Anonymous Referee #2

We thank this reviewer for helpful comments and suggestions. Below we provide a point-by-point response to this referee's comment. The page numbers refer to the original version published in ACPD.

Comment

1. Sulphuric acid modelling

As the authors state, the MATLE model clearly underestimates the H2SO4 concentration in all the cases presented. However, it seems to me that the problem lies mainly with the time period of the rising concentrations before noon: there seems to be a clear time delay of 2 hours between the rise of the measured and simulated concentrations, while the decay of the concentration in the afternoon is predicted quite well. If this is due to the underestimation of OH production from HONO photolysis, this would then have also effects on the estimate of condensing and nucleating vapours produced in the model. I think this should be discussed more extensively when evaluating the simulation results and their goodness.

Response

It is true that the better agreement was found in the afternoon (12:00-18:00; Slope=0.88, R=0.81) compared to that in the morning (06:00-12:00; Slope=0.62, R=0.78). As we stated in the article, the possible explanation is that the underestimation of HONO concentrations in the model, which further lead to the missing OH concentrations. In the revised manuscript, we have added more evidences to discuss the HONO photolysis:

"In MALTE, the sulfuric acid concentrations are underestimated compared with the observations, especially during the morning rush hours. The modelled sulfuric acid concentrations only account for 62% of the observations (Table 2). One possible explanation is that we potentially underestimate the nitrous acid (HONO) concentration. The HONO concentrations were not measured continuously during the whole campaign, hence we did not use the measurement data as input in the model. A previous study (Kurtenbach et al., 2001) pointed out that traffic emissions can produce considerable HONO concentrations. Meanwhile, the photolysis of HONO is proved to be a significant source of the OH radical, especially in the early morning (Su et al., 2008). Direct measurements of HONO concentrations were only obtained in 3 days of the total 12 selected cases. On average, the observed HONO concentrations were one order of magnitude higher than the simulated ones during 6:00-12:00. Hence, the significant elevations of sulfuric acid concentrations were observed in the case of measured HONO concentrations as input data. As a result, the sulfuric acid concentrations could be enhanced by 1.5-2.5 times at the peak of around 8:00. Therefore, the lack of measured HONO concentrations in the model might lead to the substantial underestimation of sulfuric acid concentrations, especially at the urban site with heavy traffic emissions during the morning rush hour.”

Comment

2. Aerosol formation modelling

First and foremost, I am interested in whether simulations of aerosol formation utilized simulated or measured sulphuric acid concentrations. The simulated nucleation particle concentrations seem to follow measured concentrations very closely (Fig 3 and 5); this would to me give strong support to the role of sulphuric acid if measured SA was used, but on the other hand, I would be surprised if simulated SA (which has a clear time offset) would explain the particle concentrations this well. Can the authors clarify this? As one of the main take-away points of the manuscript is that on- and offset of particle formation is well-predicted, I think this is a key issue.

Response

As the referee stated in comment 1, the sulfuric acid concentrations are underestimated before noon. Hence we used the measured sulfuric acid concentrations in the model to get the particle number size distributions. The simulated sulfuric acid concentrations were also tested in the Malte. The results showed that the on- and offset of new particle formation is also well predicted. However, the strength of the nucleation event is decreased. We have added the results and discussions in the revised version:

"Besides the measured sulfuric acid, the modelled sulfuric acid concentrations were also tested in the UHMA model. The results showed that the on- and offset of new particle formation is also well predicted. However, it should be clarified that the strength of the nucleation event is decreased, which is due to the underestimation of sulfuric acid before noon, as we mentioned above. The ratios of maximum $N_{3\text{-}6}$ values between the cases that modelled and measured sulfuric acid used in Malte are 0.78 ± 0.40 for activation nucleation and 0.64 ± 0.44 for kinetic nucleation, respectively, suggesting that the underestimation of sulfuric acid concentrations should be taken into consideration in the further simulation in case we do not have sulfuric acid measurements."

Comment

My second question concerns the performance of the simulation for so-called nonevent days. To me it seems that the model clearly overpredicts particle formation on days when no particles are formed. This is quite interesting: this is clearly not due to overprediction of sulphuric acid, but some other mechanism is at work. The fact that particle formation is predicted even on non-event days contradicts the statement in the abstract stating that on- and offset can be predicted: for me, also time periods of no formation should be predicted for this to be true.

Response

In the model, the simulated $N_{3\text{-}6}$ showed the obvious diurnal variation even on the non-event day (Fig. 3a). However, the maximum value was one order of magnitude lower than that on NPF event day. The simulated peak values were consistent with the observations, which still showed the sporadic fluctuations of newly formed particles ($N_{3\text{-}6}$). In addition, it should be noticed that the measurements of particles in the range 3-6 nm has a high uncertainty and on the edge of the instrument at such low concentrations (couple of hundreds per cm^3) is difficult to measure.

Comment

Regarding the modelling of [H2SO4][Org] - type particle formation (J_het): The temporal behavior of this type of nucleation seems to be several hours off. If I have understood correctly, the parameters going into J_het are

i) measured sulphuric acid (this I assume from visually comparing figures 1d and 5)

ii) a product that results from the reaction of simulated OH and measured (or simulated?) alpha- and beta-pinene.

iii) a nucleation coefficient K_het, which is higher than previously

From this, to me one possible explanation for the time offset would be the underprediction of OH, especially before noon (as was seen for the sulphuric acid). This situation, with both measured SO2 and measured sulphuric acid and the condensation sink, would call for a rough estimate of the OH concentration from those data and comparing that to the modelled OH concentration, to shed some light on both the sulphuric acid time offset and J_het time offset. Additionally, I would suspect that using such estimated OH would reduce the need to tune K_het to a higher value.

Response

In the modelling of [H2SO4][Org], we used the measured sulfuric acid concentrations as input data and the organic vapours are assumed as the products of alpha- and beta-pinene (measured) via OH radicals oxidation. As the referee suggested, we estimated the OH concentration. The time shift is still shown, however, the K_het is about 10% lower compared to before. We believed that the underestimation of OH concentration will influence the K_het values, but not the diurnal variation patterns.

Comment

A question of interest in studies of aerosol formation is the relative contributions of different vapours to particle growth. The simulation’s performance regrading growth has been discussed very lightly apart from the statement that a condensing organic vapour yield of 0.5% was used. This seems to me to be a very low value. A more extensive description of the possibly condensing vapours, an overview of the condensing vapour concentration, and a comparison of the simulated and measured aerosol volume/mass would give a clearer picture on the accuracy of the simulation. Also, as the properties of the condensing vapour (molecular weight, diffusion coefficient) affect the growth; what are the assumptions made regarding these properties?

Response

The main purpose of this paper is to explore the nucleation mechanism and growth properties of newly formed particles. Meanwhile, the different air masses were not included in the model which could affect larger particles. Hence in this study we only compared the volume concentrations during the nucleation event and only for the particles in nucleation mode (3-25 nm, $V_{3\text{-}25}$). Both sulfuric acid and the oxidation products of organic components by reactions with OH are assumed as the condensing vapours according to the nano-Köhler theory. In addition, water, sulfuric acid and reaction products of organic components, oxidized by OH, NO_3 and O_3, participate in the conventional condensational growth of particles. The molecular weights of the condensing molecules are 98 g/mol for sulfuric acid and 150 g/mol for the organic products, respectively. The diffusion volumes for the condensational vapours are set as 51.96 in the model. We have included these in the revised manuscript.

Moreover, we have added one figure (Figure 4 in the revised version) to show the differences between the simulated and measured particle volume concentrations ($V_{3\text{-}25}$). The results reveal that the $V_{3\text{-}25}$ is underestimated on NPF event days, but over predicted on Non-event days. The ratios of maximum values between the simulated and measured $V_{3\text{-}25}$ are 0.8±0.3 on NPF event days and 1.8±1.3 on Non-event days, respectively. We also found the time delay (~ 2 h) between the simulated and observed $V_{3\text{-}25}$ in all NPF event cases. This might be attributed to the underestimation of OH concentrations before noon (6-12 am), as we described above. In addition, the time delay could also be related to a certain amount of EL-VOC (Extreme Low

Volatile Organic Compounds) which were measured lately but not included in the model in a proper way.

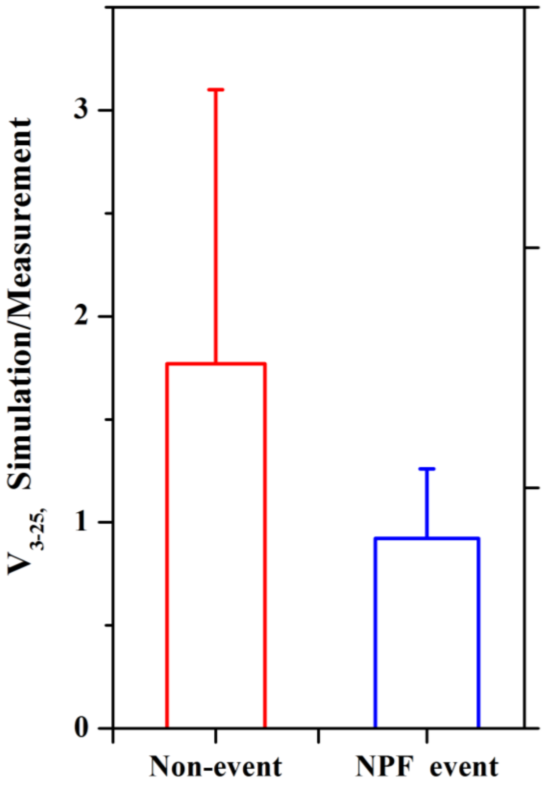

Figure 4. The ratios between the simulated and measured particle volume concentration in nucleation mode ($V_{3\text{-}25}$) on Non-event (red) and NPF event (blue) days.

Comment

It would also be of interest to see the specific contributions that the different oxidation mechanisms (OH, Ozone, NO_3) give to the added volume of aerosol, as this has been a topic of research lately.

Response

We have included this topic in the revised manuscript:

“During the nucleation event, the fraction of $V_{3\text{-}25}$ contributed by the sulfuric acid is in the average 3.2%±1.6%. This value is in the range of previous studies (Kuang et al., 2010;Stolzenburg et al., 2005;Wehner et al., 2005;Wang et al., 2013), which suggested the limited contribution of gaseous sulfuric acid to particle growth. Totally, the OH and O_3 oxidation mechanism contribute 5.5%±2.3% and 94.5%±2.6% to the $V_{3\text{-}25}$, respectively, indicating the particle growth is more controlled by the precursor gases and their oxidation by O_3, which is consistent with the field observation (Yli-Juuti et al., 2011) and laboratory study (Hao et al., 2011). ”

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