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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Isoprene oxidation products are a significant atmospheric aerosol component” *by* S. N. Matsunaga et al.

Anonymous Referee #3

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The work presented in this paper provides an estimate of the contribution of isoprene to the production of organic aerosol on a global level. The estimate is based upon field measurements of three second generation oxidation products of isoprene (methylglyoxal, glycolaldehyde and hydroxyacetone) in the gas and aerosol phase and incorporation of these data into a model calculation. This work is original and attempts to address important questions concerning the sources and composition of organic aerosol in the atmosphere. However, the paper is far too short and the level of technical detail provided on the field measurements and model calculations is inadequate. More importantly, I believe the work contains a number of significant deficiencies which cast doubt over the validity of the end result.

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1. The measurements were made using an annular denuder/filter sampling system to trap gas and particle phase compounds. This method can provide very useful information but is prone to sampling artifacts and considerable care needs to be taken to avoid or minimise these effects. Technical details on the sampling system are not provided in the present paper. However, the reader is referred to a previous article, Matsunaga et al., Journal of Geophysical Research, 109, 4302, 2004, where some information, such as the collection efficiency of the denuder are reported. For further details concerning the testing of the denuder, the reader is again referred to another article, but this is a “paper in preparation”, which to my knowledge has not been published. The result is that the authors have not convincingly demonstrated the performance of the denuder/filter sampling system in separating and collecting gas and particle phases and uncertainties therefore remain. For example, the collection efficiency is reported as being $>$90% for each of the compounds measured in this work, but no indication is given on how this was determined. Furthermore, because the denuder is not 100% efficient, small amounts of the gas-phase compounds can “break through” the first denuder and become trapped in the second denuder. In the method employed in this work, the extract of the second denuder is added to that of the filter, with the result that this gas-phase component is mistakenly identified to be part of the particulate phase. The problem could be compounded further if the first denuder becomes saturated as a result of continuous sampling for 3 hours. In this case the net result would be an overestimate of the particulate phase concentration. A number of control experiments are required to eliminate these uncertainties and no evidence that these tests have been performed is presented in any of the papers.

2. The use of the term "Aerosol Partition Ratio (APR)" is unrepresentative of gas-particle partitioning in the atmosphere. The extent to which compounds partition between the gas and particle phases depends on the amount of available particulate matter and is more accurately described by the gas-particle partitioning coefficient Kp; Kp = (F/TSP)/A, where F and A are the particle and gas-phase concentrations of the compound and TSP is the concentration of total suspended particulate matter. The

APR term does not incorporate the ambient particulate concentration and is therefore not fully representative of partitioning. The authors could convert to Kp values if the particulate mass was measured at the time of sampling. However, no mention of particulate mass measurements is provided in the experimental section of the paper.

3. The proposed linear relationship between APR and relative humidity is far from convincing. E.g. for glycolaldehyde (Figure 3a), the APR values at 100% relative humidity vary from 0.1 to 0.8 !!! This strongly suggests that other parameters, such as temperature and ambient particulate mass need to be taken into account. As a result, the equations used to calculate APR values and the resulting aerosol mass contributions (AMC) are too simplistic.

4. There is virtually no information presented about the model used to calculate the gas-phase concentrations of the three compounds. What are the branching ratios and rate coefficients used in the model? How do the errors on these parameters affect the yield values, Y, for each compound?

Additional Comments:

(i) The introduction is too short, does not take into account previous work on measurements of isoprene oxidation products in aerosol and does not contain a statement of the objectives of the work.

(ii) page 11144, line 16: glycolaldehyde, hydroxyacetone and methylglyoxal are not the major oxidation products of isoprene. They are second generation oxidation products.

(iii) A significant amount of experimental detail is missing. How were the VOCs (isoprene, methacrolein and methyl vinyl ketone etc.) measured? What was the temperature during experiments? What measures were taken to ensure that the denuder/filter sampling system was free from artifacts (see point 1 above)?

(iv) page 11146, line 23: I do not agree with the statement that the model "accurately re-produced the concentration and diurnal variation of MACR and MVKĚ" see figure 1.

(v) page 11147, line 18: As indicated in figure 3, the relationship between APR and relative humidity shows a weak dependence - not high dependence. It is fairly obvious that other parameters, including temperature and particulate mass need to be considered here (see point 3 above).

Although this work attempts to address a significant issue concerning the biogenic sources of organic aerosol in the atmosphere, it is less than convincing and contains too many uncertainties. Consequently, I do not recommend publication of this article in Atmospheric Chemistry and Physics in its current form. However, if the paper is re-written to address the deficiencies detailed above then it may be suitable for re-submission.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11143, 2005.

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