**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Formation of secondary aerosols: impact of the gas-phase chemical mechanism" *by* Y. Kim et al.

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Received and published: 4 November 2010

We appreciate the anonymous referee for reading the manuscript attentively and giving helpful comments to improve our manuscript.

Referee's general comment: this manuscript addresses the impact of two specific gas-phase chemical mechanisms (CB05 and RACM2) on resulting predictions of secondary particulate matter in Europe; the title should state this more explicitly (as opposed to generally, which gives the impression that several mechanisms were tested). Simulation of secondary particulate matter is certainly of relevance to the readership of ACP, but I will admit that I felt as if I were reading a consulting report, not a scientific manuscript. I do not feel that conclusions or interpretations beyond "these

simulation results differ between the two mechanisms because of reason x, y, or z" were made (and many of these results were intuitive). Tools and analysis techniques were unoriginal, but the scientific method used was sound. That being said, the manuscript was well written and used appropriate citations. The abstract captures the contents of the manuscript adequately. Tables provide necessary information, and the figures, while numerous and somewhat repetitive, do as well. There are no major weaknesses with this paper beyond a lack of interpretation/conclusions; however, in my opinion, this is sufficient to prevent publication.

Our responses to the general comment:

We agreed with the referee that the title of the manuscript could be misleading. It has been modified to "Formation of secondary aerosols: comparison of two gas-phase chemical mechanisms".

We have provided more details on the reasons for the differences in secondary PM formation due to the differences in gas-phase chemistry. For example, we added the following two paragraphs in the conclusion:

"The effects of a gas-phase chemical kinetic mechanism for ozone formation on SOA concentrations can be classified into three main categories: (1) direct effects that result from the design of the mechanism leading to different yields of SOA precursors (e.g., different precursor emissions due to different aggregation of molecular VOC species into VOC surrogate model species, different kinetics of VOC oxidation, different stoichiometric coefficients for VOC oxidation products such as different cresol yields in RACM2 and CB05), (2) primary indirect effects due to different concentrations of the oxidant species (OH, O_3 and NO_3), which affect the rate of oxidation of VOC species

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Discussion Paper

and (3) secondary indirect effects due to interactions among SOA species (e.g., an increase in one SOA species leads to greater organic particulate mass available for additional absorption of other SOA species).

Here, a harmonized approach was used when modifying the two mechanisms to handle SOA formation. Early treatment of SOA formation in air quality models used simple approaches where SOA formation was treated at the first oxidation step of the precursor species and only a few mechanisms have treated SOA formation at later oxidation steps (e.g. Griffin et al., 2002). We have attempted to reflect the current understanding of SOA formation by accounting for the NO_x-regime dependence of SOA formation from aromatic compounds and treating SOA formation at later oxidation steps. Accordingly, the future development of mechanisms for SOA formation will require chemical mechanisms that can account for the various gas-phase reaction steps that are important for SOA formation."

Referee's questions, suggestions and corrections

1.It should be noted that one of the major references cited (that describes the SOA model being used) [Debry et al., 2007] is not from a published, peer-reviewed manuscript. Perhaps the authors should consider providing more details on that model in this manuscript? That would certainly make an impact on the importance of this paper.

Our response: We have added a new section (Section 2.1), which provides a more detailed description of the secondary organic aerosol model (the following sections have been renumbered); a table that summarizes the SOA surrogate species, the corresponding precursors and the relevant physico-chemical properties of the

SOA surrogate species has also been added. The new Section 2.1 is presented below.

"Precursors of SOA in the model include anthropogenic compounds (aromatics, long-chain alkanes and long-chain alkenes) and biogenic compounds (isoprene, monoterpenes, and terpenoids). This model includes an explicit treatment of hydrophilic SOA species. As described by Pun et al. (2002), condensable oxidation products of VOC are grouped into two categories: hydrophobic compounds, which can be absorbed into organic particles and hydrophilic compounds, which can be absorbed into aqueous particles (typically inorganic particles containing sulfate, ammonium and possibly nitrate). When the relative humidity is very low and no aqueous particles are present, hydrophilic compounds may be absorbed into organic particles. Those condensable oxidation products are represented by a limited number of surrogate SOA species, which are selected to represent the ensemble of possible SOA species. Those surrogate SOA species are selected based on the SOA molecular constituents identified in smog chamber experiments for monoterpene precursors and their physico-chemical properties such as their octanol/water partitioning coefficient (to determine whether they are hydrophobic or hydrophilic), their saturation vapor pressure (for hydrophobic SOA species) and their dissociative properties in aqueous solutions (for hydrophilic SOA species) (see Pun et al., 2006 for details on the method for selecting SOA surrogates). Because less information on the molecular constituents of SOA is available for products of anthropogenic precursors, the surrogate SOA species were selected based on SOA molecular species derived from a theoretical chemical mechanism of the precursor oxidation (e.g., Griffin et al., 2002).

Table 1 summarizes the surrogate SOA species, their precursors, and their physico-chemical properties used in the model. For isoprene, the representation of Zhang et al. (2007) was used. Absorption of SOA into organic particles follows Raoult's law and depends on the average molecular weight of the organic particulate mixture, the

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Discussion Paper

saturation vapor pressure of the condensing SOA surrogate and its activity coefficient in the particle. Absorption of hydrophilic SOA into aqueous particles follows Henry's law and depends on the liquid water content of the particle, its pH (for mono- and dicarboxylic acids, i.e., BiA1D and BiA2D, respectively) and the activity coefficients of the dissolved species. Activity coefficients of organic compounds are calculated for both the organic phase and the aqueous phase using UNIFAC (see Pun et al., 2002 for details regarding the computational implementation of the gas/particle partitioning and activity calculations).

Oligomerization is represented according to the pH-dependent parametrization of Pun and Seigneur (2007), which applies to aqueous-phase oxo-SOA (i.e., BiA0D). In addition, it is assumed that glyoxal and methylglyoxal can oligomerize and thereby contribute to SOA formation; following Pun and Seigneur (2007), empirical gas/particle partitioning coefficients were used to that end (9.1×10^{-6} (μg / μg water) / (μg / m^3 air) for glyoxal and 5.6×10^{-12} (μg / μg water) / (μg / m^3 air) for methylglyoxal).

A major difference with previous work is the NO$_x$-dependency for SOA formation from aromatic compounds. Ng et al. (2007) showed that the SOA yields from aromatic oxidation were greater under low-NO$_x$ conditions than under high-NO$_x$ conditions. Accordingly, different yields are used for SOA formation under those different regimes with two surrogates being used for the high-NO$_x$ regimes (AnBmP and AnBlP) and one surrogate being used for the low-NO$_x$ regime (AnClP). To properly account for different yields for different NO$_x$ regimes, SOA formation is not treated as a product of the first oxidation step of the VOC precursor, but instead it is treated in later oxidation steps as discussed in Section 2.2 of our manuscript."

2.At the start of section 2.2, the authors state that oxidation of organics lowers volatility. This is not strictly always true – in some gases, fragmentation occurs that breaks

carbon chains, increasing the volatility.

Our response: We agree with the reviewer and we now mention this point for completeness as follows: "As organic gases are oxidized in the gas phase by hydroxyl radicals (OH), ozone (O_3) and nitrate radicals (NO_3), their volatility evolves. Their volatility may decrease by the addition of polar functional groups (such as hydroxyl, hydroperoxyl, nitrate and acid groups). On the other hand, oxidation products may have higher volatility than the parent organic gases due to the cleavage of carbon-carbon bonds."

3.Does copying reactions from RACM2 into CB05 as described on page 20631, line 14, homogenize the mechanisms, thereby defeating the whole purpose of this exercise?

Our response: We agree with the reviewer that our addition of reactions and species for SOA formation to RACM2 and CB05 could be confusing because it was implemented in a way that involved some duplication of parts of the RACM2 mechanism into CB05. In order to have a more harmonized approach to the modification of both mechanisms for SOA formation, we have now modified our approach slightly by adding new reactions and species for SOA formation to both RACM2 and CB05. The results are not very different but by identifying clearly the chemical species linking the gas-phase mechanism (RACM2 or CB05) to the SOA species, the SOA formation module is now better described. An example of this modification is presented in the following revised Table 2a for toluene oxidation (similar modifications were made for the xylene oxidation).

4.On page 20632, line 19, should it say that the EMEP inventory provides yearly emissions of PM, not yearly concentrations?

Our response: This has been corrected as suggested.

5.On line 24, the definitions of API and LIM should be given earlier (upon first use; those abbreviations are used previously in the text).

Our response: This has been corrected as suggested.

6.At the top of page 20633, are sea-salt emissions included in fine or coarse aerosol? Earlier the manuscript states that PM coarse is totally attributed to dust and also gives a distribution for PM fine. Is this first set of information only for emissions on land? If so, this needs to be specified. If the sea salt emissions composition is for over coastal domains, how is the sea salt distributed between fine and coarse material?

Our response: The EMEP inventory provides only anthropogenic PM emissions. For biogenic PM emissions, sea-salt emissions are included in fine and coarse aerosols. The parameterization of Monahan (1986) for indirect generation by bubbles is used. This parameterization is valid for diameters larger than 1.6 μm. The rate of sea-salt generation is assumed to be zero for diameters lower than 1.6 μm. The distribution of sea-salt emission between the different particulate sections is done by integrating the dry rate of sea-salt generation for mass between the section bounds. By assuming that the wet radius at 80% humidity is about 2 times the dry radius of particles (Gerber, 1985), 76% of sea-salt are emitted in our last section (2.5119 to 10 μm) and 28% in the section (0.6310 to 2.5119 μm). Following Seinfeld and Pandis (1998), sea-salt emissions are assumed to be made of 30.61% sodium, 55.04% chloride and 7.68% sulfate.

7.I applaud the authors' effort to evaluate the model versus observed data. However, not enough information is given regarding the temporal resolution of the data, the sites

that are used, the methodology for data generation, etc. (section 3.2).

Our response: The observations are 24-hour averages and this is now mentioned in the text. We have also inserted a new figure depicting the locations of the observation stations in the revised version of our manuscript (see Figure 1).

8.With respect to sulfate formation, the model results indicate that the predominant path-way is via SO_2 + OH. Does this occur in upper levels of the model? In general, near the surface, SO_2 deposition is thought to occur more rapidly than its homogeneous oxidation by OH.

Our response: We agree that in the planetary boundary layer, SO_2 gas-phase oxidation is commensurate with SO_2 dry deposition; however, sulfate formation via gas-phase SO_2 oxidation also occurs in upper levels of the model.

9.The statement on page 20639, line 10 concerns me in that it implies that emissions rates are different between the two mechanistic applications. This confounds their comparison of output results because, for example, you will get more SOA from compound A in a model if more of compound A is emitted. If the impact of the mechanism is to be isolated, emissions need to be identical.

Our response: The assignment of molecular organic species to the model species is an integral part of any chemical mechanism (Sarwar et al., 2008). The different emissions rates between the simulations result from the different assignment of molecular species. If one makes the emissions rates identical artificially, part of the impact of the mechanism would be hidden.

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10.The version of Figure 6 provided needs to be updated. It appears that the value being presented only has three values across the entire continent (zero, 1, and somewhere in between). I assume this is incorrect.

Our response: The figure may look confusing because of its cryptic color-bar. Nevertheless it is correct. In the figure, there are three colors: orange for $GR > 1$, green for $0 < GR < 1$ and blue for $GR < 0$. In the revised manuscript, the color-bar is displayed more clearly and we explain the color-coding of the figure in more details in the caption.

11.Corrections: 20626, lines 20 and 22, should aromatics be aromatic?

Our response: This has been corrected as suggested.

12.20627, lines 1-5, these need to be broken into two complete sentences

Our response: This has been corrected as suggested.

13.20627, line 19, references for these mechanisms should be provided

Our response: This has been corrected as suggested.

14.20627, line 20, formations should be formation

Our response: This has been corrected as suggested.

15.20629, line 17, specifies that organic reactions added/modified are described in the following paragraph. However, the following paragraph discusses N_2O_5

Our response: The statement has been corrected as "Section 2.2" instead of "the following paragraph".

16.20632, line 14, non does not need to be capitalized

Our response: This has been as suggested.

17.20637, lines 11 to 15, these need to be broken into two complete sentences

Our response: This has been corrected as suggested.

18.20638, line 11, need with between reaction and LIM; line 17, the first SOA can be removed

Our response: This has been corrected as suggested.

Additional references:

Gerber H.E.: Relative-humidity parameterization of the Navy Aerosol Model (NAM), Technical Report 8956, Natl. Res. Lab., Washington D.C., 1985.

Griffin, R.J., Dabdub, D., Seinfeld, J.H.: Secondary organic aerosol. 1. Atmospheric

chemical mechanism for production of molecular constituents, J. Geophys. Res., 107, D17, 4332, doi:10.1029/2001JD000541, 2002.

Ng, N.L., Kroll, J.H., Chan, A.W.H., Chhabra, P.S., Flagan, R.C., Seinfeld, J.H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, 2007.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20625, 2010.

Table 2a. Toluene oxidation chemistry for SVOC formation.

RACM2	CB05
TOL + HO → 0.25 TOLPAEC* + other products	TOL + OH → 0.25 TOLPAEC* + other products
TOLPAEC + HO2 → 0.78 AnClP + HO2** [†]	TOLPAEC + HO2 → 0.78 AnClP + HO2** [†]
TOLPAEC + MO2 → 0.78 AnClP + MO2** [†]	TOLPAEC + MEO2 → 0.78 AnClP + MEO2** [†]
TOLPAEC + ACO3 → 0.78 AnClP + ACO3** [†]	TOLPAEC + C2O3 → 0.78 AnClP + C2O3** [†]
TOLPAEC + NO → 0.053 AnBlP + 0.336 AnBmP + NO** [†]	TOLPAEC + NO → 0.053 AnBlP + 0.336 AnBmP + NO** [†]
TOLPAEC + NO3 → 0.053 AnBlP + 0.336 AnBmP + NO3** [†]	TOLPAEC + NO3 → 0.053 AnBlP + 0.336 AnBmP + NO3** [†]

*: new peroxy radical formed from toluene, **: oxidant species added as a product to retain the original gas-phase mechanism, [†]: new reactions added to both RACM2 and CB05 mechanisms for the SVOC formation.
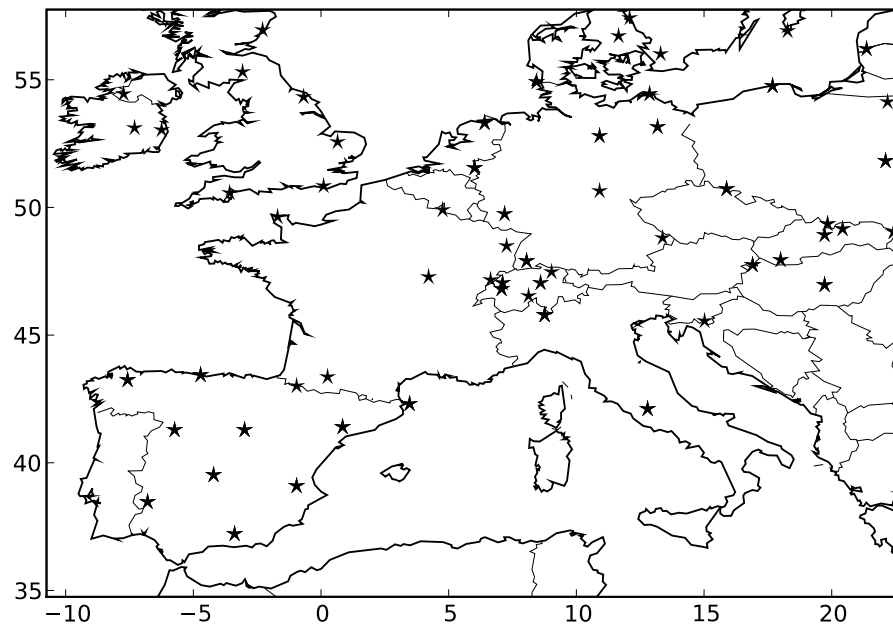
Fig. 1. Locations of the EMEP observation stations.