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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The influence of natural and anthropogenic secondary sources on the glyoxal global distribution" *by* S. Myriokefalitakis et al.

Anonymous Referee #1

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Summary

This paper focuses on a budget analysis of biogenic vs anthropogenic sources of glyoxal in the global chemical transport model TM4. Increased recognition of the role of glyoxal in secondary organic aerosol formation and as an indicator of VOC photochemical activity makes specification of its sources and distributions an important and timely topic. The existing content and organization of this manuscript are in-line with the standards of ACP. Overall, I find this to be a good paper with only a few areas that deserve more attention. It is requested that prior to publication in ACP the focus of the paper be

expanded to include further investigation of the discrepancies between observed and modeled glyoxal columns and to include the implications of such discrepancies on the budget results.

Major comments

1. As a preliminary step, model results are compared to surface measurements of glyoxal concentrations and remote measurements of the glyoxal column from SCIAMACHY. Model updates and inclusion of additional anthropogenic VOCs improves the comparison between measured and observed glyoxal columns since Wittrock et al., 2006. It is shown that bias remains globally (m=0.43) and over land (m= 0.62). It seems that not enough attention is given to this remaining discrepancy. While it is recognized that this issue is not overlooked (p1685/1686 and lines 17-23 of the conclusion), additional consideration in the text and abstract concerning the apparent missing sources of glyoxal in the model is warranted. Deference to a "forthcoming paper" unfortunately diminishes the impact of this paper, particularly as many questions are brought to mind that are critical to the subsequent budget analysis. For example, an ocean source is indicated to be missing from the model. Given the estimated glyoxal lifetime and the difference between the two lines shown in Fig 1c, what is the implied magnitude of the natural ocean source? Regarding the discrepancy over land – is it smaller or larger in industrial areas? Additional model sources of glyoxal are posited. Can comparisons between surface observations, the model and the satellite observations indicate whether discrepancies between the latter two are due to sources at the surface vs sources higher up? To what extent can uncertainties in glyoxal sinks explain the discrepancies?

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2. Uncertainty in the glyoxal concentrations and estimates of the reason for the discrepancy noted above should be reflected in the budget analysis as stated in the abstract, discussion and conclusion. For example, if indeed the model is missing a natural ocean source of glyoxal of x Tg/y, then the anthropogenic contribution to the global glyoxal burden may only be y %, and the upper bound on SOA production from glyoxal cloud chemistry given in the conclusion would be higher, etc.

3. p1686, line 28: This line states that anthropogenic hot spot areas of USA, Europe, India and China are visible from space. This signal is again mentioned on page 1689, line 2, and in the abstract: "The model results are compared with satellite observations of glyoxal columns over hot spot areas." Unfortunately, these hot spots are not identifiable in the figure given (Fig 2c, 3a,b). This is likely owing to the remote observations being degraded to TM4 resolution in these plots. It would be very helpful to see the actual SCIAMACHY data to demonstrate precisely how prominent such anthropogenic features are from space. It would be particularly useful if such plots included close-ups of glyoxal levels near some of the urban areas mentioned on page 1689, line 8.

Minor comments

1. In the budget analysis of anthropogenic vs natural influences of secondary formation glyoxal from VOC oxidation, the present work considers the anthropogenic sources of VOCs. Are anthropogenic influences on the oxidant levels also an important factor?

2. p1676: There are many proposed mechanisms for SOA formation involving glyoxal. The authors may also wish to consider works such as Ervens et al. (2004),

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Lim et al. (2005), Barsanti and Pankow (2005), Crahen et al. (2004), Warneck (2003,2005), Schweitzer et al. (2004), Kalberer et al. (2004), and Hastings et al. (2005).

3. p1677, line 22: suggest 'chemical' or 'chemistry and' instead of 'chemistry.'

4. 1684, line 6: The phrase 'overall reasonable agreement' is a bit vague. A more in-depth analysis of the surface measurements vs model estimates, or just the surface measurements themselves, would be appreciated. For example, that point concentrations near sources are likely underestimated in the model owing to sub-grid scale variability is well taken, but what about urban points that are modeled higher than the observations (i.e. the MIT measurements by Sinreich et al., 2007)? In Las Vegas, could the difference between observed summer and winter values indicate the contribution of primary anthropogenic sources to glyoxal concentrations?

5. p1685, line 26: Is the difference in the slope of the high (0.62) and low (0.60) resolution model simulations statistically significant?

6. page 1689, line 10-11: This seems like "good" rather than "excellent" agreement.

7. section 2.1: suggest a table listing emissions

8. p 1679, line 7: It's interesting that emissions of toluene and xylene here (26 Tg/y) from the POET inventory are significantly higher than the widely used EDGAR inventory of $\sim$15 Tg/y.

9. p1690, line 15: Volkamer 2006a seems to be the correct reference for the Pearl River Delta.

10. References: Several of the citations have capitalized article titles while others (most) do not. For example, Volkamer 2006a vs Volkamer 2007.

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11. References: There isn't a Volkamer 2007a, just a Volkamer 2007.

12. Figure 1: The black circles in 1c are the same data points as the blue circles in 1d. For clarity, they could be made the same color in both panels.

13. The anomalous high values of the observed glyoxal column near a few ice/water borders in Fig 2c and 3a,b are owing to ...?

14. The method of binning the SCIAMACHY data could be explained a bit more clearly. It appears that the satellite data is also binned onto the TM4 grid, as would be expected, though this isn't clearly stated.

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