Atmos. Chem. Phys. Discuss., 11, C11653–C11659, 2011
www.atmos-chem-phys-discuss.net/11/C11653/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of the isoprene photochemical cascade on tropical ozone" *by* F. Paulot et al.

Anonymous Referee #2

Received and published: 9 November 2011

"The impact of the isoprene photochemical cascade on tropical ozone" by Paulot et al. thoroughly explores the sensitivity of tropical ozone to various changes in the isoprene oxidation mechanism. It uses both forward sensitivity experiments and adjoint sensitivity experiments to examine these sensitivities. Besides including a thorough sensitivity study the paper does a few additional things very nicely: it gives convincing physical explanations for the results, it includes some thoughts on projected results with forecast increases in tropical NOx emissions and it includes a section on how experimental observations can help reduce the uncertainty.

In summary I think this paper is very solid with interesting results. However, I think there are a number of important items that need to be addressed before publication.

(i) The paper includes no comparison with observed measurements. The paper uses

a rather coarse version of GEOS-chem (4 x 5) in the base simulation and changes a number of reactions in this version of GEOS-chem. For the results in the paper to be valid the authors need to show the reference simulation compares reasonable well with measurements. For example Figure 1 shows the tropospheric column from satellite- the authors could easily show the model comparison here. Can one tell if the reference simulation gives a better representation of relevant HOx measurements vis-à-vis the standard GEOS-chem version?

(ii) The reader really gets little sense of the magnitude of the changes in tropical ozone to changes in the reaction mechanism. Are the actual changes large or small? This could be easily remedied by showing a "high and low" impact on tropical ozone from the sensitivity tests. Also, it would be interesting if the authors could give the overall sensitivity of tropical ozone to the reaction of OH and CH4 versus that to changes in isoprene yield and isoprene nitrate recycling (e.g., integrate local changes in Figure 5 zonally and give the average sensitivity). Figure S5 gives a hint of this but the units are not particularly helpful.

(iii) The paper presents a complex subject – however I found it somewhat difficult to read. Below I include a number of suggestions of how the authors could help out the reviews to make the paper more readable. Other suggestions are given in the minor comments.

1) The readability of the paper would be improved by providing more of a road-map of what the paper is about and where it is going.

- P25607, l 21-24. At the outset another sentence of two about how the paper goes about diagnosing the isoprene chemical cascade would be helpful (e.g., if the authors would say something about diagnosing the impact of isoprene nitrates as simulated in a chemistry-transport model).

- I think it would be much clearer if the oxidation mechanism given in the supplement is moved to the text. It is very difficult to understand the paper without referring to this

supplementary table. The discussion in the introduction would also be much clear and more concrete if it referred to the reaction mechanism used. Thus I would recommend that the reactions and discussion given in the introduction be consistent with the set of reactions given in the supplement.

- The clarity could be improved by providing a road map at the end of the introduction as to what the various sections in the paper discuss.

Minor comments:

(i) Please define NOx and Ox in the abstract.

(ii) The set of reactions given in the supplement refer to the reactions that differ from the standard GEOS-chem mechanism. What is the standard GEOS-chem mechanism? Please give an explicit reference to this mechanism or preferably publish the relevant parts of this mechanism in the paper.

(iii) Footnotes in the supplementary table of reactions have not been completed. Also please reference where the rates come from.

Page 25608.

(iv) line 8 – Nitric acid is not always a terminal sink. It would be more accurate to qualify this sentence somewhat, e.g.:"Unlike nitric acid, usually a terminal sink for NOx in the tropical boundary layer". . .

Page 25609.

(v) A little more explanation is required as to what x and y are in equation (7) and the range of values. It looks like they are given specific values in the reactions in the supplement. Please explain the relation between this equation as given in text and that given in the reaction table in the supplement.

Page 25610,

(vi) The yield "Y" is not adequately defined in the text. Its definition is much clearer referring to the mechanism in the supplement. This is another reason for moving the supplementary reaction table in the main text.

Page 25611

(vii) l 8 : knows-known

(viii) l 10: Should read "the RO2 and HO2 reaction"

(ix) l 15 Instead of isoprene do you mean isopo2?

Beginning Page 25612.

(x) The model description is given (page 25612) before we even know what the model and its adjoint are used for. A brief description of the overall simulation plan would be helpful here.

(xi) In my opinion the emphasis in the text on describing the GEOS-chem model and the adjoint model should change. This reference to GEOS-chem is rather old (10 years). Does Bey et al. give a complete description of the version used in this study? If not give a summary of the changes. In particular convective and boundary schemes utilized may have large impacts on this study. Additional information that should be included is: what is the convective scheme used, the boundary layer scheme used, the scheme for lightning NOx parameterization? What are the global lightning NOx emissions? On the otherhand, in my opinion the adjoint sensitivity is described in too much detail. I don't think anything is particularly new in the description given here. I would suggest skipping the details. If someone already understands the mathematics the adjoint the description here will not be very informative. On the otherhand for someone not versed in the adjoint this section is not sufficiently detailed to be helpful. It seems important to emphasize the parameters you are taking the sensitivity to, the units of the sensitivity and the fact it is a linear sensitivity. I think the details of the adjoint equations should be skipped (or put in the supplement).

(vi) The rather coarse horizontal resolution may have an important impact on the results. The NOx and Isoprene emissions are not properly segregated. The authors should comment on this. What will be the projected impact of the rather coarse resolution on the results?

Page 25616

(vii) line 8: allows → "allows us"

(viii) line 13: how is the recycling set? Presumably through alpha. Please be explicit.

Page 25612, (ix) l 2: Figure 5 does not give the isoprene emissions.

(x) l 10 : on a carbon basis is not necessary here. On any basis.

Page 25614,

(xi) What are the global lightning emissions?

Page 25616,

(xii) line 18: It would help if you would give a rough estimate in the text about how much is oxidized outside the boundary layer?

Page 25617

(xiii) line 5: what is HPALD?

(xiv) Sensitivity simulations: Please explain (or recap) why these are the critical sensitivity simulations to explore.

(xv) Figure 2 – The dry-dep and wet-dep colors are hard to distinguish here. Also, it would be much more convenient if you put the abbreviations for locations in the figure captions.

(xvi) lines 24-28. I don't think alpha has been explained at this point and Y is barely mentioned. You might want to repeat definitions of these parameters or emphasize to

a greater extent in the preceding text. Again reference to a reaction mechanism within the text would be very useful.

Page 25618,

(xvii) line 16 and beyond. This discussion would be more concrete if appropriate reactions in supplementary table are explicitly referred to.

Page 25622,

(xviii) line 9: it would help here and perhaps in other strategic locations to remind readers of the notation: e.g., to explicitly state "the sensitivity of tropical ozone to African variations in Y is. . .." – this would make the text less difficult read. (xix) line 10: Could you give more explicitly how the adjoint sensitivity is related to variations in Ding. Are you saying that the seasonal and regional variations in each follow the same pattern?

(xx) Beginning line 11: Can you relate the overall average sensitivity of Y in comparison to that of methane oxidation? It would be informative if the authors gave a quantitative comparison of the two sensitivities averaged over the entire tropics (this also relates to point (ii) in the main points: what is the relative importance of the questions addressed in this paper?).

(xxi) Line 12: The notation here without a subscript to the left of S is initially confusing. While it becomes obvious eventually, it would be easier on the reader if the authors could clarify at the outset.

(xxii) Line 16. But OH is presumably not small throughout the column. Please comment.

Page 25624

(xxiii) line 19, Please remind readers of the timing of the biomass burning season over this part of Africa.

(xxiv) line 20: It is not clear how Figure 7 shows Ox is very low in the boundary layer

over South America.

(xxv) Line 21: “this competition”. Please remind the reader what competition “this” refers to.

(xxvi) Overall comment: What is the role of the reaction of isoprene and ozone?

Comment on Figures

(xxvii) Figure 5. I believe the sensitivity is not to methane but to methane oxidation

(xxviii) Why do you use $\sim$1%? It should be .028% shouldn't it?

(xxix) What is small s in Figure 8? I thought small s referred to a region.

(xxx) I find Figure 9 confusing. This figure seems to sum up a lot of the discussion in the paper. However, it is passed over with barely a mention in the text and not well described in the figure caption. Can you describe in more detail?

(xxxi) Figure 10 is also barely mentioned in the text and the notation in the figure caption is confusing. What is (H-NOx)? Please spend some more time explaining this figure or leave out of the text.

(xxxii) Figure S5: This seems potentially like a good figure to show in the paper (not in the supplement), although I don't quite understand exactly what the normalized standard deviation refers to here. Do you mean spatially? Might I suggest showing the absolute changes in the ozone column in response to major point 2 above.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25605, 2011.