**Atmospheric
Chemistry
and Physics
Discussions**

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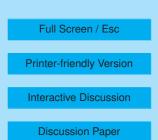
T. Stavrakou et al.

jenny@oma.be

Received and published: 21 September 2009

On behalf of all authors, I would first like to thank the reviewer for his constructive and insightful comments. A point-by-point reply follows. Reviewer's comments are *italicized*.

4D-Var data assimilation of HCHO and CHOCHO columns is used to estimate missing continental sources of glyoxal in the IMAGESv2 model. Inverse model solutions are primarily validated through comparison of the optimized model estimates to surface observations of glyoxal. The robustness of the solution is tested by additional sensitivity runs with different model setups. It is concluded that the observations and the model

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

are most consistent with an additional secondary source of glyoxal of more than 50 Tg/y. This paper is well written, the subject is timely and the approach is novel. I have questions about a few aspects of the inverse modeling that feel a bit glossed over and some suggestions for additional analysis to strengthen the presentation of the conclusions. My main suggestion for addition research is to perform a few more inverse modeling tests that begin with higher than a 108 Tg/y source of glyoxal in order to determine if this inverse modeling framework really can provide a bounded estimate from both sides, and to further discuss the implications on tropospheric chemistry of the inferred secondary glyoxal source.

Comments

1. Overall, I would appreciate seeing more in this paper about the inverse modeling approach. Having established a track record of 4D-Var data assimilation with the IMAGES adjoint, I agree there is no need for the authors to repeat content about adjoint model derivation, optimization, etc. Yet, I think they could still provide additional discussion in the introduction that connects this piece to the young, yet growing, body of literature on inverse modeling emissions of chemically reactive species using adjoints of CTMs. Many readers are still skeptical if not dismissive of top-down emissions constraints, so I think further discussion along these lines is warranted.

The reviewer can now find a brief discussion on this point in the second paragraph of the introductory section.

2. Related to the previous comment, it struck me right away that this is the first adjoint model to consider SOA formation. Nobody has yet applied 4D-Var to SOA, so that could be mentioned in the conclusions and/or abstract.

The present version of the model does not include the adjoint of the SOA formation module, and therefore, it does not account for the feedback of the SOA concentration

changes inferred by the inversion on the glyoxal sink. This is now made clear in the beginning of Section 4.1.

3. 13601.4: Since ISORROPIA is used in the forward model, has the adjoint of ISOR-ROPIA been made for the IMAGES adjoint model? If so, then that is something specifically worth highlighting, as it would be a very valuable development. If not, please mention which chemical/physical interactions are only included in the forward model.

Note that EQSAM, not ISORROPIA is used in the forward. The adjoint of EQSAM has not been developed in the current version of the model. The inorganic aerosol surface densities are calculated in a forward model simulation and are kept constant throughout the inversion. A mention on that is included in the beginning of Section 4.1.

4. 13595.13: I could not help but wonder why the study is limited to continental sources. Later, there is mention that including ocean sources would be beyond the current scope of the paper, but since adjoint methods can address any number of emissions simultaneously, I just was not sure the reasons for excluding this potentially very interesting piece of the current glyoxal puzzle. It might be better if the reasons are clearly stated up front in the introduction.

The authors agree that marine sources of glyoxal are of particular interest. The reason for limiting this study over the continents lies at the inherent difficulty to retrieve glyoxal columns over water due to the interference from liquid water absorption (Wittrock et al., 2006). The interference may lead to negative values over the oceans (blank regions on Fig.1). On the other hand, the HCHO column amounts over the oceans lie close to the instrument detection limit, and they are not expected to offer strong constraints to the inversion. As suggested by the reviewer, a comment is now added in the second paragraph of the introduction.

5. 13596.4: Why is the missing source necessarily biogenic in origin?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The spatiotemporal patterns of the observed glyoxal columns suggest the existence of a source of biogenic origin, the leaf area index being considered as a proxy for this source. However, contributions from pyrogenic and anthropogenic sources are not excluded, and the inversion scheme is also inferring emission updates for these two categories.

6. 13596.16: ". . . organic aerosols is another potentially significant source of glyoxal." Yet, this and other papers focus more on SOA as being a sink for glyoxal, especially when considering, as is done here, irreversible SOA formation. So why is SOA being mentioned here as a source?

Glyoxal could be released from SOA generated from other precursors. In addition, although throughout this study glyoxal is considered to be irreversibly transformed to SOA, a reversible partitioning to aerosol liquid water with a very high effective Henry's constant could also account for observed glyoxal concentrations in Mexico City (Volkamer et al., 2007, Section 2.4). The implementation of alternative parameterizations lies within our future plans.

7. 13597.7: "monthly mean ECMWF reanalysed wind fields". Why use the monthly mean winds if the model takes 24h time steps?

This is a feature of the model. The daily variability is accounted for through diffusion coefficients.

8. (a) Are the NOx emissions inventories mentioned? (b) NOx levels will affect lifetimes and inferred emissions. (c) While understandably outside the scope of this article, it could be suggested that NOx observations potentially provide additional constraints for future inverse modeling studies.

(a) Anthropogenic NOx emissions are obtained from the EDGARv3.3 inventory for 1997 (Olivier et al. 2001), emissions from biomass burning are distributed accord-

ing to GFEDv2 (van der Werf et al., 2006). Biogenic NOx emissions are obtained by using the parameterization of Yienger and Levy, 1995 combined with fertilizer statistics and ECMWF fields for precipitation and soil temperature. It is globally scaled to 8.2 Tg N/yr. The horizontal distribution of lightning emissions (scaled globally at 3 Tg N/yr) combined a space-borne climatology (LIS/OTD) for the number of flashes with a parameterization (Price and Rind, 1993; Martin et al., 2007), which uses ECMWF meteorological fields (cloud top height, convective precipitation rate). The emissions are distributed vertically following Pickering et al., 1998.

The inclusion of a paragraph on the NOx emission inventories would lengthen the paper without bringing additional insight, so the authors prefer to keep the section on the emissions in its present form.

(b) This is true. Note, however, that photolysis is by far the dominant sink for both HCHO and CHOCHO, whereas oxidation by OH is much less significant (ca. 20% of the global sink). Therefore, both species should not be much affected by moderate updates in the NOx emissions used to drive the model.

(c) The authors agree with the reviewer that NOx (also CO) observations can help to better constrain future inversion studies.

9. section 2.6, which describes the surface glyoxal measurements, is missing. Perhaps it would answer why diurnal variations are not considered for model comparisons to the surface observations.

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. The reader is referred to the cited literature of Table 3 for a thorough description of the ground-based observations.

10. 13605.16: "The thresholds has been adjusted so as to avoid the existence of large disparities in the number of unknowns to be optimized from the different categories." It is not obvious why such disparity would be a problem. Could this be explained further?

Disparities in the number of unknowns for anthropogenic, pyrogenic, and biogenic emissions is not a problem for the inversion from the computational point of view. By setting the threshold to a specific value for a category we want to make sure that there are enough control variables from this emission category to be inferred by the inversion.

11. Results: One of the most important parts of the results section is the attempt to verify or discredit the different inverse modeling solutions. In this manuscript, then approach is to compare estimates from the various optimized models of surface glyoxal concentrations to observations. The analysis would be strengthened by including quantitative metrics of this comparison for each of the sensitivity analysis. For example, the results of sensitivity studies C-F can be compared to the surface measurements, and the resulting correlations and biases summarized in Table 3, or even as labels in Fig. 8. This would be more satisfactory than the textual summary given in lines 23-25 of page 13608.

Comparison to the HCHO measurements also provides an additional constraint, but since these observations were used in the inverse modeling procedure themselves, the utility of such comparisons for validating the inverse modeling solution is different. Still, it would be nice if analysis similar to Fig. 3 was included for runs C-F. Providing a quantitative metric along with these plots would help (for example the % of the converged cost function owing to HCHO observations), because at first glance it does appear that B is better than A, which would be nice to know.

A new table (Table 4) is included which summarizes the results of the inversion experiments. The global mean model/data biases (b) and spatiotemporal correlation coefficients (r), the average biases b_{situ} and the root mean square deviations (RMSD)

calculated from the comparisons with the in-situ measurements of Table 3 are given on this table. As shown by this comparison, most of the studies yield results quite similar to the inversion B, except for the case E and F where the calculated bias with respect to surface measurements worsens. The cost function reduction is more efficient in inversion B (50%) compared to A (40%), whereas for the sensitivity studies it ranges between 45% (E) and 55% (F). The sensitivity cases exhibit negligible differences compared to case B in Fig. 3, and therefore they are not included in the new manuscript.

12. For nonlinear optimization problems, there is no guarantee that the inverse model has converged to a global minimum. The authors could and should explore this possibility by trying an additional inversion or two wherein the initial guesses for the CHO-CHO or UVOC sources are much higher than those from Inv A or B. This would demonstrate that the inverse model truly is capable of bounding the value of the missing source. Otherwise, the results could simply indicate a lower bound for the missing sources since the model is constrained to the a priori source levels.

To reply to the reviewer's concern and following his suggestion, we have performed an additional inversion exercise where the a priori global UVOC source strength is chosen to be four times higher than in the standard setup, i.e. 80 Tg/yr. The a priori global CHOCHO source is then estimated to 134 Tg/yr. After inversion, the UVOC global source is reduced to 63 Tg/yr. This value is by 17% higher than in inversion B. The global CHOCHO source (113 Tg/yr) is only slightly higher than in inversion B. The average bias with the surface glyoxal measurements of Table 3 is equal to 1 pptv and the root mean square deviation is equal to 5.2. A brief comment on this inversion scenario is included in the section 4.2.

13. Lastly, I think there is room for additional discussion of the impacts of the inferred glyoxal source beyond those on concentrations of glyoxal, formaldehyde and SOA. For example, did the concentrations of species such as NOx and O3 change much in

the IMAGES model after the inversion? Are these changes con- sistent with current understandings of tropospheric chemistry?

Overall, the 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 (Fig. 6) 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%.

It is worth mentioning, however, that in the light of the recent work by Lelieveld et al., Nature, 2008 and J. Peeters, et al., PCCP, 2009, the currently used degradation mechanism of isoprene, which is based on the Master Chemical Mechanism, should undergo significant revision, and therefore, the formaldehyde and glyoxal yields from isoprene might be quite different from those assumed by the MCM and used in this study. This introduces an additional uncertainty in our results.

As recommended by the reviewer, a discussion is now included in the section 4.2 of the revised manuscript.

Lelieveld, J., T. M. Butler, J. N. Crowley, T. J. Dillon, H. Fischer, L. Ganzeveld, H. Harder,

M. G. Lawrence, M. Martinez, D. Taraborrelli, and J. Williams: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, 2008.

J. Peeters, T. L. Nguyen and L. Vereecken, HOx radical regeneration in the oxidation of isoprene, Phys. Chem. Chem. Phys., 2009, 11, 5935–5939, DOI: 10.1039/b908511d.

Minor comments and clarifications

13595.27: replace "lanfd" by "land"

Corrected.

13599.11 replace "by 16%" by "which is 16%"

Corrected.

13606.16: replace "thresholds has been" by "thresholds have been"

Corrected.

Ratio plots: strongly suggest using a traditional blue-white-red plot for these types of values. Otherwise, it can not be quickly determined which changes are increases vs decreases. A log scale may also be more appropriate.

The ratio plots have been improved in the revised manuscript so that the green color corresponds to a ratio equal to 1. We think that the multiple colors of this scale allow for a more precise determination of the values on the plot compared to the blue-white-red scale.

13606.25: biogenic isoprene fluxes "biogenic fluxes" because the biogenic emissions sector includes other VOC species, correct?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Yes, corrected.

13606.26: "in excellent agrement". Typo in agreement. Also, I would strongly suggest providing the quantitative support for this claim, which would make it all the more impressive.

Corrected. The sentence becomes : "The optimized isoprene source amounts to 476 Tg/yr, and is equal to the inferred isoprene source from a previous inversion constrained by HCHO columns (Stavrakou et al. 2009b)".

13609.15: replace "source, major" by "source, a major"

Corrected.