Atmos. Chem. Phys. Discuss., 10, C14327–C14335, 2011
www.atmos-chem-phys-discuss.net/10/C14327/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and externally mixed CCN-inactive soot particles" *by* D. Rose et al.

D. Rose et al.

d.rose@mpic.de

Received and published: 4 March 2011

Response to Referee #2

We thank Referee #2 for the review and the constructive suggestions for improvement of our manuscript, which will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee comment:

P26843L9: What kappa_a,p, kappa_org etc. mean? Abbreviations should be used following their definition.

Author response:

Indeed we did not explicitly give the definitions of some of the abbreviations in the abstract. We will implement them in the revised manuscript.

Referee comment:

P26845L8: I suggest authors to add a paragraph that summarizes (1) what has been already done to reveal the relationships between CCN activity and chemical composition, mixing state etc, and (2) what kind of questions are unanswered. Some studies have already investigated the relationships between CCN data with AMS (e.g., Cubison et al., 2008) and VTDMA data (e.g., Kuwata and Kondo, 2008). What kind of novel knowledge the authors are going to add? This paragraph will be useful in clarifying the scientific role of the paper.

Author response:

We will revise the introduction accordingly and add the suggested references.

Referee comment:

P26847L2: I am concerning about the potential influence of water in particles. RH = 33% is almost equivalent to efflorescence relative humidity of (NH4)2SO4. This means that sampled particles potentially contained significant amount of water. Please discuss how it affects the data reported in the manuscript as well as the discussion

ACPD

10, C14327–C14335, 2011

(i.e., I do not think that it is possible to derive kappa values precisely when particles contain water). RHs for CCN measuring instrument, DMPS, VTDMA, and AMS were the same? If not, how it affects the data analysis?

Author response:

As mentioned in Sect. 2.2.1 the RH for the DMPS and VTDMA was the same as for the CCNC, and the RH for the AMS was 30-45%. Indeed, the efflorescence RH of ammonium sulfate is close to our average aerosol humidity of (33±7) %. According to the Köhler curve, the size of an average mixed particle (kappa = 0.3) at 40% RH would be ∼6% larger than its dry size. That means, if we selected a particle of a certain size at 40% RH, its actual dry diameter would be 6% smaller. If we assumed the size at this RH to be the dry size, we would underestimate the kappa by ∼20%. (At 33% RH, the underestimation in kappa is still ∼13%).

In our measurement setup, however, the sheath air flow of the DMA was dried with a silica gel diffusion dryer. The silica gel was exchanged regularly and the average RH in the sheath flow was <5%. In this setup the particles are rapidly dried upon entering the DMA (Mikhailov et al., 2009). Thus, size selection is effectively performed under dry conditions, and the relative deviations in particle diameter should be < 1% (Mikhailov et al., 2009). We will include this information in the revised version of our manuscript (P.26848, L.1).

Referee comment:

P26848L24: I have concerns on this paragraph regarding (1) actual value of density, and (2) potential size-dependence in density. 1.7 g cm-3 is almost equal to the density of (NH4)2SO4. Considering that observed particles contained significant fraction of organic compounds, the real density would be lower than this value. The authors refer Cheng et al. (2006) and Zhang et al. (2006) as references for the value. However,

ACPD
10, C14327–C14335, 2011

Zhang et al. (2009) investigated optical properties of particles observed at Beijing, which is located thousands kilometers away from PRD region. Cheng et al. (2006) assumed density as 1.7 g cm-3. Figure 2 clearly demonstrates size-dependence in chemical composition. This indicates density is also size-dependent. It may be difficult to derive size-dependent particle density; however, it would be possible to discuss how assumptions in density affect the data interpretation.

Author response:

Assuming a particle density of 1.7 g cm-3 we are on the upper limit that can be expected for a mixed aerosol with an organic fraction of on average 50%. Calculations based on the DMPS and AMS measurements performed during this campaign yielded a density increasing with particle size from ∼1.5 g cm-3 at 100 nm to ∼1.7 g cm-3 at 200 nm (Wolfram Birmili, personal communication). For a density correction factor lower than 1.7, the resulting mobility diameter would turn out to be larger than what we calculated (13% larger for a factor of 1.5). The mass concentrations and mass fractions displayed in Figs. 1 and 2 would be linearly shifted to the right and accordingly also the kappa_a,p values would be shifted (Fig. 11). Since we observed an increasing inorganic mass fraction with particle size (Fig. 2), this shift would lead to a smaller kappa_a,p value at a particular size. However, the effect would be on average very little because the size dependence was, except during the biomass burning event, only small. For example, a density factor of 1.5 instead of 1.7 would give changes in kappa_a,p of ∼1% at 50 nm or ∼3% at ∼200 nm (∼3% and ∼12%, respectively during the BBE). We will add this information in Sect. 2.2.3 of the revised manuscript.

Referee comment:

P26849L13: It seems that the authors (implicitly) assume soot particles do not contain organic compounds. However, laboratory studies and atmospheric observations have showed that they are coated by primary organic matters. This means that the present

ACPD

10, C14327–C14335, 2011

data analysis is possibly over-estimating the fraction of organic compounds included in non-soot particles. Please describe the assumptions on mixing state, and how they affect the data interpretation.

Author response:

As stated on P. 26849 L. 23-29, we are aware and do not exclude that soot particles may contain organic compounds. In our data analysis, we refer to the total organic material detected by AMS, including organic material from soot particles. We consider it likely that refractory organic compounds that cannot be detected by the AMS are also not water soluble. As indicated by the comparison between CCN and VTDMA data, the externally mixed weakly CCN active (soot) particles are most likely not coated by large amounts of non-refractory organic material.

Referee comment:

P26853L8: I am not sure if the assumption is acceptable or not. Density of POA (e.g., n-alkanes) would be around 0.8 g cm-3, which is so much different from 1.7 g cm-3 for inorganic compounds. Do the authors have any additional comments regarding this point?

Author response:

Our data from this and other field campaigns in various environments (Amazonian rainforest: Gunthe et al., 2009; rural and alpine Central Europe: Dusek et al., 2010 and Rose et al. (in preparation)) demonstrate that mass fractions can indeed be used for efficient approximation. For investigations aimed at very high accuracy (e.g., detailed laboratory studies) it would certainly be better to account for differences in density.

Referee comment:

ACPD

10, C14327–C14335, 2011

P26854L2: I am wondering the significance of the statement. If the authors observed significant influence of primary organic matters (e.g., biomass burning, transportation from megacities located at the vicinity of the observation site), it does not make any sense to compare the value with those of SOA. Kappa_org for SOA can be higher than 0.1 if significant fraction of water-insoluble primary organic matters were present. It would be useful if the authors can add some statements on the data scattering shown in Figure 3. Is it from the noise in the original data, or does it indicates potential fluctuation in kappa_org?

Author response:

Indeed, we find it noteworthy that the average effective hygroscopicity parameter of the organic fraction observed in a megacity environment is similar to the average values observed in field and chamber studies of SOA. We will clarify the manuscript text accordingly: "Extrapolation of the fit line to f_org = 1 yielded kappa_org = 0.10$\pm$0.02 for the organic fraction. This is similar to the average hygroscopicity parameters found in field measurements and chamber studies of secondary organic aerosol (SOA) (King et al., 2009; Gunthe et al., 2009; Dusek et al., 2010). Apparently, the differences between more and less water-soluble and hygroscopic organic compounds present in SOA and POA (e.g., carboxylic acids, levoglucosan, polyfunctional aliphatic and aromatic hydrocarbons, proteins, ...) tend to cancel out in the course of atmospheric mixing and chemical aging."

Referee comment:

P26855L26: Figure 5 shows (1-MAFf) vs Da relationship. Is it appropriate to use Da as x-axis? Particles larger than Da determines (1-MAFf). It would be more appropriate to use other parameters e.g., Da + 3 sigma.

Author response:

ACPD

10, C14327–C14335, 2011

Many thanks for your suggestion. Actually we had also thought about but missed to follow up on it. In the revised version we will implement this approach.

Referee comment:

P26857L20: It seems that the same equation has already been used by other studies (e.g., Kuwata et al., 2007). The authors will be able to demonstrate appropriateness of the definition by referring some of the previous studies.

Author response:

Many thanks for the hint. We had not recognized that the same approach had already been taken by Kuwata et al., 2007. In the revised version will of course refer to that study. So far we are not aware of any other study using the same approach.

Referee comment:

L26857L24: Is it really due to the uncertainty of the measurement? What happens if the assumptions in deriving the equation (2) are not correct?

Author response:

With regard to the general scattering and uncertainty of the measurement data (generally +/-10-20%, see error bars in Fig. 8, and Figs. 1 and 3 of Rose et al., 2010), we consider it most likely that the negative value is due to measurement uncertainties. Nevertheless we agree that it might be also influenced by deviations from the assumption that the lv-particles correspond to the non-activated particles. This will be clarified in the revised manuscript: "... is slightly negative. The deviation from zero is within the range of measurement uncertainties, and it might also be influenced by deviations from the assumption that the lv-particles correspond to the non-activated particles."

ACPD

10, C14327–C14335, 2011

Interactive Comment

Referee comment:

Figures 3 and 4: At which supersaturation authors measured the data shown in the figure?

Author response:

As stated in P. 26849, L. 16-18 in the correlation analysis between AMS and CCN data, CCN efficiency spectra with D_a−sigma_a<50nm were excluded, which includes all spectra measured at S = 0.87% and some measured at S = 0.47%. Thus in Figs. 3 and 4 data points were measured at S = 0.068%, 0.27%, and 0.47%.

Referee comment:

Figure 12: This figure contains too many panels, which makes it difficult to focus on each panel. Can the authors select important panels?

Author response:

We regard all panels in this figure relevant and would like to keep them. This figure is meant to give an overview of the diurnal cycles of different types of aerosol parameters observed during PRIDE-PRD2006. For better readability, we intend to increase the panel size in the revised manuscript.

References:

Dusek, U., Frank, G. P., Curtius, J., Drewnick, F., Schneider, J., Kürten, A., Rose, D., Andreae, M. O., Borrmann, S., and Pöschl, U.: Enhanced organic mass fraction and decreased hygroscopicity of cloud condensation nuclei (CCN) during new particle formation events, Geophys. Res. Lett., 37, L03804, doi: 10.1029/2009GL040930,

ACPD

10, C14327–C14335, 2011

2010.

Gunthe, S. S., King, S. M., Rose, D., Chen, Q., Roldin, P., Farmer, D. K., Jimenez, J. L., Artaxo, P., Andreae, M. O., Martin, S. T., and Pöschl, U.: Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity, Atmos. Chem. Phys., 9, 7551–7575, 2009.

King, S. M., Rosenøern, T., Shilling, J. E., Chen, Q., and Martin, S. T.: Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings, Atmos. Chem. Phys., 9, 2959–2971, 2009.

Kuwata, M., Kondo, Y., Mochida, M., Takegawa, N., and Kawamura, K.: Dependence of CCN activity of less volatile particles on the amount of coating observed in Tokyo, J. Geophys. Res., 112, D11207, doi:10.1029/2006JD007758, 2007.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491–9522, 2009.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26841, 2010.