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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Boundary layer nucleation as a source of new CCN in savannah environment" *by* L. Laakso et al.

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The authors thank the referee for the critical and fair comments that have helped to improve the manuscript. In several comments the referee criticized the authors' attempt to interpret observations with a model due to the lack of agreement between the results. In the revised manuscript this is no longer attempted. Rather, the observations and model results are compared side by side. New model runs were also performed to increase our understanding about the reasons for the differences in results. All of the referee's suggestions have been taken into account to the best of our ability, and the manuscript has been revised accordingly.

General comments:

R2: In this work, the authors investigated particle formation and growth in the South African savannah region environment. They found that CCN-sized particles during the dry winter season are from biomass burning, while CCN-sized particles during the wet summer season are mainly from boundary layer new particle formation and growth. They suggested that the higher growth rates during the wet season are attributed to vapors of biogenic origin. Global model results were presented here to interpret the observations at the Botsalano game reserve site. This is a very interesting and important work, one that has a good potential to deepen the understanding on biogenic emissions and the factors controlling nucleation and growth in such savannah environment. I would ultimately like to see the results of this effort published. However, the lacks of a critical analysis of the results and the large uncertainties of model simulation at the Botsalano game reserve site made the current version of this manuscript could not be accepted for publication in ACP. Based on the assessment above, I recommend major revision of the manuscript in its present form.

Most of the detailed discussions about the observed new particle formation, growth, and the contribution due to sulfuric acid at the Botsalano game reserve site during the same period have already been published in Vakkari et al. (2011). The potential highlight of this work is the discussion of the contributions of biogenic organic vapors to new particle formation and growth in such savannah environment. However, there was no attempt to look at the detailed measurements at this site to provide a convincing idea about the role of biogenic organic vapors in the formation of CCN-sized particles. It is no surprise that biogenic organic vapors are important in savannah environment. But the more interesting part is how biogenic organic vapors affect new particle formation and growth in such environment.

A: We agree that this is an important aspect. Unfortunately the measurements were limited and no reliable data of organic vapours achieved (However, we are currently analyzing a one year VOC-data set 2011-12 from another site (www.welgegund.org) approximately 200 km south-west of Botsalano).

R2: The simulated new particle formation and growth are only approximately 10-20% of the observations. It means amount of unknown sources and physical processes are missed in this simulation. The model does not provide acceptable results for boundary layer nucleation at this site, which is closely related to the major conclusion made in this study. When we use the model simulation to interpret the observations, one of the basic requirements is that model simulation should show good/reasonable agreement with the measurements. Otherwise, this kind of interpretation could mislead the readers' understanding.

A: This is a valid point and it is much more clearly stated in the revised manuscript. We no longer aim to explain the observations with the model, but rather focus on the differences between the two and discuss their probable causes. Actually, we consider this as one of the interesting and useful results of the study - the model utilized, GLOMAP, has shown good performance earlier: why does it now produce poorer results when applied for CCN-formation in savannah environment? In the revised version we discuss these issues in much more detail.

In the revised manuscript we tested, besides kinetic H2SO4 particle formation, a second particle formation mechanism depending on both sulfuric acid and secondary organics, and have doubled the secondary organics production. Even this change does not improve the results in a significant manner, so admittedly we cannot fully understand what's going on. There seems to be far more condensing material than predicted with the current emission inventories. Also the observed nucleation rates appear to be higher than those predicted by the parameterizations, which are based on observations from other sites

In the abstract we say:

"The observations are compared to simulations by a global aerosol model GLOMAP. To our surprise, the global aerosol model utilized to explain the observations was not capable of re-producing the characteristics of particle formation and the annual CCN

cycle, despite earlier good performance in predicting the particle concentrations in a number of diverse environments, including the South African savannah region. We assume that the poor performance related to particle underestimation of formation and particle growth rates is due to deficiencies in organic emission inventories and model's inability to reproduce wet removal in the free troposphere."

The agreement between the actual CCN number concentrations leads us to the following hypothesis: in an environment with enough solar radiation, precursors and seasonal variability, there is a pool of CCN which is filled by competing mechanisms: primary emissions during the dry season and secondary particle formation when pre-existing particle surface is reduced. Now if the physical mechanisms are correct, but magnitude of either primary emissions or nucleating/condensing vapours is incorrect, we may get a correct number of CCN, but for wrong reason. This is discussed in the conclusions.

Special comments:

R2: 1. There are a number of citation errors of references. For example, the manuscript of Laakso et al. (2008) appeared several times in this manuscript is not included in references list. Please check the citations carefully in the manuscript.

A: Checked and corrected.

R2: 2. P8505, L4-6. In addition to particle number concentration, aerosol composition and mixing statement are also very important for cloud properties.

A: Added.

R2: 3. P8507, L17-18. How about the frequency of electricity breaks at the observation site? How to consider the missing data in the statistical analysis? Will the frequent electricity breaks bring any trends to the statistical analysis?

A: No, it does not. The experimental data shown here is averaged for each specific calendar month. There were several gaps in data; however, when combining the whole

18 months data set, we got for each month at least 23 days of data. The results are averages (or medians) for this data. While breaks may lead to increased variability, they should not cause any systematic trends. A sentence trying to clarify this was added.

R2: 4. P8509, L26-28. Carbonaceous aerosol emission from large scale biomass burning is important for the simulations of primary particle number concentration and condensation sink, especially in this region. van der Werf et al. (2010) pointed out that the Global Fire Emissions Database version 3 (GFEDv3) monthly inventory data were highly variable. Therefore, the GFEDv3 data based on satellite data averaged over the years 1997–2002 is not suitable here. I suggest the authors to use the GFED3 emission monthly inventory for individual years (2006-2008) to do the simulation. Carbonaceous aerosol emission from large scale biomass for the individual years can be found in http://www.falw.vu/ gwerf/GFED/GFED3/partitioning/.

A: This was a mistake in writing, as GFEDv1 averaged over the years 1997-2002 was used in first initial simulations, but was later changed to the new GFEDv3 inventory. All submitted results use GFEDv3 for the individual years (2006-2008). The mistake has been corrected in the revised manuscript.

R2: 5. P8510, L13-14. Biogenic monoterpenes are major sources of the condensable secondary organic vapors which are suggested to have significant contribution to particle growth here. Did the modeled monoterpenes emissions taken from the GEIA database have seasonal variation? What are the major differences between GEIA biogenic monoterpenes emissions and those from MEGAN?

A: The modeled monoterpene emissions have a monthly variation, but no daily cycle. GEIA is an older model than MEGAN, which is an improved version. Both are based on Alex Guenther's work. Our understanding is that the global emissions are similar in magnitude, but differences in regional emissions and in the monthly cycle exist.

R2: 6. P8513, L19-21. As shown in Fig.3 (a) and (b), the simulated particle formation rate is only approximately 10% of the observations. It means 90% of the observed

particle formation rate could not be explained by model simulation. And it is clear that the model shows an opposite cycle in particle formation rate. The large differences between the observations and model simulations indicate that the simulation of new particle formation at this site may miss some important underlying physical processes which dominate the performance of nucleation here. Therefore, the following discussions and conclusions which are based on the modeling study are not strongly supported.

A: We completely agree. To address this comment, we have performed a full set of new simulations based on nucleation of sulfuric acid and secondary organics according to a recent parameterization of Paasonen et al. (2012), with doubled secondary organic production rate. We would have expected increased nucleation rates as well as an improved yearly cycle, but this does not appear to be the case even with the new parameterization. In the revised version we aim not to overstate the importance of modeling results in the interpretation of the observation. Rather, we focus in the discussion of the issues leading to discrepancies as thoroughly as we can. About the underestimation of the modeled particle formation rates we say:

"Due to the low growth rates and the wrong seasonal cycle in the modeled particle formation rate, we tested another nucleation scheme including H2SO4 and secondary organics (Eq. 2) with the doubled yield of condensable organic vapours (red curves in Fig. 4 b and d). The dry season peak in the 10 nm particle formation rate obtained with kinetic H2SO4 nucleation was no longer pronounced when the involvement of secondary organics in the nucleation process was included, but the observed peak in the particle formation during the wet season was not produced either (Fig 4b, red curve). A plausible reason for this would be too slow particle growth. As described in Kerminen et al. (2004), particle survival from 3 nm to 10 nm is a non-linear competition between growth and scavenging. If particles grow in size too slowly, also the formation rate of 10 nm particles, despite original nucleation mechanism, is reduced. Doubling the secondary organics yield resulted in an overall shift of both pre-existing

and BL nucleated particles to larger sizes, without improving the overall characteristics of particle growth when compared to observations. The growth rates obtained with the visual method remained nearly equal, or were even slightly reduced (Fig. 4d, red curve). However, we note that the lack of increased growth may partly be related to deficiencies in the analysis method since the modelled nucleation events lasted longer when Eq. 2 was used. In conclusion, it seems that deficiencies in condensable organic emissions alone are not sufficient to explain the differences between the model results and observations. The differences arise mainly from too high modelled concentrations of background particles. These particles consume too much of the condensing and/or nucleating vapours for sufficient growth or particle formation to take place. ”

R2: 7. P8513, L21-23. What is the role of vapors of organic origin in particle formation? Can it cover the rest 90% of the observed particle formation rate which is not captured by the model simulation in this study?

A: As mentioned in the previous reply, organic nucleation mechanism is now tested in the revised manuscript. This parameterization, as the previous one, is also based on observations on other sites. Even with the new parameterization and doubled organic vapor production rates the model still explains only around 10% of the particle formation rate at 10 nm.

R2: 8. P8514, L13-15. The simulated particle growth rate in this study is only approximately 10-20% of the observations. I do not think model simulation presented here is suitable to interpret the observations at the Botsalano game reserve.

A: The modeled concentrations were indeed too low. We have performed new model runs with doubled organic vapor production rates. The doubled organic vapor production did not improve the growth rates, as also the nucleation bursts lasted somewhat longer (the prolonged nucleation burst has the tendency to reduce the growth rates obtained with the visual method). But it would seem that much higher concentrations of condensable species would be needed in order to reach the observed growth rates.

However, we do emphasize that the modeled seasonal cycle of growth rates follows the modeled seasonal cycle of secondary organics production. The referee is also right that GLOMAP may not be suitable to explain the observations, but in contrast, further thinking of the results based on feedback from referees revealed important and interesting aspects of functioning of global models in predicting the concentrations and origin of CCN in different environment. We changed the manuscript to focus more to this aspect.

R2: 9. P8515, L1-2. Figure 4 (a) suggests that approximated fractions of particle growth due to sulfuric acid are less than 20% during the whole year. But model simulation shows that approximated fractions of particle growth due to sulfuric acid from May to October are high up to 40%. In my opinion, the observation and the simulation provide opposite conclusions. The observation suggests that sulfuric acid is not an important role in particle growth at this site. In contrast, model simulation suggests that sulfuric acid play a comparable role in particle growth at this site during dry winter. In additional, if organic vapors are important for seasonal cycle of particle growth rates at this site, the model employed in this study, which has large uncertainties of organic vapors simulation, is not suitable to interpret the observations.

A: This is partly true. We no longer aim to interpret the observations with model results, but rather to understand the reasons behind the differences. For the most part the observations are sufficient to explain themselves without further backup from modeling: BL nucleation rates produces more CCN during the wet season, and the growth rates have a similar cycle as biogenic production. The figure comparing the contributions to growth has the same seasonality in the observed and modeled results, which emphasizes the likely contribution of secondary organics. However, it is not an interpretation of the observed result per se. On the other hand, observed growth fractions are based on approximated sulfuric acid concentrations, which may well be somewhat inaccurate. The observation figure does not rule out the importance of sulfuric acid on particle growth entirely, but shows that sulfuric acid is even more unlikely to explain the

growth during the wet season.

R2: 10. P8515, L6-7. The model significantly underestimates particle formation rate and growth rate. Why can the model still capture the absolute number of different CCN-sized particles?

A: We thank the referee for this comment, as it brings out a very important point: It appears that CCN concentrations in Botsalano as in many other environments are fairly buffered: if CCN is not originating from local emissions and transport, it is produced by in-situ particle formation and growth.This is now explained in conclusions:

"The comparison of observations and modelling results revealed several interesting results. First of all, earlier analysis (Spracklen et al., 2010) showed that GLOMAP produced realistic concentrations of CCN-sized particles in diverse environments including our measurement site Botsalano. However, when the contribution of one of the mechanisms producing CCN, boundary layer nucleation, was studied, we found that the number of CCN produced via BL nucleation was significantly different from the observations. This leads us to the following hypothesis: in an environment with enough solar radiation, precursors and seasonal variability, there is a pool of CCN which is filled by competing mechanisms: primary emissions during the dry season and secondary particle formation when pre-existing particle surface is reduced. If in a model the physical mechanisms are correct, but magnitude of either primary emissions or nucleating/condensing vapours incorrect, we may get a relative correct number concentration of CCN, but for wrong reasons or due to wrong sources."

R2: 11. P8516, L1-9. The discussion of observed and simulated CCN indicates that model simulation significantly underestimates the contribution of new particle formation to CCN number concentration in wet season. It indicates that the model cannot capture the major characteristics of new particle formation at the site. Therefore the discussion of the contributions of primary particles, upper tropospheric nucleation, and boundary layer nucleation, which is based on model simulation here, is not convincing.

A: This in now removed.

R2: 12. P8526, Figure 2. Latitude and longitude should be marked on the map. The legend for the colored trajectories should be added here.

A: The figure is completely redrawn.

References:

Paasonen, P.; Nieminen, T., Asmi, E., Manninen, H. E., Petäjä, T., Plass-Dülmer, C., Flentje, H., Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A., Laaksonen, A., Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, Atmos. Chem. Phys., 10, 11223-11242, 2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8503, 2012.