

Anonymous Referee #1

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

Provide the instruments used for basic gas concentrations (ozone, NO, NO₂, SO₂, CO) and detection limits (p. 14982) to allow readers to check for methods and detection sensitivities compared to other measurements.

Response

We have added one paragraph to describe the instruments for gas measurements in the revised manuscript:

“Measurements of the gas concentrations were carried out by using commercial analyzers (Ecotech Inc.). The instrument models are EC9810 for O₃, EC9830 for CO, EC9850 for SO₂ as well as EC9841 for NO and NO_x, respectively, with the lower detection limits 0.5 ppb, 50 ppb, 0.5 ppb and 0.5 ppb. All the trace gas instruments were maintained and calibrated routinely and the measurements are reported with uncertainties of 1% on average.”

Comment

Uncertainties are 1%? I am sure the authors mean on average. However the NO detection limit is dependent on ambient concentrations.

Response

Yes, the uncertainty for NO is dependent on the ambient concentration and 1% is average value.

Comment

Organic chemistry is rather complex and a multitude of species not measured may show up. It is being stated that (calibrated) PTR-MS measurements are used instead of

emission modules in MALTE. That's reasonable. However what about compounds with different structures but of the same mass, e.g. monoterpenes, xylene and ethylbenzene as well as ketone, alcohols or alkenes with the same number of basic atoms? This is not distinguishable by PTR-MS and would have implications to atmospheric chemistry. What about transport effects and vertical or horizontal gradients? How may those have affected the results?

Response

During the CAREBeijing 2008 campaign, besides the PTR-MS measurement, the air samples were also taken using fused silica-lined stainless steel canisters and quantified by GC-MS-FID. Hence the compounds with the same m/z like monoterpenes were separated by the GC-MS-FID results. We have clarified this in the revised manuscript.

In this study, we used the zero-dimensional version of MALTE for model simulation. Hence, we had to assume that the species were mixed homogenous in the boundary layer, and the transport effects and vertical or horizontal gradients were ignored.

Comment

p. 14984, l. 18: What is meant by 'K_{het} is chosen as $3.0 \pm 3.4 \times 10^{12} \text{ cm}^3 \text{ s}^{-1}$? Did the authors use a negative K_{het}? Please correct with different upper and lower uncertainty ranges.

Response

Unlike the activation nucleation coefficients A and kinetic nucleation coefficients K , the nucleation coefficient K_{het} could not be obtained from the field measurements because we did not have the direct measurements of organic vapours (M_{TOP} in this study). In this study, the K_{het} value for each day was obtained based on the comparisons between ambient measurements and model simulations. The investigated 8 NPF cases were totally different from each other. Hence the K_{het} values varied in a huge range, with the standard deviation of $3.4 \times 10^{12} \text{ cm}^3 \text{ s}^{-1}$.

Comment

The aspect of 0.5% partitioning of all organic compounds is highly critical. Certainly the exact identity is so far unknown. But having the first order compounds saturation vapour pressures can be estimated by a number of simple methods (e.g. Stein and Brown, 1994) and applying a certain organic fraction, again unknown this may be a more realistic description since the primary compounds will further affect the local chemistry, i.e. the aromatic ones will. Everything seems to work like a big tuning of processes specific to the site. It may be appropriate it may be not. But at least those have been considered.

Response

In this study, 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, NO₃ and O₃, participate in the conventional condensational growth of particles. We have added one figure (Figure 4 in the revised version) to show the differences between the simulated and measured particle volume concentrations in nucleation mode (V_{3-25}). The similar growth patterns of V_{3-25} are observed in all NPF event cases, however, the time delay (~ 2 h) between the simulated and measured V_{3-25} are also found, too. 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. Nevertheless, the results reveal that the ratios of maximum values between the simulated and measured V_{3-25} are 0.8 ± 0.3 on NPF event days and 1.8 ± 1.3 on Non-event days, respectively.

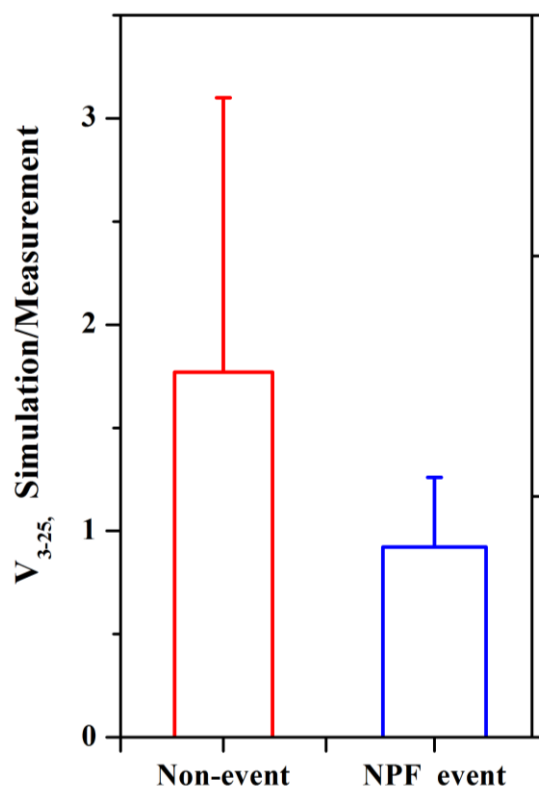


Figure 4. The ratios between the simulated and measured particle volume concentration in nucleation mode (V_{3-25}) on Non-event (red) and NPF event (blue) days.

Comment

p. 14986: The fit of MATLE data with sulfuric acid data essentially depends on getting OH correct. How accurate the NO measurements and as the authors suggested the HONO simulation (in comparison with other sites) are, because that's commonly the weak point?

Response

As the referrer stated, the simulation of sulfuric acid data essentially depends on getting OH correct, which is influenced by the HONO photolysis, especially in the urban environment. During the CAREBeijing 2008 campaign, HONO concentrations were only obtained in 3 days of the total 12 selected cases. We have added these discussions in the revised manuscript:

“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.”

References

Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lörzer, J. C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, *Atmos. Environ.*, 35, 3385-3394, 10.1016/s1352-2310(01)00138-8, 2001.

Su, H., Cheng, Y. F., Shao, M., Gao, D. F., Yu, Z. Y., Zeng, L. M., Slanina, J., Zhang, Y. H., and Wiedensohler, A.: Nitrous acid (HONO) and its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China, *J Geophys Res-Atmos*, 113, D14312, 10.1029/2007jd009060, 2008.