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Interactive comment on "Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high– NO_x conditions" by M. M. Galloway et al.

Anonymous Referee #2

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This paper provides experimental data convincingly showing the production of small yields of glyoxal, glycolaldehyde and hydroxyacetone as first generation products from isoprene. They also report first generation methylglyoxal formation from MVK and MACR. Gas-phase glyoxal was continuously monitored using a laser induced phosphorescence instrument and chemical ionization mass spectrometry (CIMS) was used for on-line measurement of gas-phase glycolaldehyde and hydroxyacetone.

The authors included their data in the Master Chemical Mechanism (MCM) improving its initial performance. Further improvement of the MCM resulted from lowering the

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first generation glyoxal production from C5 carbonyls (hydroxcarbonyls??), suggesting the importance of further experimental data on the fate of these C5 carbonyls. This is an important study, but its presentation could be improved by including additional experimental details. Specific comments that should be addressed are as follows:

p. 10396, lines 24-26: The authors mention the upper limit of Orlando et al. (1999) for methylglyoxal from MACR, they should also note the yield measured by Tuazon and Atkinson (1990b).

p. 10697: The authors should provide more details concerning the experimental methods: Were the lights black lamps? What NO2 photolysis rate did 100% lights correspond to? What were the initial HONO concentrations? At what stage during the experiment did O3 formation begin? What were the total irradiation times?

p. 10698, line 3: the units for the limit of detection for glyoxal are not clear, why are they in ppt s-1? For 30 s time resolution, what is the limit of detection in ppt?

p. 10698, lines 7-8: since the paper describing the "lifetime methylglyoxal detection method" is in preparation, a brief description of the method would be useful for the reader.

p. 10701, line 5-7, this sentence needs clarification: I assume the authors mean that because MACR and MVK are less reactive than isoprene the reactions of products are more apparent earlier in the MACR and MVK reactions than in the isoprene reactions.

p. 10701, equation 3, is there any theoretical basis for this equation or is it merely empirical?

p. 10701, line 28: I suggest that the authors replace "this" with the "Dibble mechanism".

p. 10702, lines 9 and 10: The entry from Paulot et al. (2009a) for methylglyoxal from MACR in Table 2 is 0% - either this entry is incorrect, or the statement on lines 9-10 is incorrect. Also on line 9, the "and Atkinson (1989)" should be "and Atkinson (1990b)".

p. 10704, line 12: Again a problem with the entry from Paulot et al. in Table 2 being inconsistent with the text.

p. 10705, line 5 onward: I assume the C5 carbonyls are, in fact, C5 hydoxycarbonyls. With regard to reactions of C5 hydroxycarbonyls, Berndt and Boge (J. Phys. Chem. A, 2007 111, 12099) measured glycolaldehyde and glyoxal yields from OH + 4-hydroxy-2-butenal of 40 +/- 6% and 17 +/- 4%, respectively. Baker et al. (Envir. Sci. Technol., 2005, 39, 4091) observed glycolaldehyde from OH + 1,3-butadiene and ascribed it to essentially unit formation from OH + 4-hydroxy-2-butenal. These apparently conflicting observations may be reconciled, at least in part, if glycolaldehyde is also formed as a first generation product from OH + 1,3-butadiene.

Table 1: "C1" should be footnoted as data from Chan et al., 2009?

"Table 3" appears in the text when referring to both Table 2 and Table 3.

Table 2 provides very important values, some of which appear to be in incorrect columns. The first line of data for isoprene, MVK and MACR should be footnoted as the experimental values from this work (if this is correct). In the table title: are these "molar" yields? For MVK in Table 2, what is presently listed as hydroxyacetone yields for the Tuazon and Atkinson and Paulot et al. entries are the methylglyoxal yields. For the present work listed in Table 2 (and in the text, e.g., p. 10701, line 15) what are the error limits (for example, 1 or 2 standard deviations or what).

A more descriptive Table caption on Table 3 is necessary to avoid confusion.

Figures 2 and 3, it would be useful if the yields of the various model parameters (for example, the yields of products modeled) were given in the figure caption.

Figure 4, line 2 of caption, I suggest the authors replace "attenuated" with adjusted or some other verbiage.

Most of the information in the Supplement is not referred to in the manuscript.

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Table S2. What are the criteria used for "Excellent", "Good" etc. in the agreement of the model with the measurements?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 10693, 2011.