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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling secondary organic aerosol formation through cloud processing of organic compounds" *by* J. Chen et al.

J. Chen et al.

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Response to anonymous reviewer 2: We thank the reviewer for his/her comments. We address the comments below:

Comments: There are, however, some concerns regarding the structure of the model, in particular of the zero-dimensional one. There are large inhomogeneity in the level of complexity of the model: while gas-phase reactions are treated in much details, and part of the aqueous-phase mechanisms up to carbon number four are also based on exact kinetic models, a very large fraction of potential organics with carbon number greater than four (which together could be more important in SOA formation than the few low MW compounds) are treated as surrogates using very simple assumptions

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(Page 8956 line 10-11). Basically, it is assumed that aldehydes are converted into their corresponding carboxylic acids in clouds. So it is to some extent trivial that cloud reactions that decrease the volatility of a great many compounds in surrogates will inevitably increase the amount of SOA formed. Larger MW aldehydes (e.g. pinonaldehyde) are generally assumed to contribute directly (but only in a small fraction due to their volatility) to SOA mass, and in OH reactions they do not oxidize further but even decompose to small gaseous species. Thus cloud reactions which not only preserve these abundant species but convert them into less volatile (and more stable) species, will add mass to SOA, no question about it. Thus the entire complex model is pending on a single and simple assumption which still awaits confirmation in chemistry. This would make the model an order of magnitude estimate at best, but certainly would not justify reporting percentage increase up to 3 significant digits (such as Page 8964 Line 20). In their paper, the authors do not expressly emphasize this important limitation and its consequences on the entire model study. They simply refer to it as part of the modeling approach, and give reference to a relevant but not very recent paper (Aumont et al., 2000). Furthermore, among the model assumptions, clouds seem not to affect gas-phase photolysis at all (Page 8959, Line 11-12). In addition, clouds are also treated in a very simplistic way: monodisperse clouds are assumed to occupy the entire boundary layer of 1000 m height for three hours each day. It would have been interesting to see how important cloud reactions remain if clouds occupy part of the boundary layer and affect actinic flux as they normally do. In general, the paper is very valuable as a comprehensive modeling study, but its limitations must be explicitly stated (also in the Abstract and Discussion) and the conclusions need to be formulated in the light of these limitations.

Responses: 1). Regarding several assumptions used in zero-dimensional model studies, many of these assumptions have been used in other similar studies. For example, occupation of the clouds over the entire boundary layer (Lim et al., 2005); cloud droplets are monodisperse (Gelencser and Varga, 2005; Lim et al., 2005); clouds do not affect gas-phase photolysis rates (Ervens et al., 2004; Lim et al., 2005). A sensitiv-

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ity analysis of the zero-dimensional model simulation indicated that the model results changed very little when the photolysis rates in clouds were reduced by 50% compared to clear sky conditions. In addition, the three-dimensional model simulation represents more realistically atmospheric conditions. Resolved cloud information is from meteorological input and is dependent on each grid cell (approximately 10 vertical layers were used for the boundary layer in the three-dimensional model) and hour. The effect of clouds on photolysis rates is also considered in the CMAQ model.

2). Regarding the assumption of complete conversion of aldehydes to the corresponding carboxylic acids, we have added explicit words about its limitation in the abstract and the conclusion. At the end of the abstract part, we added "Because aldehydes of carbon number greater than four are assumed to convert fully to the corresponding carboxylic acids upon reaction with OH in cloud droplets and this assumption may overestimate carboxylic acid formation from this reaction route, the present study provides an upper bound estimate of SOA formation via this pathway.". In the conclusion part (the second paragraph of Section 4), we added "The assumption that aldehydes of carbon number greater than four fully convert to the corresponding carboxylic acids may overestimate the yield of carboxylic acids from the reaction of aldehydes with OH in clouds. Thus the results from the current study represent an upper-bound estimate of SOA formation via this route in clouds." Finally, the numerical results are now reported up to two significant digits at most throughout the entire paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8951, 2007.