

Interactive comment on “Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs low-yield pathways” by D. K. Henze et al.

Anonymous Referee #2

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This manuscript applies in a global model the results of recent laboratory findings on the NO_x-dependence of aromatic SOA formation. Ng et al (2007) from the same Cal Tech group have reported high non-volatile yields for SOA formed under low-NO_x conditions, while SOA formed under high-NO_x conditions is similar to previous results from Odum et al. (1996, 1997). Several new patterns emerge, including a large contribution of benzene to aromatic SOA formation in the far field where NO_x has been depleted, and more SOA formation in the summer than the winter due to higher HO₂/NO ratios. This topic belongs in ACP and the paper is clearly written and of appropriate length. I recommend publication in ACP after some revisions to address the items below.

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Main Items

* An important comment relates to the degree of uncertainty of these results. Here a relatively simple chemical mechanism derived from smog chamber experiments under high concentrations and short times (~ 8 hr) is applied to the global atmosphere where much lower concentrations and longer times are relevant. Most importantly, the results for benzene under low-NO_x are based on a single chamber experiment (#9 on Table 3 of Ng et al, 2007), which produced 3x the yield of the one previous low-NO_x experiment (Martin and Wirtz, 2005). Also the NO_x levels for the high-NO_x experiments are 1-2 orders of magnitude higher than in the urban atmosphere. Although the authors argue in the paper that this is not important based on known chemistry, non-anticipated secondary chemistry is possible and could yield surprises as it has before (for example Docherty and Ziemann, 2003). Other parameters such as effects of NH₃ (Na et al., 2006), RH (Cocker et al., 2001), and seed composition (Song et al., 2007) on the low-NO_x pathway have not been explored. This paper is a very valuable exercise in propagating the new results of Ng et al. into a global context. However the remaining uncertainties are very large and much more research is needed on this topic. It seems to me that the paper doesn't quite communicate that degree of uncertainty in its text, and would benefit from more precisely acknowledging it. A quantitative estimate of the uncertainties would be a very useful addition to the paper.

* The low-NO_x mechanism is less relevant under urban or near-field polluted conditions and the high-NO_x yields have not changed compared to those of Odum et al. Then the studies of de Gouw et al. (2005), Volkamer et al. (2006), and Kleinman et al. (2007), all of which find about an order of magnitude more SOA than predicted from the aromatic yields of Odum et al., show pretty conclusively that there are additional precursors contributing to anthropogenic SOA formation. The wording in the manuscript of "it would appear there are additional pathways" (abstract and end of section 5) seems much too weak in this context. Based on those studies, it is very likely that total anthropogenic SOA is several times larger than calculated here (see for ex-

ample the estimate in Volkamer et al., 2006), and a global apportionment of the order of 30 anthrop / 70 biogenic seems more likely to me based on current evidence than the 10 / 90 presented here. I suggest that this context is discussed in the revised paper.

Various Detailed Comments

* The SOA formation mechanisms in clouds (Turpin, Ervens, and others, for example Lim et al. (2005)) and from intermediate volatility precursors (Robinson et al., 2007) deserve mention in the paper.

* Page 14571 line 5; SOA can also be formed through cloud processing or heterogeneous reactions, not only gas-phase reactions.

* Page 14571 line 13: Johnson et al. (2006) and Kleinman et al. (2007) can also be cited here.

* Page 14571 line 15; I suggest replacing "are generally considered" with "have been traditionally considered." As discussed above, there are many recent results that point to the importance of other precursors.

* Page 14572 line 5; it seems that a citation is missing for the updated runs of the Tsigaridis model with the Song et al yields.

* Page 14572 line 9; this should be clarified: it reads as if Pun and Seigneur had identified benzene as an important SOA precursor, when the credit really belongs to Martin and Wirtz (as properly credited by Pun and Seigneur).

* Page 14576; the NO_x emissions inventory used should also be mentioned and a citation given, since use of a different inventory could result in different amount and distribution of aromatic SOA.

* Page 14577 line 18: recent work by Song et al (2007) indicates that primary organic material may not serve as partitioning mass for SOA. Although more research in this topic is needed, this possibility would reduce the amount of SOA formed in the model

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and should at least be mentioned in the paper.

* Page 14580 line 20; both the burden and annual production rates should be given here. Currently the annual production from this study of 3.5 Tg/yr is given in the abstract but not in the text.

* Page 14581, line 3; the new global burdens would be most accurately described as "more than three times the range of previous estimates."

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