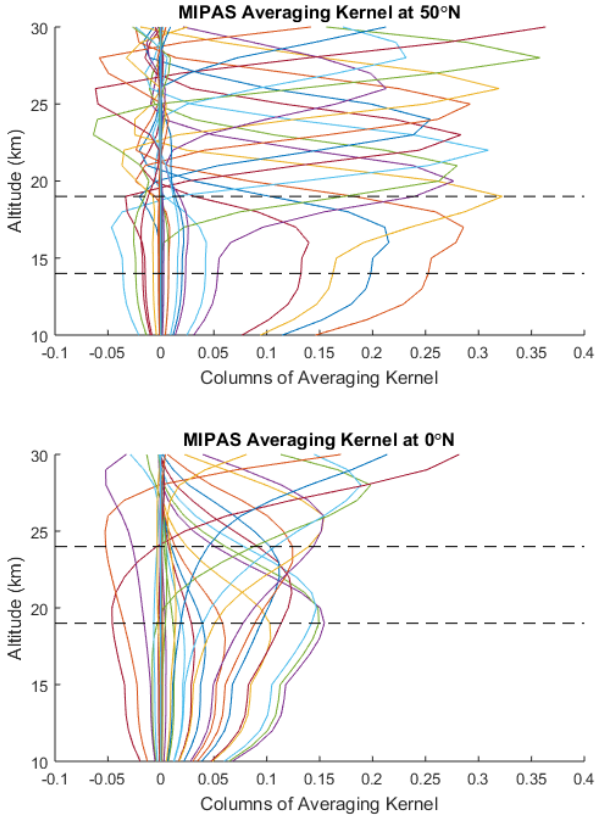

Fig. 4. Columns of representative MIPAS averaging kernels at (top) 50°N and (bottom) 0° latitude.

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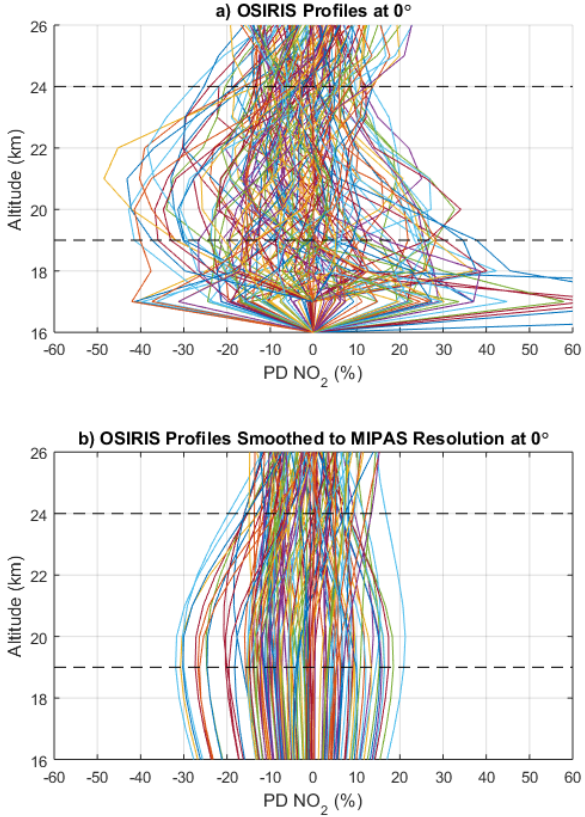

Fig. 5. Monthly mean NO2 percent difference profiles measured by OSIRIS (a) at original resolution and (b) smoothed using the OSIRIS averaging kernel at 0° latitude.

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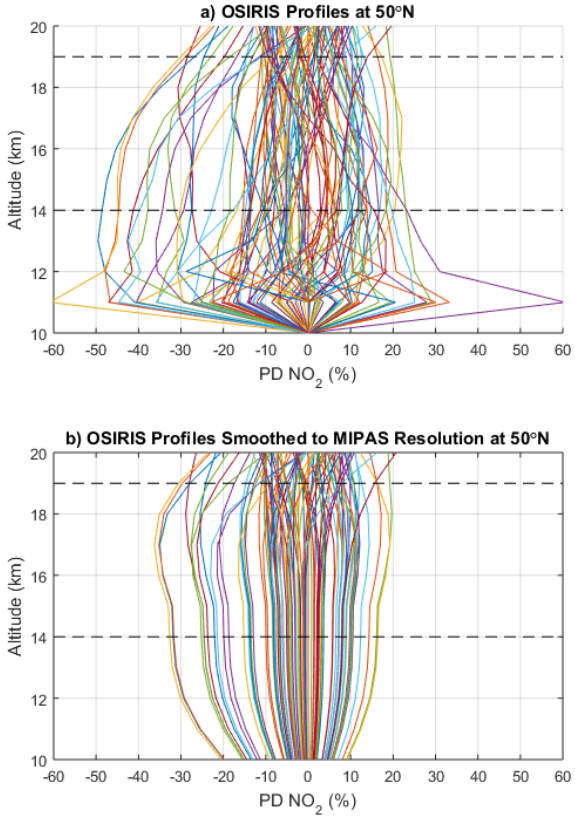

Fig. 6. As for Figure 5, for 50°N.

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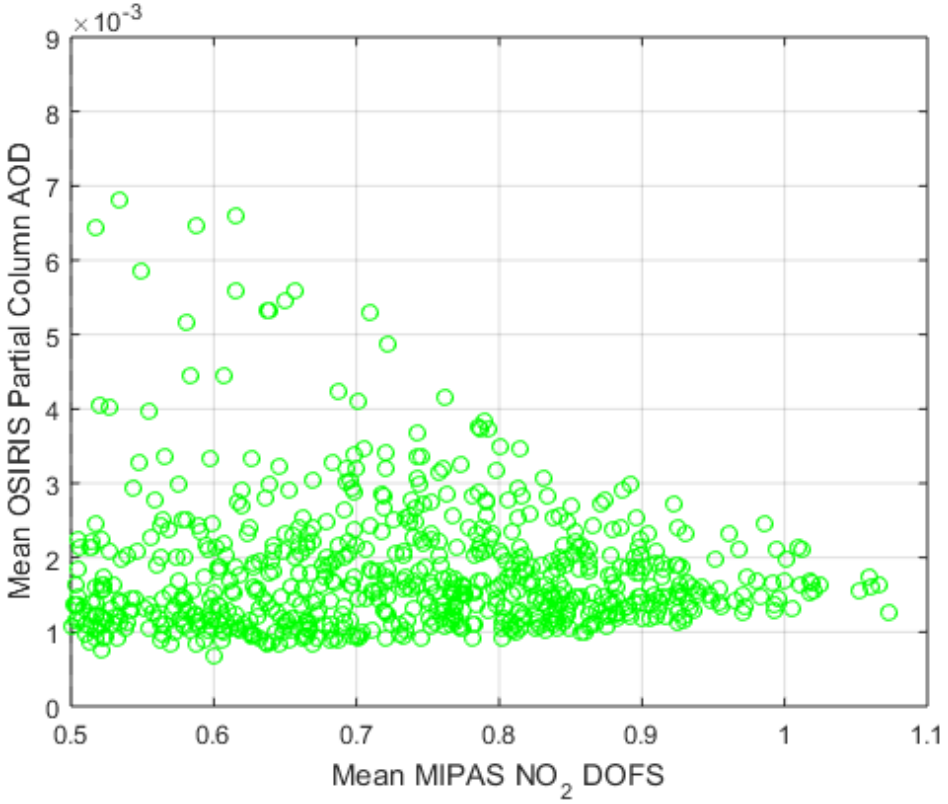

Fig. 7. For all latitude bins and dates included in the analysis, the mean MIPAS DOFS for NO2 versus the OSIRIS partial column AOD.

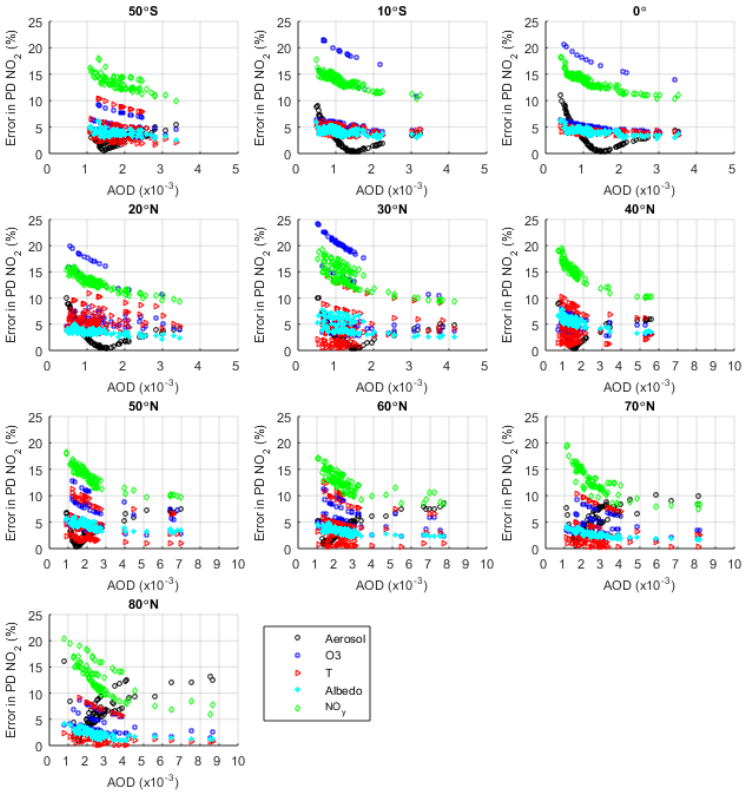

Fig. 8. Breakdown of parameters used to estimated total model uncertainty in Fig. 5 of the paper.

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Discussion paper

Effect of volcanic aerosol on stratospheric NO_2 and N_2O_5 from 2002-2014 as measured by Odin-OSIRIS and Envisat-MIPAS

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Abstract. Following the large volcanic eruptions of Pinatubo in 1991 and El Chichón in 1982, decreases in stratospheric NO_2 associated with enhanced aerosol were observed. The Optical Spectrograph and InfraRed Imaging Spectrometer (OSIRIS) likewise measured widespread enhancements of stratospheric aerosol following seven volcanic eruptions between 2002 and 2014, although the magnitudes of these eruptions were all much smaller than the Pinatubo and El Chichón eruptions. In order to isolate and quantify the relationship between volcanic aerosol and NO_2, NO_2 anomalies were calculated using measurements from OSIRIS and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS). In the tropics, variability due to the quasi-biennial oscillation was subtracted from the ~~timeseries~~time series. OSIRIS profile measurements indicate that the strongest ~~relationships~~ anticorrelations between NO_2 and volcanic aerosol extinction were for the 5-km layer starting ~3~~-7~~ km above the mean tropopause at the given latitude. ~~, where~~ OSIRIS stratospheric NO_2 partial columns ~~for ~3-7 km above the tropopause~~in this layer were found to be smaller than baseline NO_2 levels during these aerosol enhancements by up to ~60% with typical Pearson correlation coefficients of R ~ -0.7. MIPAS also observed decreases in NO_2 partial columns during periods ~~of~~ affected by volcanic aerosol, with percent differences of up to ~25% relative to baseline levels. An even stronger ~~relationship~~ anticorrelation was observed between OSIRIS aerosol optical depth and MIPAS N_2O_5 partial columns, with R ~ -0.9, although no link with MIPAS HNO_3 was observed. The variation of OSIRIS NO_2 with increasing aerosol was found to be ~~quantitatively~~ consistent with simulations from a photochemical box model ~~in terms of both magnitude and degree of non-linearity toward larger aerosol extinction values~~, within estimated model uncertainty.

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1 Introduction

Major volcanic eruptions can increase levels of sulfate aerosols in the stratosphere, which provide surfaces on which heterogeneous chemical reactions take place. This, in turn, can affect photochemistry with some of the largest impacts expected for the partitioning of reactive nitrogen, NO_y ~~(where NO_y= NO+NO_2+HNO_3+N_2O_5+$ClONO_2$+$BrONO_2$)~~ species (where $[NO_y]$= $[NO]$+$[NO_2]$+$[HNO_3]$+2$[N_2O_5]$+$[ClONO_2]$+$[BrONO_2]$, e.g., Coffey, 1996). The two key heterogeneous reactions that compete with gas-phase chemistry at all stratospheric temperatures are (1) and (2)~~,~~ below (e.g., Cohen and Murphy, 2003). In the presence of volcanic aerosol, the rate of N_2O_5 conversion to HNO_3 increases as shown in Eq. (1):

$$N_2O_5 + H_2O \xrightarrow{Aerosol} 2HNO_3 \quad , \qquad (1)$$

leading to an increase in levels of HNO_3, and a decrease in levels of N_2O_5. Since N_2O_5 is a reservoir species for NO_x (where $[NO_x] = [NO_2] + [NO]$), levels of NO_x also decrease. The hydrolysis of $BrONO_2$, shown in Eq. (2):

$$BrONO_2 + H_2O \xrightarrow{Aerosol} \mathrm{HOBr} + HNO_3 \quad , \qquad (2)$$

can also lead to decreased levels of NO_2 in the lower stratosphere, which are particularly significant toward high latitudes in the summer (Randeniya et al., 1997). The hydrolysis of chlorine nitrate can also play a significant role inside the polar vortex, (Wegner et al., 2012), but is not considered here because measurements were taken outside the polar vortex.

Following the large 1982 and 1991 El Chichón and Pinatubo volcanic eruptions, several studies measured significant decreases in NO_2. Total columns of NO_2 measured by ground-based instruments decreased by ~15-70% following these eruptions (Coffey, 1996; Johnston et al., 1992; Koike et al., 1993; Mills et al., 1993). Fahey et al. (1993) measured in situ NO_x/NO_y aboard aircraft following Pinatubo and found that NO_x/NO_y decreased with increasing aerosol surface area, with a saturation effect toward larger aerosol surface areas.

The effects of the Pinatubo eruption on HNO_3 and N_2O_5 were also assessed in several studies. Some studies noted increases in HNO_3 and attributed these increases to Eq. (1), but this was not consistently observed across various ground-based, in situ, and satellite datasets (e.g., Coffey, 1996; Rinsland et al., 1994). Rinsland et al. (1994) found decreases in N_2O_5 following Pinatubo, which is also ~~consistent with~~ implied by Eq. (1).

Berthet et al. (2017) assessed the impact of the more recent Sarychev eruption in June 2009 on lower stratosphere chemistry using remote sensing, situ measurements, and model calculations. Measured profiles of NO_2 and aerosol extinction were anti-correlated in the lower stratosphere following the eruption, with layers of enhanced aerosol coinciding with smaller NO_2

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mixing ratios. Using model calculations, they estimated that NO_2 decreased by ~45% and HNO_3 increased by ~11% over the August-September 2009 period below 19 km following the volcanic eruption.

The Optical Spectrograph and InfraRed Imaging System (OSIRIS) has observed enhancements in stratospheric aerosol from multiple volcanoes since it began taking measurements in 2001 (Bourassa et al., 2012a). The effect of these more recent volcanoes on stratospheric NO_2, also measured by OSIRIS, is investigated in the present study. Stratospheric ~~SO_2,~~ NO_2, HNO_3, and N_2O_5 from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) are also considered. Variations in NO_2, HNO_3 and N_2O_5 with aerosol are also studied using a photochemical box model. ~~To the authors' knowledge, this is the first study that measures the effect of increased volcanic aerosol on NO_2, HNO_3, or N_2O_5 following these smaller, more recent eruptions.~~

This paper is organized as follows. The OSIRIS, MIPAS, and photochemical model datasets are described in Sect. 2. Monthly average NO_2, HNO_3, and N_2O_5 anomalies and baseline values are calculated from these data using the methodology given in Sect. 3. The relationships between these anomalies and volcanic aerosol measured by OSIRIS are presented in Sect. 4, with conclusions given in Sect. 5.

2. Satellite and model datasets

2.1 OSIRIS MART aerosol extinction and NO_2

OSIRIS (Llewellyn et al., 2004; McLinden et al., 2012) is a Canadian satellite instrument on-board the Odin spacecraft (Murtagh et al., 2002), which was launched 20 February 2001 into a sun-synchronous orbit at ~600 km altitude and a descending node equatorial crossing time of ~06:30 local time (LT). OSIRIS measures limb-scattered radiances ~~with near-global coverage in the summer hemisphere~~ from 82°S to 82°N, with nearly full coverage in the summer hemisphere.

The OSIRIS Multiplicative Algebraic Reconstruction Technique (MART) v5.07 NO_2 (Bourassa et al., 2011) and aerosol extinction at 750 nm (Bourassa et al., 2007) data products were used for this study. Data were collected by the optical spectrograph, which measures from 280-810 nm, with a ~1 nm spectral resolution using an optical grating and a charge-coupled device detector. The SASKTRAN spherical forward model is used in the inversion and accounts for multiple scattering and ground albedo (Bourassa et al., 2008). OSIRIS MART aerosol extinction is consistent with SAGE III to ~10% (Bourassa et al., 2012b) and to within ~20% with SAGE II, although the conversion to 525 nm adds uncertainty ~~makes the comparison more difficult~~ (Rieger et al., 2015). The OSIRIS MART NO_2 data product is consistent with the OSIRIS Chalmers NO_2 data product (Bourassa et al., 2011).

For both aerosol extinction and NO_2, OSIRIS data from the descending portion of the orbit~~node~~, with solar zenith angle (SZA) ~~<~~ less than 88° were used in this analysis. For aerosol, an extinction threshold ~~of >~~ greater than $2x10^{-3}$ km^{-1} was used to terminate the profiles at lower altitudes. This excludes some lower stratospheric altitudes where an aerosol saturation effect occurs in fresh volcanic plumes (Fromm et al., 2014). Similarly, values of NO_2 ~~>~~ greater than $5x10^9$ mol/cm^3 were removed from the profiles. Data below the thermal tropopause, calculated using lapse rates from the National Center for Environmental Prediction (NCEP) reanalysis data (Kalnay et al., 1996), were excluded. As discussed further in Sect. 2.3, below, in order to account for the diurnal variation of NO_2, a photochemical model (Brohede et al., 2008; McLinden et al., 2000) was used to scale all NO_2 profiles to a common local time of 06:30 LT. Profiles for SZA greater than 88° at 06:30 LT ~~> greater than 88°~~ were also excluded from the analysis in order to prevent scaling data to periods near sunrise when NO_2 is varying rapidly.

2.2 MIPAS IMK/IAA ~~SO_2,~~ NO_2, N_2O_5, and HNO_3

MIPAS (Fischer et al., 2008) is on board the Environmental Satellite (Envisat), which was launched on 1 March 2002 into a Sun-synchronous polar orbit at 800 km altitude with 14.4 orbits per day. MIPAS measured limb radiances in the mid-infrared from 4.1-14.7 µm (685-2410 cm^{-1}) until communication with the satellite was lost in April 2012.

For this study, ~~SO_2,~~ N_2O_5, HNO_3, and NO_2 from retrievals performed by the Institute of Meteorology and Climate Research (IMK) and Instituto de Astrofisica de Andalucia (IAA) were used. The version V5R_NO2_220/V5R_NO2_221, V5R_N2O5_220/V5R_N2O5_221, V5R_HNO3_224/V5R_HNO3_225~~, V5R_SO2_220/V5R_SO2_221~~ data from January 2005 to April 2012 were considered. Prior to 2005, data are available, but MIPAS operated with a different spectral resolution and only minor volcanic eruptions occurred. Retrievals for NO_2 (Funke et al., 2005, 2014), N_2O_5 (Mengistu Tsidu et al., 2004), and HNO_3 ~~(von Clarmann et al., 2009), and SO_2 (Höpfner et al., 2013)~~ are performed using a constrained multiparameter nonlinear least squares fitting of measured ~~and modelled~~ spectra with modelled ones (von Clarmann et al., 2009). Data unaffected by clouds and with diagonal terms of the averaging kernel ~~>~~ greater than 0.03 were used for the analysis. Only daytime measurements (SZA ~~<~~ less than 88°), taken at 10:00 LT, were used for consistency with OSIRIS.

2.3 Photochemical modelling

A stratospheric photochemical box model (Brohede et al., 2008; McLinden et al., 2000) was used to help interpret the satellite data. The model is constrained with climatological profiles of ozone and temperature. Long-lived species (N_2O, CH_4, H_2O) and families (NO_y, Cl_y, Br_y) are based on a combination of three-dimensional model output or tracer-correlations. All remaining species are calculated to be in a 24-hour steady-state by integrating the model ~~over~~ for as many as 30 days, but where the model remains fixed ~~to a~~on the original specified Julian day. Heterogeneous chemistry on background stratospheric sulfate aerosols is included ~~using the aerosol surface area climatology of Thomason et al. (1997)~~, but polar stratospheric clouds

are not included. Brohede et al. (2008) demonstrated that this model can accurately simulate stratospheric nitrogen partitioning.

The model is typically used for two purposes: (i) to adjust the local time of the OSIRIS measurements to a common value through a photochemical scaling factor (e.g., Brohede et al., 2008, 2007), and (ii) to model the behavior of NO_2 and other species for varying levels of aerosol. In this latter application, the aerosol surface area, *SA* ($\mu m^2/cm^3$), is adjusted so that it matches the extinction coefficient, k (km^{-1}), measured by the OSIRIS instrument, using the expression,

$$SA(z) = \frac{4000}{\bar{Q}} \cdot k(z) \quad , \qquad (3)$$

derived in Appendix A, where $\bar{Q}$ is the effective scattering efficiency. A scattering efficiency of 0.40 was calculated using Mie theory for background spherical sulfate particles (based on a log-normal distribution with size parameters of r_e = 0.08 µm and σ_e=1.6). However, volcanic eruptions alter the size distribution, as SO_2 rapidly forms sulfuric acid, which can condense to form new small particles or increase the size of existing ones. This change in size distribution will affect the scattering efficiency, but the sign of this change is unknown. For example, two months after the Kasatochi eruption, there was a shift in the ambient size distribution toward smaller particles (Sioris et al., 2010) whereas Sarychev led to a shift toward larger particles (O'Neill et al., 2012). As a result of these mixed findings, we elected to keep the scattering efficiency constant, using $SA = 10000 \cdot k$, but tested a non-linear *SA* dependence on k, and included it in the model uncertainty estimates, as described in the paragraph below.

Table 1 summarizes the parameters used to estimate uncertainty in the modelled NO_2 percent differences. The model calculations were repeated, successively varying one key geophysical input or assumption, in order to assess its impact on the results. In total, eight such sensitivity calculations were performed and their individual NO_2 percent difference values were added in quadrature to estimate a total sensitivity or uncertainty. To account for potential errors and variability over 2002-2015 in our background *SA*, we scaled 10000 by factors of 3 and 1/3. The large factor is based on the sensitivity of scattering efficiency to the aerosol size parameters for the particle sizes and wavelengths considered here. For example, a change in effective radius by a factor 2 leads to a change in scattering efficiency by a factor of 3 (see Hansen and Travis (1974) Fig. 8). The dependence *SA* on k was estimated by analogous to that from Thomason et al. (1997), and incorporated it into an uncertainty. For this, we considered $SA \propto k^p$ with p=1.3 for an increase in particle size following an eruption, and p=0.7 for a decrease, analogous to that from Thomason et al. (1997). Furthermore, to account for potential errors in our background *SA*,

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~~we scaled 10000 by factors of 3 and 1/3 and folded these into the overall uncertainty.~~ In order to account for uncertainty and variability in the climatological input profiles~~—~~, ozone, NO_y, and temperature profiles were perturbed by +10%, +20%, and +5 K, respectively. Surface albedo was changed from the original model setting of 0.1 to 0.3. For ozone, NO_y, temperature, and albedo, half the perturbation was applied as a systematic error, affecting both the monthly NO_2 and baseline NO_2, and half the perturbation was applied as a random error, which would account for year-to-year variability between conditions for baseline and monthly NO_2. The $NO+O_3$ reaction rate and NO_2 absorption coefficient were both perturbed by 10%, and applied as a systematic error only.

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3 Calculation of monthly averages, anomalies, and baseline levels

3.1 OSIRIS and MIPAS

Volcanic eruptions and periods affected by volcanic aerosol were identified using monthly averages of latitude-binned OSIRIS aerosol extinction. In order to isolate the effect of volcanic aerosol on NO_2, HNO_3, and N_2O_5, anomalies and baseline levels in the absence of volcanic aerosol were estimated for each month and latitude. Partial vertical column densities (VCDs) and partial aerosol optical depth (AOD), as well as vertical profiles were considered. Partial columns were used, instead of, e.g., volume mixing ratios at a fixed altitude, because the largest observed aerosol extinction ratios related to volcanic aerosol were observed at different altitude layers for different latitudes and times. The partial column altitude range was selected to include most of these large extinction ratios. Furthermore, MIPAS NO_2 measurements have low resolution at the altitudes affected by volcanic aerosol and therefore are better presented as partial columns. Calculations were made for each month and latitude, and for the profiles, each altitude layer was considered separately. Latitudes south of 50°S were excluded from the analysis because there is no evidence of volcanic aerosol at these southern hemisphere high latitudes and OSIRIS AODs are dominated by seasonal variation. The steps for these calculations are described in the paragraphs below.

Monthly average profiles of aerosol extinction, and of ~~SO_2,~~ NO_2, N_2O_5, and HNO_3 number densities were calculated in 10° latitude bins. At least five measurements were required for each bin. Partial column AOD and partial VCDs of ~~SO_2,~~ NO_2, N_2O_5, and HNO_3 were all calculated from the sum of these monthly mean profiles for ~~the~~ a ~~five measurement layers~~5-km altitude range ~~from~~ starting at ~3~~-7~~ km above the mean NCEP thermal tropopause at each latitude. If a profile d~~oe~~sid not have valid data over all five measurement layers, it ~~i~~was not included in the analysis. This altitude range typically corresponded to the highest levels of volcanic aerosol observed by OSIRIS. Bins were tested for smaller latitude and time ranges, but yielded similar ranges of AODs, suggesting that smaller bin sizes did not capture more detailed processes in the volcanic plume.

MIPAS volume mixing ratio profiles were converted to number densities using MIPAS temperature and pressure profiles. Note the calculated VCDs for OSIRIS and MIPAS are offset by 0.5 km because their measurement altitude grids are offset by

0.5 km. MIPAS degrees of freedom for signal (DOFS) were calculated from the trace of the averaging kernel over the partial column altitude range. MIPAS VCDs with DOFS ~~<~~ less than 0.5 were excluded from the analysis, leaving mean DOFS of ~~1.3 for SO_2,~~ 0.7 for NO_2, 1.8 for N_2O_5, and 2.1 for HNO_3.

Bins affected by volcanic aerosol were identified using thresholds based on OSIRIS aerosol extinction measurements. For the partial AODs, this threshold was set at $2x10^{-3}$, which was approximately the 75th percentile of monthly mean partial column AODs across all latitudes for 50°S to 80°N. For the profiles, the threshold was set using an extinction ratio = 1.2, which was approximately the 90-95th percentile of monthly mean extinction ratios across all latitudes for 50°S to 80°N. The extinction ratio (OSIRIS-measured extinction divided by the Rayleigh extinction) has less dependence on altitude than the extinction and was calculated using air density profiles from European Centre for Medium-Range Weather Forecasts analysis data.

In order to remove the seasonal variation from the NO_2 time series, ~~In order to remove t~~he NO_2 anomaly (dNO_2) was calculated for each bin of the monthly mean NO_2 VCDs as follows ~~seasonal variation from the NO_2 timeseries, for each bin of the monthly mean NO_2 profiles and VCDs, the NO_2 anomaly (dNO_2) was calculated:~~.

$$dNO_2(y,m,lat) = NO_2(y,m,lat) - \overline{NO_2^{No\ Volc}(m,lat)} \quad , \qquad (4)$$

where $NO_2(y,m,lat)$ is the NO_2 VCD for the given year/month/latitude bin, and $\overline{NO_2^{No\ Volc}(m,lat)}$ is the mean ~~of binned~~ NO_2 ~~values~~ VCD for the given month/latitude across all years for bins that were not affected by volcanic aerosol, as determined by the AOD ~~extinction~~ threshold~~s~~. For the profile analysis, the NO_2 anomaly was calculated separately ~~separately~~ at each altitude from NO_2 number densities, with bins affected by volcanic aerosol identified using the extinction ratio threshold.

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The quasi-biennial oscillation (QBO), with a mean period of ~28 months, is the dominant internal mode of climatic variability in the tropical stratosphere (see review by Baldwin et al., 2001). NO_2 can vary by ~~>~~ more than 25% in the tropics near the tropopause due to QBO (Hauchecorne et al., 2010), which is on the same order of magnitude ~~of~~ as the variation of NO_2 observed during periods of enhanced volcanic aerosol in this study. Therefore, the QBO was fit using a robust regression to the NO_2 anomaly ~~timeseries~~time series for each latitude bin between 40°S to 40°N. Bins that were affected by volcanic aerosol were excluded from the fit. The fit was only performed if at least ten NO_2 anomaly values were available, and included the first two principal components of QBO, calculated with stratospheric winds from http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html (Naujokat, 1986). The two QBO principal components and 40°S to 40°N latitude range were selected based on the results of Bourassa et al. (2014). The QBO fits were subtracted from the NO_2 anomaly ~~timeseries~~time series for each latitude bin between 40°S to 40°N. For the profile analysis, this procedure was applied separately at each altitude.

An example of the QBO fitting procedure is shown for 20.5 km at 0° latitude in Figure 1. The ~~timeseries~~time series of extinction ratios shows several distinct periods with extinction ratios above the extinction ratio threshold of 1.2 (panel a). The QBO fit to the NO_2 anomaly ~~timeseries~~time series includes only data collected during time-periods with extinction ratio ~~<~~ less than 1.2 (panel b) in order to avoid fitting out some of the variability due to volcanic aerosol. The fit includes a constant and the two QBO principal component terms only. After subtracting the fit, the NO_2 anomaly ~~timeseries~~time series has stronger negative anomalies during the periods with enhanced volcanic eruptions (panel c).

Baseline NO_2 profiles and VCDs were ~~also~~ estimated for periods that ~~are not~~were not affected by volcanic aerosol. For mid-latitudes and high latitudes (50°S ~~– 80°S~~ and 50°N – 80°N), $\overline{NO_2^{No\ Volc}(m, lat)}$ was used directly for baseline NO_2. For 40°S – 40°S, the fitted~~NO_2~~ response to the QBO, as illustrated by the red dashed line in Figure 1b, was added to $\overline{NO_2^{No\ Volc}(m, lat)}$ in order to estimate the variation of baseline NO_2 with the QBO. The addition of the QBO signal had a minor impact on this analysis (~5-10%).

~~The~~ NO_2 ~~was presented as a~~ percent difference ~~in NO_2~~ ($100\% \times \frac{NO_2\ Anomaly}{Baseline\ NO_2}$) ~~was used~~ for all figures and calculation of correlation coefficients in this study. Replacing percent difference NO_2 with the NO_2 anomaly has a minor influence on the shape of scatter plots and Pearson correlation coefficients (R) between NO_2 and aerosol extinction.

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For N_2O_5 and HNO_3, anomalies and baseline values were calculated using the same approach as for NO_2. For aerosol extinction profiles and partial AODs, variations due to seasonal cycles are small and variations due to QBO in the tropics are ~~<~~ less than 10% for 20-26 km (Hommel et al., 2015), while volcanic perturbations in aerosol extinction are often ~~>~~ greater than 100%. Therefore, monthly averages of aerosol extinction and partial AODs were used directly in this analysis, without calculation of relative anomalies ~~or baseline values~~.

3.2 Photochemical model

A similar approach was used to assess variations in modelled aerosol extinction, NO_2, N_2O_5, and HNO_3 partial VCDs and profiles. The photochemical model was run monthly at 10° latitude intervals for a range of aerosol surface areas at the approximate OSIRIS measurement time (06:30 LT). For the column amounts, partial VCDs and partial column AODs were calculated over the 5 km layer, ~~s~~starting ~3~~-7~~ km above the tropopause for each of the model runs. Then, for each latitude and month, percent differences in NO_2, N_2O_5, and HNO_3 partial VCDs were calculated for a range of partial column AODs using ($100\% \times \frac{NO_2\ (AOD) - Baseline\ NO_2}{Baseline\ NO_2}$), where *$NO_2$(AOD)* is the modelled NO_2 for the ~~given~~ AOD/month/latitude and *Baseline NO_2* is the modelled NO_2 for the given month/latitude, interpolated to the baseline partial column AOD. The baseline partial column

AOD was calculated from OSIRIS measurements at the given latitude. For the profiles, a similar interpolation procedure was used at each altitude layer using OSIRIS-measured aerosol extinction.

3.3 Conversions between partial column AODs, aerosol extinction, and extinction at various wavelengths

All AODs and aerosol extinctions presented here are for 750 nm, which is the wavelength of the OSIRIS retrievals. The partial column AODs are for a 5 km altitude range, and therefore can be related to the mean extinction (km^{-1}) over the given altitude range by dividing the partial column AOD by 5. In order to convert aerosol extinctions from 750 nm to other typical wavelengths, the conversion factors given in

Table 2 can be used.

4 Results

4.1 NO_2, N_2O_5, and HNO_3 VCDs

We first examine an example of the modelled variation of NO_2, N_2O_5, and HNO_3 partial VCDs with volcanic aerosol, shown in Figure 2 for 60°N in August. This latitude was affected by enhanced volcanic aerosol in August from the 2009 Sarychev Peak and the 2011 Nabro eruptions, as discussed in further detail below. The maximum partial column AOD observed by OSIRIS at this latitude, $8x10^{-3}$, is indicated on the figure. Levels of NO_2 decrease ~~almost exponentially~~ strongly in the presence of ~~toward~~ larger partial column AODs, reaching percent differences of -45% relative to baseline levels for AOD=$8x10^{-3}$ at the approximate local time of OSIRIS measurements. At the MIPAS local time, reductions in NO_2 are slightly smaller, reaching -40% for AOD=$8x10^{-3}$. Percent differences in N_2O_5 decrease even more steeply than NO_2, reaching up to -86% relative to baseline levels for AOD=$8x10^{-3}$. HNO_3 increases slightly with partial column AOD, but is only +5% higher than baseline levels for AOD=$8x10^{-3}$. This is because HNO_3 is the dominant NO_y species in the lower stratosphere. Therefore, even major changes in the partitioning due to heterogeneous chemistry on sulfate aerosol would have only a marginal relative impact on HNO_3.

Turning to the measurements, seven periods with volcanic aerosol enhancements were identified in the OSIRIS AOD ~~timeseries~~time series, most of which were associated with negative NO_2 anomalies. This is apparent in the ~~timeseries~~time series of AOD and percent difference NO_2 VCDs, shown in Figure 3 and summarized in Table 3. Note that only volcanoes with clear signals in the OSIRIS AODs are identified here, and therefore this is not a comprehensive list of all volcanoes known to have influenced the stratosphere. Höpfner et al. (2015) ~~See,~~provide a list of ~~e.g.,~~ volcanoes identified in MIPAS SO_2 ~~(Höpfner et al., 2015)~~. ~~.~~

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~~For some of these volcanic eruptions, a brief signature in MIPAS SO_2 partial VCDs is also apparent during the early part of the AOD enhancements. Stronger SO_2 enhancements are observed after the higher latitude 2008 Mt Okmok / Kasatochi and 2009 Sarychev Peak eruptions. Weaker enhancements are observed after the tropical 2006 Soufrière Hills and 2011 Nabro eruptions. The weaker signal in the tropics is likely because the conversion to sulfate is faster in the tropics due to higher levels of OH. Furthermore, in the tropics, the relative humidity in the troposphere is higher, increasing the scavenging by frozen hydrometeors that trap SO_2 as the eruption column rises through the troposphere (Rodríguez et al., 2008; Textor, 1999). No obvious enhancement in SO_2 was observed after the 2010 Mt Merapi volcano, which is consistent with the weaker signal~~

~~in OSIRIS AOD for this volcano. MIPAS SO_2 data did not meet the filtering criteria for this study following the 2005 Mt Manam eruption and was unavailable for the 2014 Kelut eruption.~~

The OSIRIS NO_2 percent differences compared to baseline levels are largely negative during the AOD enhancements (~~cyan~~thick black contours) and return to baseline levels when AODs decrease. This is consistent with reduction in NO_2 due to heterogeneous chemistry on the surface of sulfate aerosol. In the MIPAS data, NO_2 anomalies tend to be negative during periods affected by volcanic aerosol. However, this relationship is weaker than observed with the OSIRIS NO_2 data and MIPAS measurements are not available for the largest observed OSIRIS AODs, as they did not meet the filtering criteria for this study. The variability of NO_2 outside periods of volcanic aerosol (standard deviation of the NO_2 anomaly divided by the mean baseline levels of NO_2 in each latitude bin) was ~~<~~ less than 14% for both OSIRIS and MIPAS.

Figure 4 shows the correlation between NO_2 VCD percent differences and AOD for all times/latitudes. ~~Note that data between 60°S and 80°S are excluded from the correlation coefficients due to large variability in the AOD, perhaps due to polar stratospheric clouds.~~ For OSIRIS, there appears to be a negative linear relationship, with R=-0.68. For larger AODs ~~>~~ (greater than $4x10^{-3}$), OSIRIS VCDs are ~20-60% lower than under baseline conditions. For MIPAS, the relationship between NO_2 percent difference and AOD is weaker, with R = -0.37. When only MIPAS data from 40°~~S~~ N to 80°N are considered, the anticorrelation is somewhat stronger, with R = -0.50. Compared with OSIRIS, there are fewer monthly average MIPAS measurements available when AODs are high, which likely contributes to the weaker correlation. For AODs ~~>~~ greater than $4x10^{-3}$, 18 out of 19 latitude-binned MIPAS VCDs have negative percent differences, typically in the range of ~5-25%.

The effect of volcanic aerosol on NO_2 is smaller for MIPAS than for OSIRIS. From the model simulations in Figure 2 it appears that the difference in local time of the measurements, 10:00 LT vs. 06:30 LT, can explain only a small part of this difference. These discrepancies could not be attributed to differences in sampling between OSIRIS and MIPAS, since MIPAS and OSIRIS both sample throughout the monthly 10° latitude bins. MIPAS measurements are not clustered in parts of the bin where smaller OSIRIS AODs were observed. ~~Likely a~~A larger contributor to the smaller MIPAS NO_2 anomalies is a damping effect as many of the VCDs had DOFS ~~<~~ less than 1, with smaller DOFS for larger OSIRIS partial column AODs. For OSIRIS partial column AODs ~~>~~ greater than $5x10^{-3}$, the average MIPAS DOFS was ~0.6. The sub-optimal DOFS is accompanied by coarse altitude resolution which smooths NO_2 from higher altitudes where aerosol levels are not enhanced. In other words, the coarse altitude resolution leads to a smaller amplitude in the local NO_2 variation in the MIPAS data. In order to test this, representative MIPAS averaging kernels were applied to the OSIRIS NO_2 percent difference profiles at 50°N and 0° latitudes. Representative averaging kernels were used because MIPAS NO_2 is retrieved in the logarithmic domain and the averaging kernel thus refers to the logarithm of the mixing ratio. By applying the averaging kernel directly to the percent difference profile, the MIPAS a priori profile does not need to be included in the calculations. The magnitude of the largest percent differences in the NO_2 percent difference profiles decreased from approximately -45% in the original OSIRIS profiles to

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approximately -30% in the smoothed OSIRIS profiles, demonstrating this damping effect. These tests did not account for variation of MIPAS DOFS with partial column AOD. The smaller MIPAS DOFS observed for larger OSIRIS partial column AOD would lead to further damping of the MIPAS NO_2 percent differences. Also, correlation due to an NO_2 retrieval dependency on aerosol is expected to be small for OSIRIS because of the differential nature of the measurement and the spectral proximity of the selected strongly and weakly absorbing wavelengths (Bourassa et al., 2011).

The relationship between the MIPAS N_2O_5 anomaly and OSIRIS aerosol is also shown in Figure 3 and Figure 4. Strong anticorrelation between the N_2O_5 anomaly and AOD is observed, with R = -0.86 for 50°S to 80°N and R = -0.90 for 40°S N to 80°N. The percentage decrease in N_2O_5 cannot be inferred due to the known low bias in the MIPAS data at these altitudes. Despite this low bias, the DOFS of ~1.8 suggest that real variability in N_2O_5 is observed.

MIPAS HNO_3 VCDs were also considered in this analysis (not shown here) using the same methodology as for NO_2 and N_2O_5, but no relationship with partial column AOD was apparent in the timeseriestime series, with |R| < less than 0.2 for most latitudes and altitude ranges considered. This is consistent with results from the photochemical model which suggest that HNO_3 should increase by less than 10% relative to baseline levels for all latitudes and partial column AODs observed in this study. Such small relative increases in HNO_3 would be difficult to observe over background variability.

Scatter plots for OSIRIS AOD versus NO_2 VCD percent difference, at latitudes where at least one AOD > greater than $3x10^{-3}$ was recorded, are shown in Figure 5. At all latitudes, higher AODs are associated with lower levels of NO_2, with R ranging from -0.40 to -0.85 at the various latitudes. For smaller AODs (< ~$3x10^{-3}$), this relationship appears to be somewhat linear. For larger AODs, however, this relationship displays greater curvature with additional aerosol having an increasingly smaller impact, which is consistent with the saturation at higher aerosol levels (e.g., Fahey et al., 1993). The larger AODs are all measured following volcanic eruptions (Table 3). The modelled NO_2 percent differences, interpolated to the OSIRIS month, latitude, and partial column AOD are also shown. The modelled data agrees well quantitatively with the OSIRIS measurements across latitudes and AOD ranges and reproduces the shape of the curve approaching saturation. The modelled data agree well with the OSIRIS measurements and are within the estimated model errors for most OSIRIS data points. For larger AODs (greater than $5x10^{-2}$), the modelled data agree well with the OSIRIS measurements and are within the estimated model errors for most OSIRIS data points. For smaller AODs, both the model and OSIRIS show a negative relationship between percent difference NO_2 and AOD. However, there is variability in the OSIRIS NO_2 percent differences that is not captured by the model. This is expected as the model is responding only to changes in AOD and not other sources of natural variability in NO_2.

Other species are expected to be affected by increased aerosol, including $BrONO_2$, from Eq. (2), and by extension, BrO, where BrO is also measured by OSIRIS (McLinden et al., 2010). An analysis of the OSIRIS BrO product indicated no significant

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impact following the eruptions. This is consistent with a model-estimated increase in BrO of only 5-10% for AOD=$8x10^{-3}$ (not shown here), and the reduced sensitivity of the OSIRIS BrO product below 20 km.

4.2 OSIRIS NO_2 profiles

The OSIRIS NO_2 and aerosol extinction profiles were used to assess the altitude range over which levels of NO_2 decreased in the presence of volcanic aerosol. The MIPAS NO_2 and N_2O_5 profiles were not considered for this purpose because of limitations in the vertical resolution in the lower stratosphere.

The ~~timeseries~~time series of OSIRIS extinction ratio and OSIRIS and modelled NO_2 percent difference profiles are shown for 0° in Figure 6. Negative NO_2 anomalies are apparent during the periods of enhanced aerosol for altitudes between ~16-24 km, with maximum decreases in NO_2 typically at ~20 km in both the OSIRIS and model datasets. These altitudes coincide approximately with the largest observed extinction ratios. OSIRIS measured percent differences in NO_2 of up to ~ -50% after the 2006 Soufrière Hills volcano, up to ~ -40% after the 2014 Kelut volcano, up to ~ -35% after the 2011 Nabro volcano, and up to ~ -25% after the 2005 Manam volcano. In the model dataset, similar qualitative features are observed, but with somewhat smaller reductions in NO_2. Modelled percent differences reach up to ~ -20% after the Nabro and Manam volcanoes and up to ~ -30% after the Soufrière Hills and Kelut volcanoes. This is consistent with the modelling comparisons of VCDs and partial column AODs (Figure 5), in which modelled NO_2 percent differences at 0° latitude are biased somewhat low compared with OSIRIS. Only the aerosol extinction is varied inter-annually in the model, while other parameters such as NO_y, ozone, and temperature are from monthly climatologies, which likely why the model displays less variability than OSIRIS during non-volcanic periods.

At 50°N, both OSIRIS and modelled negative NO_2 anomalies are similarly related to the times and altitudes of enhanced levels of aerosol, as shown in Figure 7. ~~At this latitude, decreases in NO_2 are observed between ~10-20 km.~~ Decreases in NO_2 of up to ~ -50% are observed after the 2009 Sarychev Peak volcano, up to ~ -40% after the 2011 Nabro volcano, and up to ~ -30% after the 2008 Kasatochi/Okmok volcanoes. The modelled percent difference profiles are similar to the OSIRIS data, reaching ~ -40% for the Sarychev Peak and Nabro volcanoes and ~ -30% for the Kasatochi/Okmok volcanoes. The observed and modelled decreases in NO_2 for the Sarychev Peak eruption are consistent with Berthet et al. (2017), who calculated ~45% decrease below 19 km using model calculations.

The OSIRIS-measured variability in NO_2 outside of the periods of volcanic aerosol (standard deviation of the NO_2 anomaly divided by the mean baseline levels of NO_2 in each latitude/altitude bin) was ~~<~~ less than 20% for most latitude/altitude bins. Therefore, the OSIRIS-measured decreases in NO_2 of up to ~ -30~~-~~ to -50% after these volcanic eruptions are significant compared to background variability.

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At both 0° (Figure 6) and 50°N (Figure 7), positive NO_2 anomalies are also observed, in particular before 2005. This is in part because baseline NO_2 is calculated using measurements taken for aerosol ratios ~~<~~ less than 1.2. Below this threshold, levels of aerosol still vary, and tend to increase after ~2005 at most latitudes (see, for example, Figure 1). This leads to positive anomalies in NO_2 during periods with lower levels of volcanic aerosol, as are reflected in the photochemical model results, which are based entirely on aerosol levels. There are some differences between the OSIRIS measurements and model results during periods with positive anomalies. For example, at 0° (Figure 6), positive anomalies are stronger in the OSIRIS data than in the model output, suggesting that the observed anomaly may~~is~~ not be fully explained by aerosol levels and may be related to other sources of variability.

At each altitude and latitude, the correlation coefficient between the OSIRIS percent difference in NO_2 and the aerosol extinction was calculated and is shown in Figure 8. Negative correlations between NO_2 and aerosol are observed at most latitudes and altitudes in the lower stratosphere. Altitudes and latitudes that were affected by volcanic aerosol for at least one month in the ~~timeseries~~time series are given by the magenta and green contour lines. For these altitudes and latitudes, the relationship between NO_2 and extinction tends to be stronger. In each latitude bin, the strongest correlation coefficient across altitudes is similar to the correlation coefficients for the partial VCDs and partial column AODs shown in Figure 5. In some cases, the strongest correlation coefficient within the profile is slightly lower than for the partial VCDs and partial column AODs, suggesting noise in either the NO_2 or aerosol extinction profiles or both. ~~For 60°S to 90°S, some positive correlation coefficients are observed. The variability in OSIRIS aerosol extinction at these latitudes is largely unrelated to volcanic aerosol.~~

5 Conclusion

Between 2002 and 2014, seven periods with enhanced volcanic aerosol were observed by OSIRIS and, in most cases, were associated with reduced levels of NO_2 observed by both OSIRIS and MIPAS. For the partial column AODs between 5-7x10^{-3}, OSIRIS and MIPAS NO_2 VCDs decreased relative to baseline levels by ~20-50% and ~5-25%, respectively. For AODs ~~>~~ greater than 7x10^{-3}, decreases in OSIRIS NO_2 reached ~40-60%. No MIPAS NO_2 measurements were available for AODs ~~>~~ greater than 7x10^{-3}. MIPAS observed a smaller decrease in NO_2 than OSIRIS, which was found to be consistent with the effect of the MIPAS DOFS less than 1 at these latitudes~~is consistent with differences in the DOFS < less than 1 for the MIPAS measurements~~.

The relationships between the percent differences in NO_2 relative to baseline levels and AODs are ~~somewhat linear~~~~observed~~found for both OSIRIS and MIPAS, with R between approximately -0.4 and -0.8 depending on the altitude and latitude range. ~~Perfect linearity is not expected because heterogeneous~~ Heterogeneous chemistry becomes saturated toward larger aerosol concentrations (e.g., Fahey et al., 1993) and can vary throughout the ~~timeseries~~time series with other factors,

such as temperature and available sunlight (e.g., Coffey, 1996), all of which can affect the linearity of the correlation . The variation of OSIRIS percent differences in NO_2 with partial column AOD was compared against photochemical model runs and was found to be consistent within estimated uncertainty. ~~They were found to be consistent both in terms of the magnitude of percent difference and the shape of the curve as it approaches saturation~~.

A strong anticorrelation~~negative relationship~~ was observed between MIPAS N_2O_5 and OSIRIS AOD, with R ~ -0.9, however, no relationship was observed between MIPAS HNO_3 and OSIRIS AOD. The photochemical model suggests that increases in HNO_3 would be ~~<~~ less than 10% for the observed partial column AODs, and therefore would be difficult to detect above other sources of variability.

The reductions in NO_2 observed in the present study would amount to ~~<~~ less than 20% of the total column in the tropics and ~~<~~ less than 10% of the total column toward higher latitudes, even for the largest aerosol events. This is much smaller than the column reductions of up to 50-70% observed after the Pinatubo and El Chichón volcanoes (e.g., Coffey, 1996), where the largest reductions in the total column of NO_2 occurred for periods with aerosol enhancements above 25 km (Koike et al., 1993), where the bulk of the NO_2 column resides. The results presented here are consistent with the smaller stratospheric aerosol loads and lower altitude range of the more recent volcanoes (e.g., Rieger et al., 2015).

Appendix A: Relationship between aerosol extinction and aerosol surface area

Let $n(r)$ represent the number of particles, per unit volume, with a size between radius *r* and *r*+*dr*, such that

$$N = \int_0^\infty n(r)dr \quad \text{(A1)}$$

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is the total number of particles per unit volume. The surface area density, SA, is then

$$SA = \int_0^\infty 4\pi r^2 n(r)dr \quad \text{(A2)}$$

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and the extinction, k, is

$$k = \int_0^\infty \sigma(r)n(r)dr \quad \text{(A3)}$$

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where $\sigma(r)$ is the extinction cross-section. It is convenient to use an extinction efficiency, $Q(r)$, such that $Q(r) = \sigma(r)/\pi r^2$ which represents the ratio of the extinction cross-section to the geometric cross-section. In this case

$$k = \int_0^\infty \pi r^2\, Q(r)n(r)dr \quad \text{(A4)}$$

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If it is assumed that $Q(r)$ can be replaced by an effective value, $\bar{Q}$, then

$$k = \bar{Q} \int_0^\infty \pi r^2 n(r) dr = \left(\frac{\bar{Q}}{4}\right) SA \quad \text{(A5)}$$

where

$$\bar{Q} = \frac{\int_0^\infty \pi r^2 Q(r) n(r) dr}{\int_0^\infty \pi r^2 n(r) dr} \quad \text{(A6)}$$

$Q(r)$ can be calculated for spherical particles using Mie theory; see, e.g., Hansen and Travis (1974). For a sulfate aerosol and a lognormal size distribution with r_g=0.08 μm and σ_g=1.6, $\bar{Q}$ =0.4. Since both surface area density and extinction are proportional to r^2, and the extinction efficiency is a weaker function of size than the absolute cross-section, it is advantageous to use this approach when the size information is less accurately known. Note an additional factor of 10^3 is required to adjust between the common units of extinction (km^{-1}) and surface area density ($\mu m^2/cm^3$).

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Acknowledgments and Data

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References

Baldwin, M. P., Gray, L. J., Dunkerton, T. J., Hamilaton, K., Haynes, P. H., Randel, W. J., Holton, J. R., Alexander, M. J., Hirota, I., Horinouchi, T., Jones, D. B. A., Kinnersley, J. S., Marquardt, C., Sato, K. and Takahashi, M.: The Quasi-Biennial Oscillation, Rev. Geophys., 39(2), 179–230, doi:10.1029/1999RG000073, 2001.

Berthet, G., Jégou, F., Catoire, V., Krysztofiak, G., Renard, J., Bourassa, A. E., Degenstein, D. A., Brogniez, C., Dorf, M., Kreycy, S., Pfeilsticker, K., Werner, B., Lefèvre, F., Roberts, T. J., Lurton, T., Vignelles, D., Bègue, N., Bourgeois, Q.,

Daugeron, D., Chartier, M., Robert, C., Gaubicher, B. and Guimbaud, C.: Impact of a moderate volcanic eruption on chemistry in the lower stratosphere: balloon-borne observations and model calculations, Atmos. Chem. Phys., 17, 2229–2253, doi:10.5194/acp-17-2229-2017, 2017.

Bourassa, A. E., Degenstein, D. A., Gattinger, R. L. and Llewellyn, E. J.: Stratospheric aerosol retrieval with optical spectrograph and infrared imaging system limb scatter measurements, J. Geophys. Res. Atmos., 112, D10217, doi:10.1029/2006JD008079, 2007.

Bourassa, A. E., Degenstein, D. A. and Llewellyn, E. J.: SASKTRAN: A spherical geometry radiative transfer code for efficient estimation of limb scattered sunlight, J. Quant. Spectrosc. Radiat. Transf., 109, 52–73, doi:10.1016/j.jqsrt.2007.07.007, 2008.

Bourassa, A. E., Degenstein, D. A., Elash, B. J. and Llewellyn, E. J.: Evolution of the stratospheric aerosol enhancement following the eruptions of Okmok and Kasatochi: Odin-OSIRIS measurements, J. Geophys. Res. Atmos., 115, D00L03, doi:10.1029/2009JD013274, 2010.

Bourassa, A. E., McLinden, C. A., Sioris, C. E., Brohede, S., Bathgate, A. F., Llewellyn, E. J. and Degenstein, D. A.: Fast NO_2 retrievals from Odin-OSIRIS limb scatter measurements, Atmos. Meas. Tech., 4, 965–972, doi:10.5194/amt-4-965-2011, 2011.

Bourassa, A. E., Robock, A., Randel, W. J., Deshler, T., Rieger, L. A., Lloyd, N. D., Llewellyn, E. J. and Degenstein, D. A.: Large Volcanic Aerosol Load in the Stratosphere Linked to Asian Monsoon Transport, Science (80-.)., 337(6090), 78–81, doi:10.1126/science.1219371, 2012a.

Bourassa, A. E., Rieger, L. A., Lloyd, N. D. and Degenstein, D. A.: Odin-OSIRIS stratospheric aerosol data product and SAGE III intercomparison, Atmos. Chem. Phys., 12, 605–614, doi:10.5194/acp-12-605-2012, 2012b.

Bourassa, A. E., Degenstein, D. A., Randel, W. J., Zawodny, J. M., Kyrölä, E., McLinden, C. A., Sioris, C. E. and Roth, C. Z.: Trends in stratospheric ozone derived from merged SAGE II and Odin-OSIRIS satellite observations, Atmos. Chem. Phys., 14, 6983–6994, doi:10.5194/acp-14-6983-2014, 2014.

Brohede, S., McLinden, C. A., Urban, J., Haley, C. S., Jonsson, A. I. and Murtagh, D.: Odin stratospheric proxy NO_y measurements and climatology, Atmos. Chem. Phys., 8, 5731–5754, doi:10.5194/acp-8-5731-2008, 2008.

Brohede, S. M., Haley, C. S., McLinden, C. A., Sioris, C. E., Murtagh, D. P., Petelina, S. V., Llewellyn, E. J., Bazureau, A., Goutail, F., Randall, C. E., Lumpe, J. D., Taha, G., Thomasson, L. W. and Gordley, L. L.: Validation of Odin/OSIRIS

stratospheric NO_2 profiles, J. Geophys. Res. Atmos., 112(D07310), 1–22, doi:10.1029/2006JD007586, 2007.

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kold, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M. and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18, Jet Propulsion Laboratory, Pasadena, USA. [online] Available from: http://jpldataeval.jpl.nasa.gov, 2015.

Coffey, M. T.: Observations of the impact of volcanic activity on stratospheric chemistry, J. Geophys. Res., 101(D3), 6767–6780, doi:10.1029/95JD03763, 1996.

Cohen, R. C. and Murphy, J. G.: Photochemistry of NO_2 in Earth's Stratosphere: Constraints from Observations, Chem. Rev., 103, 4985–4998, doi:10.1021/cr020647x, 2003.

Fahey, D. W., Kawa, S. R., Woddbridge, E. L., Tin, P., Wilson, J. C., Jonsson, H. H., Dyes, J. E., Baumgardners, D., Borrmans, S., Toohey, D. W., Avallone, L. M., Proffitt, M. H., Pargitan, J., Loewenstein, M., Podolske, J. R., Salawitch, R. J., Wofsy, S. C., Ko, M. K. W., Andersonss, D. E., Schoeberl, M. R. and Chan, K. R.: In situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion, Nature, 363, 509–514, 1993.

Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehhalt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopmann, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G. and Zander, R.: MIPAS: an instrument for atmospheric and climate research, Atmos. Chem. Phys., 8, 2151–2188, doi:10.5194/acp-8-2151-2008, 2008.

Fromm, M., Kablick III, G., Nedoluha, G., Carboni, E., Grainger, R., Campbell, J. and Lewis, J.: Correcting the record of volcanic stratospheric aerosol impact: Nabro and Sarychev Peak, J. Geophys. Res., 119(17), 10343–10364, doi:10.1002/2014JD021507.Since, 2014.

Funke, B., López-Puertas, M., von Clarmann, T., Stiller, G. P., Fischer, H., Glatthor, N., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Mengistu Tsidu, G., Milz, M., Steck, T. and Wang, D. Y.: Retrieval of stratospheric NO_x from 5.3 and 6.2 μm nonlocal thermodynamic equilibrium emissions measured by Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on Envisat, J. Geophys. Res., 110, D09302, doi:10.1029/2004JD005225, 2005.

Funke, B., Stiller, G. P. and von Clarmann, T.: Mesospheric and stratospheric NO_y produced by energetic particle precipitation during 2002 – 2012, J. Geophys. Res., 119, 4429–4446, doi:10.1002/2013JD021404, 2014.

Hansen, J. E. and Travis, L. D.: Light scattering in planetary atmospheres, Space Sci. Rev., 16, 527–610, doi:10.1007/BF00168069, 1974.

Hauchecorne, A., Bertaux, J. L., Dalaudier, F., Keckhut, P., Lemennais, P., Bekki, S., Marchand, M., Lebrun, J. C., KyröÏla, E., Tamminen, J., Sofieva, V., Fussen, D., Vanhellemont, F., Fanton d'Andon, O., Barrot, G., Blanot, L., Fehr, T. and Saavedra de Miguel, L.: Response of tropical stratospheric O_3, NO_2 and NO_3 to the equatorial Quasi-Biennial Oscillation and to temperature as seen from GOMOS/ENVISAT, Atmos. Chem. Phys., 10(18), 8873–8879, doi:10.5194/acp-10-8873-2010, 2010.

Haywood, J. M., Jones, A., Clarisse, L., Bourassa, A., Barnes, J., Telford, P., Bellouin, N., Boucher, O., Agnew, P., Clerbaux, C., Coheur, P., Degenstein, D. and Braesicke, P.: Observations of the eruption of the Sarychev volcano and simulations using the HadGEM2 climate model, J. Geophys. Res. Atmos., 115, D21212, doi:10.1029/2010JD014447, 2010.

Hommel, R., Timmreck, C., Giorgetta, M. A. and Graf, H. F.: Quasi-biennial oscillation of the tropical stratospheric aerosol layer, Atmos. Chem. Phys., 15, 5557–5584, doi:10.5194/acp-15-5557-2015, 2015.

Höpfner, M., Boone, C. D., Funke, B., Glatthor, N., Grabowski, U., Günther, A., Kellmann, S., Kiefer, M., Linden, A., Lossow, S., Pumphrey, H. C., Read, W. G., Roiger, A., Stiller, G., Schlager, H., von Clarmann, T. and Wissmüller, K.: Sulfur dioxide (SO_2) from MIPAS in the upper troposphere and lower stratosphere 2002–2012, Atmos. Chem. Phys., 15, 7017–7037, doi:10.5194/acp-15-7017-2015, 2015.

Jégou, F., Berthet, G., Brogniez, C., Renard, J.-B., François, P., Haywood, J. M., Jones, A., Bourgeois, Q., Lurton, T., Auriol, F., Godin-Beekmann, S., Guimbaud, C., Krysztofiak, G., Gaubicher, B., Chartier, M., Clarisse, L., Clerbaux, C., Balois, J. Y., Verwaerde, C. and Daugeron, D.: Stratospheric aerosols from the Sarychev volcano eruption in the 2009 Arctic summer, Atmos. Chem. Phys., 13, 6533–6552, doi:10.5194/acp-13-6533-2013, 2013.

Johnston, P. V., McKenzie, R. L., Keys, J. G. and Matthews, W. A.: Observations of depleted stratospher NO_2 following the Pinatubo volcanic eruption, Geophys. Res. Lett., 19(2), 211–213, doi:10.1029/92GL00043, 1992.

Kalnay, E., Kanamisu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K. C., Ropelewski, C., Wang, J., Leetmaa, A., Reynolds, R., Jenne, R. and Dennis, J.: The NCEP/NCAR 40 Year Reanalysis Project, Bull. Am. Meteorol. Soc., 77, 437–471, doi:http://dx.doi.org/10.1175/1520-0477(1996)077<0437:TNYRP>2.0.CO;2, 1996.

Koike, M., Kondo, Y., Matthews, W. A., Johnston, P. . V. and Yamazaki, K.: Decrease of stratospheric NO_2 caused by Pinatubo volcanic aerosols, Geophys. Res. Lett., 20(18), 1975–1978, doi:10.1029/93GL01800, 1993.

Kravitz, B., Robock, A. and Bourassa, A.: Negligible climatic effects from the 2008 Okmok and Kasatochi volcanic eruptions,

J. Geophys. Res., 115, D00L05, doi:10.1029/2009JD013525, 2010.

Llewellyn, E. J., Lloyd, N. D., Degenstein, D. A., Gattinger, R. L., Petelina, S. V., Bourassa, A. E., Wiensz, J. . T., Ivanov, E. V., McDade, I. C., Solheim, B. H., McConnell, J. C., Haley, C. S., von Savigny, C., Sioris, C. E., McLinden, C. A., Griffioen, E., Kaminski, J., Evans, W. F. J., Puckrin, E., Strong, K., Wehrle, V., Hum, R. H., Kendall, D. J. W., Matsushita, J., Murtagh, D. P., Brohede, S., Stegman, J., Witt, G., Barnes, G., Payne, W. F., Piché, L., Smith, K., Warshaw, G., Deslauniers, D.-L., Marchand, P., Richardson, E. H., King, R. A., Wevers, I., McCreath, W., Kyrölä, E., Oikarinen, L., Leppelmeier, G. W., Auvinen, H., Mégie, G., Hauchecorne, A., Lefèvre, F., de La Nöe, J., Ricaud, P., Frisk, U., Sjoberg, F., von Schéele, F. and Nordh, L.: The OSIRIS instrument on the Odin spacecraft, Can. J. Phys., 82, 411–422, doi:10.1139/p04-005, 2004.

McLinden, C. A., Olsen, S. C., Hannegan, B., Wild, O., Prather, M. J. and Sundet, J.: Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, J. Geophys. Res., 105(D11), 14653–14665, doi:10.1029/2000JD900124, 2000.

McLinden, C. A., Haley, C. S., Lloyd, N. D., Hendrick, F., Rozanov, A., Sinnhuber, B.-M., Goutail, F., Degenstein, D. A., Llewellyn, E. J., Sioris, C. E., Van Roozendael, M., Pommereau, J. P., Lotz, W. and Burrows, J. P.: Odin/OSIRIS observations of stratospheric BrO: Retrieval methodology, climatology, and inferred Br_y, J. Geophys. Res., 115, D15308, doi:10.1029/2009JD012488, 2010.

McLinden, C. A., Bourassa, A. E., Brohede, S., Cooper, M., Degenstein, D. A., Evans, W. J. F., Gattinger, R. L., Haley, C. S., Llewellyn, E. J., Lloyd, N. D., Loewen, P., Martin, R. V., McConnell, J. C., McDade, I. C., Murtagh, D., Rieger, L., Von Savigny, C., Sheese, P. E., Sioris, C. E., Solheim, B. and Strong, K.: Osiris: A Decade of scattered light, Bull. Am. Meteorol. Soc., 93, 1845–1863, doi:10.1175/BAMS-D-11-00135.1, 2012.

Mengistu Tsidu, G., von Clarmann, T., Stiller, G. P., Höpfner, M., Fischer, H., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., Milz, M., Steck, T. and Wang, D. Y.: Stratospheric N_2O_5 in the austral spring 2002 as retrieved from limb emission spectra recorded by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), J. Geophys. Res., 109, D18301, doi:10.1029/2004JD004856, 2004.

Mills, M. J., Langford, A. O., O'Leary, T. J., Arpag, K., Miller, H. L., Proffitt, M. H. and Solomon, S.: On the relationship between stratospheric aerosols and nitrogen dioxide, Geophys. Res. Lett., 20(12), 1187–1190, doi:10.1029/93GL01124, 1993.

Murtagh, D., Frisk, U., Merino, F., Ridal, M., Jonsson, A., Stegman, J., Witt, G., Eriksson, P., Jiménez, C., Megie, G., Noë, J. D. La, Ricaud, P., Baron, P., Pardo, J. R., Hauchcorne, A., Llewellyn, E. J., Degenstein, D. A., Gattinger, R. L., Lloyd, N. D., Evans, W. F. J., McDade, I. C., Haley, C. S., Sioris, C., von Savigny, C., Solheim, B. H., McConnell, J. C., Strong, K.,

Richardson, E. H., Leppelmeier, G. W., Kyrölä, E., Auvinen, H. and Oikarinen, L.: An overview of the Odin atmospheric mission, Can. J. Phys., 80, 309–319, doi:10.1139/p01-157, 2002.

Nagatani, R. M. and Rosenfield, J. E.: The Atmospheric Effects of Stratospheric Aircraft, in Report of the 1992 Models and Measurements Workshop, NASA Ref. Publ. 1292, edited by M. J. Prather and E. E. Remsberg, pp. A1–A47, NASA, Washington, D.C., 1993.

Naujokat, B.: An Update of the Observed Quasi-Biennial Oscillation of the Stratospheric Winds over the Tropics, J. Atmos. Sci., 43(17), 1873–1877, doi:10.1175/1520-0469(1986)043<1873:AUOTOQ>2.0.CO;2, 1986.

O'Neill, N. T., Perro, C., Saha, A., Lesins, G., Duck, T. J., Eloranta, E. W., Nott, G. J., Hoffman, A., Karumudi, M. L., Ritter, C., Bourassa, A., Abboud, I., Carn, S. A. and Savastiouk, V.: Properties of Sarychev sulphate aerosols over the Arctic, J. Geophys. Res., 117, D04203, doi:10.1029/2011JD016838, 2012.

Olsen, S. C., McLinden, C. A. and Prather, M. J.: Stratospheric N2O-NO2 system: Testing Uncertainties in a three-dimensional framework, J. Geophys. Res., 106(D22), 28,771–28,784, 2001.

Prata, A. J., Carn, S. A., Stohl, A. and Kerkmann, J.: Long range transport and fate of a stratospheric volcanic cloud from Soufrière Hills volcano, Montserrat, Atmos. Chem. Phys., 7, 5093–5103, doi:10.5194/acp-7-5093-2007, 2007.

Randeniya, L. K., Vohralik, P. F., Plumb, I. C. and Ryan, K. R.: Heterogenous $BrONO_2$ hydrolysis: Effect on NO_2 columns and ozone at high latitudes in summer, J. Geophys. Res., 102(D19), 23543–23557, doi:10.1029/97JD01655, 1997.

Rieger, L. A., Bourassa, A. E. and Degenstein, D. A.: Merging the OSIRIS and SAGE II stratospheric aerosol records, J. Geophys. Res., 12(17), 1–15, doi:10.1002/2015JD023133, 2015.

Rinsland, C. P., Gunson, M. R., Abrams, M. C., Lowes, L. L., Zander, R., Mahieu, E., Goldman, A., Ko, M. K. W., Rodriguez, J. M. and Sze, N. D.: Heterogeneous conversion of N_2O_5 to HNO_3 in the post-Mount Pinatubo eruption stratosphere, J. Geophys. Res. Atmos., 99(D4), 8213–8219, doi:10.1029/93JD03469, 1994.

Sioris, C. E., Boone, C. D., Bernath, P. F., Zou, J., McElroy, C. T. and McLinden, C. A.: Atmospheric Chemistry Experiment (ACE) observations of aerosol in the upper troposphere and lower stratosphere from the Kasatochi volcanic eruption, J. Geophys. Res., 115, D00L14, doi:10.1029/2009JD013469, 2010.

Thomason, L. W., Poole, L. R. and Deshler, T.: A global climatology of stratospheric aerosol surface area density deduced from Stratospheric Aerosol and Gas Experiment II measurements: 1984–1994, J. Geophys. Res., 102(D7), 8967–8976,

doi:10.1029/96JD02962, 1997.

von Clarmann, T., Höpfner, M., Kellmann, S., Linden, A., Chauhan, S., Funke, B., Grabowski, U., Glatthor, N., Kiefer, M., Schieferdecker, T., Stiller, G. P. and Versick, S.: Retrieval of temperature, H2O, O3, HNO3, CH4, N2O, ClONO2 and ClO from MIPAS reduced resolution nominal mode limb emission measurements, Atmos. Meas. Tech., 2, 159–175, doi:10.5194/amt-2-159-2009, 2009.

Wegner, T., Grooß, J.-U., von Hobe, M., Stroh, F., Sumińska-Ebersoldt, O., Volk, C. M., Hösen, E., Mitev, V., Shur, G. and Müller, R.: Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex, Atmos. Chem. Phys., 12, 11095–11106, doi:10.5194/acp-12-11095-2012, 2012.

Table 1: Parameters considered for model perturbation tests.

Parameter	Model Settings	Perturbation(s)	Perturbation Comment
SA to *k* linear scaling factor	10000	Model Setting × 3; Model Setting × 1/3	Accounts for range in aerosol size distributions
Degree of *SA* to *k* non-linearity	$SA \propto k^{1.0}$	$SA \propto k^{1.3}$; $SA \propto k^{0.7}$	Following Thomason et al. (1997)
Ozone profiles	OSIRIS climatology (Bourassa et al., 2014)	Model Setting +10%	Estimate of uncertainty and variability in monthly mean
NO_y profiles	From 3D model simulations (Olsen et al., 2001)	Model Setting +20%	Estimate of uncertainty and variability in monthly mean
Temperature	Climatology from Nagatani and Rosenfield (1993)	Model Setting +5 K	Estimate of uncertainty and variability in monthly mean
Surface albedo	0.1	0.3	Difference between mean, effective albedo with and without clouds
NO + O_3 reaction rate coefficient	JPL Publication 15-10 (Burkholder et al., 2015) [$A=3\times10^{-12}$; E/R=1500]	Model Setting +10%	Estimated uncertainty from Burkholder et al. (2015)
NO_2 absorption coefficient	JPL Publication 15-10 (Burkholder et al., 2015) [Table 4C-2]	Model Setting +10%	Estimated uncertainty from Burkholder et al. (2015)

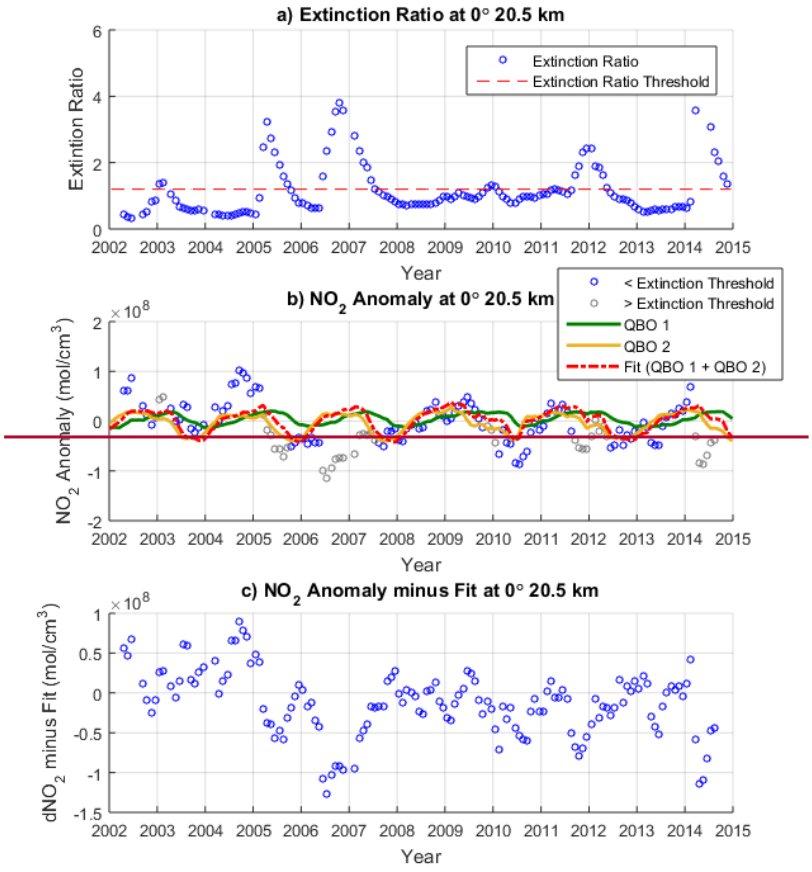
Table 2: Conversion factors for aerosol extinctions measured at various wavelengths.

Conversion (nm)	**Angstrom coefficient**	**Conversion factor (ratio of extinctions)**
1020 → 525	2.5	5.42
750 → 525	2.3	2.27
1020 → 750	2.8	2.39

Table 3: Summary of volcanoes observed in OSIRIS partial column AOD and associated OSIRIS NO_2 VCDs. References given in footnotes describe stratospheric aerosol following these eruptions. Note that this table ~~only include~~lists eruptions that were followed by significant increases in OSIRIS aerosol extinction. Therefore, it does not include all volcanoes known to have affected the stratosphere during this time-period.

Volcano Name[a]	**Eruption Date**	**Eruption Latitude**	**Extent of aerosol enhancement observed by OSIRIS**[b]	**Effect on OSIRIS-observed NO_2 partial VCD**
Manam[c]	27 Jan 2005	4°S	Both hemispheres, confined to the tropics	Minimal effect on observed NO_2
Soufrière Hills[d]	30 May 2006	17°N	Both hemispheres, reaching high latitudes in spring 2007	For 50°S-0° and 40°-60°N, NO_2 is lower by ~10-40%
Mt Okmok[e] Kasatochi[e]	12 Jul 2008 7 Aug 2008	53°N 52°N	Combined effect of both volcanoes, reached tropics in Dec 2008-Jan 2009	For 40-80°N NO_2 is lower by ~20-40%
Sarychev Peak[f]	12 Jun 2009	48°N	Large AODs until Dec 2010, mostly confined to northern hemisphere mid-latitudes and high latitudes	For 30-80°N, NO_2 is lower, reaching reductions of up to ~45-55% for 40-80°N
Mt Merapi	4 Nov 2010	7°S	Both hemispheres, small signal confined to tropics in northern hemisphere and extending to higher latitudes in southern hemisphere in Jan 2011	Minimal effect on observed NO_2
Nabro[g]	12 Jun 2011	13°N	Large AODs throughout the northern hemisphere until Jan 2012, with smaller AODs until Jun 2012	20-80°N, NO_2 is lower, reaching reductions of up to ~50-55% for 50-80°N
Kelut	13 Feb 2014	8°S	Both hemispheres, confined to the tropics	For 10S°-0° NO_2 is lower by ~20-40%

[a] Eruption dates and latitudes from (Höpfner et al., 2015) and reports available at http://volcano.si.edu/.
[b] OSIRIS does not measure AOD in the winter hemisphere and therefore may not capture the full extent of aerosol enhancement.
[c] (Bourassa et al., 2012b)
[d] (Prata et al., 2007)
[e] (Bourassa et al., 2010; Kravitz et al., 2010; Sioris et al., 2010)
[f] (Haywood et al., 2010; Jégou et al., 2013; O'Neill et al., 2012)
[g] (Bourassa et al., 2012a)


a) Extinction Ratio at 0° 20.5 km
Extinction Ratio
Extinction Ratio Threshold
Extintion Ratio
Year
b) NO2 Anomaly at 0° 20.5 km
< Extinction Threshold
> Extinction Threshold
QBO 1
QBO 2
Fit (QBO 1 + QBO 2)
NO2 Anomaly (mol/cm3)
Year
c) NO2 Anomaly minus Fit at 0° 20.5 km
dNO2 minus Fit (mol/cm3)
Year

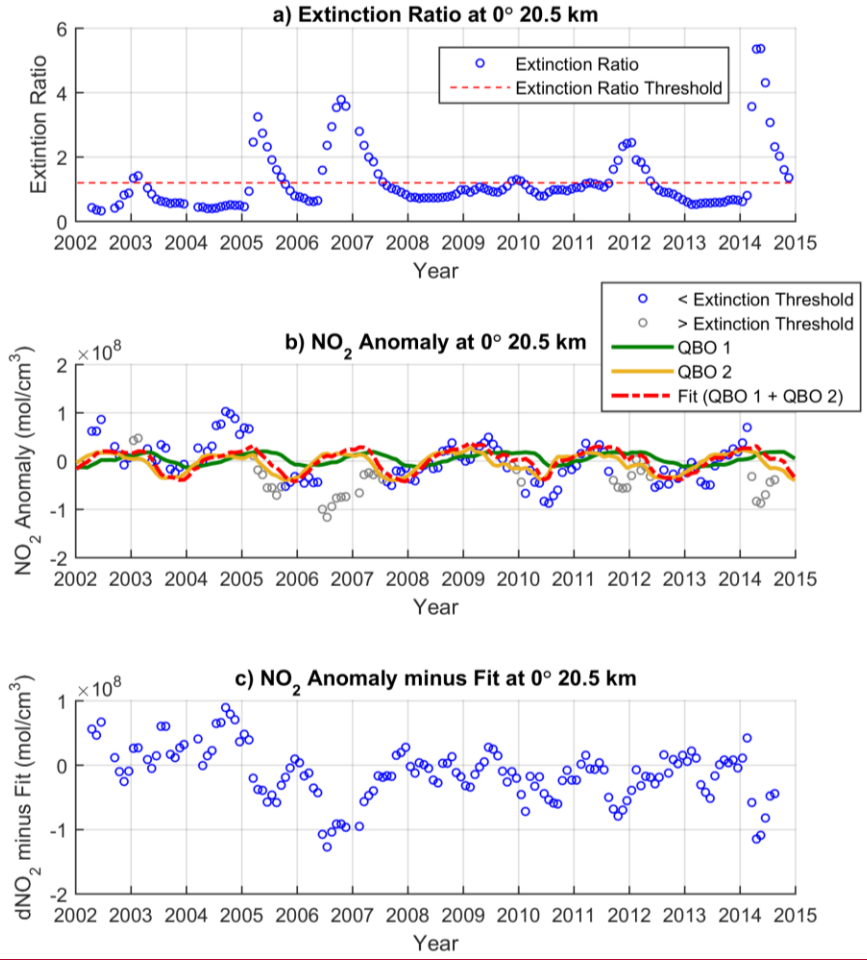
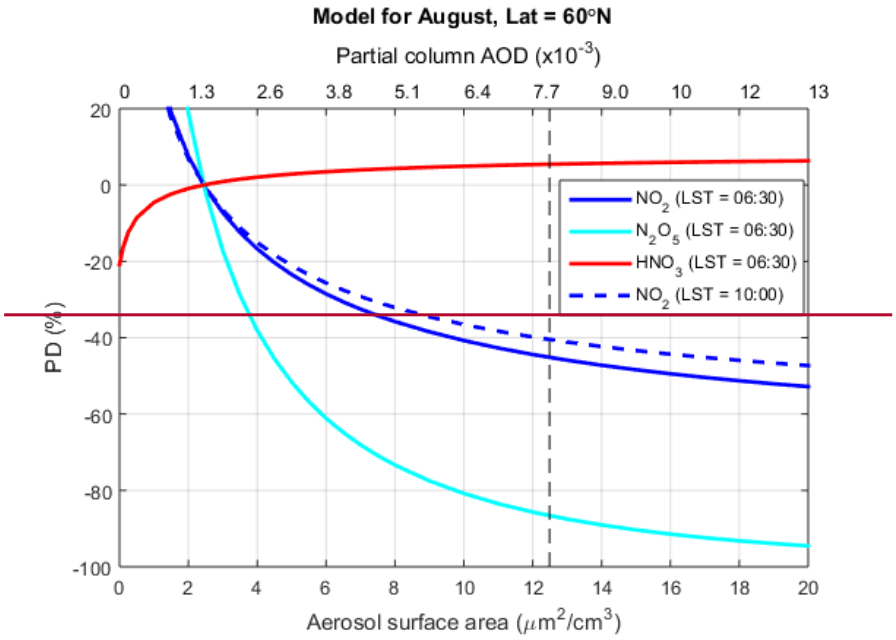


Figure 1: QBO fitting results for 0° latitude at 20.5 km. (a) Extinction ratio ~~timeseries~~time series (blue circles) with extinction ratio threshold (red dashed line). (b) NO_2 anomaly ~~timeseries~~time series for time periods with extinction ratio ~~<~~ less than extinction ratio threshold (blue circles) and time periods with extinction ratio ~~></~~ greater than extinction ratio threshold (grey

circles). The fits for the two QBO principal components – QBO 1 (green line) and QBO 2 (yellow line) – as well as the total fit (red dashed lined) to the NO_2 anomaly ~~timeseries~~time series during time periods with extinction ratio ~~<~~ less than extinction ratio threshold are also shown. (c) NO_2 anomaly ~~timeseries~~time series after subtraction of the fit.


Model for August, Lat = 60°N
Partial column AOD (x10-3)
0
1.3
2.6
3.8
5.1
6.4
7.7
9.0
10
12
13
20
0
-20
-40
-60
-80
-100
PD (%)
0
2
4
6
8
10
12
14
16
18
20
Aerosol surface area (μm2/cm3)
NO2 (LST = 06:30)
N2O5 (LST = 06:30)
HNO3 (LST = 06:30)
NO2 (LST = 10:00)

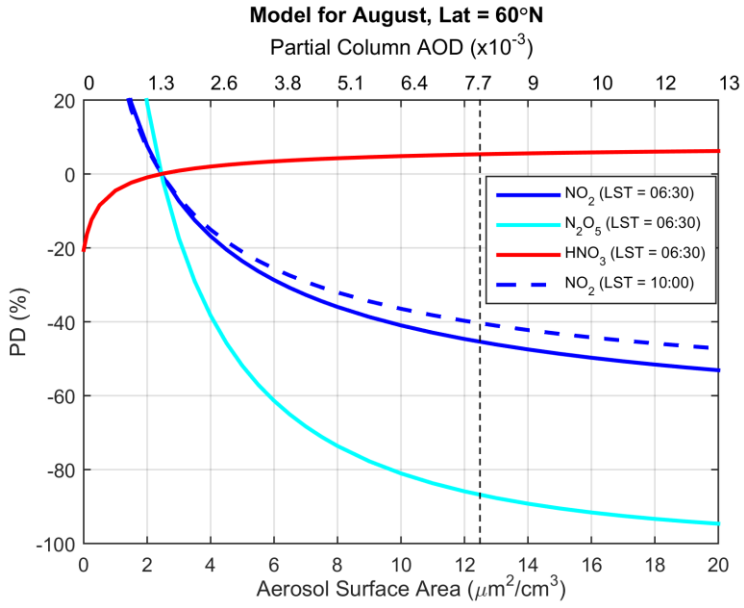
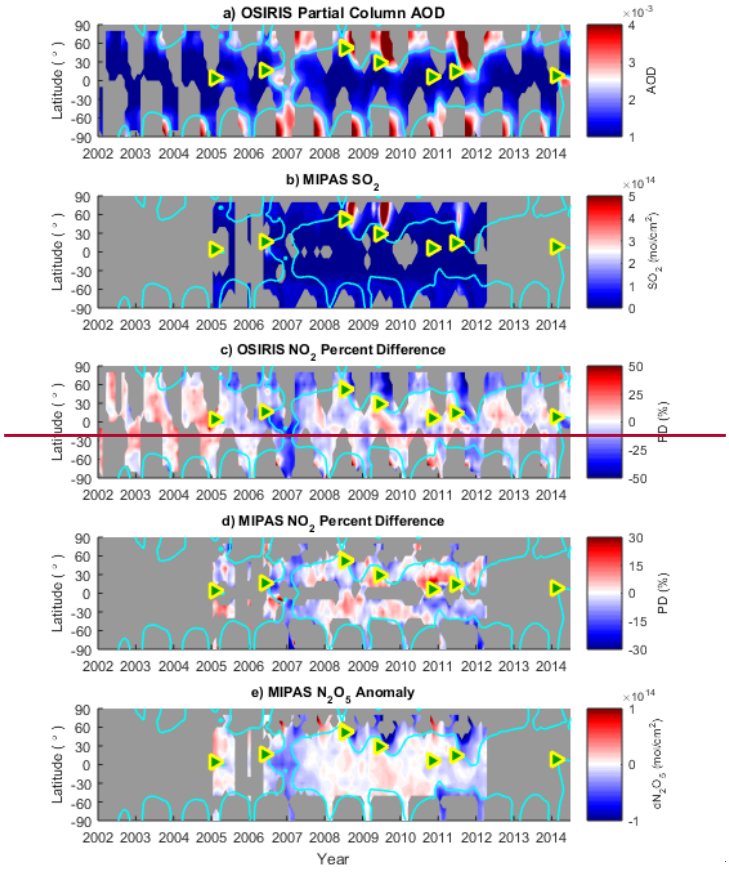


Figure 2: Modelled variations of NO_2, N_2O_5, and HNO_3 with stratospheric aerosol at 60°N in August. Aerosol surface area (bottom x-axis) and partial column AOD (top x-axis) are both shown. The y-axis gives the percent difference (anomaly – baseline)/baseline for partial VCDs of NO_2 (blue line), N_2O_5 (cyan line), and HNO_3 (red line) at the approximate OSIRIS local time (06:30 LT), and for NO_2 (blue dashed line) at the approximate MIPAS measurement time (10:00 LT). AODs and VCDs were calculated for a 5 km layer, starting ~3 km above the tropopause. The black dashed line indicates partial column AOD = $8x10^{-3}$, approximately the largest value in the OSIRIS measurements.


a) OSIRIS Partial Column AOD
b) MIPAS SO2
c) OSIRIS NO2 Percent Difference
d) MIPAS NO2 Percent Difference
e) MIPAS N2O5 Anomaly
Latitude (°)
Year
AOD
PD (%)

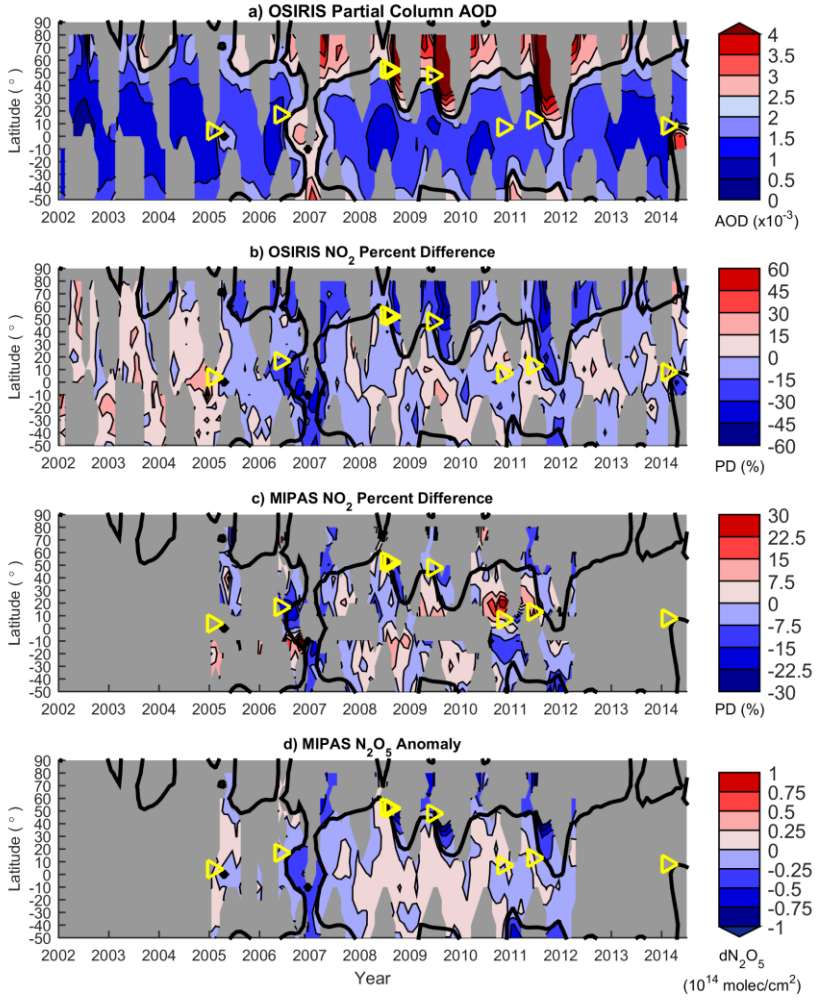
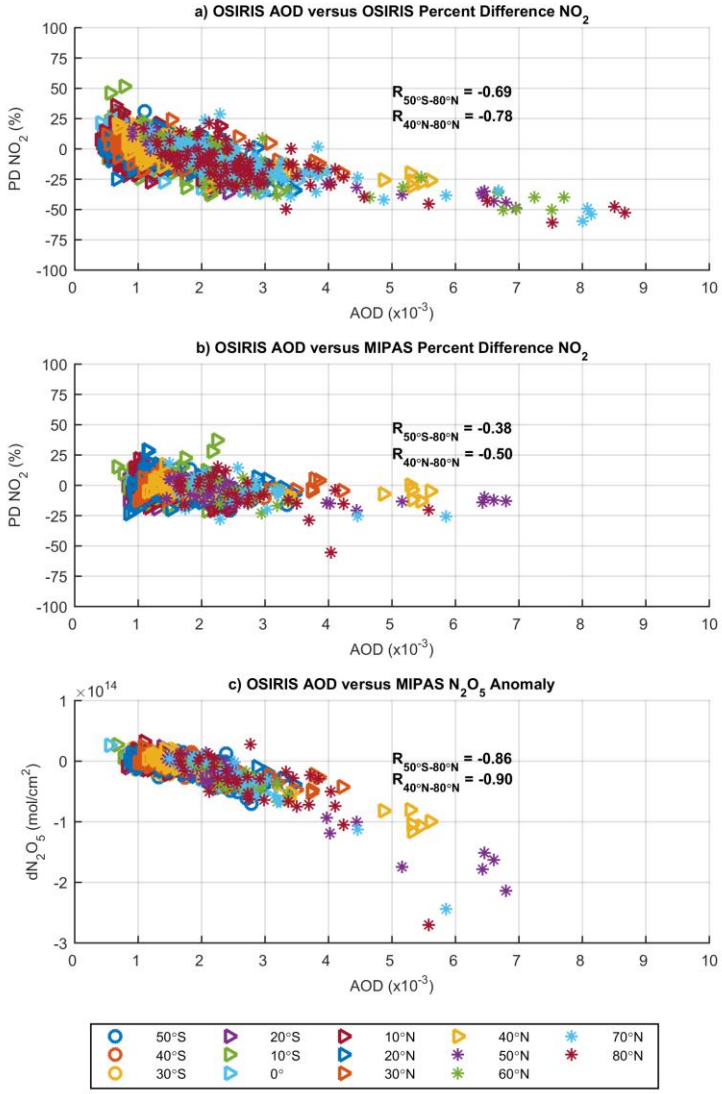

a) OSIRIS Partial Column AOD
b) OSIRIS NO2 Percent Difference
c) MIPAS NO2 Percent Difference
d) MIPAS N2O5 Anomaly
Latitude (°)
Year
AOD (x10-3)
PD (%)
PD (%)
dN2O5
(1014 molec/cm2)

Figure 3. Contour plots of time (x-axis) versus latitude (y-axis) versus (a) OSIRIS partial column AODs, ~~(b) MIPAS SO_2 VCDs,~~ (~~c~~b) percent difference of OSIRIS NO_2 VCDs, (~~d~~c) percent difference of MIPAS NO_2 VCDs, and (~~e~~d) MIPAS N_2O_5 anomaly. The partial column AODs and VCDs are calculated for ~~3-7~~5 km layer starting ~3 km above the thermal tropopause. Percent differences are relative to baseline levels of NO_2. Note that different colour-scale ranges are used for OSIRIS and MIPAS NO_2 percent differences. The ~~cyan~~ thick black contour lines show OSIRIS AOD = $2x10^{-3}$, extrapolated to latitudes/times where data were unavailable. The yellow~~/green~~ triangles indicate the volcanic eruptions ~~identified in~~that were followed by significant increases in OSIRIS aerosol extinction, as listed in Table 3.


a) OSIRIS AOD versus OSIRIS Percent Difference NO2
PD NO2 (%)
AOD (x10-3)
R50°S-80°N = -0.69
R40°N-80°N = -0.78
b) OSIRIS AOD versus MIPAS Percent Difference NO2
PD NO2 (%)
AOD (x10-3)
R50°S-80°N = -0.38
R40°N-80°N = -0.50
c) OSIRIS AOD versus MIPAS N2O5 Anomaly
×10^14
dN2O5 (mol/cm2)
AOD (x10-3)
R50°S-80°N = -0.86
R40°N-80°N = -0.90
50°S
40°S
30°S
20°S
10°S
0°
10°N
20°N
30°N
40°N
50°N
60°N
70°N
80°N

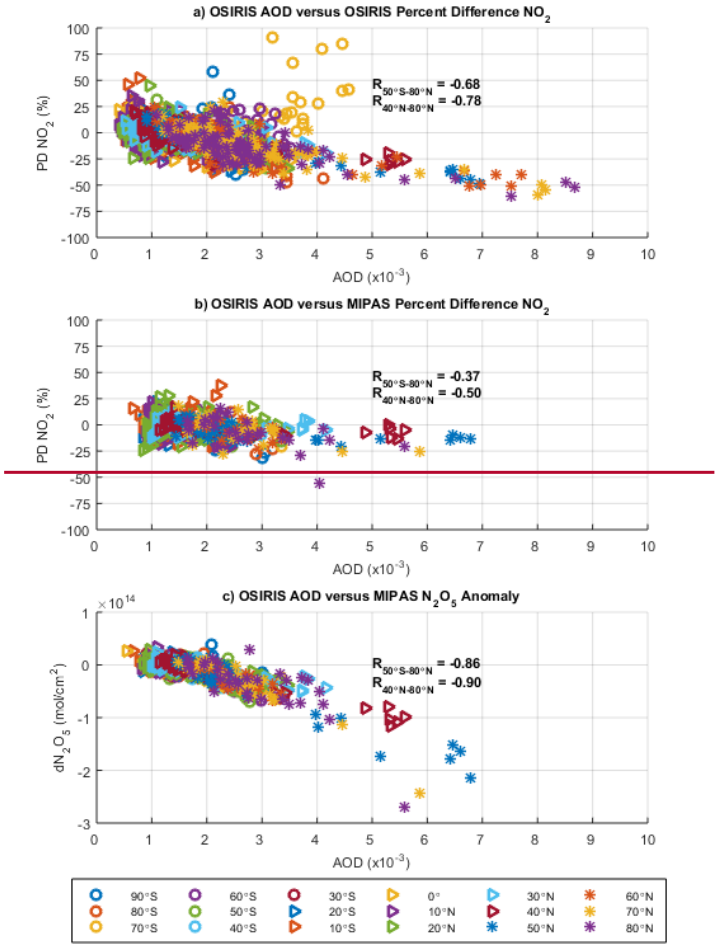
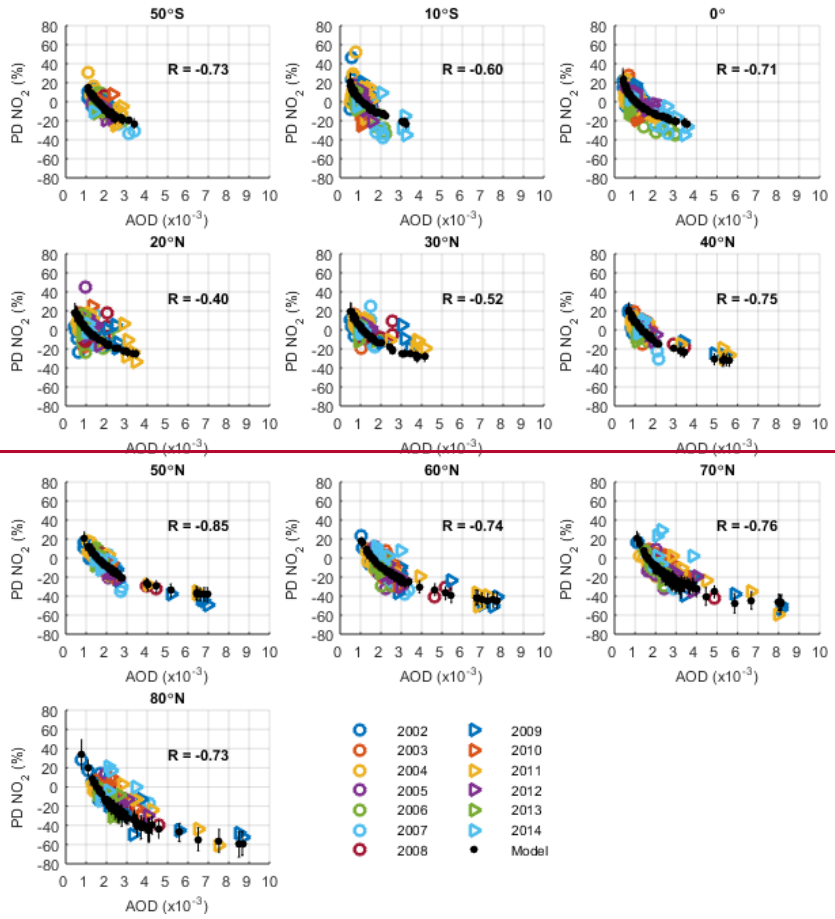


Figure 4. Scatter plots of OSIRIS AOD versus (a) OSIRIS and (b) MIPAS percent difference of NO_2 VCD relative to baseline levels and (c) MIPAS N_2O_5 anomaly. The legend shows the measurement latitude. R for NO_2 percent difference and AOD for data collected between 50°S and 80°N, and 40°N and 80°N are given in the plot. The p-values for all calculated R are ≤ less than $1x10^{-8}$.


50°S
R = -0.73
10°S
R = -0.60
0°
R = -0.71
20°N
R = -0.40
30°N
R = -0.52
40°N
R = -0.75
50°N
R = -0.85
60°N
R = -0.74
70°N
R = -0.76
80°N
R = -0.73
PD NO2 (%)
AOD (x10-3)
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
Model

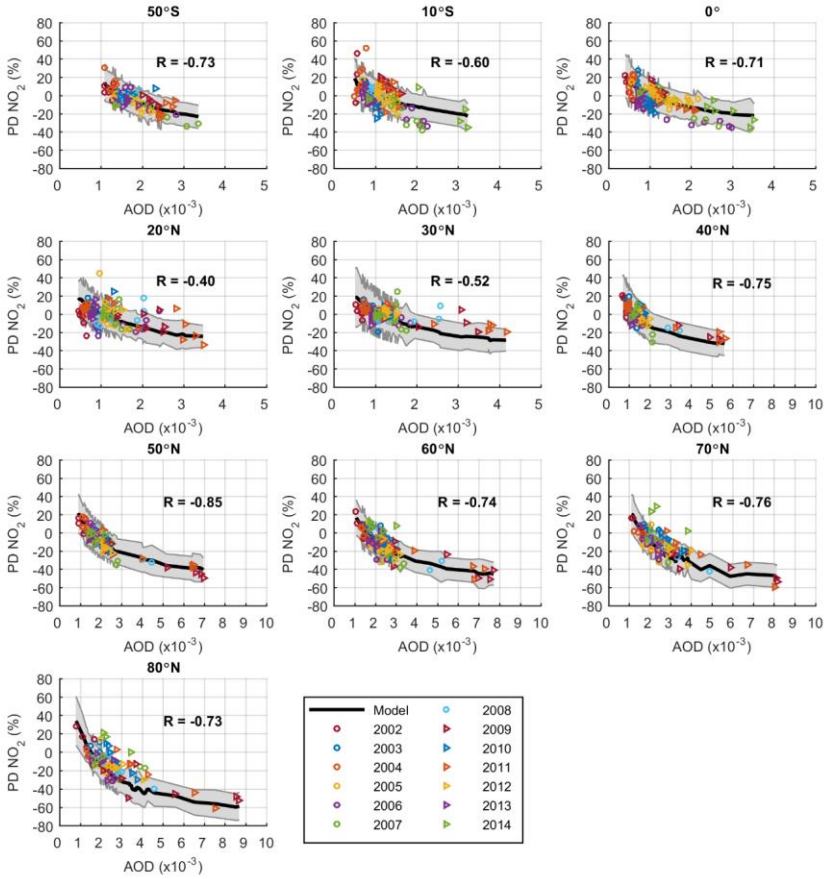
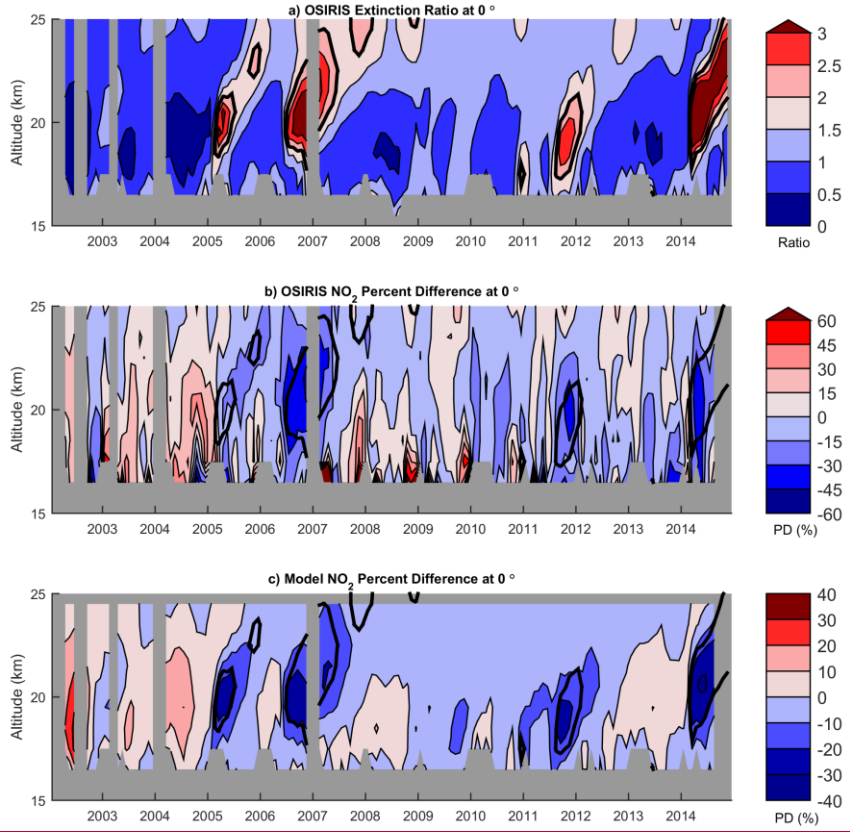


Figure 5. Scatter plots of OSIRIS AOD versus OSIRIS NO_2 percent difference in VCD relative to baseline levels for various latitudes, with R given in the plot. The legend shows the measurement years. Modelled values are shown with black ~~dots~~line, with ~~error bars~~shaded region representing uncertainties in aerosol extinction to aerosol surface area conversions and model

input parameters, as described in Sect. 2.3. The p-values for R in all panels are ~~<~~ less than $1x10^{-5}$. Note that the scale of the x-axis varies between panels so that the data can be seen more clearly.


a) OSIRIS Extinction Ratio at 0 °
Altitude (km)
25
20
15
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
3
2.5
2
1.5
1
0.5
0
Ratio
b) OSIRIS NO2 Percent Difference at 0 °
Altitude (km)
60
45
30
15
0
-15
-30
-45
-60
PD (%)
c) Model NO2 Percent Difference at 0 °
Altitude (km)
40
30
20
10
0
-10
-20
-30
-40
PD (%)

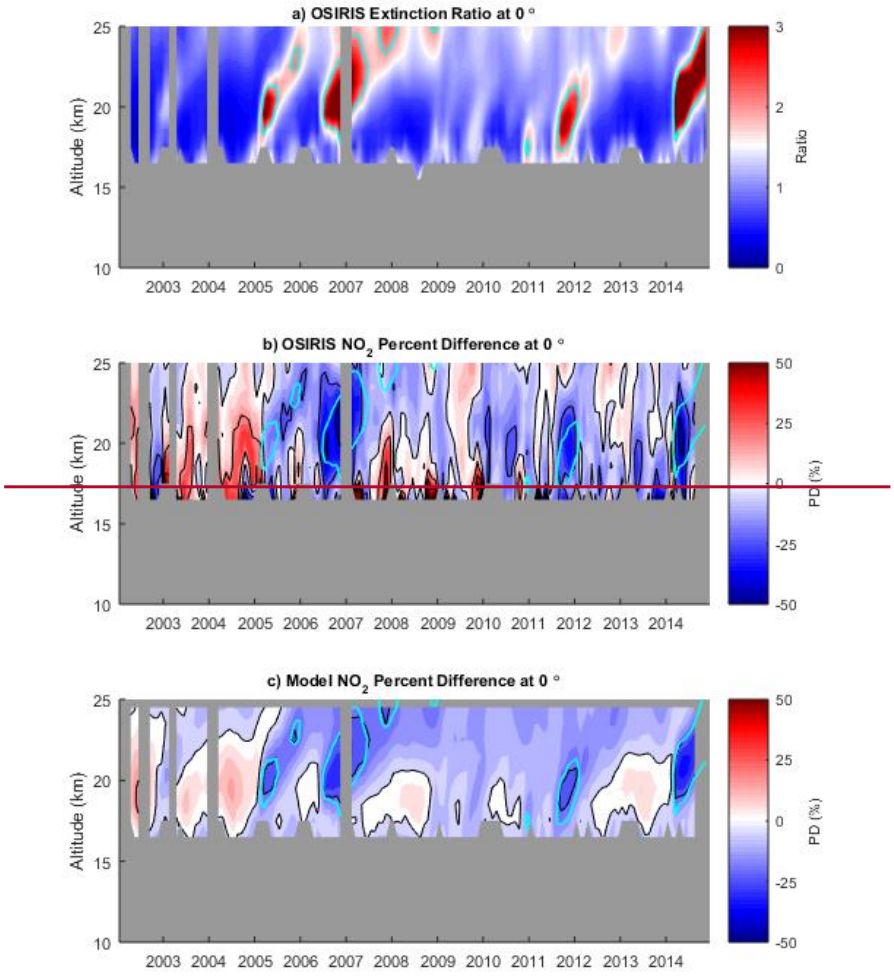
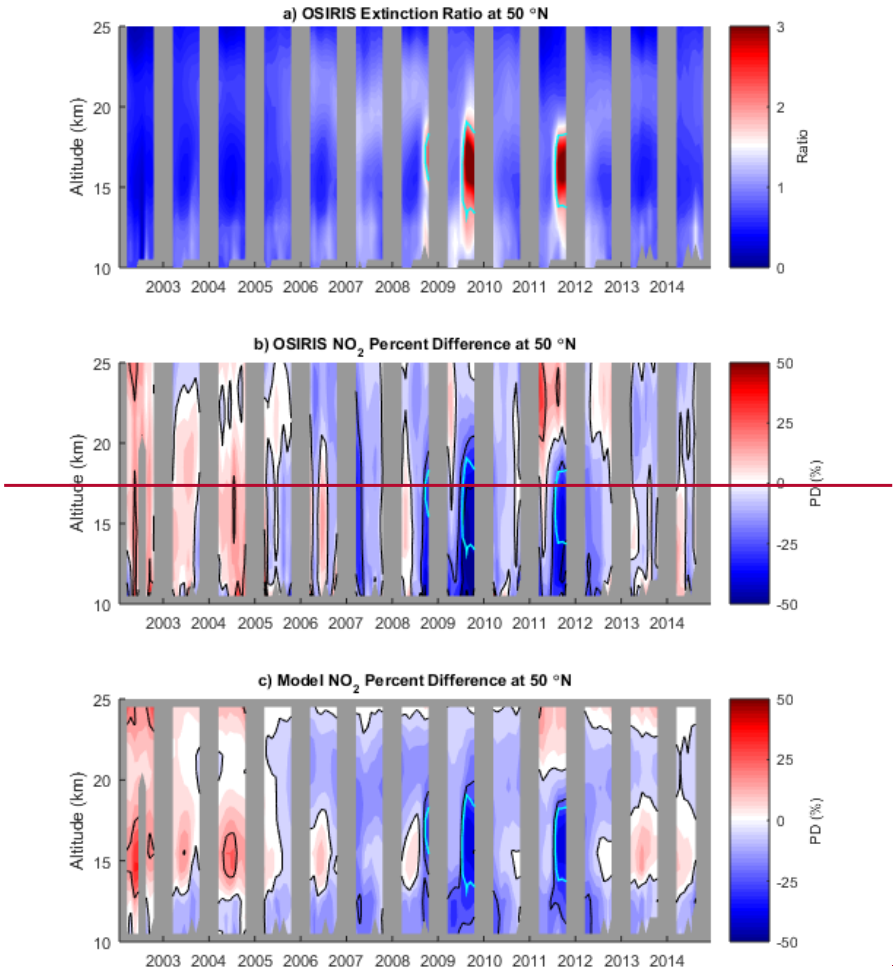


Figure 6. Profiles of aerosol extinction ratio and NO_2 percent difference at 0°. ~~Timeseries~~Time series of (a) OSIRIS extinction ratio, (b) OSIRIS percent difference NO_2 relative to baseline levels, and (c) modelled percent difference NO_2 relative to

baseline levels. Note that different colour-scale ranges are used for the OSIRIS and model percent differences. ~~The thin black contour lines indicate -40%, -20%, 0%, and +20%.~~ The ~~cyan~~ thick black contours are for extinction ratios = 2.


a) OSIRIS Extinction Ratio at 50 °N
Altitude (km)
25
20
15
10
2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014
3
2
1
0
Ratio
b) OSIRIS NO2 Percent Difference at 50 °N
Altitude (km)
25
20
15
10
2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014
50
25
0
-25
-50
PD (%)
c) Model NO2 Percent Difference at 50 °N
Altitude (km)
25
20
15
10
2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014
50
25
0
-25
-50
PD (%)

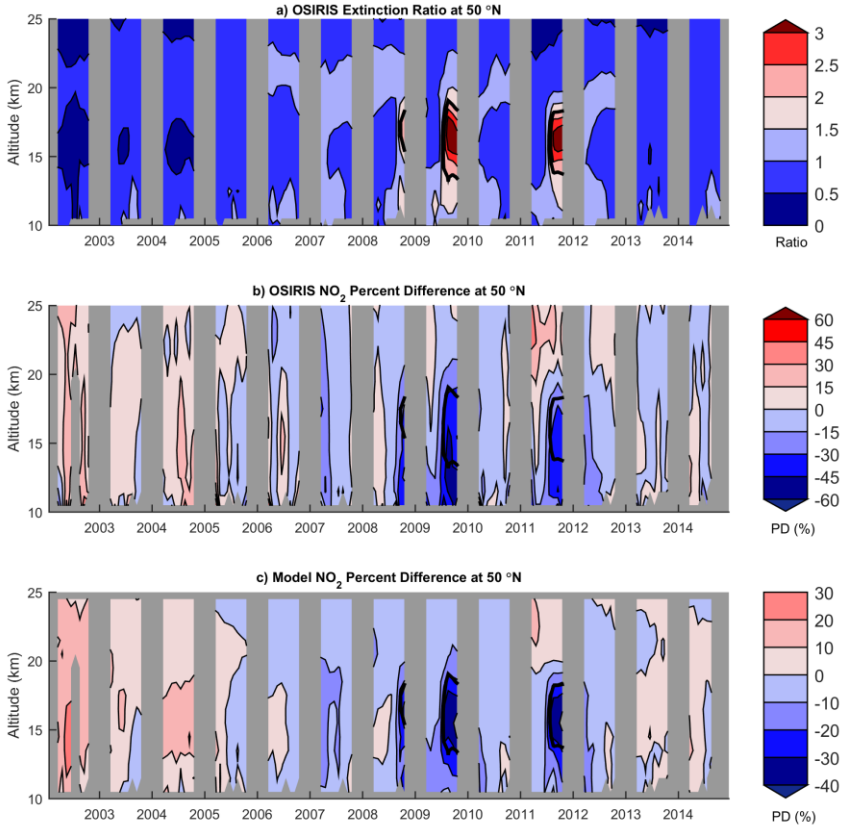
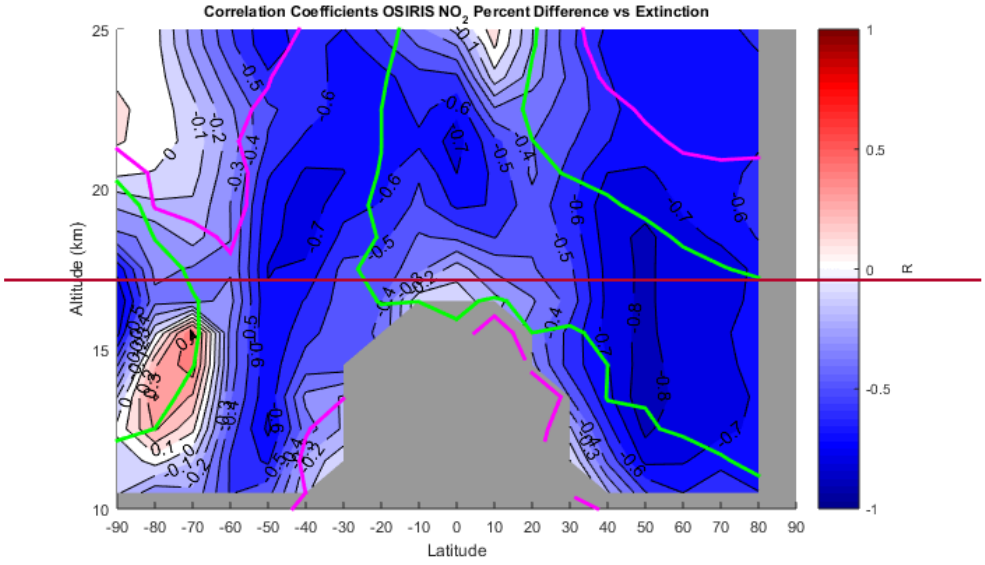


Figure 7. Profiles of aerosol extinction ratio and NO_2 percent difference at 50°N. ~~Timeseries~~Time series of (a) OSIRIS extinction ratio, (b) OSIRIS percent difference NO_2 relative to baseline levels, and (c) modelled percent difference NO_2 relative to baseline levels. Note that different colour-scale ranges are used for the OSIRIS and model percent differences. ~~The thin black contour lines indicate -40%, -20%, 0%, and +20%.~~ The ~~cyan~~ thick black contours are for extinction ratios = 2.


Correlation Coefficients OSIRIS NO2 Percent Difference vs Extinction
Altitude (km)
Latitude
R

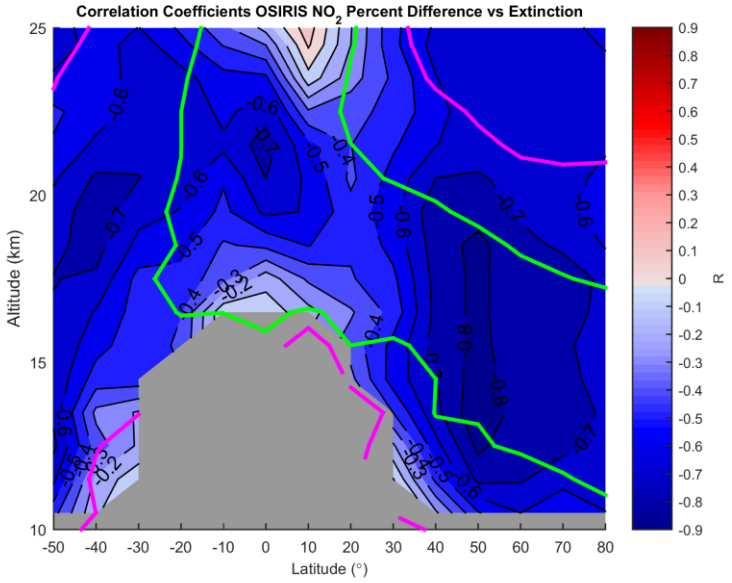


Figure 8. ~~R~~ Correlation coefficient for ~~timeseries~~time series of OSIRIS percent difference in NO_2 versus aerosol extinction for each latitude and altitude, the magenta and green contours are for latitudes and altitudes at which maximum extinction ratios over the ~~timeseries~~time series was 1.2 and 2, respectively.