Atmos. Chem. Phys. Discuss., 3, S1067–S1070, 2003
www.atmos-chem-phys.org/acpd/3/S1067/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global modelling of secondary organic aerosol in the troposphere: A sensitivity analysis" *by* K.Tsigaridis and M. Kanakidou

K.Tsigaridis and M. Kanakidou

Received and published: 22 July 2003

We would like to thank Serena Chung for the time she has spent to read and comment our manuscript. We find her comments very useful pointing out the parts of our manuscript that are not clear to the reader. Consideration of her comments will definitely improve the presentation of the manuscript so that the readers will understand the details of our work.

Specifically:

Major comments

1. Evaporation

We do know that some of our simulations are extreme cases but they are not 'mathe-

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matically' wrong. The presented sensitivity studies aim to give upper and lower limits to the SOA production since the fate of the condensed SOA compounds is not yet satisfactorily investigated in chamber experiments.

In the revised manuscript we will rephrase the discussion starting from line 8 on page 2889, to clarify the aim of the performed simulations that correspond to two groups of extreme cases:

- In the first one in which the total aerosol phase has the potential to fully evaporate, the equilibrium is calculated considering the sum of the gas and aerosol phase. This approach neglects any possible chemical reaction on aerosol and particularly those leading to non-volatile products (cases S1 and S3).

- The second one that provides an upper limit of the SOA production, considers that all semi-volatile organics undergo chemical or physical processes on particles (e.g. chemical reactions to form non-volatile compounds and/or inhibition of evaporation by other non-volatile components on the particle) that suppress the evaporation of SOA (cases S2 and S4). In this latter case, the equilibrium equation is applicable only to the gas phase of the semi-volatile compounds. Mathematically this leads to the same result with the assumption that Aio=0 in the equation of page S870 of the interactive comment.

However, none of these groups reflects the reality, since it is expected that some reactions do occur on the particles but they do not necessarily transform the total amount of SOA to non-volatile. To make this clear, we will rephrase the description of the equation (21) in the revised manuscript. We will also rephrase the description of the simulations in Table 4, replacing 'without evaporation of pre-existing SOA' by 'with 100% conversion of pre-existing SOA to non-volatile constituents'.

2. Simulation S1.3

To our understanding, the chamber experiments do not disqualify our approach for the secondary oxidation products. To support this, we performed simple box model calculations of the aerosol yield for both cases (S1 and S1.3): without and with the assumption of the secondary oxidation of the products (a-pin-P1, a-pin-P2, equations 4 and 5).

The following reactions have been considered in these cases.

For Case S1 - without the secondary oxidation of the products:

a-pinene + O3 -> a1 (a-pin-P1) + a2 (a-pin-P2) + other gas phase products (equation 2 of the manuscript)

For Case S1.3 - with the secondary oxidation of the products: a-pinene + O3 -> a1 (a-pin-P1) + a2 (a-pin-P2) + other gas phase products (equation 2 of the manuscript)

a-pin-P1 + oxidants -> Bb + other gas phase products (equation 4 of the manuscript)

a-pin-P2 + oxidants ->Bb + other gas phase products (equation 5 of the manuscript)

For the box model simulations we fixed O3 at the increased pattern measured during the Griffin et al. (1999a) chamber experiment (figure 9 in Griffin et al., 1999a), OH at 1E6 molecules/cm3 (Odum et al., 1997), temperature at 298 K and adopted an initial a-pinene concentration of 70 ppbv consistent with some of the chamber experiments performed by Griffin et al. (1999a).

Under these conditions, the lifetimes of a-pin-P1 and of a-pin-P2 (with respect to their reactions with O3 and OH) are about 32 and 1.5 times longer than the precursor molecule, a-pinene, respectively. For both simulations SOA mass was calculated as described in the manuscript for the 3-d model. Then the aerosol yield (Y) was derived by:

Y= Delta Mo/Delta HC

The calculated difference in the aerosol yield between S1 and S1.3 (box model simulations) exceeds 1%, 2% and 3% after about 7.5, 11 and 19 hours of simulation, respectively. To our knowledge, most chamber experiments do not last long enough to detect these expected differences in the aerosol yield that are also within the uncertainty of the experimental data. Therefore, simulation S1.3 is not inconsistent with the published chamber experiments.

3. Black Carbon can absorb SOA.

Indeed, in our study we consider that the semi-volatile products can partition also on black carbon (BC). As commented by S. Chung the so-called ’BC’ consists both from graphitic carbon and organic material at percentages not precisely quantified. Therefore, in our study we include black carbon as an absorptive medium for SOA with decreased ability compared to the pre-existing SOA. This is parameterized using an activity coefficient of 0.7 (for insoluble BC) to 0.8 (for soluble BC) that is smaller than that of 1.0 adopted for SOA (equation 19; table 2). The discussion concerning BC as absorptive matter for SOA will be extended to include the above mentioned clarifications.

Summarizing, we do believe that the cases S1.3, S2 and S4 provide insight in totally unexplored topics related to SOA occurrence in the atmosphere and enrich the discussion.

Finally, case S1 is definitely NOT the base case of our work, but just A reference case for the various sensitivity studies. We do not wish to present a base case simulation since the related uncertainties due to missing knowledge remain important.

Minor comments

- On page 2883, line 20, the reference will be corrected in the revised version.

- In equations (23) and (24) the notation of Ki will be changed to avoid confusion between the partitioning and the absorption rate coefficients.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2879, 2003.