

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

D. K. Henze et al.

Received and published: 7 January 2008

Reviewer comments are italicized. References to specific text of the revised manuscript are given as sYpZ for section Y, paragraph Z.

** 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 ex-*

periment (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.

A new section (Section 5) devoted to discussion of uncertainty is now included in the revised manuscript. Uncertainties arising from several aspects of the model are discussed, and they are quantified when possible. The resulting qualified estimate of SOA production from aromatic hydrocarbons is reported as 2 – 12 Tg/yr. Specifically, the issues raised by the reviewer in the above comment are addressed as follows. First, uncertainty associated with the SOA yields of benzene are assessed. The yields determined by Martin-Reviejo and Wirtz (2005) are taken to constitute a lower bound, see s5p1 and response to comment (2) of reviewer #1, yielding an SOA production of 0.5 – 1.0 Tg/yr from benzene as a lower estimate. The consequences of a lack of preexisting organic aerosol are estimated to underestimate SOA production by a factor of two at most. The consequence of additional factors, such as the effect of RH on partitioning and the specification of the available substrate for partitioning, are discussed with references to works of Cocker et al. (2001) and Song et al. (2007). Though the effect of acid vs non-acid seed was found to be negligible in Ng et al. (2007), the work of Na et

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al. (2006) is cited as a source of uncertainty resulting from heterogeneous chemistry that is not accounted for by the current mechanism, s5p4.

** 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 example 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.*

Interestingly, the more recently determined high NO_x yields are actually a few percent higher than those from Odum et al. (1996), see Figure 11 of Ng et al. (2007). However, it is indeed an important conclusion that anthropogenic sources beyond those considered here likely contribute to SOA formation. Additional comments to this effect, beyond those already given in the initial submission, expand up this in s6p2, and the wording has been made stronger in the abstract and conclusion.

** 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.*

The section on uncertainty now includes discussion of mechanisms for SOA forma-

tion from aromatics not included in the present work. In the conclusion (s7p5) and elsewhere (s6p2), there is now a discussion of sources of anthropogenic SOA beyond partitioning of the semivolatile gas-phase products considered here. This discussion necessarily considers the formation of SOA from intermediate volatility precursors (Robinson et al., 2007).

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

Good point. The sentence has been reworded to read “A significant fraction of organic aerosol material results from the physical and/or chemical processing of volatile gas-phase hydrocarbons to yield less volatile products that condense into the particulate phase; this is referred to as secondary organic aerosol (SOA).”

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

The work of Kleinman et al. (2007) is an additional observationally based study that is referenced at this point in the revised manuscript. It would already have been included had it been published prior to the initial submission. We now cite Johnson et al. (2006), though at a later point (the third paragraph), as this work focuses more on modeling.

** 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.*

Done.

** 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.*

The reference to Tsigaridis et al. (2006) has been added.

** 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).*

The sentence has been rewritten as “SOA formation from benzene, as identified by Martin-Reviejo and Wirtz (2005), has been noted to be an important additional pathway in the box model studies of Pun and Seigneur (2007) and the Lagrangian trajectory model of Johnson et al. (2006).”

** 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.*

The section on aromatic emissions is now expanded to include a description of the NO_x, isoprene, and primary organic aerosol emissions, see s3.1p2.

** 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 and should at least be mentioned in the paper.*

This is now mentioned in s5p2, which reads “In contrast to models that assume any organic aerosol mass as part of the available substrate, Song et al. (2007) found that the presence of a hydrophobic organic seed did not enhance partitioning. The implications would be an overestimate of SOA formation in the current model near sources of primary (hydrophobic) organic aerosol.”

** 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.*

Done.

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

True. Revised estimates from Heald et al. (2007) make the range slightly narrower, so the sentence now reads “Overall, the range of estimated global burdens of aromatic SOA from recent simulations (0.04 – 0.08 Tg) is nearly three times the range of earlier estimates of 0.01 – 0.03 Tg (Tsigaridis and Kanakidou, 2003).”

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14569, 2007.