Atmos. Chem. Phys. Discuss., 13, C11870–C11878, 2014
www.atmos-chem-phys-discuss.net/13/C11870/2014/

Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "Measured and modelled Cloud Condensation Nuclei (CCN) concentration in São Paulo, Brazil: the importance of aerosol size-resolved chemical composition on CCN concentration prediction" *by* G. P. Almeida et al.

Anonymous Referee #2

Received and published: 4 February 2014

The paper by Almeida et al. presents CCN concentrations measured in the Sao Paulo Metropolitan Area in Brazil. The measurements were compared with chemical composition data from an aerosol chemical ionization monitor leading to the conclusion that a size-resolved chemical composition is necessary to predict CCN concentrations reasonably well. The information given in this manuscript is relevant for the readers of ACP and of interest for the community in general. However, there are still quite some issues as detailed below that have to be addressed by the authors before I can recommend the paper for publication in ACP.

Major comments:

1. Calibration of the CCNC

You mention that “the factory calibration based on (NH4)2SO4 was used (”P. 32360, L. 7-8). However, DMT recommends calibrating the instrument’s supersaturation regularly. And indeed, as shown by Rose et al. (2008) it is necessary to carefully calibrate the supersaturation in the CCNC, since the relation between the supersaturation and temperature gradient along the flow tube strongly depends on the operating conditions (air pressure, air temperature, flow rate). The factory calibration was performed in Boulder at about 1700 m asl. As your measurements were performed in Sao Paulo at 700 m asl there is about 100 hPa difference in air pressure between the two operating conditions. As demonstrated in Fig. 9 of Rose et al. (2008) an increase in pressure by 100 hPa leads to a relative increase in supersaturation of at least 10% (the increase is larger at small supersaturations). Taking this into account the actual supersaturation levels during your campaign were rather something like 0.22%, 0.44%, 0.66%, 0.88%, and 1.1%. Since the CCN concentration strongly depends on the supersaturation, this is an important fact if you want to compare your results with other measurements.

In the revised version of your manuscript you would definitely need to discuss this point. You should provide values of supersaturation that are corrected for differences between operating conditions during the campaign and during factory calibration. Maybe it is even possible to still calibrate your instrument under conditions similar as during the campaign.

Note that changing supersaturation values have a significant influence on the prediction of CCN concentrations. I assume that with supersaturation levels being actually higher you result in a smaller critical diameter of CCN activation, which would in turn yield higher CCN number concentrations. How much higher depends of course on the particle size distribution.

2. Relevance of measured mass composition for the size range of CCN measurements

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As you point out correctly in Sect. 3.2.1 the mass of particles with larger size contributes much more to the bulk chemical mass than the mass of particles with smaller size. Therefore the question rises whether the bulk mass you measured with ACSM is at all relevant for the size range in which the particle activation happens. I wonder if there is a correlation between your CCN data and the bulk particle composition data. I would appreciate if you could test the correlation between kappa_ACSM and kappa_CCN, where kappa_ACSM = f_org * kappa_org + f_inor*kappa_inor. kappa_CCN can be calculated by first looking for the diameter above which the integrated DMPS measured size distribution equals the measured CCN concentration, and secondly calculating kappa from your Eq. 3 inserting the supersaturation measured with CCNC and the just calculated diameter. Such a correlation has been made e.g. in Juranyi et al. 2010. From my experience this correlation is generally not very good but improves for decreasing supersaturation. Nevertheless, it may help you in the interpretation of your predicted CCN concentrations.

3. CCN prediction assuming size-dependent chemical composition (Sect. 3.2.2)

As far as I understood you did not have any size-resolved chemical composition data in the time period of your CCN measurements. Therefore you try to use the results of MOUDI samples taken during a previous campaign to account for the size dependence in the composition. However, I am not able to understand how exactly you did that. There is a lot of information missing. I suggest fully revising Sect. 3.2.2 to clearly describe the applied approach. The following questions may help you with that: Are the size distributions you show in Fig. 6 the results from the MOUDI samples? Where exactly were they taken? – The same location as your CCN measurements? If not, are the measurement sites comparable to each other? What was the average total mass concentration for the MOUDI samples and ACSM measurements? – Are they about the same? How exactly did you calculate the size-dependent composition during your CCN period? Did you fit a function through the size-resolved sulfate mass fraction and multiplied by the mass fraction measured by ACSM? Which size range did you assume to be relevant for particle activation, i.e., for which size range did you calculate kappa? Which value did you assume for kappa_org? What is the purpose of the paragraph in P. 32368, L. 13-22? Where do the AMS measurements come from?

4. Terminology: aerosol vs. particle

The term “aerosol” defines as “solid or liquid particles suspended in a gas”. So, you have to differentiate between the term “aerosol”, which means always the total population of particles in the air and the term “particles”. Instead of talking of e.g. “total aerosol concentration” you should write “total particle number concentration” since it is the number of particles per cubic centimeter of air. Or instead of “aerosol diameter” you should rather say “particle diameter”. I would really appreciate if you could check the whole manuscript with regard to the terminology and write “aerosol” only if you want to talk of the total population of particles. Otherwise you should always use the term “particle(s)” or “aerosol particle(s)”.

5. English and captions

The manuscript needs major improvement in language. In some parts it is really difficult to read and understand. Also, please thoroughly revise your figure and table captions. It must be possible to understand the meaning of a figure or table from the caption alone!

Minor comments:

P. 32356, L. 7-10: This sentence is not quite correct. The ability of a particle to act as CCN depends on its size (not size distribution) and chemical composition. The rest of the sentence is okay: Knowledge of particle number size distribution and chemical composition would suffice to predict ambient CCN concentrations.

P. 32360, Sect. 2.2.2: Which type of DMA did you use? A size range of 10 to 500 nm appears quite broad to me. At which flow rates did you operate the DMA? The size distributions you show in Fig. 3 reach only up to 400 nm. Why not up to 500 nm?

P. 32383, Fig. 2: Could you please also plot the time series of the total CN concentration for comparison?

P. 32362, L. 8-11: From the plots shown in Fig. 2 and from the numbers in Tab. 1 I think you are not able to draw the conclusion that the high variation in CCN number concentration is mostly due to variations in chemical composition rather than shape of the size distribution. In fact, I guess the opposite is true: A change in aerosol composition leads to changes of the critical diameter needed for cloud droplet activation but that in turn leads only to a small change of the CCN concentration (when the CN size distribution is kept constant). Instead, keeping the chemical composition constant (i.e., keeping the activation diameter constant) a change in the (shape of the) size distribution leads to a much higher relative change in the CCN number concentration. This has been shown intensely, e.g. by Dusek et al., 2006 and Juranyi et al., 2010.

P. 32363, L. 5: What is “aerosol mean diameter and volume”? Please define more exactly. I guess you mean the number and volume mean diameter. According to Seinfeld and Pandis (2006) the number mean diameter is the “average diameter of the population”, and the volume mean diameter is the “diameter of the particle whose volume equals the mean volume of the population”.

P. 32363, L. 6-8: I wouldn’t say that the total particle number concentration has a secondary peak at 18:00 LT. In Fig. 3e the value at 18:00 is only little higher than the values one hour before and after. For me the overall trend is rather a decreasing concentration from 11:00 to (even) 05:00. I suggest showing a so-called box or whisker plot of the whole statistics (median, quartiles, etc.) here. That would present a clearer picture of trends and peaks. Also, what kind of information do you have on the traffic emissions? Maybe statistics on the average diurnal variation of vehicles in a street? Could you provide a graph?

P. 32363, L. 11-12: I don’t understand the meaning and purpose of this sentence. It seems not to be related to anything you say before or after, nor can it be proven by any figure.

P. 32364, L. 2-5: What do you mean with this sentence? Something like that?: “The contribution of organics and BC to the total mass was much larger than observed in previous studies in this area. Among all components BC exhibited the largest variability”.

P. 32364, L. 5-7: I do not agree with this statement. The diurnal variation of the organic mass concentration is not more than the diurnal variation of the inorganic components. Only the minima and maxima occur at different times.

P. 32364, L. 7-9: I also do not see that there is agreement in the diurnal variation between organic mass and total particle concentration. What about the diurnal variation of BC? Is it related to the number of vehicles?

P. 32365, L. 21-22: Which measured parameters did you use for the calculation of f_org and f_inor? Since you talk of “ACMS/MAAP derived kappa”, is the BC mass measured by the MAAP somehow used in this calculation? You cite Dusek et al. (2010) and Rose et al. (2011) here, but they calculated only AMS derived kappa values.

P. 32366, L. 2-3: I do not understand this sentence. Do you mean that the calculated kappa value experienced large variations because of the strong variation in f_inor?

P. 32366, L. 4: “0.10 +/- 0.03 for inorganic fraction”: This value is meaningless.

P. 32366, L. 13-18: Please revise this paragraph and write exactly how you calculated the total CCN concentration. I guess what you did is the following: 1. calculating kappa from f_org and f_inor; 2. calculating the critical diameter at the supersaturation under consideration by Eq. 3 using kappa; 3. integrating the DMPS derived particle number size distribution above the critical diameter. Note that since you have only 22 size channels for the whole size distribution it is necessary to interpolate it in order to be able to integrate properly.

P. 32370, L. 5-6: “. . . presenting peaks that alternate with low N_CCN values”: This phrase is meaningless.

P. 32370, L. 22: None of your graphs is showing “an increase in aerosol hygroscopicity in the afternoon”. For this you would have to plot the diurnal variation of kappa (kappa_CCN as explained above), which would actually be interesting to see.

Technical corrections:

Figures: Can you please plot all graphs showing average diurnal cycles (e.g., Fig. 2c) from 0 to 24 LT.

P. 32355, L. 10-11: mention what the numbers are, e.g.: (arithmetic mean ± standard deviation)

P. 32355, L. 14: define SS

P. 32355, L. 22: define N_CCN

P. 32356, L.12-14: “. . . of droplets in clouds and decrease their sizes. . .”

P. 32356, L. 24: define N_CCN

P. 32357, L. 7: “. . . to act as CCN is a difficult task.”

P. 32357, L. 8: “. . . is often . . .”

P. 32357, L. 9: “. . . to be internally mixed. . .”

P. 32359, L. 25: do you want to name the supersaturation as “SS” or “S”? Please choose only one symbol.

P. 32359, L. 27: define SS_crit

P. 32360, L. 1: “Droplets leaving the column. . .” instead of “particles”

P. 32360, L. 2: “CCN” without “s”

P. 32363, L. 8: Fig. 3e shows no figure on traffic emissions

P. 32366, L. 7: "This is a result of the relatively low inorganic mass fraction."

P. 32366, L. 19-20: "The modeled results indicate an overestimation of N_CCN, which is increasing with increasing supersaturation." It is not the "critical supersaturation".

P. 32369, L. 12: "CCN concentration" instead of "CCN spectra"

P. 32370, L. 11: "higher mass fractions" instead of "volume fractions" since you talk of mass fractions throughout the paper

P. 32370, L. 12: What do you mean with "charge" of aerosols?

P. 32382, Fig. 1: "Time series" instead of "diurnal variation".

References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 32353, 2013.