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

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In this study the contribution of three water-soluble isoprene oxidation products (methylglyoxal, glycolaldehyde, and hydroxyacetone) to global organic aerosol loading is estimated. Calculated loading is found to be substantial (10-120 Tg/year). Such estimates are necessary given the observations by Matsunaga and coworkers (in this work and in other recent studies) that such compounds are present in high concentrations in the aerosol phase. This mechanism of aerosol growth may play a role in the observations of SOA formation in recent chamber studies of isoprene oxidation (Edney et al., 2005; Kroll et al., 2005), and should be included in global modeling studies.

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However, the model used has some inherent weaknesses which are not addressed, and so uncertainties in particulate loading may be much larger than those reported. Improvements to the model could reduce these uncertainties substantially. Most important is the unrealistic treatment of gas-particle partitioning; partitioning is expressed in terms of an "Aerosol Partition Ratio" (APR), the fraction of a compound found in the aerosol phase. The APR's used in the model are weakly dependent on relative humidity (RH) but are otherwise assumed to be constant under all other atmospheric conditions. However, it is well-established that partitioning is highly dependent on the amount of ambient particulate matter available into which the condensable compound may partition. Partitioning is more accurately described by K_H^*, the effective Henry's Law constant (or K_p, the gas-particle partitioning constant). The partitioning coefficient equals P/(G*SP), in which P and G are the mass concentrations of the compound in the particle and gas phases, and SP is mass concentration of suspended particulate matter (aqueous only in the case of water-soluble compounds); it may also be highly temperature dependent. Neglect of the roles of SP and T likely accounts for the very large scatter in APR measurements, as well as the observed weak dependence of APR on RH (as RH may affect the total water content of aerosols). If the sampling sites are not representative of global tropospheric conditions in terms of T and SP, the errors in gas-particle partitioning will be much higher than implied by the scatter in Figure 3.

Further, the authors should examine in greater detail the calculated gas-phase yields of the isoprene oxidation products (Y_{GA}, Y_{HA}, and Y_{MG}). The total aerosol mass contribution (AMC) from each product is sensitive to these yields, and the authors associate large errors with these values (factors of 1.5-2.1). Only a small fraction of this error is ascribed to deviations of parameterized yields (Eqs. 4a-c) from the results of a chemical box model. However, it is not clear that the parameters in Eqs. 4a-c are valid for all atmospheric conditions. It is stated they are statistically obtained by multiple regression of results from 25 box model runs, over a wide range of [O_3], [NO_x], and

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[isoprene]. It is not mentioned whether temperature, pressure, and background levels of other species (which may affect radical chemistry) were varied as well, or whether cross-validation techniques were used, comparing yields to box model results in conditions different than the ones used to generate the regression data. Such tests are necessary if yields are to be parameterized globally; otherwise uncertainty is substantially greater than the stated values of 13%-18%. Additionally, how well does the box model upon which the parameterization is based describe isoprene chemistry globally? It is shown to reproduce measurements in the Duke Forest (Figs. 1 and 2), but this is a test under high-NO_x conditions only. How well are low-NO_x conditions (important in remote regions such as the Amazon) represented? Comparison of model results with low-NO_x measurements would be useful. At the very least, the chemical mechanism of isoprene oxidation used in the model, with branching ratios and rates, should be shown, and assumptions made should be stated explicitly.

Minor point: Assuming uptake of these products is reversible, when a particle is transported to a cleaner environment, its constituent organics will begin partitioning back into the gas phase. In that case, partitioning of these products into the condensed phase may be only a temporary reservoir for such products. In other words, Eq. 3 calculates gross production of aerosol from these products but not net production (or else it assumes uptake is irreversible). This should be stated explicitly. This distinction can make a substantial difference in estimates of global SOA production (Chung and Seinfeld 2002, Tsigardis and Kanakidou 2003), and models which calculate the gross production tend to provide relatively high estimates of global SOA (Kanakidou et al 2005).

- *Jesse H. Kroll, Daven K. Henze, and John H. Seinfeld*

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References Cited

Chung, S. H., and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, J. Geophys. Res. 107, 4407, doi10.1029/2001JD001397, 2002.

Edney, E. O., Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Wang, W., and Claeys, M.: Formation of 2-Methyl Tetrols and 2-Methylglyceric Acid in Secondary Organic Aerosol from Laboratory Irradiated Isoprene/NOx/SO2/Air Mixtures and Their Detection in Ambient PM2.5 Samples Collected in the Eastern United States, Atmos. Environ., 39, 5281-5289, 2005.

Kanakidou, M., et al.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., and Seinfeld, J.H.: Secondary organic aerosol formation from isoprene photooxidation under high-NOx conditions, Geophys. Res. Lett., 32, L18808, doi:10.1029/2005GL023637, 2005.

Tsigardis, K., and Kanakidou, M.: Globel modelling of secondary organic aerosol in the troposphere: a sensitivity analysis, Atmos. Chem. Phys., 3, 1849-1869, 2003.

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

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