Response to referee #2

We thank the referee for the positive review of our manuscript. Below we give detailed responses to the major comments and questions posed in the review.

GENERAL COMMENTS

The main general concern that I have relates to the fact that there is not sufficient discussion on why the photolysis rate simulations are actually different when applying MBA as compared to BA. There is a fairly thorough description of the MBA scheme, but even in this model description section (Section 2), the major differences of the two schemes are not clearly stated. Later, there is a quite thorough analysis of the chemical drivers of differences in the two TM5 model versions, but, before that, there is not much discussion on the physical drivers that may be making photolysis rates drastically different in some cases. There is no need for a very detailed analysis of each individual driver, but some more discussion (and perhaps evidence) could enhance the value of that section.

We have briefly now included more details regarding the main differences between the two schemes, thus:

One major advantage of the MBA over the BA is the removal of the parameterization used to account for the overhead optical depth by explicitly calculating both the absorption and scattering components introduced by gases, aerosols and clouds at each specific model level (Williams et al., 2006). For computational efficiency the BA typically requires the use of offline look-up tables containing pre-calculated scaling ratios (δ_i) (see below) using a standard atmosphere, that are subsequently indexed with respect to temperature, pressure and total optical depth. The explicit nature of the MBA increases the flexibility of the approach compared to the BA in terms of updating molecular absorption properties (σ-values; ϕ-values) and the addition of new J-values into CTMs. Other improvements pertain to instances of high SZA, where additional constraints and spectral band limits are applied when calculating the J-values (see below).

For brevity and to keep the paper focused on the application of the MBA we reference the paper of Williams et al. (2006) which contains an in-depth discussion regarding the development and error analysis associated with the MBA. Direct comparisons against the BA for an identical atmosphere are also shown for a variety of tropospheric J-values, where the error is shown to drop significantly for both J(O1D) and J(NO2) at solar zenith angles > 71°. By summarising sensitivity tests made with respect to the TOA solar spectrum and the findings from additional box modelling studies, which differentiates the effects introduced by changes in the absorption characteristics of photolytically active gases from those associated with differences in the flux of the incident radiation, we already include some discussion of what is the most likely causes of the decreases in the J(O1D) and JNO2 in the middle troposphere. (e.g. pg 2291, lines 2-8). The heavily parameterized nature of the BA (where the pre-calculated δ_i values are used for a standard atmosphere) means that comparing quantities like for like is not possible.

For example, the representation of clouds is being mentioned a few times as a potential source for differences, but rather speculatively, and without making the reader understand why the cloud treatment may have had such an effect and why the new treatment is better. I believe that a more focused discussion on such aspects could be rather illuminating, especially for the readership of GMD.

We have now performed some additional sensitivity simulations for clear-sky conditions and where the aerosol OD is set equal to zero in order to differentiate the influence of the different scattering components introduced. We include the following text to address this point:

For clouds the OD introduced by the Slingo (1989) parameterization is around 0.5-1, therefore perturbing J-values to a much greater extent than the aerosol OD simulated in the model. Performing a sensitivity study using a clear-sky atmosphere shows that both J values decrease (increase) in the boundary layer (free troposphere (FT)) by the order of ~10-30% (~2-20%) due to the presence of clouds, which agrees with previous findings in the literature (e.g. Tie et al, 2003; Voulgarakis et al, 2009b). This is due to increased scattering of light at the cloud top as a result of increased shortwave albedo (Twomey, 1977). The increase in r_{eff} *in the MBA will subsequently result in a higher albedo in the BA than the MBA for a given flux of incident radiation at the cloud-top.*

By applying a parameterization which allows the calculation of variable cloud droplet sizes we feel that we are improving on the BA which adopts a fixed cloud droplet size of 8uM.

SPECIFIC COMMENTS

ABSTRACT

Line 15: “which induced :” : Are we sure ozone changes are the main reason? I would expect that the changes in the photolysis of ozone are also important.

We modify the abstract to address this point.

Line 15: Does the negative sign refer to the changes in high northern latitudes in Fig. 4a? If yes, that is not so important, and thus the _ in here is a bit misleading.

Re-examining Figures 4 and S3 shows that in many instances larger differences of ±10% occur especially over land. The negative sign applies to large regions of the southern hemisphere (SH).

SECTION 1

Page 2281, Line 8: Why is longitude not mentioned?

Now added

Page 2281, Line 15: What about surface reflections (albedo)?

The effect is implicit in the dependence of the path length on the extent of single and multiple scattering from the surface and e.g. clouds.

Page 2282, Line 5: Sentence starting “J–values :” seems a bit out of place here.

We now add “In general, … “ at the beginning of the sentence.

Page 2282, Line 21: Liu et al. (2006) is probably the reference for which the authors intended, so it is correct here, but there is a different one listed in the References section (the 2009 paper). See the full 2006 citation at the end of this review.

Error now corrected.

Page 2282, Line 25: What about chemistry–climate models?

In the version presented here we do not account for photolysis below 202nm or account for the spherical effects (refraction) of the incident radiation at high solar zenith angles so as to optimize the code for use in large scale tropospheric models. The full version of the approach outlined in Williams et al (2006) has been developed for tropospheric-stratospheric chemistry transport and chemistry-climate models.

SECTION 2

Page 2283, Line 20–23: The sentence starting with "One" is not enough for the user to understand all the differences and advantages of MBA compared to BA. Since this is not clearly done in another part of the manuscript either, I would recommend that at this point there should be a small paragraph outlining the main differences/advantages of MBA as compared to BA (not in terms of results, but in terms of structure, principles, user–friendliness etc).

The paragraph has now been re-written to outline the main differences between the BA and MBA. Please see the response to the first point in the general comments.

Page 2284, Line 16: If I understand the method it correctly, it would be clearer if you add "single" before "pre–defined".

Done

Page 2285, Second half of the page: I understand that LWC is the only input to the photolysis calculations, when it comes to clouds. But it is not clear where this LWC comes from. Please specify.

The LWC values are calculated from the ECMWF ERA-interim meteorology used to drive the CTM. We now clarify this point.

Page 2286, Paragraph starting at Line 11: So, for let's say, the free troposphere of a fully oceanic region, there will be a single optical depth value used everywhere?

In the free troposphere a homogeneous aerosol type is use globally. Inhomogeneities are introduced into to total optical depth by the variable cloud component.

Page 2286, Line 17: So, only isotropic scattering is being considered? Please clarify.

We now clarify this point.

Page 2286, Lines 20: Look–up tables of what? Please clarify.

We now add " … for the additional scattering component".

Page 2287, Lines 3 and 5: Please add "," after "For this" and "For the BA".
Page 2287, Lines 23–24: The albedo values used in the equation do not seem fully consistent with the surface types.

Now corrected.

Page 2289, Lines 1–15: Are these stratospheric ozone values used for the radiative transfer and photolysis calculations as well?

The photolysis rates calculated below the tropopause are dependent on the vertical distribution of the stratospheric ozone column, where the OD is both temperature and pressure dependant.

Page 2289, Lines 18–20: What does "either: : :or" mean in this case? When are GEIA and when are ORCHIDEE emissions used? Please clarify.

We only use the GEIA estimates for the ocean emissions. All land-based emissions originate from the ORCHIDEE climatology. This is now clarified in the text.

SECTION 3
Page 2290, Line 5: Please add "(BA and MBA)" after "approaches".
Page 2290, Line 7: Please add "," after "effects".

Page 2290, Line 10: It would be better to rephrase to ": : :namely the photolysis of ozone to produce excited oxygen (O1D) atoms J(O1D): : :" and change JO3 to J(O1D) throughout the manuscript, in order to be more specific/accurate.

Done

Page 2291, Lines 7–9: (Please also see my general comment) How do we know that clouds and aerosols are responsible? This needs some more discussion and convincing evidence. To strengthen this argument (although this may not be enough), the authors could also cite past studies, which have demonstrated that clouds and aerosols can drive large changes in photolysis rates in large spatial scales (e.g. zonal mean).

Both the BA and MBA include the effects of scattering and absorption from cloud and aerosol during the calculation of the height resolved actinic flux values. It is not our intention to expand the article to include a detailed analysis of cloud and aerosol effects on tropospheric J values as (i) GMD deals specifically with model development rather than scientific studies and (ii) the focus of the paper is predominantly concerned with the application of the MBA in a large-scale CTM rather than the individual components of the system which we feel is not of interest to the reader. However, we do now include some further details in the text regarding the quantification of effects in order to satisfy the referee's requests.
For aerosols the BA includes the aerosol OD implicitly in the actinic flux values stored in the offline look-up table. Therefore it is difficult to quantify the extent to which the aerosol OD has changed between approaches, although the total AOD is 0.38 at 320nm. We have performed an additional sensitivity study where the aerosol OD in the MBA simulation is set to zero in order to quantify the effect more robustly in both the boundary layer and the free troposphere. We find that the effects are rather small for aerosols due to the low aerosol OD of 0.01 at 320nm calculated with the Shettle and Fenn (1979) approach.
For clouds both approaches use the ECMWF cloud fraction and LWP for calculating effects (although the BA uses maximum overlap whilst the MBA uses random overlap). In that the cloud droplet size is now modified away from the fixed size of 8uM will reduce the amount of attenuated radiation above any typical cloud layer (see text). Tests using a clear sky set-up indicate that clouds decrease (increase) J values in the boundary layer by the order of ~10-20% (~2-20%) depending on the extent of the cloud coverage taken from the ECMWF meteorology.

Page 2291, Lines 25–29: This sentence needs rephrasing.
Page 2292, Line 17: Please add "," after "surface".

This sentence has now been re-structured.

Page 2292, Line 23: What is AFGL? Please explain.

We now define the acronym.

Page 2292, Line 25: Please change "For the tropics" to "For the region lying in the tropics".
Page 2293, Line 12: Please change "Finally" to "Also".
Page 2293, Line 13: Please add "," after "OH".

Done

Page 2293, Up to line 22: It would be nice to actually see some of these photolysis rate comparisons with measurements here, and also the improvements (?) seen when using MBA instead of BA. The discussion about these feels a bit too brief, taking into account how crucial the accurate representation of photolysis is in such a study, and also what the readership of this journal would expect.

Comparisons against direct measurements made on specific days are heavily constrained by the scarcity of suitable data for our chosen evaluation year of 2006. We have chosen this simulation year so that our manuscript can be compared directly to the benchmark paper of TM5 published last year (Huijnen et al (2010)). We have looked through the literature an found that empirical relationships of both J(O1D) and J(NO2) have been derived in the past (e.g. Harvey et al, 1977; Dickerson et al, 1982). One drawback of such empirical relationships is that the rate constants used to deconvolute the values of J(O1D) and J(NO2) from chemical actinometry studies have also been revised in the latest recommendations meaning that the empirical relationships do not necessarily hold when using present day recommendations. However, we have added a multi-year comparison of the resident concentration of OH vs JO1D against measurements made at the Meteorological Observatory Hohenpeissenberg (Rohrer and Berresheim (2006)) as an additional figure and supply associated text.

SECTION 4

Page 2294, Line 14: Please change sentence starting with "The corresponding reductions in surface NOx show that increases in surface O3: : :" to "The corresponding reductions in surface NOx and the increases in O3 loss via photolysis imply that increases in surface O3: :"

Done

Page 2295, Lines 7–12: STE is actually too small, compared to past multi–model intercomparisons (e.g. Stevenson et al. (2006)). Please state this clearly. Is this feature of ERA–interim an improvement compared to the operational analyses or not?
Also, net chemistry (Prod.–Loss) is too small. But it is worth commenting on the fact that MBA changes both Prod. and Loss towards the right direction (based on Stevenson et al., 2006).

The value of STE for TM5-chem-v3.0 is ~52% lower than that given for the TM5 version in Stevenson et al. (2006) due to the nudging height in the stratosphere being reduced (Huijnen et al. 2010). The use of the ERA-interim re-analysis meteorology results in a further reduction in STE of ~10%, where tracer transport from the stratosphere into the troposphere has been shown to be more realistic using the ERA-interim reanalysis by Monge-Sanz et al. (2009). From this we assume that using the ERA-interim reanalysis in our simulations provides a more realistic description of STE, although the value is on the low side. The MBA causes an additional reduction of ~9% due to the introduction of JO2 increasing O_3 in the UT. Additional text has been added containing these details.

Page 2295, Line 12: Maybe "recycling of NOx" is what you meant to write?

Now corrected

Page 2295, Lines 25–28: Less titration or more efficient production, as mentioned earlier?

When analysing the chemical budget terms for the lower troposphere the enhanced NO_x recycling does amplify the chemical production term for O_3 to a great extent than the chemical loss term, resulting in a net gain in the concentrations of surface O_3 shown in the supplementary material. However, both the redistribution of NO_x into the free troposphere and the repartitioning into more stable reservoirs does mitigate this increase to a certain extent. We now clarify this in the text.

Page 2296, Line 19: "especially during DJF": I would also say during spring.

Now changed to "winter and spring".

Page 2296, Lines 22: Please make "over estimate" one word.
Page 2296, Lines 24: S3 is for the albedos. Please change.

Done

Page 2297, Lines 8: Also, please mention reduced photolysis rates as a potential reason for higher HNO_3.

We now include a statement on the lifetime of HNO_3 in the free troposphere being increased due to the lower photolysis rate.

Page 2297, Lines 7–10: I would say that a possible explanation is that reduced photolysis of NO2 in the free troposphere in MBA leads to more NO_x, which then translates to more HNO3. Please comment and change text if needed.

OH also exhibits simultaneous increases (see Fig. 4) which enhances in-situ HNO_3 formation in the free troposphere. Analysis of the chemical budget terms show that the increase in the net regeneration of NO_2 from the photolysis of HNO_3 is much smaller than the increase in the OH + NO_2 term, therefore we remove the statement regarding the influence of enhanced HNO_3 on NO_2.

Page 2297, Lines 10–13: Do we understand why PAN is reduced in MBA?

This is due to the enhanced production of HNO_3 depleting the NO_2 available to form PAN in the boundary layer i.e. there is a repartitioning of reactive nitrogen between reservoirs.

Page 2297, Line 27: Please make the sentence end like ": with a negative bias in most of the cases.", as the bias is not seen for all the months/locations.

Done

Page 2299, Lines 15–17: Yes, but chemical production and loss change by roughly the same amount, in relative terms, while production is larger in absolute terms, so how can it be that the burden is increasing? Please comment.

This section refers to the chemical budget terms for formaldehyde as given in Table 4. As noted by Referee #1 there was an error in the chemical production term which has now been corrected. The change in the tropospheric burden is negative (c.f. Fig 8) therefore we do not understand the referees point.

Page 2300, Line 4: Please change "anthropogenic emission" to "anthropogenic CH2O emission source".
Page 2300, Line 6: Please add "almost" before "inverted".
Page 2300, Line 8: Please add "to" after "difficult".

Done

SECTION 6
Page 2301, Lines 16–20: Some possible drivers of the changes seen when moving from BA to MBA are mentioned here, but it would be nice to know which of them may have played the most crucial role. This relates to the general comment made at the beginning. Also, this list of differences could be mentioned clearly at the beginning of the model description (see comment on Page 2283, Line 20–23).

We have modified the details given in the model description to highlight the differences between the BA and MBA as previously requested by the referee. Again, the pre-calculation of the scaling ratios in the BA means that unfortunately a directly comparison of F_{act} values is not feasible in this study. It is expected that the use of one type of standard atmosphere profile during the calculation of the scaling ratios used to produce the look-up table for the BA will also impose a large effect on the scaling ratios, although this cannot be explored further due to implicit nature of the way the BA has been implemented. Therefore we have to use the sensitivity studies to give us some indication as to the magnitude of effects introduced into the MBA by the different changes. Therefore we do not list the changes in order of importance in the summary.

Page 2301, Last paragraph: Are there any plans to add more photolysis reactions in the mechanism? If yes, which?

The modified CBM4 scheme is rather fixed but we have tested a hybrid version which explicitly declares the C1-C3 organic components rather than lumping them in the CBM components for higher hydrocarbons. This new photolysis scheme allows us to include complex photolysis rates such as that of acetone much more easily.

TABLES/FIGURES

Table 2: Not sure what "MBA/BA" ratio mean. If it is a ration how can it often be negative (assuming these quantities do not change sign)?

This error is now corrected. It should have been percentage differences rather than a ratio.

It would be helpful to have the loss term below the production one, for immediate comparison. Same for Tables 3 and 4.

This is now moved as suggested by the reviewer.

Table 5: It would be very useful to add a line with mean (mass weighted) OH concentrations and their changes.

We choose not to adopt this point as a tropospheric average for OH is not so informative considering that the mass changes presented in Table 6 are the result of differences in regional oxidation budgets.

Table 6: I cannot see any blue color.

This aspect of the Table has now been removed.

Figure 3: Please add a legend instead of the lines in the parentheses in the caption.

The type of grid cell for which the comparisons of the monthly mean J-values are made are now given in the figure rather than the caption.

Figures 4a, b: The blue color in the stratosphere for ozone is misleading. Also, the units are not clear. Finally, 0.0 and 0.1 appear twice on the colorbar.

We now redefine the color bar and correct the format of the legend to amend these points.

Figures 7 and 8: Please use consistent colors with Figures 5 and 6. Also, please add legend. I would also say that the fonts used in the x/y titles and panel titles is much better in 7 and 8 than in most of the previous figures. Please increase font size wherever it looks too small.

There is a trade-off between covering a wide range of values such as in Figure 4 and the font size due to merging of the values on the color bar. We do try and increase the font size wherever possible.

References

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