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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isoprene emissions in Africa inferred from OMI observations of formaldehyde columns" *by* E. A. Marais et al.

E. A. Marais et al.

emarais@fas.harvard.edu

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Specific comments.

1) As is acknowledged by the authors in the conclusion, one of the biggest impediments to retrieving isoprene emissions from satellite HCHO columns is the current problems in understanding the oxidation of isoprene under low-[NOx]. An attempt to address this issue in this work is made by using both the standard MCM isoprene oxidation scheme, and a modified scheme by Paulot et al. (2009) which produces more OH during isoprene oxidation. The more radical (with respect to OH) scheme of Peeters et al. is discounted based on recent experimental results. However, I would suggest that this consideration of a single possible modification of the isoprene oxidation scheme is overly optimistic, and barely scratches the surface of this complex parameter space.

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Recent studies (Stone et al., 2011; Archibald et al., 2010) have shown that the amount of additional OH produced by the Paulot et al. scheme is nowhere near enough to explain the field measurements of OH. Thus, whilst it may represent a step forward, this scheme alone is clearly not the answer to the problems in understanding isoprene oxidation. In Fig. 4, Marais et al. show the potential modification to the amount and timescale of HCHO yields due to the use of the Paulot et al. scheme relative to the standard one. The modifications at low and very low [NOx] shown in Fig. 4 are substantial, and perhaps indicative of the magnitude of changes that may be induced by modifying the isoprene oxidation scheme. However, there is no reason to believe that further future revelations regarding isoprene oxidation will not result in larger differences in HCHO yields compared to the standard scheme at low-mid [NOx] than the Paulot et al. scheme does. Given the current unknowns I think the authors have made an reasonable effort to address this problem. However, I would contend that the statements made on pg. 7495, line 23 and pg. 7499, line 2 that the errors from smearing are larger than those from the chemical scheme cannot be justified given the current poor understanding of isoprene oxidation. I suggest that the authors note this, and mention that true isoprene oxidation may differ significantly from both of the schemes used here.

Response (1): We now include in Figure 4 (attached and labeled "Figure 1") the time-dependent yields of HCHO (in green) that result from a mechanism that includes generation of 3OH molecules as a result of oxidation of isoprene hydroperoxides as proposed by Lelieveld et al. (2008). The low sensitivity of HCHO yields to changes in OH concentration is discussed in Section 3.2.

2) Following on from the previous point, on pg. 7491, line 26 it is suggested that the negligible smearing of HCHO (at high wind speeds) in the AMMA observations may be a result of the relatively high [NOx] conditions, whilst the much larger smearing across Central Africa (at low wind speeds) is due to more moderate [NOx] levels. However the reported NOx mixing ratios are similar (360 pptv NOx for AMMA and âĹij400 pptv

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NO2 for Central Africa). Thus based on Fig. 8, I would disagree that the AMMA observations are close to the threshold between high and low [NOx] conditions (which appears to occur at âĹij1 ppbv), as stated on pg. 7494, line 25, and instead suggest that the NOx regimes in AMMA and Central Africa are similar (as also suggested in Fig. 6), and these differences in smearing are evidence of our poor understanding of isoprene oxidation chemistry (based on both satellite and MEGAN estimates of isoprene emissions in Fig. 9, the AMMA and Central Africa transects both show substantially different isoprene emissions, and therefore likely the influence of isoprene on the overall atmospheric chemistry of the two regions differs). I think the text should be changed to reflect this.

Response (2): A new Figure inserted between Figures 5 and 6 (attached and labeled Figure 2), as suggested by referee #1 (comment #1), shows the percentage contribution of RO2+NO reaction to overall loss of RO2 in Africa for July 2006 in GEOS-Chem. In central Africa the low-NOx reaction pathway dominates as isoprene emissions are very high leading to a high isoprene:NOx ratio. Conversely, in AMMA isoprene emissions are low and so the isoprene:NOx ratio is low. We elaborate on this on page 7492 line 4 for AMMA and page 7492 line 25 for central Africa.

3) Potentially how substantial is the isoprene emission from the excluded grid squares? Perhaps a first assessment could be done by summing up the bottom-up emissions from MEGAN for these grid squares?

Response (3): The percentage isoprene emissions for excluded gridsquares due to biomass burning and anthropogenic influences is now stated on page 7483, line 16: “These excluded areas account for 27% of African isoprene emissions in the MEGAN inventory (Sect. 3.3).” The relative contribution of gridsquares filtered due to smearing influences is already provided on page 7494, line 9.

4) Large numbers of grid-square-months are removed due to the effect of smearing (Section 4.2). However, these removed HCHO values are indicative of emissions in

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their source grid square. As I understand it, this lost fraction of HCHO is implicitly accounted for by assuming that GEOS-CHEM correctly simulates the real smearing (and therefore loss of HCHO from a grid square via transport) and thus calculates the right ratio of ΩHCHO to EISOP. I think this assumption should be spelled out to the reader.

Response (4): We have adjusted page 7494 lines 3-8 to clarify that the smearing is diagnosed in the model: "We find that 41% of gridsquare–months in GEOS-Chem over Africa have S > 4 × 10ˆ3 s, which is higher than HCHO yields from isoprene emission would allow. This reflects smearing as diagnosed in the model and mainly affects regions where isoprene emissions are very low (such as the vast desert expanses as well as coastal gridsquares)."

Minor comments.

Pg. 7477, line 16. This final sentence is too strong given the uncertainties in the topdown method. I suggest replacing with, "Our results suggest a large overestimate of central African rainforest emissions in the state-of-the-science MEGAN inventory."

Response: We now include the following final statement in the abstract: "Our results suggest that isoprene emission from the central African rainforest is much lower than estimated by the state-of-the-science MEGAN inventory."

Pg. 7477, line 22. Guenther et al. (2006) only report isoprene emission estimates. A further reference is needed to justify this 50% figure, or else use the 44% value from Guenther et al. (1995).

Response: We have corrected this to include the references that quote estimates of NMVOC emissions from biogenic and anthropogenic emission inventories, resulting in about a 50% contribution from isoprene, after taking into account variability across emission inventories.

Pg. 7481, line 27. "...only a few hours, whereas..."

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Response: Done.

Pg. 7481, line 27. I think this sentence refers to oxygenated VOCs emitted by biomass burning? In which case this should be made more explicit to avoid apparently contradicting the point made on pg. 7478, line 25 regarding isoprene dominating HCHO production from NMVOCs.

Response: We have adjusted line 27 (page 7478) to indicate that screening of HCHO for biomass burning and anthropogenic influences is necessary before using the underlying HCHO columns to estimate isoprene emissions: “Contributions from other biogenic or anthropogenic NMVOCs are generally much weaker because emissions are lower and/or HCHO production is slower (Palmer et al., 2003), although care is needed to screen biomass burning and large anthropogenic influences (Fu et al., 2007; Barkley et al., 2008).”

Pg. 7490, lines 18, 20, 23, 25 and pg. 7492, line 15. As pressure increases with decreasing height it would be more explicit to say "below the 900 hPa level", etc.

Response: We switched to altitude (km) for clarity.

Pg. 7491, line 8. "...there is no signiïňĄcant smearing of these species and provides..."

Response: Done.

Pg. 7491, line 17. This sentence assumes we are conïňĄdent of HCHO formation pathways and yields from the isoprene oxidation scheme. See main comment above.

Response: We have amended the sentence to include a statement about the minor contribution of secondary HCHO to the ultimate yield of HCHO: “Because HCHO is produced together with MVK+MACR and this first-stage production accounts for 80-90% of the ultimate HCHO yield under the AMMA conditions (see below), it would be difficult to account for a model bias in HCHO but not in MVK+MACR.” On page 7489, line 18-20, we have already referenced literature in which GEOS-Chem HCHO yields have been validated against ground-based and aircraft observations under conditions

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in which HCHO yields are realized within a few hours, indicating that we are confident in HCHO yields for the high-NOx reaction pathway.

Pg. 7492, line 27. Please provide boundary layer mixing ratio equivalents of these NO2 columns to aid the reader.

Response: We have edited this section of the paper to include a discussion of the relative contribution of the RO2+NO reaction pathway (i.e. Figure 6) as per the suggestion from reviewer #1. In this section we identify central Africa as a region with 15% contribution from the RO2+NO reaction pathway compared with 50% in the AMMA region as determined in GEOS-Chem. We also include the boundary layer NOx conditions for central Africa in GEOS-Chem (300 pptv).

Fig. 7. "MEGAN" should be in the key with the other variables, rather than floating. Presumably the arrow shows wind direction, in which case this should be stated.

Response: Done.

Fig. 9. Two extra panels showing OMI + and - the calculated error would be very informative for the comparison with MEGAN, particularly as this error varies with NOx regime.

Response: The annual error would be considerably smaller than the error we calculated for 8-day average HCHO columns, due to temporal averaging of the OMI HCHO observations.

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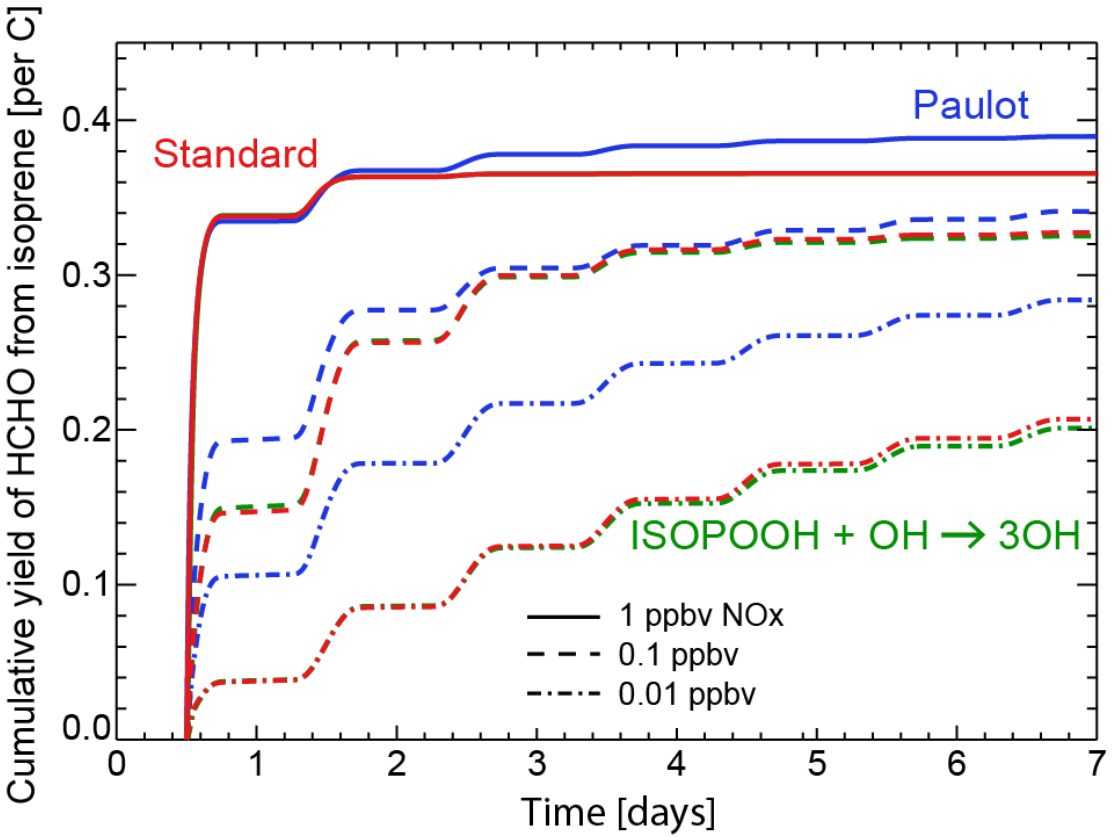

Fig. 1.

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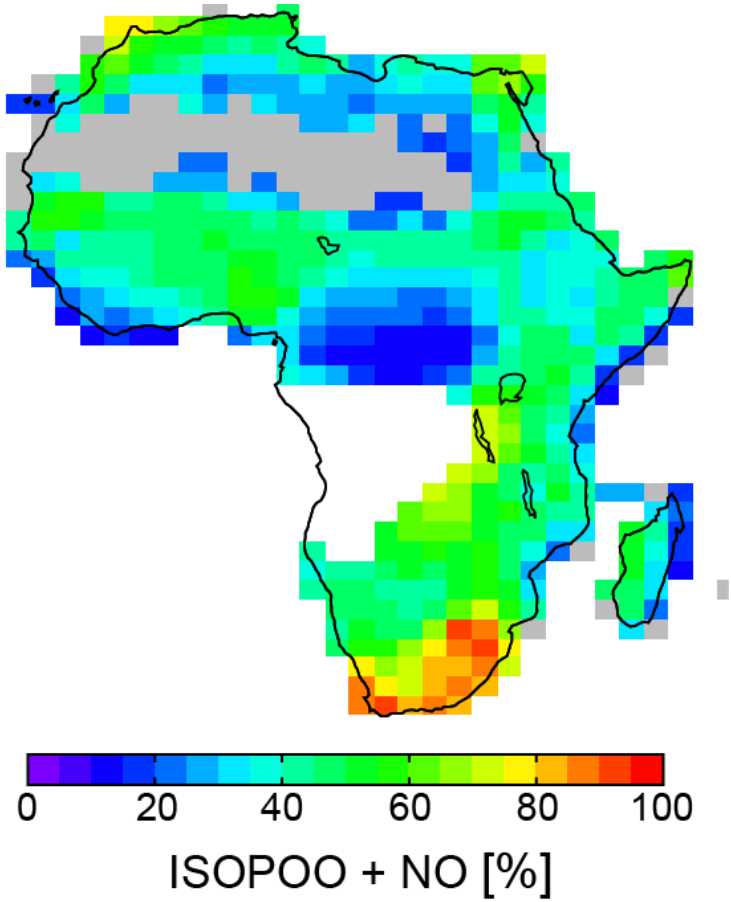

Fig. 2.

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