We thank the referee#2 for his/her review of our submitted manuscript and respond to the specific points raised.
Since performing the simulations presented in the ACPD manuscript, modeling errors were found in both the vertical distribution of lightning NO_x and the also in the declaration of coefficients used in the deposition parameterization. Examining the resulting differences introduced shows that increases in the chemical production term occur increasing the resident mixing ratios of CH_3ONO_2 by a few ppt at global scale, especially in the Northern Hemisphere and the tropical column. Therefore, the final version of the manuscript will use these improved simulations although the magnitude of differences is rather small.

1) To provide context to the entire study, I suggest the authors present an annually averaged, globally-integrated budget of CH_3ONO_2 early in the manuscript.

We agree with the referee on this point and now merge the old Section 5 into Section 3.

a. What is known about the day-to-day and regional variability of oceanic biogenic CH_3ONO_2 emissions? Do any of the cited papers provide an estimate of the uncertainty, the variability? b. The same questions with regards to deposition.

The cited literature states that there is a strong link between the presence of chlorophyll and alkyl nitrate concentrations in the seawater meaning that the biogenic source flux will be dependent on both seasonal temperature and nutrients available in the ocean. This will introduce a large degree of regional and seasonal variability. We already mention this in the text and make an analogy to the release of isoprene from the ocean, as well as propose future work to make a direct link between the chlorophyll distribution observed by satellites and monthly mean emission fluxes. There is a large uncertainty associated with quantifying such oceanic emissions due to the lack of comprehensive measurements at different longitudes in the tropics with which to constrain emission fluxes, leading Chuck et al. (2002) to conclude that a precise value of the uncertainty is difficult to quantify. It is also somewhat dependent on the different parameterizations used to calculate the degree of phase transfer out from the oceans surface. In that the ocean water is typically supersaturated with respect to alkyl nitrates (e.g. Dahl et al, 2005) means that emissions are likely to occur throughout the day, without a strong diurnal cycle. From their modeling study Neu et al. (2008) provide an uncertainty of between 0.2-0.6 Tg N/yr, or ~66% of their derived global flux for alkyl nitrates, based on the measurements of Blake et al (2003), although they neglect direct chemical production meaning their estimate could be rather high. Moreover, estimates provided by Chuck et al. (2002) are smaller by a factor of 3, showing the sensitivity of the uncertainty to the location at which measurements have been taken.

Concerning deposition, Russo et al (2010) found a minimum in CH_3ONO_2 in the early morning, where they found similarities between the diurnal variability of tropospheric O_3 and CH_3ONO_2 under stable nighttime conditions thus imply a similar value for the dry deposition term. Our deposition parameterization (Ganzeveld and Lelieveld, 1995) does account for different surface resistances from e.g. snow cover (c.f. Figure 2) therefore this seasonal variability over land is implicitly accounted for at a 3 hourly time resolution from the ECMWF ERA interim meteorological data fields used to drive TM5.

c. What is the global annual average concentration observed at all of the ground sites and what is simulated in each of the scenarios?

This is generally in the order of 2-10 ppt as shown in the horizontal means in Figure 1. To provide more information on the temporal variability in near-surface mixing ratios we will include a figure showing the annually averaged surface distribution of CH_3ONO_2 for a number of the simulations, along with the associated annual mean values at a selection of surface sites as requested by the referee.

2) In general, the organization of the experimental setup (the series of simulations), the paragraphs describing the observations, and figures are challenging to follow. More detailed comments are given in the minor comments below. Since the authors refer often to the sensitivity simulations, it would be helpful to reconsider the naming scheme (E.g., using names like EMISS, EMISSDD and DEMISS and EMISSPT to assess chemical production is confusing).

We agree to change the names of a few of the simulations, namely EMISSDD becomes DDEP and EMISSPT becomes FULL. We feel that BASE, EMISS, DEMISS and FLIGHT are self explanatory.

Also, maintain consistency within the figures, and clear figure headings (e.g., difference of EMISSPT and EMISS in Fig. 1 and difference of BASE and EMISSPT in Fig. 2).

We now changed Figure 3 to show the differences between the BASE and EMISSPT.

Is the BASE simulation necessary for this analysis?

Yes the BASE simulation is deemed necessary otherwise you cannot assess the impact of introducing CH_3ONO_2 emissions and chemical formation on the oxidative capacity in the modified CB05 chemical mechanism. The differences introduced allows a direct comparison with the findings presented in Neu et al. (2008).

3) To narrow the focus, I suggest removing analysis of the CARIBIC dataset. The NOy measurements have a stated uncertainty of 8%, alkyl nitrates only make up approximately 10% of NOy on average, and CH_3ONO_2 are only a small fraction of that.

Since it is important that the model is reasonable with regards to NOy, I suggest the authors include a sentence like "the model has been compared to NOY datasets, including measuremnts from the CARIBIC campaign and found to have reasonable agreement with: : :. ". I also suggest dropping discussion of higher order alkyl nitrates and associated figures and tables (Fig 3, Table 4, Fig 7).

We disagree on this point as this paper should also serve to validate the performance of TM5 with respect to both RONO2 and NO_y in the upper troposphere. The modified CB05 chemical mechanism has not been validated previously in terms of nitrogen reservoirs and we want this manuscript to partially fulfill this task. The CARIBIC data is novel in that it allows us to do this on seasonal time scales across a wide latitudinal range in the tropical upper troposphere. Given the time and expense associated with publishing this manuscript we feel that has to serve as a future reference concerning the performance of TM5 in terms of organic nitrates.

Also, I presume that the behavior of species XO2N is not widely known by the larger atmospheric chemistry community, and thus should be avoided (E.g., Table 4).

In order to close the global chemical budget associated with RONO2 we need to show all individual terms. The nature of the Carbon Bond Mechanism (CBM) means that some proxies are introduced, XO2N being one of them, in order for the scheme to capture data from smog-chamber measurements whilst providing a condensed mechanism that can be used in large-scale atmospheric models. This CBM approach is used in a number of regional chemistry-transport models and thus is somewhat familiar to the global modeling community.

4) For the observations used, please include a figure with three or four map panels that show the simulated annual-average CH_3ONO_2 with standard emissions and 1%, 0.3% and Flocke et al., 1998 branching ratios and some indication of surface measurements(i.e. colored scatter plots for average observed values).

See response above related to the additional Figure that will be included related to the surface distribution for the various sensitivity runs.

Furthermore, I would suspect that the CO signature of each source category would be quite different (and easy to show with the models), and could be used to better constrain the relative size of each source.

Due to the relatively long tropospheric lifetime of CO (1-2 months) for one to be able to truly attribute the history (location) of any air mass would require simulations containing individual tagging of CO from different emission sources such as biomass burning, which is a strong tropical emission source exhibiting large inter-annual variability. Although we agree there should be some anti-correlation with CO from direct oceanic emissions, using CO peaks to attribute the anthropogenic component would not necessarily provide a clear answer without differentiation between CO emission sources.

Consider including the HIPPO dataset in the analysis. After downloading the data and sorting, there are 1160 reported values for MeONO2. The measurements span the Central Pacific from approximately 80 degree S to 80 degree N and the full troposphere. The dataset could be useful for constraining the source of CH_3ONO_2 due to its latitudinal coverage. For example, in Figure 1, the authors show that the meridional gradient over the Central Pacific is very sensitive to MeONO2 formation rate (for 0.3% branching ratio, 0 -10 ppt at Equator and Antarctic, 10-20 ppt at S mid-latitudes and 30-40 ppt in the N mid-latitudes), a region covered by HIPPO.

We feel that the HIPPO dataset has rather similar coverage to the PEM-tropics B dataset which is already used in the manuscript. Moreover, we cannot find a validation or treatise of these measurements in the literature, as for the other measurements we have chosen to use. However, in the light of the referees concerns related to global coverage we now perform an additional comparison against data made as part of the POLMIP measurements campaign which was conducted in the year 2008 at Northern latitudes in and around the Arctic, and therefore is ideally suited to investigating the vertical distribution around this location.

5) Please discuss the large discrepancy between the observed and simulated vertical profile of CH_3ONO_2 in more detail (i.e. Fig 6). There appear to be a consistent increase of CH_3ONO_2 from 8 km to 10 km. The authors state that the discrepancy is instead due to transport (P20129, L29), which I find unlikely. It appears that the models that include chemical production of CH_3ONO_2 simulate a similar feature albeit at much smaller magnitude while emissions only sources have nothing like it.

Figure 1 shows the zonal mean differences in CH_3ONO_2 mixing ratios, where the highest mixing ratios occur in the free troposphere of the northern hemisphere, where most NO_x is emitted. Analysing the monthly mean distribution in the Free Troposphere for March shows that southerly transport of CH_3ONO_2 occurs away from the continents, explaining the simulated increases between 8-10km in e.g. EMISSPT. We add additional details in the text regarding this.

Do the authors know of any possible temperature or pressure dependent source? Do they know of any that have been hypothesized?

Apart from a discredited source related to PAN decomposition (pg 20115, ln 22-25), the only other chemical formation route not considered is the reaction of CH_3O with NO_2. However, Flocke et al (1998) estimate a very low formation efficiency of CH_3ONO_2 under ambient NO_2 mixing ratios, meaning it would only be an efficient source under relatively high NO_x conditions or in the lower stratosphere. In our model simulations the coarse horizontal resolution means that high NO_x emissions are somewhat diluted across a wider area, therefore the sequestration of NO_2 by CH_3O would be dampened if included in the model. Again any additional CH_3ONO_2 formed under such conditions would need to be subsequently transported towards the tropics.

The most efficient mechanism at global scale is the one that we introduce in our study.

We do now add the following text to the introduction: "The formation of CH_3ONO_2 from the sequestration of NO_2 by CH_3O is also a possible source, but not considered to be significant at global scale because of the high NO_2 mixing ratios which are necessary for the reaction to be significant (Flock et al, 1998)".

Is it possible that the CH_3O_2 + NO reaction rate has a strong temperature dependence?

This is already accounted for in the rate expression for CH_3O_2 + NO in TM5.

Abstract: Edit to fit with changes made to manuscript. Please give some estimate of the range of branching ratios that seem possible given the observed values

We now provide an estimate of the branching ratios based on the various simulations which have been conducted and explicitly state that the most probable branching ratio is <0.3%.

20113 - L6) What about CO?

We now include a mention of the OH + CO reaction.

20113 – L20) Awkward discussion of O_3-NO_2-NO steady-state. NO + O_3 is a fast in many locations, and slower at high NO_x (O_3 titrated to 0).

We now amend to: "Loss of NO may also occur via the titration of O_3, Reaction (R6), which moderates O_3 mixing ratios in high NO_x environments."

20114 – L 6) "long-lived nitrogen reservoirs" to oxidized nitrogen species or NO_y, PAN and some AN's are not long-lived.

Although this has now been changed as requested, we think that PAN can be rather long lived once lofted out of the boundary layer into a lower temperature regime and is important for the global redistribution of NO_x as shown by e.g. Moxim et al (1996) and Fischer et al. (2013).

20114 – L 11: Please use more standard terminology for alkyl nitrates (i.e. $RONO_2$).

We agree that this could introduce confusion and therefore rename lumped higher alkyl nitrates to $RONO_2$ throughout the manuscript.

20114 – L 14: Awkward conversation of radical chemistry. Maybe only discuss HO_x-NO_x chain terminating reactions in previous paragraph and drop this paragraph. HO_x-HO_x reactions dominate the global budget.

We now remove the paragraph discussing the bi-molecular reactions involving peroxy-radicals.

20114 – L 14: In this instance maybe should be “may be”; correct through out manuscript please. (**Corrected**)

20115 – L28: Possibly mention different methods typically used to measure ANs, differences between specific and sum ANs (i.e., TD-LIF)

We now add : “ … typically by analysing flask measurements, although in some instances techniques such as Gas Chromatography with electron capture (Roberts et al, 1998), Gas Chromatography/Mass Spectrometry (GC-MS) (e.g. Dahl et al, 2005) and thermal dissociation laser induced fluorescence (TD-LIF) (e.g. Farmer and Cohen, 2008) have been used directly at the measurement location.”

20116 – L13: Change “nitrogen reservoirs” to “reactive N” (**Corrected**)
20116 – L13: delete “direct” “additional” “without the need of long range transport” (**Corrected**)
20116 – L20-25: Do any of these studies provide estimates of the variability or uncertainty of these processes at a global scale. I.e., does that range justify the range of sensitivity simulations used in this work.

In that different regional sources are used in the literature to explain observations made at different measurement sites shows that there is a large degree of uncertainty as to the strength and location of individual sources. For our study we include the location of oceanic emission sources solely based on the various independent measurements made directly over the ocean on ships, rather than those made in the Free Troposphere by aircraft (i.e.) we impose no direct emission in the Southern Hemisphere. The range of emissions that have been used are based on adopting an initial estimate from a previous modeling study, along with an increased emission flux which improved the agreement of the simulated vertical distribution of CH_3ONO_2 in TM5 when compared against aircraft measurements use to derive the initial estimate of the oceanic emission flux. Both the chemical mechanism and oxidative capacity of TM5 determine the best correlation, allowing us to provide our own best estimate for the direct emissions. By accounting for the additional chemical source term we aim to provide an updated estimate compared to recent studies.

20118) Write out ODIN, UARS (**Corrected**)
20118 – L25: Add “Further updates to the model used in this study include” (**Corrected**)
20119 – L17: correct “described Williams” (**Corrected**)
20120 – L25-: Should this description be moved to section 2.1 Model description?

For clarity we remind the reader of what assumptions are made with respect to the oceanic emissions before discussing effects.

20121: Possibly shorten description of each measurement site and provide references for those interested in more detail

We think that providing some brief description of each measurement site used places it in context with respect to the proximity towards any potential oceanic source without the reader having to access additional papers to find these details themselves.

20122 – L17: Hourly not hly. (**Corrected**)
20123 – L18: use "simulated" instead of "shown" (**Corrected**)
20124 – L13: Yes CH_3ONO_2 has a higher solubility than higher ANs, but that does not mean it has a higher solubility than PAN, the value adopted. I would prefer to see some mention of the range of possible values for similar compounds to gauge the uncertainty in the deposition rate.

Examining the uptake co-efficients for aqueous solution across chemical species shows that indeed the solubility of CH_3ONO_2 is ~75% of PAN, meaning even our default value could be considered to be on the high side. However, Russo et al. (2010) imply a much larger deposition flux to explain their nighttime measurements, whereas most other papers associated with measurements do not discuss deposition terms at all but rather concentrate on source terms. Therefore the uncertainty based on this rather limited sample over one terrain type is ~200%. This shows that to fully understand the processes which determine the global distribution of CH_3ONO_2 requires more measurements at different (background) locations where the magnitude of the deposition fluxes are rather unknown. The sensitivity study we define uses a different of ~100% from the default, which we feel is representative of the current uncertainty.

20124 – L23-28: Awkward. consider revising.

We now re-write this section so as to introduce the global budgets for CH_3ONO_2 and thus modify the text accordingly.

20125 and throughout: consider using global average ppt as units instead of burden. Budget terms in Tg/ yr is good though.

We wish to keep the discussion related to the global impacts of CH_3ONO_2 framed in Tg N yr so that they can be directly compared to other emission sources of NO_x (i.e. N).

20126 – L19: add simulated to "shows the daily variability" I think Fig 4 would be improved by scaling the data or using a y-log scale. Also, it is also unclear to me whether this data shows any measurements. Please clearly distinguish measurements from simulated values.

The figure will be reworked to improve the visibility of the measurements points.

20128- L5: Check values with Table and earlier mention of same site (**Corrected**).

20129 – L14: Please discuss whether this variability is useful to differentiate oceanic and chemical sources, if not in the observations, than in a model.

Any variability observed in high frequency observations is not captured well in a global CTM due to both the vertical and horizontal resolution employed for computational efficiency, and that the time-step for calculating transport and chemistry typically varies between 15-30 minutes. Although we do interpolate to the vertical, latitudinal and longitudinal position of the aircraft, we still use values representative of a wide area (using a 3º x 2º horizontal resolution), which exhibit much less variability compared to what actually occurs. One further artifact with this analysis is that all longitudes are averaged into a single latitudinal point resulting in the 1-σ deviation being quite large, therefore not particularly useful for partitioning sources compared with using the various sensitivity studies..

20130 – L18: Please use consistent percent units for the branching ratio. Is this 0.0045%?

We now clarify this in the final version of the manuscript.

20131 – 20134: Much of this seems beyond the scope of this work and could be summarized in a sentence or two.

Please see our response concerning general model validation above.

Tables: (See major comments above) – The names of the model simulations confused me throughout, please consider changing. Also, location names in Table 1 would be useful.

Please see our response above regarding the choice of names for the various simulations. .

Table 5 Figures: In general, use different color scales for difference plots and include some header that describes what the plot is showing (e.g., Fig 1. ECH3ONO2-only and impact of PCH3ONO2)

We feel that referring to the acronyms defined in section 2 suffices otherwise it is difficult to link the discussion provided in the text directly with the figure. The figure legend describes what the plot is showing.

I found Figs 3, 7 and 8 to be beyond the scope of this paper. Also, Fig. 7 is where some of my confusion about ORGNTR occurred. Is ORGNTR all RONO2 or is it just C-1-5 compounds?

RONO2 represents C2-C4 organic nitrates making it directly comparable with the higher organic nitrates measured in the PEM-tropics campaign. We now clarify this in the text. Of course the C1 nitrate is explicitly included as CH3ONO2 in the study, as described in Section 2.

Fig 2- This figure may be unnecessary (the description of deposition in the text seems sufficient). But if you keep, please use units that are useful to compare with budget terms.

These are standard units used to define annually averaged deposition terms. The corresponding value in terms of Tg N/year is already given in Table 3. To improve the use of Figure 2 we also now show the location of the surface observations used in a later section such that the reader can use the variability with respect to location in a more defined way.

Fig 4: The observed values (short green lines?) are very difficult to see.

In response to referee #1 we now improve the clarity of the measurement lines and change the measurements into black lines.

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