Interactive comment on "Dynamically controlled ozone decline in the tropical mid-stratosphere observed by SCIAMACHY" *by* Evgenia Galytska et al.

Anonymous Referee #2

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We thank the Referee for the time spent on reading and reviewing this manuscript, as well as raising some important points. Below we address these points one by one. Our responses are highlighted in blue. We refer to the manuscript using, for instance, **P1 L12**, which means page 1, line 12.

The authors aimed to understand the negative ozone change seen in the middle tropical stratosphere, and in doing so made the link that increases in NO2 as a result of dynamical changes were causing the loss of ozone in the region of focus around 30-35 km. However, they were not able to link this to a statistically significant change in the age of air, which is also an interesting result. Nevertheless, the importance of understanding multiple chemical and dynamical drivers in the stratosphere is highlighted and the authors present interesting results and raise questions worth investigating further.
Although annual changes in AoA are statistically insignificant we discovered that seasonal changes in AoA are significant and result in specific physico-chemical mechanisms that control the O_3 amount and its changes in annual means. The N_2O, NO_2, and O_3 responses to the changing BDC and AoA are non-linear. We changed the text to point out this issue more strongly, i.e. on **P19 L19-33.**

However, my concern is that some of the points made, and hypotheses, are not well supported by what is presented, or the authors are not explicit and careful with how they present results (e.g. correlation coefficient, below).
I think this work is useful, and should be published, but changes are needed to make it explicitly clear what (i) can definitely be said from the observations, model and comparisons, (ii) what are the hypotheses the authors are putting forward, and (iii) what are the clear open questions that need to be addressed in future.
To address this comment, we rewrote the discussion of model-satellite comparison in Sect. 3.4. SCIAMACHY data, yielding statistically significant and insignificant gradients are both plotted in Fig. 12 (see our reply to Reviewer #1). The discussion of the possible reasons for the differences between the model and measurements has been rewritten (**P19 L5-11**). We also explained better our hypotheses of the non-linear relationship between AoA and $N_2O/NO_x/O_3$ (**P19 L19-33**). Concerning the issue (iii) mentioned by the Referee "what are the clear open questions that need to be addressed in future" we explicitly described in the last two paragraphs of the Summary (**P20 L20-P21 L5**), i.e. possible causes of the observed seasonal AoA variations.

Comments: 1. I am in agreement with the other referee that the non-significant, even opposite signal (and sign of trend) in February, though non-significant (in the supplement), is not addressed head on. Data is often messy and difficult to deal with especially when comparing with a model, and should be presented front and centre even if there is a contradiction or lack of evidence to contend with. This actually requires a deeper discussion, because if the model disagrees with the data in the sign of the trend (and it appears consistent between NO2 and O3 in February in the supplementary materials despite the non-significance) then that raises questions that need to be highlighted (for example, is it a model or an observational problem?). I won't labour on this point further, or repeat points raised by the other referee, as the other referee has spent quite some time on points related to this.

We agree with the Referee in his criticism and we replotted Fig.12. We included the SCIAMACHY measurements yielding insignificant gradients in Fig. 12c,d; we noted statistically significant at 2-sigma level changes as solid lines, and insignificant changes as dashed lines (see also our reply to Reviewer #1).

We also rewrote the explanations of the behaviour observed in Fig. 12:

- We mention that SCIAMACHY measurements do not show statistically significant changes for NO_2 and O_3 time series of Januaries and Februaries in **P19 L2-3**: 'SCIAMACHY measurements show statistically insignificant changes of NO_2 and O_3 during Januaries and Februaries (Fig. 12c,d, Supplements Fig. S4)'.
- We also mentioned that contrary to model simulations, SCIAMACHY measurements do not show a NO_2 decrease and an O_3 increase when analysing changes for any particular calendar month (**P19 L3-5)**: "Contrary to the TOMCAT simulations, SCIAMACHY measurements do not show a statistically significant NO_2 decrease and O_3 increase when analysing changes for any particular calendar month'.
- We also discuss possible reasons for the model-measurements differences (Fig. 12c,d) on **P19 L5-11**: 'From September to February, the gradient of O_3 time series increases, becoming more positive for both SCIAMACHY and TOMCAT data, resulting for February in small, statistically insignificant negative gradients for SCIAMACHY observations and small but statistically significant positive gradients for TOMCAT. Similarly for NO_2 mixing ratios, from September to February the gradients decrease i.e. they become more positive for both, SCIAMACHY and TOMCAT results. The SCIAMACHY data show larger errors on gradients of the time series for individual months, than those of the TOMCAT model. This results from the stronger oscillating structure in the SCIAMACHY time series. The reasons for the observed oscillations and their strength are not yet unambiguously identified and are under investigation'.

2. Page 4, L20-23: is this relationship specifically in the 30-35 km tropical region of the study (see comment 2 below).

The sentence on **P4 L20-23** could indeed be misleading the way it is. We removed the reference of Plummer et al. (2010) because he was dealing with tropical, but lower stratosphere. However, we leave the reference of Kracher et al. (2016), in the manuscript as we consider that this research addresses the impact of tropical upwelling on the N_2O lifetime. Also, to avoid the confusion with regard to their results, we rewrote **P4 L20-23** as follows: 'While accelerated tropical upwelling enhances transport of N_2O from its source towards the stratosphere, it reduces its lifetime (e.g. Kracher et al., 2016). The amount of NO_x is then affected by a shorter N_2O residence time causing its lower production via Reaction (R8a), and as a consequence less O_3 loss in the tropical mid-stratosphere'.

3. Page 4, L26: actually I would argue that the decrease Kyrola et al., 2013 found was up to 6-8% at its core (Fig. 16), which is more in line with that quoted for Gebhardt et al 2014. However, the core of the negative region in Gebhardt et al., 2014 is upward of -18% (Fig. 8). Fig. 16 of Kyrölä et al. (2013) shows the change of O_3 trends between the two periods. In our manuscript, we refer to O_3 change during the specific period 1997-2011 from Kyrölä et al., 2013, as it is the closest to our period 2004-2012. Consequently, we believe Fig. 15 from Kyrölä et al. (2013) is the most suitable. We improved the sentence on **P4 L26-28** as follows: 'Kyrölä et al. (2013, Fig.15) showed a statistically significant negative trend of O_3 of around 2-4% per decade in the tropical region (10° S-10° N) at altitudes 30-35 km for the period 1997-2011 from the combined Stratospheric Aerosol and Gas Experiment (SAGE) II-Global Ozone Monitoring by Occultation of Stars (GOMOS) dataset '.

Could the authors be clear in what they mean here since I believe the -10% refers to the 20S-20N (Fig 7) profile; since the authors focus in on +/-10 deg. latitude region, the higher value seems more appropriate but then the estimate in this manuscript is almost 2x smaller. We mixed up the 10°S-10°N defined as the tropical region in our study with the 20°S-20°N region used in other studies, e.g. Gebhardt et al. (2014). Since we provided the definition of tropics on **P3 L5-6** as 10°S-10°N, we modified the sentence on **P4 L26-31** as follows:
'Kyrölä et al. (2013, Fig.15) showed a statistically significant negative trend of O_3 of around 2-4% per decade in the tropical region (10° S-10° N) at altitudes 30-35 km for the period 1997-2011 from the combined Stratospheric Aerosol and Gas Experiment (SAGE) II-Global Ozone Monitoring by Occultation of Stars (GOMOS) dataset. Gebhardt et al. (2014, Fig.8) identified much stronger negative O_3 trend of up to 18% per decade in the same altitude and latitude range for the period August 2002-April 2012 from SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) observations'.

I assume, though perhaps the authors should check, this difference is due to a different time period and set of regressors used? At the very least please be explicit about what region the numbers represent and are comparable to the region focused on in this manuscript. To address this point, we now say on **P8 L22** that SCIAMACHY O_3 changes were 'reaching 12% per decade' rather than 'reaching around 10% per decade'. We would also like to highlight that Gebhardt et al. (2014) applied SCIAMACHY limb O_3 scientific dataset v2.9, which was suffering from a drift. In our research we use the O_3 scientific dataset v3.5 (as mentioned on **P6 L21**), which drift-corrected in contrast to v2.9.

4. Page 8, L4-9: I am not sure I agree that it is consistent to ignore the monthly autocorrelation when using all months. It seems to me consistent not to use it for single month (i.e. Jan only, etc) estimates (since there should be no autocorrelation between the months 12 months apart) and to indeed consider autocorrelation for the full time series since that is typically the case if they are next to each other in a continuous time series. This is only reasonable if you can state explicitly that there is no change in the significance - does considering it have an effect on your conclusions?
Autocorrelation of the noise affects errors of the trends but does not affect the value of the trends themselves. As the major focus of current manuscript is the seasonal changes of transport and chemical compounds, the use of autocorrelation of the noise is not needed. We do not apply it in our Multivariate Linear Regression applied to the annual averages. In Fig. 2 and Fig. 3a,d our focus is on the similarities of the observed patterns of the SCIAMACHY measurements and TOMCAT model in the tropical mid-stratosphere. Nedoluha et al. (2015) , who analysed tropical O_3 trends from HALOE and MLS, also did not apply an autocorrelation term.

5. Page 9, L14: the inference the authors make from Fig.3 is that chemistry has little impact on the 30-35 km tropical region; for O3 and N2O I think this is reasonable. But for 3d-f it seems that in the box, NO2 is roughly split 70/30 or maybe 50/50 in the peak positive change. So it isn't clear to me if this statement is fully backed up by the plot (or perhaps its a non-linear interaction?). Please could the authors comment on this, perhaps with values.
For the simulations used in the fixed dynamical (fDYN) case, N_2O (Fig. 3i) shows statistically significant but weak positive changes in the tropical mid-stratosphere. Consequently, an increase of NO_2 (Fig. 3f) is also expected due to Reaction (R8a), $N_2O + O(^1D)$. As a result, a small statistically significant NO_2 increase in the tropical mid-stratosphere (~3% per decade), caused by the chemical mechanism, does lead to a statistically significant O_3 decrease. However in the fSG TOMCAT simulation, NO_2 shows positive changes in the tropical mid-stratosphere (Fig. 3e) similar to TOMCAT CNTL simulation (Fig. 3d) and SCIAMACHY measurements (Fig. 2b). We infer that the major impact of the positive changes of NO_2 comes from the dynamics i.e. the slower transport of N_2O. We provided minor correction on **P10 L1** from '...around 1-3 % per decade' to '...around 3 % per decade'.

6. While Fig 4a. shows a combined non-linear shape, it appears that the anticorrelation (linear slope for each level) reduces with higher altitude, being almost flat at 35 km (green). Why does this happen? Does this indicate that the mechanism proposed is no longer operating as efficiently in the upper part of the box?
We indeed found the drop of anti-correlation between N_2O and NO_2 at the altitude of around 35 km. Although, N_2O and NO_2 on average highly anti-correlate in the tropical middle stratosphere (r=-0.9, Fig. 6). This anti-correlation becomes weaker at 35 km altitude in the tropics during May-July and November and anti-correlation varies from -0.52 to -0.57 (these results are not included in the manuscript). In particular, at altitudes above 35 km, produced NO (via Reaction R8a) reacts rapidly with N ($NO + N \rightarrow N_2 + O$) and therefore converts NO back to N2. Therefore the N_2O-NO_2 anti-correlation becomes weaker in the upper edge of our target altitude region and above.

7. Fig 6, 10, and all discussion related to the Rˆ2 statistic: this is very confusing and needs to be stated explicitly and correctly. Rˆ2 is formally the "coefficient of determination", which can be the square of, but not same as the "correlation coefficient". Further Rˆ2 can only range from 0 to 1, while the correlation coefficient can range from -1 to +1. Please check all instances of this and be correct in its usage; in many places this is confusing and leads the reader to have to try and work out what the authors mean.
We agree with the Referee that R^2 was misleading and we removed R^2 from the text of manuscript entirely and reformulated the sentence on **P12 L15-16** as follows: 'Recognising the tight relationships within the tropical mid-stratosphere N_2O-NO_x-O_3 chemistry, seen in Figs. 4 and 5, we further calculated Pearson correlation coefficients, between the chemical species as well as with the dynamical AoA tracer'.

8. Page 16, L5: 0.6 is an arbitrary threshold; please state this explicitly.
We improved the sentence as suggested on **P16 L4-5**: 'Horizontal dashed lines indicate an arbitrary threshold of moderate correlation, which is represented by the value of -0.6.'
We also corrected the caption of Fig. 10 accordingly.

9. Fig. 11: is this also integrated over 10S-10N?
Yes, to avoid any misunderstanding we rephrased the caption of Fig. 11 as follows:
'Annual cycle of monthly mean N_2O (ppbV, contours, 15 ppbV interval) and AoA (years, colours, 0.2 yr interval) as a function of altitude from TOMCAT run CNTL in the tropical region, averaged over the period January 2004–April 2012.'

10. Page 19, L4-5: Is this a hypothesis or a demonstrable fact? I do not understand why it is a limitation of the measurements, given the description earlier of the limb observations being well-distributed in the tropics and the period being considered is the same for the model data. If the effect is demonstrable, then this would provide good evidence the model is correct and why we don't have to worry about the insignificance and/or inverse correlations. If it is a hypothesis, please state explicitly this is the case.

We reworked the hypothesis of larger errors of SCIAMACHY gradients/linear changes on **P19 L8-11** as follows: 'The SCIAMACHY data show larger errors on gradients of the time series for individual months, than those of the TOMCAT model. This results from the stronger oscillating structure in the SCIAMACHY time series. The reasons for the observed oscillations and their strength are not yet unambiguously identified and are under investigation'.

11. Page 19, L16-22. I'm afraid I found this explanation difficult to follow. Please rewrite to be clearer. Is the summary that the N2O "changes do not cancel in the yearly average" because photolysis has an affect that AoA is not impacted by?

We reworked the explanation of N_2O-AoA non-linear relation on **P19 L19-33** as follows (see also reply to reviewer #1): 'The negative AoA gradients for the 2004-2012 period during the boreal winter months (January and February) and positive AoA gradients during the boreal autumn months (September and October) cancel, i.e. there is no statistically significant linear

change/gradient in the annual mean AoA (Fig. 8b). In contrast, the monthly gradients over the same periods for the chemical species N_2O, NO_2 and, as a result of the NO_x ozone catalytic destruction cycle, O_3 do not cancel in the annual means. This effect is primarily attributed to the non-linear relationship between AoA and N_2O. This is explained by the following: 1) AoA strongly depends on the speed of the BDC, with lower AoA values indicating an acceleration, and higher AoA indicating deceleration of the vertical transport. In the absence of significant photolytic loss of N_2O via the Reaction (R7), the changes in stratospheric N_2O would be controlled only by changes of the rate of the tropical upwelling of the BDC (or simply by AoA), i.e. faster upwelling would enhance transport of N_2O to the stratosphere, and vice versa. Without photolytic loss, the rate of change of N_2O concentration would be inversely proportional to the AoA change; 2) the dominant chemical loss mechanism of N_2O is through its photolysis. The amount of photolysed N_2O depends on the residence time of N_2O and this in turn depends on the transport speed, i.e. AoA. Longer residence times of N_2O result from a transport slow-down. Consequently, there is more time for photolytical destruction of N_2O; 3) as the amount of N_2O is controlled by both transport and photochemistry, its changes do not cancel in the annual average; 4) the amount of NO_2 and O_3 are chemically linked to that of N_2O. Overall, the changes of NO_2 and O_3 are dependent on both the amount of N_2O transported to the stratosphere and its residence time'.

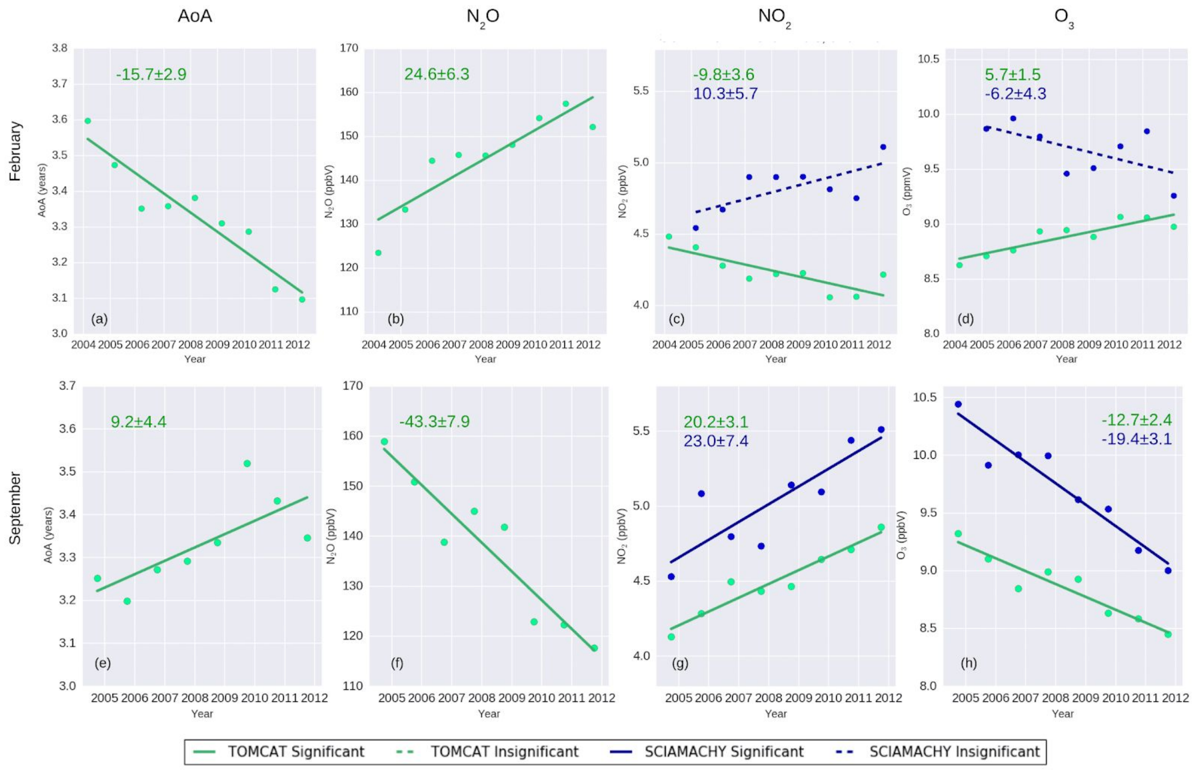

Figure 12. Linear changes of AoA, N_2O, NO_2, and O_3 minus QBO effect averaged over (a-d) Februaries 2004-2012 and (e-h) Septembers 2004-2011 in the tropical stratosphere between 30 and 35 km altitude. Colour coding indicates the data source: TOMCAT CNTL simulation (green), and SCIAMACHY measurements (dark blue). Colour-coded trend values and their errors (in % per decade) are shown in each panel. Solid lines indicate statistically significant linear changes at the 2σ level, dashed lines indicate statistically insignificant changes.