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## ***Interactive comment on “Modeling secondary organic aerosol formation from isoprene oxidation under dry and humid conditions” by F. Couvidat and C. Seigneur***

### **Anonymous Referee #1**

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Review comments on modeling secondary organic aerosol formation from isoprene oxidation under dry and humid conditions, by F. Couvidat and C. Seigneur

General comments:

This paper presents a new module for simulating secondary organic aerosol (SOA) from isoprene based on recently published laboratory experimental data and chemical kinetic data for important oxidation reactions. This work is very important and interesting to both air quality and climate research communities, as it focuses on SOA that has significant impacts on particle pollution (because SOA is a significant component of PM<sub>2.5</sub>) and climate change (because SOA has a large activation potential and can

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serve effectively as cloud condensation nuclei (CCN) under both polluted and clean conditions such as coastal areas where isoprene emissions from oceanic phytoplankton may be significant), yet subject to largest uncertainties in its formation mechanisms, in particular, SOA from isoprene. It is also very timely. Although there have been several modules developed for simulating isoprene SOA in 3-D models (e.g., either based on simple yield approach, or an absorption approach under low NO<sub>x</sub> conditions, or assuming a linear interpolation between the low and high NO<sub>x</sub> incremental SOA mass such as the work presented by Stroud et al. at the 2009 CMAS annual meeting in the U.S.), none of them were physically-based modules that are able to simulate isoprene SOA formation under both low and high NO<sub>x</sub> conditions.

Despite some uncertainties associated with some assumptions, the physically-based SOA module presented in this paper distinguishes it from previous work on this subject in two main aspects. First, the new module developed in this work is applicable to both low (including none) and high NO<sub>x</sub> conditions, whereas nearly all other isoprene SOA modules that are currently used in 3-D air quality models were developed under low NO<sub>x</sub> conditions. Although isoprene SOA formed under low-NO<sub>x</sub> conditions generally dominates, that formed under high-NO<sub>x</sub> conditions may also be important under some atmospheric conditions (e.g., some areas with high biogenic emissions from either terrestrial or marine sources yet with high NO<sub>x</sub> emissions from power plants, vehicle exhausts, and marine vessels). Second, the new module accounts for the impact of high ambient humidity on isoprene SOA formation via changing the hydrophilic properties of SOA, which is often neglected by other existing isoprene SOA modules. One major finding of this work is a significant enhancement of isoprene SOA formation under high humidity conditions. This important finding attests itself the importance of accounting for such an impact in modeling SOA.

The authors have done a rigorous work to develop the module, design the model calculation, test it with experimental data, and examine major model sensitivity to key parameters and processes. The methodology is technical sound. All calculations are

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well thought-out and the material is well organized and presented. I found little to add except that some clarifications are needed for several places to provide a bit more detailed information regarding the new SOA module (e.g., molecular weight of SOA species, UNIFAC-activity coefficient calculation, etc, see specific comments (3), (15), (22)), clarify a couple of confusing points (e.g., see specific comments (7), (9), (17), (27)) elaborate the explanation of results in a few tables and figures (e.g., see specific comments (8), (11), (13), (14), (16), (18), (19), (31)), and cite a few additional references (e.g., see specific comments (1), (2), (5), (21), (33)).

To summarize, this is a well-written paper that fills in our knowledge gap in simulating isoprene SOA and addresses one of the major uncertainties in aerosol and climate modeling. The results are very important and represent a significant contribution to SOA modeling. I would strongly recommend its acceptance for publication on ACP. Only minor revisions are needed to clarify a few points and to address other specific issues as described in specific comments below.

Specific comments:

(1) Page 20561, lines 19-29, the paragraph starting “Isoprene...”, some important references should be cited in this overview paragraph, e.g.,

The work done by Jang et al. (Science, 298, 814-817, 2002) on isoprene SOA formation via particle-phase reactions and a recent review paper on isoprene SOA by Carlton et al., ACP, 9, 4987-5005, 2009.

(2) Page 20561, line 21, a reference is needed for the following statement:

“Until recently, isoprene was believed not to be a major SOA precursor, despite its large emission flux, due in part to the high volatility of its first generation oxidation products (such as methacrolein and methyl vinyl ketone).”

(3) Page 20562, lines 21-22, “under both low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions”, need to define them in terms of the ranges of ppb. What is the cutoff value between the two

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regimes selected in the SOA module?

(4) Page 20563, lines 23-24, were UNIFAC-activity coefficient calculation done once for each simulation or it requires iteration? This info is important for the application of the new SOA module in 3-D air quality models.

(5) Page 20566, line 11, R5 and line 15 about the rate constant for R5, where were they from? A reference is needed.

(6) Page 20566, lines 25-27, it stated that “The loss of SOA could be due to either gas-phase reactions (consumption of the partitioning compounds may drive equilibrium away from the particle phase) or particle-phase reactions”. First, some references should be added for each of the loss pathways. Second, what about loss due to surface absorption/adsorption/oligomerization for hydrophobic SOA and that due to aqueous dissolution and reaction/oligomerization pathways for hydrophilic SOA?

(7) Page 20568, lines 7-10, in the first statement of this paragraph, it stated “In the atmosphere, concentrations of ISOP are not typically sufficient for Reaction (R8) to be dominant”. But in the last statement, it stated “those radicals are likely to be in higher concentrations in the atmosphere and BiMT could be formed by this pathway.” The two statements seem to be contradictory because even if MO<sub>2</sub> and ACO<sub>3</sub> radicals are high in the atmosphere, BiMT formation via R10 cannot be significant if ISOP level is low. As shown in Figure 3(a), the mass of BiMT is < 1 ug m<sup>-3</sup> when ISOP is about 64 ppb. The ambient concentration of isoprene is typically in the range of 2-10 ppb, which leads to even lower BiMT. Some clarifications are needed here.

(8) Page 20568, lines 12-21, the paragraph describing Tables 2-3 and Figures 2-3a. Table 2 was derived under an ambient T of 25 °C. So were all test simulations shown in Table 3 and Figure 3. These values would need to be extrapolated under other temperature conditions. How was the extrapolation done for these values under other temperature conditions? Given a large range of T values in the atmosphere, brief discussions should be added regarding the appropriateness of the extrapolation of the

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optimal values in Table 2 under other higher or lower temperature conditions.

(9) Page 20569, lines 1-2, the statement “the pathway by which the SOA loss occurs should be clarified (particle-phase reaction, gas-phase reaction, photolysis).” This statement seems to be out of place and some transition statements are needed to place this in the context of discussions in this paragraph and also to clarify what exactly it means. For example, does it refer to the SOA loss shown in Figure 3b? Are those three causes for SOA loss based on speculations or some references? For calculated SOA, were any particle-phase reactions explicitly included? What gas-phase reactions can contribute to SOA loss under the simulated/measured conditions? For photolysis that causes SOA loss, do they occur in the gas-phase or aqueous-phase? It would be useful to give a couple of examples along with references if any for each of the loss pathways.

(10) Page 20570, lines 4-5, is the simple parameterization developed in this work? If not, a reference is needed.

(11) Page 20570, lines 16-17, some discussions should be added regarding the appropriateness of the extrapolation of optimal values used in the results in Table 4 under other temperature and RH conditions.

(12) Page 20570, lines 19-20, activity coefficients of what species?

(13) Page 20570, lines 21-26. In addition to the case with the lowest NO<sub>x</sub> level, it would also be interesting to discuss another case with initial NO = 98 ppb and NO<sub>2</sub> = 31 ppb, for which the calculated SOA is ~9-26% lower than measured, in contrast to the case with the lowest NO<sub>x</sub> level. Why will the likely causes for overestimation (e.g., too much radical HO<sub>2</sub> or missing some reactions for OH did not occur for this case? What are the possible causes for this underestimation under the relatively low NO<sub>x</sub> cases? This explanation is important, because 3 out of 6 cases show underestimation by 5-12% based on measured mean values.

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(14) Page 20571, in addition to NO<sub>x</sub> level and physical parameters such as Temp., OH radical will affect isoprene SOA formation. Brief discussions should be added regarding the effect of OH conc. on SOA formation and why this was not included in the sensitivity study in this section.

(15) Page 20571, lines 7-9, this paragraph fits better in page 20563, after “as described below”, as it offers a big picture on what were modified in the original RADM2 mechanism. In addition to the new reactions added, could the authors provide info regarding the molecular weight, enthalpy of vaporization, partitioning coefficients (or saturation concentrations) used for each ISOP SOA precursors (e.g., BiPER, BiDER, BiMGA, etc.)? A table with such info would be useful.

(16) Page 20571, lines 19-21, the statement “According to the model results, the amount of SOA decreases strongly only for low [NO<sub>2</sub>]/[NO] ratio and is below the amount of SOA formed in no-NO<sub>x</sub> conditions for very high concentrations of NO<sub>x</sub>. . .” What is the amount of SOA formed under in no-NO<sub>x</sub> conditions? Could the authors add a curve for each of the three conditions in Figure 5 to show this (or at least show one curve at low [NO<sub>2</sub>]/[NO] ratio? Please explain why SOA formation under low [NO<sub>2</sub>]/[NO] ratio and very high concentrations of NO<sub>x</sub> is lower than that formed in no-NO<sub>x</sub> conditions. What are the possible reasons for inhibition of SOA formation under such conditions?

(17) Page 20571, lines 23-24, “For higher [NO<sub>2</sub>]/[NO] ratios, it seems that the SOA yield is higher under high-NO<sub>x</sub> conditions than under low-NO<sub>x</sub> conditions.” This statement refers to the case with [NO<sub>2</sub>]/[NO] = 1, but it is not accurate for the whole range of initial NO<sub>x</sub> concentrations. As shown in Figure 5, SOA conc. are higher when NO<sub>x</sub> conc. is in a range of ~150-350 ppb than that under the low NO<sub>x</sub> conc., but SOA conc. is indeed lower under NO<sub>x</sub> > 350 ppb than that under the low NO<sub>x</sub> conc. Please reword this statement for accuracy.

(18) Page 20572, lines 5-8, there are several interesting trends for the SOA yield at

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various NO<sub>x</sub> concentrations in Fig. 7 that may be worth to explain. First, SOA yield decreases significantly when NO<sub>x</sub> increases from 100 ppb to 300 ppb, but when NO<sub>x</sub> further increases from 300 to 500 ppb, SOA yield increases in some ranges of ISOP concentrations. What are the possible reasons for such a variation trend? Second, the dependence of SOA yield on initial ISOP conc. at NO<sub>x</sub> = 100 ppb is just the opposite to that at NO<sub>x</sub> = 500 ppb for ISOP conc. > 160 ppb, why?

(19) Page 20572, section 3.2, Influence of temperature, Could the authors link the effect of T on SOA formed to the formulations/parameters that account for such dependence?

(20) Page 20572, line 19, change “by about 2 ug m<sup>-3</sup>” to “by 0.5-2 ug m<sup>-3</sup>”, because Figure 7 shows only ~0.5 ug m<sup>-3</sup> increase in SOA mass when T drops from 10° to 0° when [NO<sub>2</sub>]/[NO] = 0.1 for most initial NO<sub>x</sub> conc.

(21) Page 20573, lines 17-19, the statement “However, the study of aqueous-phase reaction (Ervens et al., 2008) was considered outside the scope of this work and was not modeled here.” The Ervens et al., 2008 ref. is for aqueous-phase reaction in cloud droplets, a more recent paper by Volkamer et al., ACP, 9, 1907-1928, 2009 indicated that isoprene SOA may be formed on aqueous aerosol particles via aqueous oxidations, which should be cited as well.

(22) Page 20574, lines 10-20, and Page 20575, lines 5-6. What is temperature for those Henry’s law constants from other references and shown in Table 6? Provide this info in the text and Table 6.

(23) Page 20575, lines 8-18, what is the activity coefficient for the organic phase in Case 1? Figure 9 shows that the SOA mass formed in Cases 1 and 4 follows a similar curve, but with different magnitudes. It would be interesting to discuss the dependence of SOA mass on activity coefficients assumed in cases 1 and 2 shown in Figure 9 (e.g., is there any linearity or non-linearity?).

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(24) Page 20575, line 14, the statement “A value of  $50 \mu\text{gm}^{-3}$  was used in the second case.”, change it to “A value of  $50 \mu\text{gm}^{-3}$  of liquid water was used in the second case.”

(25) Page 20575, line 20, the statement “(maximum of SOA formed is  $0.27 \mu\text{gm}^{-3}$ )”, should  $0.27 \mu\text{gm}^{-3}$  be  $0.027 \mu\text{gm}^{-3}$ ? The values under the Case 1 shown in Figure 8 seem all below  $\sim 0.03 \mu\text{gm}^{-3}$ .

(26) Page 20576, lines 12-13, the statement “But, contrary to the low-NO<sub>x</sub> conditions, the third case shows that a significant part of the surrogates may condense on the organic phase.” Although SOA formed on organic phase in case 3 in Figure 9 is much higher than that in Case 3, its absolute value ( $\sim 0.12 \mu\text{g m}^{-3}$ ) is still much lower as compared with SOA formed on an aqueous-phase in case 3. So, I would not say “a significant part of the surrogates may condense. . .”, instead, something like below may be more appropriate:

“But, contrary to the low-NO<sub>x</sub> conditions, the third case shows that a non-negligible (or noticeable) amount of the surrogates may condense on the organic phase.”

(27) Page 20576, lines 16-17, it stated that “Whereas, the measured SOA yield was higher for dry conditions under high-NO<sub>x</sub> conditions than under low-NO<sub>x</sub> conditions,” Some clarifications are needed for this statement, as some laboratory studies (e.g., comparing Kroll et al., 2006 under low-NO<sub>x</sub> conditions vs. Kleindienst et al., ES&T, 40, 3807-3812, 2006 under high-NO<sub>x</sub> conditions) show lower SOA yields under high-NO<sub>x</sub> conditions than under low-NO<sub>x</sub> conditions.

(28) Page 20577, lines 1 and 5 and Page 20578, line 25, change “a M<sub>water</sub>/M<sub>organic</sub> ratio” to “an M<sub>water</sub>/M<sub>organic</sub> ratio” or “a ratio of M<sub>water</sub>/M<sub>organic</sub>”

(29) Page 20577, line 9, define “AEC” before its first use.

(30) Page 20577, line 17, should “highly hydrophilic” be “highly hydrophobic”?

(31) Page 20577, lines 21-25, several questions: (a) should “see Fig. 8” be “see Fig. 9”? as Figure 11 shows results under high-NO<sub>x</sub> condition, which is the same condition

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as Fig. 9, instead of Fig. 8. (b) Fig. 9 was obtained at ISOP = 50 ppb, but Fig. 11 was obtained at ISOP = 10 ppb. Could Fig. 11 be replaced with a figure at ISOP = 50 ppb so that both figures can be directly compared? (c) In lines 24-25, it stated that “In this case, the mass of SOA is underestimated by the AEC hypothesis by 11%”, does this refer the SOA mass shown in Figures 9 and 11? Note that Fig. 11 shows  $\sim 0.68 \mu\text{gm}^{-3}$  SOA mass at hour 10, which is indeed higher (instead of lower) by  $\sim 13\%$  than the value of  $0.6 \mu\text{gm}^{-3}$  shown in Figure 9. Please clarify or support this statement with respective figures.

(32) Page 20578, section 4.3, what is additional CPU needed to account for oligomerization and additional absorption on top of the baseline treatment? This info may be important for the implementation of the new SOA module in 3-D models.

(33) Page 20578, section 4.3 on oligomerization, cite some work done by others on this (e.g., Liggió et al., ES&T, 39, 1532-1541, 2005).

(34) Page 20578, line 20, add an “s” at the end of “phase”.

(35) Page 20578, line 28, add “when its absorption is accounted for” after the statement “BiNGA can then be considered hydrophilic.”

(36) Page 20579, line 8, add ““when its oligomerization is accounted for” after the word “hydrophilic”

(37) Page 20589, Table 3. The measured SOA from Kroll et al. (2006) were obtained under NO<sub>x</sub>-free conditions, not low-NO<sub>x</sub> conditions.

(38) Page 20588-20590, please add a footnote to indicate the assumed atmospheric conditions (e.g., T = 25 °C for all Tables, RH = 5 % for Table 4).

(39) Pages 20594-20596, please indicate the conditions assumed for calculation in Figures 2-4.

(40) Page 20597, Figure 5. Change NO<sub>2</sub>/NO to [NO<sub>2</sub>]/[NO] in the figure legend to be

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consistent with its definition.

(41) Page 20602, Figure 10, the figure legend box should not be placed on top of curves in the Figure.

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