Atmos. Chem. Phys. Discuss., 12, C6589–C6598, 2012
www.atmos-chem-phys-discuss.net/12/C6589/2012/

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.

L. Laakso et al.

lauri.laakso@fmi.fi

Received and published: 5 September 2012

The authors thank the referee for the fruitful comments that have helped to improve the manuscript. We try to answer all the questions as thoroughly as we can and change the manuscript accordingly.

R1: This study compared global model simulation of aerosol nucleation events with the 18-months observations conducted in a site over the South African savannah region. The observation data have been discussed in another paper, so the focus of this study is to deduce aerosol formation and growth mechanisms from the difference between model and observation results. The subject is certainly interesting and suitable for publication in ACP. However, the main conclusion that biogenic organic vapor is an important source of aerosol for this region is not strongly supported by their analysis.

The authors should try to rule out other possibilities as well as evaluate the uncertainties in the model. This manuscript may be considered for publication if the following comments can be responded satisfactorily.

A: The main objective was to study the formation of CCN in the savannah region based on observation. These observations clearly show that new particle formation produces a substantial part of CCN, particularly during the wet season when the biological production peaks. To further deepen the analysis, we applied a global model to the area trying to reproduce observations. To our surprise, the model produced somewhat poor results, which was not clearly enough reflected to the submitted version of the manuscript – this is now changed. In the revised manuscript we have focused much more on evaluating and understanding the discrepancies between the measurements and the model results. Please also see the reply to the referee 2.

Major comment:

R1: 1. A main point of this paper is to relate the underestimation of aerosol production and growth in the model to the omission of organic vapor. I have quite a few concerns about this assumption (seems to be regarded as a conclusion in this paper).

(1) No direct supporting evidence is provided. For example, is there any measurement of secondary organics in the aerosol?

A: Unfortunately, we do not have such data. Based on modeling study by Guenther et al. (1995) organic emissions are many folds during the wet season. In 2011-12, we have conducted a vegetation survey in a grassland savannah site (www.welgegund.org) approximately 200 km south-west of Botsalano. The results (unpublished) show that leaf area index (LAI) of the trees is more than 10-fold during the summer. Thus the biogenic emissions (proportional to LAI) during the dry season have to be significantly lower than during the wet season, as stated by Guenther et al as well.

The reasoning behind the importance of the organics is the following: 1) We see highest GR during the wet season (with significant biogenic emissions). 2) In contrast, emissions from fires are highest during the dry season 3) Estimated H2SO4 concentrations based on SO2, radiation and pre-existing particle surface measurements do not show significant seasonal cycle. -> Thus, there is a missing condensing component during the wet season 4) The most probable condensable species are the biogenic organics (as found in many other environments) as there are no other probable candidates.

But as the referee states, this is not direct evidence. This is now clarified in the text.

R1: (2) The model that used seems to consider OC aerosol emission (p. 5). Does it consider mechanisms for organic aerosol formation? If so, then a sensitivity test could further elucidate the importance of organics. Figure 4a shows the fraction of growth from H2SO4. What are the rest of the fraction composed of (any information on OC)?

A: The model uses only secondary organics derived from oxidation products of monoterpene as the second condensing species besides H2SO4. In the model all growth is therefore due to H2SO4 and secondary organics. In the measurements the amount of H2SO4 is approximated using a similar proxy calculation for the whole year. The absolute fraction of the growth explained by H2SO4 is not known; however, what is important is the seasonal cycle, which shows that during the wet season sulphuric acid explains a smaller fraction of the growth than during the dry season indicating some non-sulphate compounds participating in growth. As anthropogenic and biomass burning emissions are lower during the dry season, we conclude that the growth have to be by biogenic organic aerosol compounds (please see also the reasoning for comment (1)).

R1: (3) The evolution of size spectrum is not totally controlled by nucleation and condensation. Other factors, such as coagulation and emission are also important, and the inaccuracy in them may contribute to the discrepancies in Figs. 3-5. For example, the biomass burning emission used in the simulation is based on climatological satellite data, but the real biomass burning evens are usually sporadic and have strong inter-annual variations. Such an uncertainty might invalidate the suggestion of a strong contribution from organic vapor (e. g., the model may simply underestimated biomass emission). The uncertainty in biomass emission was mentioned in section 3.3 to explain the difference in CCN-sized particles, and this should be applied to Fig. 3 also.

A: Certainly there are uncertainties in processes besides nucleation and condensation (like uncertainties in emitted particle sizes) that may contribute to the discrepancies between observations and model results. The emitted size distribution of primary particles differs for each individual factory, for example. So does the time that it takes for the particles to travel from each point source to the measurement site, as well as the time they have for coagulation during the transport, while emissions inventories have a limited resolution. These kinds of issues have to be dealt with using standard approximations, and admittedly they bring about a lot of uncertainty to model results.

For biomass burning emissions, we used best available monthly emission inventories for the period of the measurements, thus inter-annual variability should not affect the results. However, there is a concern with the use of monthly averaged emissions. We agree that the daily variability may be high, especially if the fires are close to the observations site. However, biomass burning takes place only during the dry season and thus cannot affect CCN production during the wet season when the highest growth rates are observed and the highest suggested contribution of organic vapor takes place.

R1: (4) The general underestimation of particle production and growth in Fig. 3 could also be due to the inaccuracy of the model physics. For example, Chen et al. (2011, Atmos. Chem. Phys., 11, 7171–7184) argued that surface tension decreases with particle size, and ignoring this effect would result in underestimation in both nucleation rate and condensation rate. Also, the lack of RH dependence in Eq. 1 could lead to a lack of minimum in the particle production during the dry season.

A: In the model we do not use classical nucleation theory as a basis for the nucleation parameterization, but empirical relationships derived from a large set of observations from around the globe. All observations show that nucleation always depends on the sulfuric acid concentration to power 1 or 2, and possibly on the concentration of secondary organics to power 1 or 2 as well, and the parameterizations based on these observations do not include RH dependency. In the corrected manuscript we use a method based on sulfuric acid and secondary organic nucleation, as suggested be referee 2. Classical nucleation theory would predict a much steeper dependency between nucleation rates and concentrations of these species than the applied parameterizations, and it cannot explain the observed particle formation events, as pointed out in several recent papers. In the condensation parameterization we assume both sulfuric acid and secondary to condense kinetically. These are standard approaches for many of the current day models. Therefore, neither nucleation parameterization nor the condensation parameterizations depend on surface tension.

R1: 2. p.3, 8-5 lines to the bottom: I do not have access to the Zhou (2001) thesis and thus don't know why there should exist a 50% RH threshold. The hygroscopic growth (or the threshold of it) depends on chemical composition as well as whether efflorescence occurs. For example, sulfuric acid solution does not dehydrate under typical conditions, so there is no RH limit for the hygroscopic growth such droplets.

A: Laakso et al., 2004 estimated hygroscopic growth correction factors based on earlier measurements of aerosol particles measured in Hyytiälä Smear II station. The original parameterization was based on PhD-thesis of Zhou. Later on this study was confirmed by Birmili et al. (2009). These parameterizations give GF of 1.047 for our observed average 37% humidity during the particle growth.

As the referee states, the hygroscopic growth depends on aerosol chemical composition. In 2010-11 we carried out 1-year measurements of PM1 chemical composition by ACSM approximately 200 km from Botsalano. Those studies (so far unpublished) show that PM1-aerosol is a mixture of organics (~50 %), sulphate (30%), ammonia

(10%) and other minor compounds. Adam et al., 2012 (Fig. 6) studied GF of slightly less acidic ambient aerosol in Ispra, Italy showing that GF at 40% relative humidity is less than 1.1.

Another study (Wiedensohler et al, 2012) states that aerosol should be dried below 40% to be dry – this is more than the average ambient RH of our analysis.

Based on these studies and unpublished information of PM1 chemical composition, we assume our approximation is safe. We have added an additional reference (Wiedensohler et al, 2012) to the revised manuscript.

R1: 3. p. 5, Eq. 1: Eq. 1 seems to be very crude. According to the nucleation theory, H2SO4-H2O binary nucleation is a strong function not only [H2SO4] but also relative humidity and temperature. This could be part of the reason why the modeled fresh particle formation rates do not show a minimum in the dry season as in the observation. Another question is why it is necessary to use a different scheme for the boundary layer than for the free-troposphere since both assume H2SO4-H2O binary nucleation?

A: As discussed in the reply to the previous comment, the nucleation parameterization applied in the boundary layer is based solely on observations and not on classical nucleation theory. Classical nucleation theory for H2SO4-H2O system cannot produce enough particle formation in the boundary layer, and therefore cannot be used. However, H2SO4-H2O nucleation based on classical theory seems to reasonably describe nucleation in the free troposphere. Why this is so is an open question, but may be related to other chemical species in the BL such as the secondary organics, amines, etc.

However, on a global scale the applied crude parameterizations in the BL seem to describe particle formation fairly OK in terms of annual trends in total particle concentrations and CCN when looking at a large set of observation sites. One of the motivations for this paper was to see if these kinds of crude parameterizations actually capture the characteristics of nucleation events in a specific site. Unfortunately, this does not appear to be the case in Botsalano, which means that we indeed need more specified parameterizations and better understanding of the physics of particle formation and growth.

Minor comments:

R1: 1. p.4, line 17-18: “minimum, mean and maximum sizes that growing particles reach during the event” How do you define “growing particle”? Some of the particles might be pre-existing. Are you also assuming that there is no atmospheric advection or spatial inhomogeneity?

A: Completely true. There is unfortunately no thoroughly valid way to estimate from field measurements which of the particles grow to CCN. I’m (Laakso) currently participating in a manuscript addressing this problem. We have, however, excluded cases with clear air mass changes (based on air mass trajectories and visual inspection of the aerosol size distributions) from the data-analysis. In general, the approach used here for determination of particle formation and growth is utilized in the analysis of practically all surface observation data – the effect of advection and spatial inhomogeneity is dealt with excluding suspicious data.

R1: 2. Fig. 3 This figure shows the seasonality of particle formation or growth rates as a means to verify model results. The seasonality is a rather crude parameter in relating to the particle formation mechanisms. Why not show the dependence of “particle formation rate” on more direct physical or chemical parameters such as SO2 concentration, solar radiation etc.?

A: The original reason for not trying to explain the microphysics behind the new particle formation was our limited observations: based on experiences from other field stations, several different types of cluster and aerosol mass spectrometers are necessary for such studies to get something new out. However, we do have some discussion on such issues in our earlier paper by Vakkari et al. (2011).

Another reason for our approach is the aim to really merge the observation and modeling results together. Field observations provide only a limited and often crude picture of the atmospheric processes, and many of the analysis methods are equally crude and not well confirmed. For example, a previous study by Spracklen at al. (2010) utilizing our observations show a nice correlation with observations. Now looking the situation from a different perspective show that actually the good correlation earlier observed may be for wrong reason.

Our feeling is that there is always a pool of CCN in the atmosphere (in areas with enough solar radiation for photochemistry throughout the year). A simple comparison of concentrations does not tell how this “pool” is filled: by upper atmospheric nucleation, BL nucleation, or primary particles – now looking the earlier results from BL nucleation point of view the contribution of the processes may be different than earlier model studies, based just on comparisons of particle number show.

R1: 3. p. 7, last paragraph: It is unclear what the “dip in accumulation mode” means. Are the authors referring to the dip in the tri-modal (or multi-modal) distribution that suggested by Whitby? The authors seem to relate the missing of the “dip” to wet removal (specifically rain scavenging). If the authors are referring to the Greenfield gap concept, then the scavenging process should produce a maximum in the accumulation mode, not a dip. More detailed explanation is needed for general readers to understand what message the authors are trying to convey.

A: We have changed the confusing term “dip in accumulation mode” to “decrease in accumulation mode concentrations” during the onset of nucleation burst. This decrease is most probable due to dilution of the boundary layer air with free troposphere /residual layer air. In the paragraph we now say:

“When the simulations data were studied in more detail, we found that unlike in observations, the pre-existing particle concentrations did not show a decrease in accumulation mode concentrations during the onset of new particle formation. This is most probably due to the underestimated aerosol removal mechanisms in residual layer/free troposphere especially during wet season, leading to an overestimation of the condensation to the pre-existing particles. Characteristic for the area, a major fraction of the precipitation comes from multi-cell thunderstorms with strong updrafts (Tyson and Preston-Whyte, 2000), leading to challenges in estimating the particle wet removal mechanism in global models."

R1: 4. It would be helpful if the authors can demonstrate the performance of the aerosol model by showing the simulated evolution of size spectrum and compare it with Fig. 1.

A: We have added Figure 2 to show such demonstration.

References:

Adam, M., Putaud, J. P., Martins dos Santos, S., Dell'Acqua, A., and Gruening, C.: Aerosol hygroscopicity at a regional background site (Ispra) in Northern Italy, Atmos. Chem. Phys., 12, 5703-5717, doi:10.5194/acp-12-5703-2012, 2012.

Birmili, W., Schwirn, K., Nowak, A., Petäjä, T., Joutsensaari, J., Rose, D., Wiedensohler, A., Hämeri, K., Aalto, P., Kulmala, M. & Boy, M. Measurements of humidified particle number size distributions in a Finnish boreal forest: derivation of hygroscopic particle growth factors. Boreal Env. Res. 14: 458–480, 2009.

L. Laakso, T. Petäjä, K. E. J. Lehtinen, J. Paatero, M. Kulmala, U. Hõrrak, H. Tammet and J. Joutsensaari "Ion production rate in a boreal forest based on ion, particle and radiation measurements", Atmos. Chem. Phys., 4, 1933-1943, 2004

Spracklen, D. V., Carslaw, K. S., Merikanto, J., Mann, G. W., Reddington, C. L., Pickering, S., Ogren, J. A., Andrews, E., Baltensperger, U., Weingartner, E., Boy, M., Kulmala, M., Laakso, L., Lihavainen, H., Kivekäs, N., Komppula, M., Mihalopoulos, N., Kouvarakis, G., Jennings, S. G., O'Dowd, C., Birmili, W., Wiedensohler, A., Weller, R., Gras, J., Laj, P., Sellegri, K., Bonn, B., Krejci, R., Laaksonen, A., Hamed, A., Minikin, A., Harrison, R. M., Talbot, R., and Sun, J.: Explaining global surface aerosol number concentrations in terms of primary emissions and particle formation, Atmos. Chem. Phys., 10, 4775-4793, doi:10.5194/acp-10-4775-2010, 2010.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjäraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grüning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H.-G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Löschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657-685, doi:10.5194/amt-5-657-2012, 2012.

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