

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

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

However, the authors make it clear in their introduction that their goal is to present a meaningful and conservative estimate of SOA from AVOC in a global context. Such ambition necessarily requires a critical discussion of how meaningful the precursors and processes represented in their model really are for the atmosphere. Such discussion is rather limited in the current manuscript, and the literature that provides for relevant discussion points is currently incompletely represented. The inherent assumption

made by the authors is that “SOA from aromatics as the result of the partitioning of semivolatile oxidation products” can for all practical means and purposes be equated with “anthropogenic SOA”. This assumption is weakly supported by the recent literature. The effect is that the paper creates an arguable impression, i.e., that the model is indeed to make meaningful estimates of SOA formation from AVOC, while in fact a lower limit number is estimated.

There are several reasons why estimates of SOA formation from these pathways in the current model can not be taken strictly as a lower bound. See response to comment (2) and (4), and also uncertainty associated with factors mentioned by other reviewers, such as the effective ΔH_v of SOA (s5p2), the inclusion of hydrophobic organic aerosol as a substrate for partitioning (s5p2), and variability between models (s5p5).

The level of certainty of the model output remains difficult to judge from the current manuscript, and would benefit from an expanded discussion of uncertainty. Such discussion should address (1) the quantitative uncertainty of the precursors and processes currently represented in their model, and (2) uncertainty due to precursors and/or processes of SOA formation that are currently not represented in their model but relevant to the topic of SOA formation from AVOC.

An entire new section (Section 5) devoted to uncertainty in the model is now included. The estimated range of uncertainty for the SOA production from aromatics via the pathways identified here is 2 – 12 Tg/yr (s5p6). Remaining uncertainty owing to processes not included is also addressed (s5p4), as is the likelihood of additional sources of anthropogenic SOA (s6p2). These points are reiterated in the conclusion (s7p4–5) and the abstract.

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1) *The paper explicitly equates “SOA from the partitioning of semivolatile oxidation products from aromatic VOC” as “SOA from anthropogenic hydrocarbons” (on page 14571, line 15 it reads “Among anthropogenic hydrocarbons, aromatic compounds are generally considered to be the most important SOA precursors”). Throughout the following manuscript the validity of this fundamental assumption remains not further supported.*

This sentence is simply a statement of historical context (Chung and Seinfeld, 2002; Kanakidou et al., 2005). Rather than an assumption, this sentence is addressed as a hypothesis in clear need of revision given recent advances in our understanding of the SOA yields from aromatics (Ng et al., 2007) since the work of Odum et al. (1996, 1997) upon which it is based. To clarify, the wording has been changed to read “has previously been” instead of “are generally.” As is now clear, the present work does not propose that aromatics constitute the exclusive source of anthropogenic SOA.

It is limited to rather vague mentioning in the abstract “it would appear there are additional pathways beyond those accounted for here for production of anthropogenic SOA”, and on page 14582 line 16 “it would appear that additional mechanisms for anthropogenic SOA formation still exist beyond those presently considered”. The associated uncertainty remains unaddressed in the present manuscript. This vague discussion is not representative of the considerable level of certainty emerging from the recent literature, i.e., that SOA from AVOC is much larger than the 3.5 Tg/yr suggested by the authors. For example, the effect of missing precursors and/or missing processes that form SOA from AVOC could produce up to 25 Tg/yr SOA (Volkamer et al. 2006), i.e., this is seven times the estimate presented by the authors.

That such updated estimates still fall considerably short of SOA production implied by recent field campaigns is indeed an important conclusion. The original manuscript

makes this point more saliently than the reviewer suggests (see lines 5 - 18 of page 14582). Nevertheless, this is now given more explicit attention in the conclusion (s7p5), the abstract, and in the discussion of anthropogenic SOA (s6p2). An upper theoretical limit, assuming aromatics form SOA with more than a 100% yield, is in the range of 25 – 30 Tg/yr (s5p6).

As argued in that study up to one third of SOA could be from AVOC. The primary uncertainty in the extrapolations of a few data points obtained in a highly polluted atmosphere (Volkamer et al. 2006) to the global atmosphere, consists in whether abundant amounts of organics in the aerosol phase could lead to increased partitioning of semivolatile organic vapors, that would not be relevant for SOA from AVOC emitted in less polluted regions. This extrapolation appears however to be justified in light of recent findings by Kleinman et al. 2007, which corroborate the previous results from Mexico City extending them to lower organic aerosol concentration levels, and further present a direct comparison to the eastern U.S., where organic aerosol levels are considerably lower. Kleinman et al. 2007 mention in their abstract that 8221;a comparison of OA/CO in Mexico City and the eastern U.S. gives no evidence that aerosol yields are higher in a more polluted environment.8221; A meaningful model estimate of SOA from AVOC in a global context requires a critical discussion of how meaningful the precursors and processes represented in the model really are.

Several references that provide plausible explanations for additional SOA sources from AVOC are currently missing in the manuscript (see Goldstein and Galbally, 2007; Robinson et al., 2007; Volkamer et al., 2007). Discussion of how these studies would affect the results should be included. This should include discussion of (1) the uncertainty in extrapolating chamber data to the atmosphere (in terms of the deviation of oxidation pathways of aromatics at high NO_x, and additional SOA from low-NO_x chemistry of

aromatics, see also below points 2-4), (2) the uncertainty from missing precursors and missing processes, and (3) the uncertainty due to additional positive feedbacks from increased partitioning in more abundant organic aerosol if these precursors / processes were represented in the model. An attempt would be useful to set error bars to the global production from AVOC, which will be much higher, possibly up to ten times larger than the SOA production currently estimated by the authors. This major uncertainty in the atmospheric relevance of the processes / precursors reflected in their model is currently not adequately reflected in the manuscript. It would be very useful if an attempt could be made to quantify this uncertainty.

The studies of Kleinman et al. (2007) and Volkamer et al. (2007) were published after our article was submitted, so clearly they were not purposefully excluded from our discussion. Given the pace at which research is being performed in this area, we ask for some lenience regarding full consideration of works that have been published after our article was submitted. References to these works, and to the works of Goldstein and Galbally (2007) and Robinson et al. (2007), are now given in s1p1, s5p4, s6p2 and s7p5. Also included in the revised manuscript is discussion of uncertainty due to (1) extrapolating chamber data to the atmosphere (s5p1), (2) missing precursors and missing processes (s5p4), (3) feedbacks from partitioning (s5p2).

2) Another primary point made clearly by the authors refers to the NO_x dependence of SOA yields from aromatics. On page 14573 line 3ff it is said that the single experiment on the SOA yield from benzene at low NO_x from Ng et al. 2007 yielded an about three times higher yield than two consistent experiments by (Martin-Reviejo and Wirtz 2005) conducted under similar experimental conditions, but in the absence of a seed. One may argue that the presence of a seed accelerates SOA formation (Kroll et al. 2007), or that the absence of yield parameters (saturation yields and

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partitioning coefficients), and, as argued in the following text “Additional factors, such as the uncertainty in the benzene threshold concentrations⁸²²¹; in (Martin-Reviejo and Wirtz 2005) complicate a comparison to (Ng et al. 2007). However, while a seed may accelerate SOA formation, as argued in (Kroll et al. 2007), the existence of a benzene threshold concentration has a small effect on the SOA yields (overall yields are only 25-35% smaller than the maximal yields) compared to the difference in SOA yields (a factor of 3). It is noted that the authors call for additional experiments in this context. However, the difference between the two studies appears difficult to resolve based on the existing data. The uncertainty that arises from choosing the Ng et al. 2007 number should be quantified, i.e., what are the implications if the numbers by (Martin-Reviejo and Wirtz 2005) were used instead?

Assuming that the yields of Martin-Reviejo and Wirtz (2005) are for irreversible SOA formation, then it is easy to apply these yields (either total or max yield) both from the NO_x free experiments (6.1 – 6.7% or 8.1 – 8.7%, neglecting 170703B) and from the NO_x experiments (10.5 – 14.3% or 13 – 25%) to the amount of benzene estimated to proceed via the low (51%) vs high-NO_x pathways (49%) in our model. With a total benzene source of 6.1 Tg/yr, then the estimates for SOA formation from benzene using the data from Martin-Reviejo and Wirtz (2005) are in the range of 0.5 – 1.0 Tg/yr, which is less than the value of 1.68 Tg/yr that we estimate using the data from Ng et al. (2007). These estimates are given in s5p1.

There are further potentially relevant details in the study by (Martin-Reviejo and Wirtz 2005). For example, a constant SOA yield was observed for benzene in the absence AND in the presence of NO_x, i.e., at constant NO_x levels of 5-7 ppb. It should be noted, that the study by (Martin-Reviejo and Wirtz 2005) is breaking novel ground in keeping NO_x controlled, and constant. There is no previous study of SOA formation with this level of

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control on the employed NO_x concentrations. The results are in apparent conflict with the curvature of Odum curves that are widely used to parameterize SOA from experiments that are subject to highly variable NO_x concentrations over the course of an experiment. Apparently SOA yields depend on the experimental procedure with which the yields are derived. The implications of a constant (and higher) SOA yield in the presence of few ppb of NO_x as observed by (Martin-Reviejo and Wirtz 2005) for benzene could be fundamental: (1) SOA yields could be independent of the organic aerosol mass available for partitioning in the absence AND in the presence of NO_x (which would simplify parameterizations of SOA yields in models), (2) it poses the question whether the NO_x dependence of SOA yields is well constrained from currently available chamber data, given that NO_x levels are highly variable in experiments of the type as they were conducted in Ng et al. (and most chamber studies), and (3) SOA yields in the presence of NO_x could be higher by up to a factor of two for typical NO_x and organic aerosol mass loadings in urban outflow.

In response to the reviewer's enumerated implications: (1) Likewise, it is easy to estimate global SOA production from such pathways. This is used to estimate the outcome of utilizing data from Martin-Reviejo and Wirtz (2005) in the calculations given in s5p1. (2) The NO_x levels in Ng et al. (2007) were not variable, at least with regards to RO₂ chemistry. They were either so high that RO₂ + NO dominated or so low that RO₂ + HO₂ dominated. (3) The possibility of enhanced aromatic yields in the presence of preexisting organic aerosol, as would be found in an urban outflow, if not much of the NH (Zhang et al., 2007), is considered as an upper bound of SOA formation of 6.8 Tg/yr, see s5p1.

3) page 14573 line 24ff: There is an error in the interpretation of the effect of elevated concentrations of NO_x on the oxidation pathway of aromatic

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hydrocarbons. It is not correct that 8221; levels of NO up to ppm8221; are not expected to affect the aromatic oxidation pathway. This misconception by the authors seems to arise from their discussion being limited to NO_x reactions of the aromatic-OH adduct. In the real atmosphere, however, the aromatic-OH is rapidly scavenged by reversible addition of O₂ to form a peroxy radical (aro-OH-O₂); the aro-OH-O₂ concentration exceeds that of aro-OH at ambient O₂ concentrations (Bohn and Zetzsch, 1999; Bohn 2001; Raoult et al. 2004). The primary effect of NO (that is neglected in Ng et al. and in the discussion of uncertainties also in this study) consists in NO to compete for the fate of aro-OH-O₂, which is relevant already at NO concentrations well below 1 ppm, i.e., on the order of 100 ppb for benzene and other alkylbenzenes (Volkamer et al. 2002; Klotz et al. 2002; Volkamer et al. 2002b). In the study by Ng et al. 2007 initial NO and NO₂ concentrations were in excess of 100 ppb for virtually all experiments (with the exception of benzene). The effect of NO on the fate of aro-OH-O₂, together with point 2, and the NO₂ effect on aro-OH add to the uncertainty of SOA estimates from AVOC, and is worthy to be acknowledged as such.

The effect of NO on the fate of the R-OH-O₂ peroxy radical is in fact considered in both the work of Ng et al. (2007) (paragraph 3 of section 4.1) and the original submission of this work (page 14573, lines 24–26: "...nor are levels of NO up to ppm expected to prevent formation of the bicyclic peroxy radical from its isomer that initially results from O₂ addition (Zhao et al., 2005; Fan et al., 2006).") It has been slightly reworded in the revised manuscript to read "...nor are levels of NO up to ppm expected to prevent formation of bicyclic peroxy radicals from the hydroxy cyclohexadienyl peroxy radicals..."

Further, the use of NO_x concentrations taken from the 2x2.5 degree model cells to assess the effect of NO_x on SOA yields (page 14578 line 18f) should be removed. The uncertainty from deviated oxidation pathways

as the result of NO_x reactions is inherent to the chamber study (Ng et al. 2007), and hence part of the parameterizations used as input to the model; it could not possibly be assessed using the model.

This sentence does not pertain to interpretation of chamber yields of SOA, rather it notes that even if additional pathways that depend upon high absolute NO_x concentrations were included in a global model, their effect would be minimal owing to representational error.

4) page 14578 line 25ff: The only two measurements of RO₂/HO₂ ratios in the atmosphere indicate values of this ratio in excess of unity, i.e., up to 5 (Stevens et al. 1997; Mihelcic et al. 2003).

There are other observations that report a 1:1 ratio, see discussion below.

These ratios were found inconsistent with the current understanding of RO_x chemical cycles (Mihelcic et al. 2003), reflecting that the chemical representation of radical cycling at low NO_x is currently not well represented in models / constrained by laboratory experiments. The field evidence in both studies is certainly of high quality, and the values derived are beyond experimental uncertainty. Use of these ratios and the kinetic data presented in the paper would suggest RO₂ self reactions could be relevant in the atmosphere, albeit these reactions are suppressed in the underlying chamber study. The current paper suggests that an uncertainty due to the suppressed RO₂ self reactions in (Ng et al. 2007) is unlikely a problem with extrapolating these yields to the atmosphere based on an argument made on page 14578 line 25ff. The argument is not transparent to the reviewer. Moreover, use of a model to create any sense of certainty does not seem justified based on the (scarce) field evidence. RO₂ self reactions

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would lower SOA yields (see also point 2 in this context), as the products are significantly more volatile than the homologue products of the RO₂+HO₂ reaction channel. Further, the effect of temperature on the RO₂ self reaction rate constants and SOA yields is not clear, and the complex mix of RO₂ species in the atmosphere may behave differently to that in the chamber.

These issues are addressed in an expanded discussion in s5p3, “Regardless of the treatment of partitioning, it is not certain that the gas-phase chemical reaction scheme inferred from the chamber studies, (R1) - (R3), will similarly dominate in the atmosphere. As noted in Section 2, this scheme does not include reaction of the bicyclic peroxy radicals with themselves or other peroxy radicals. The consequences of reaction with other peroxy radicals would likely be formation of species with different volatility than those formed from reaction with HO₂. Observational constraints of the atmospheric concentrations of RO₂ and HO₂ have found RO₂ to HO₂ ratios ranging from 1:1 (Hanke et al., 2002) to up to 5:1 (Mihelcic et al., 2003, Stevens et al., 1997), though since these were determined at ground level, they likely represent upper bounds on this ratio in the atmosphere. However, 57% of the SOA production in the present model occurs above the boundary layer, so SOA production could be likely affected by at most 43% if such competition takes place only near VOC sources. For this to happen, the peroxy radical concentrations must exceed those of NO and HO₂ by much more than an order of magnitude as the rate constant for RO₂ + R’O₂ at 298 K is slower (likely $< 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ given their level of substitution) than k_N ($8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) or k_H ($1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Hence this seems unlikely, as even the observed ratios of RO₂ to HO₂ are not that high. Self-reaction of the bicyclic peroxy radical also seems rare since estimated concentrations of even the parent aromatic species are typically on the order of only a few ppb near source regions, where modeled NO_x concentrations are of order 0.1 ppb and/or HO₂ are 10 ppt.” With respect to the other significant sources of uncertainty listed in Section 5, uncertainty associated with such additional peroxy radical chemistry seems small.

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