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Atmospheric
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Interactive comment on “The continental source of glyoxal estimated by the synergistic use of spaceborne measurements and inverse modelling” *by* T. Stavrakou et al.

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On behalf of all authors, I would first like to thank the reviewer for his/her careful reading of the manuscript as well as his/her constructive and insightful comments. A point-by-point reply follows. Reviewer’s comments are *italicized*.

This study presents a two-species inversion of global glyoxal and formaldehyde using the chemical transport model IMAGESv2 and satellite observations from SCIAMACHY. The purpose of the inversion is to constrain the continental sources of glyoxal. Glyoxal is produced by the oxidation of NMVOC from biogenic (mainly isoprene), anthropogenic, and pyrogenic sources; there is also a direct pyrogenic emission of glyoxal.

Glyoxal is removed by photolysis, oxidation, and deposition. In addition, it is assumed that glyoxal is irreversibly absorbed by clouds and aqueous aerosols to form SOA mass. Model based on a priori emissions underestimates satellite-observed glyoxal, leading to the assumption that there is an unidentified VOC (UVOC) precursor of glyoxal. The authors conducted a couple of inversions, assuming either a direct glyoxal source (Inversion A) or a secondary production from a UVOC of 5-day lifetime (Inversion B). They found that inversion B showed better agreement with satellite observation and in situ surface concentration measurements (taken in mid-latitude forests).

Main comments

The main weakness in this paper is that the scientific basis of the UVOC assumption is not well explained. Why is the missing precursor assumed to be biogenic (by scaling to LAI)? It seems also possible (from looking at Figure 2) that pyrogenic or anthropogenic emissions may be underestimated over some continents.

The spatiotemporal patterns of the observed glyoxal columns suggest the existence of a source of biogenic origin, even though other sources might be underestimated over particular areas. A reasonable hypothesis is to associate the distribution of this missing source to the leaf area index as observed by the MODIS instrument. Regarding the a priori value of 20 Tg/yr for this source, it follows the beforehand estimate of Myriokefalitakis et al., 2008, for the missing glyoxal source. However, following the suggestion of the Reviewer#2, in order to explore whether our inversion system is able to provide an upper bound for the missing source, an additional sensitivity exercise with the a priori global UVOC source strength set to 80 Tg/yr is conducted and discussed in the section 4.2 of the revised manuscript. Besides the biogenic source, adjustments of the pyrogenic and anthropogenic NMVOC fluxes are also accounted in the inversion scheme.

Assuming that UVOC is biogenic, what is the basis for the assumption of a 5-day *lifetime? The authors must have reasons to suspect one (or some) particular candidate VOC species to make such an assumption. Is the resulting glyoxal production from UVOC from the inversion consistent with the emission of that (those) candidate UVOC(s)?*

We do not suspect any particular compound for UVOC. In this study, the choice of a 5-day lifetime is somewhat arbitrary. However, the dependence of the result to the choice of a higher or lower UVOC lifetime has been investigated through sensitivity tests. The UVOC precursor is meant to be a generic species which leads to glyoxal formation after a number of intermediate steps. These compounds could be directly emitted or produced in the oxidation of short-lived biogenic precursors like terpenoids. Unfortunately, details on the oxidation mechanisms and glyoxal yield from such compounds are either missing from the literature, or are only partly available from recent chamber studies (e.g. Forester et al., 2009, Nunes et al. 2007). Even worse, the emissions of such compounds are at best estimated at a regional scale, (e.g. Helmig et al., 2007), whereas their quantification on the global scale remains extremely challenging given the high variability in the emission rates from different species, and the selection of species that have been studied so far.

References:

Forester, C. D. and J. R. Wells: Yields of carbonyl products from gas-phase reactions of fragrance compounds with OH radical and ozone, Environ. Sci. Technol., 43 (10), 3561–3568, 2009.

Nunes, F. M. N., M. C. C. Veloso, P. A. de P. Pereira and J. B. de Andrade, Gas-phase ozonolysis of the monoterpenoids (S)-(+)-carvone, (R-)-carvone, (-)-carveol, geraniol and citral, Atmos. Environ., 39, 7715–7730, 2007.

Helmig et al. D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and T. Sakulyanontvittaya: Sesquiterpene emissions from pine trees: Identifications, emission rates, and flux estimates for the contiguous United States,

Environ. Sci. Technol., 41, 1545–1553, 2007.

At a lifetime of 5 days, a significant fraction of glyoxal production will be over the ocean instead of over land. Therefore, the inverted continental UVOC emission will be directly related to the assumed lifetime (as shown by the sensitivity studies). If the assumed lifetime is 3 days, for example, the inverted emission will undoubtedly be much lower, while still maintaining a reasonable agreement between modeled and measured surface concentrations.

We agree with the reviewer. The chosen UVOC lifetime determines the amount of the emitted UVOC through the inversion scheme. Choosing one or twenty days for the UVOC lifetime does not change significantly the agreement between modelled and measured surface concentrations, as is now illustrated on Table 4 of the revised manuscript. Only in inversion A, which assumes a direct glyoxal source, the a posteriori modelled concentrations are found to be much higher than the in-situ concentrations, as shown on Table 3.

Page 13596, lines 1617: If the release of glyoxal from SOA is a potential source, is the magnitude of that glyoxal source consistent with any SOA production mechanism? In Section 2.4, SOA is assumed to be a glyoxal sink. If the glyoxal uptake is irreversible [e.g., Liggio et al., 2005], then how can SOA also be a glyoxal source? If the glyoxal uptake is reversible [e.g., Kroll et al., 2005], then the release from SOA cannot be counted as an additional source. If some other precursors is absorbed by aerosols, undergo chemical reactions, then released as glyoxal from SOA, then is the magnitude of that release consistent with the budget of the precursors?

The release of glyoxal from SOA is proposed only as a possibility which could partially account for the missing glyoxal source. However, dedicated laboratory and field studies are necessary in order to validate or not this assumption. The global budget of SOA is highly uncertain, but we note that global models tend to largely underestimate OA concetrations, in particular in the free troposphere (e.g. Heald et al., 2005). It is therefore currently not possible to estimate whether or not the magnitude of the glyoxal release is consistent with the SOA formation mechanism. The heterogeneous uptake of glyoxal is assumed to be irreversible, but we have acknowledged the high uncertainty associated to this process.

Page 13599, lines 2627: This is confusing; is methylbutenol included in the model or not?

It is now clearly stated that methylbutenol is not included in the model.

Page 13600, line 37: How is the irreversible uptake calculated for clouds and aqueous aerosols? How are the cloud droplet and aqueous aerosol surface areas calculated?

The details of the calculation of the heterogeneous sink in cloud droplets and on aqueous aerosols are now provided in Section 2 and Section 3 of the supplementary material, which is provided with the revised version.

Page 13600, lines 11–13: In the present study, is uptake calculated only under light conditions?

No, the uptake is considered in all conditions. Note, however, that glyoxal is mostly produced during the day, when photochemical activity is high.

Section 2.3, 2.4: How are dry/wet depositions of glyoxal and formaldehyde calculated? What about aerosol depositions?

Dry deposition velocities for reactive gases are calculated using a resistance-in-series scheme (Wesely, 1989). This is now added in Section 2.1. A detailed description of the wet scavenging parameterization is now presented in the first section of the Supplement provided with the revised paper.

Page 13604, lines 6-7: I am not convinced that simulated glyoxal is low over all continents. For example over North America, where isoprene is the dominant NMVOC and its emission well known, the model seems to be doing quite well. Over other continents, the comparisons between model and satellite data suggest that different NMVOC sources are may be at fault over different regions.

This is now rephrased. Over the US, the model generally underestimates the glyoxal columns, except for the Louisiana-Mississippi-Arkansas region where a moderate overestimation is observed during summetime. Over this region the a priori model overestimates also the HCHO columns. The reduction of the isoprene source over this region after inversion is driven by both observed datasets. Please see also next comment.

Page 13607, lines 69; Figure 6: There are considerable information on isoprene emissions over North America [e.g., Palmer et al., 2006], and some information over South America [e.g., Barkley et al., 2008], Africa [e.g., Shim et al., 2005], and Asia [e.g., Fu et al., 2007]. How do those compare to the isoprene inversions here? By looking at Figure 6, North American isoprene emission is greatly reduced in Inversion B, which contradicts earlier inversion studies. This may represent an over-emphasis of biogenic UVOC emission in the inversion.

A thorough comparison of the inferred isoprene emission estimates by region with previously reported literature values has been presented in Stavrakou et al., 2009b, where an inversion using only SCIAMACHY HCHO columns through 2003-2006 is performed. The reader is referred to that paper for a detailed discussion.

The updated isoprene emission strengths derived by Stavrakou et al., 2009b are found to be reduced by 35% on average over 2003-2006 in the eastern US. Previous studies (Abbot et al., 2003, Palmer et al., 2006, Shim et al., 2005, Millet et al. 2006), despite their general consistency, exhibit large discrepancies in the inferred biogenic fluxes over this region. More precisely, whereas the GOME-derived isoprene emissions is found to be by 20% lower that the GEIA estimate in Palmer er al., 2003, an increase by 20% with respect to GEIA is reported by Shim et al., 2005, although both studies have used the same HCHO retrieval (but different inversion methods). It is worth mentioning however, that the HCHO retrieved columns by De Smedt et al. (2008) used in our work are by about 30% lower that the GOME columns used in the aforementioned studies. Although the exact reasons of the discrepancy between the satellite columns from the two instruments need further inversigation, the lower isoprene emissions inferred by our study are supported by the OMI-derived biogenic fluxes (Millet et al., 2008), which are found to be by 23% lower than the a priori MEGAN estimate. Further, the MEGAN inventory is found to be overestimated by up to a factor of two in an analysis based on airborne measurements (Warneke et al., Eos Trans. AGU, 88(52) Fall. Meet. Suppl., Abstract A14D-05, 2007).

Over the Tropical South America, our a priori modelled and SCIAMACHY HCHO columns are in very good agreement, and therefore, no significant isoprene emission change is inferred by the inversion. However, in a similar study using HCHO columns from GOME a significant isoprene flux reduction with respect to the prior MEGAN inventory is needed in order to match the observations (Barkley et al., 2008).

A short comment is added in the revised manuscript in section 4.2.

Page 13607, lines 13-16: The authors should at least offer an order of magnitude estimates for the uncertainties. Otherwise it is difficult to gauge the relevance of inversion A and B.

As already mentioned in the manuscript, possible biases/errors in the satellite retrievals, uncertainties in the chemical mechanisms of the NMVOCs, as well as the representation of the glyoxal sinks in the model, are sources of errors that remain very difficult to quantify. To these uncertainties, we should add the recent findings by Lelieveld et al., 2008 and Peeters et al., 2009 which suggest that the currently used degradation mechanism of isoprene, which is based on the Master Chemical Mecha-

nism, should go through a substantial revision. Therefore, the HCHO and glyoxal yields from isoprene might be much different than those assumed by the MCM and used in this study. This introduces an important factor of uncertainty in our results that is impossible to estimate with the current means. This is now better explained in the revised manuscript (section 4.2).

However, through our sensitivity experiments we have tried to quantify the impact of the UVOC lifetime and the SOA formation sink on the derived glyoxal fluxes, as well as the capability of the inversion to provide a possible upper bound for the missing source (the last sensitivity study has been suggested by Reviewer#2). Sensitivity results are presented in Section 4.2 and illustrated in Table 4 and Fig. 8.

Page 13610, lines 14: The better comparison between measurement and inversion B is not a robust way of rejecting a direct glyoxal source (inversion A). As the authors pointed out, all surface concentration measurements were taken in mid-latitude forests, where the a priori isoprene emission in the model is already high (which is why the a priori model already agrees well with the measurements). A secondary source (with a 5-day lifetime precursor) assumed in inversion B of course will not cause large increase over the source region.

Our inversion framework is driven by both HCHO and CHOCHO datasets. The isoprene emission updates are quite similar in A and B inversions. Over the US, where most of the in situ measurements were performed, the a priori model agrees reasonably well with the satellite measurements of glyoxal but is found to be much higher than the observed HCHO columns. In particular over the southeastern US, the use of the a priori isoprene MEGAN-ECMWF database leads to an overestimation of the CHOCHO and HCHO columns during the summer season. After inversion, the updated US isoprene emissions are decreased by 15-30% in both A and B scenarios. The choice of a direct glyoxal source leads to strongly enhanced concentrations, in particular at the Georgia, Pinnacles and Blodgett sites, but also at the Japanese and European sites, and thus, is not supported by the present two-compound inversion study.

Conclusion: The authors should briefly summarize the scientific implication of the present study in a broad context.

As suggested also by Reviewer#2, a paragraph is now added at the end of Section 4.2.

Overall, the globally inferred changes in the NOx and ozone concentrations are small. The largest changes occur near the surface over tropical regions, and are mostly driven by the isoprene updates. In particular, the strong increase of the isoprene source over Southern Africa and the Amazon basin leads to a decrease of the annually averaged OH concentrations by 10-40%, and to lower NO_2 and ozone mixing ratios by 4-6% over these regions, whereas over the tropical Atlantic and the southern Indian Ocean the NO_2 concentrations increase by 5-20%, due to the transport of nitrates generated from the oxidation of isoprene over the continental regions. In constrast, the OH concentrations are found to be decreased by 40% near the surface over the eastern US and by 70% over Indonesia, in response to the reduced isoprene source over these regions. A decrease of 5-20% of the NO_2 mixing ratio and a slight decrease (up to 4%) of the ozone concentrations is predicted over the eastern Indian Ocean and the tropical Pacific. Over China, the OH mixing ratio decrease associated to the strong increase of the UVOC and glyoxal source is compensated by an enhanced HO_2 production through glyoxal photolysis, which under the high NOx regime of this region, leads to an increase of ozone concentration by 2.5%.

Table 3: What are these concentrations? Afternoon concentrations, 24-hour averages?

In fact, for most of the measurements cited in Table 3, the air samples are collected during all day (except for Spaulding et al., 2003, and Ieda et al., 2006), and the given values are 24-hour mean concentrations. Therefore, the use of diurnally averaged modelled concentrations when comparing with the data is justified. A comment on this is now added in Section 2.1.

Minor comments

Page 13595, line 27: lanfd should be land

Corrected.

Page 13598, lines 12-14: Is there a reference for the C2H2 emission adjustment?

A reference is now added.

Figures: Fonts in all figures are too small (e.g., colorbar legends, labels, axis labels)

We have improved the fonts of figures 2, 4, 6, 7 in the revised paper.