Atmospheric Chemistry and Physics Discussions

Interactive Comment

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 #1

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The study by Henze et al. "Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: High- vs low-yield pathways" investigates the global relevance of recent simulation chamber results that parameterize the NOx dependence of SOA yields from benzene, toluene and m-xylene, by Ng et al. (2007). The paper is generally well written, and presents the results on the NOx dependence on SOA yields clearly.

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

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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. 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.

Specific comments are:

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. 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 miss-

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ing 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. 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 "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." 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 NOx, and additional SOA from low-NOx 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.

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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.

2) Another primary point made clearly by the authors refers to the NOx 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 NOx 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 partitioning coefficients), and, as argued in the following text "Additional factors, such as the uncertainty in the benzene threshold concentrations" 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 ?

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 NOx, i.e., at constant NOx levels of 5-7 ppb. It should be noted, that the study by (Martin-Reviejo and Wirtz 2005) is breaking novel ground in keeping NOx controlled, and constant. There is no previous study of SOA formation with this level of control on the employed NOx concentrations. The results are in apparent conflict with the curvature of Odum curves that are widely used to parameterize SOA from

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experiments that are subject to highly variable NOx 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 NOx 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 NOx (which would simplify parameterizations of SOA yields in models), (2) it poses the question whether the NOx dependence of SOA yields is well constrained from currently available chamber data, given that NOx 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 NOx could be higher by up to a factor of two for typical NOx and organic aerosol mass loadings in urban outflow.

3) page 14573 line 24ff: There is an error in the interpretation of the effect of elevated concentrations of NOx on the oxidation pathway of aromatic hydrocarbons. It is not correct that "levels of NO up to ppm" are not expected to affect the aromatic oxidation pathway. This misconception by the authors seems to arise from their discussion being limited to NOx 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.

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

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). These ratios were found inconsistent with the current understanding of ROx chemical cycles (Mihelcic et al. 2003), reflecting that the chemical representation of radical cycling at low NOx 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 would lower SOA yields (see also point 2 in this context), as the products are significantly more volatile that 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.

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