Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-23-RC1, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Variation of CCN activity during new particle formation events in the North China Plain" *by* N. Ma et al.

Anonymous Referee #1

Received and published: 18 February 2016

General comments.

This paper presents a detailed analysis of instrumental measurements of particle physics and their cloud condensation parameters during an intensive field campaign in a highly polluted region of the North China Plain. The analysis focused on the CCN activity potential of the particles in the 20 to 200nm size range. CCN activation ratio data are unique for this region and provide results of value to the wider atmospheric sciences and cloud physics community. Chemical analysis for the size range of particles most important for CCN activity of the total particle population is lacking. The measurement of hygroscopic growth factor helps in understanding the CCN of the several events and indicated a chemical effect but the compounds or groups of compounds causing this effect cannot be identified with certainty. The data presentation via graphs is generally clear, quantitative and provides an excellent integral overview.

Specific comments.

Abstract and introduction: Mention of region and season is made. The data base of the study is different event types in one region, NCP, over one four week time period. Thus, it would be more accurate and clear to refer to the results in terms of a case study of NPF type, i.e., based on your NCP PNSD and chemical composition data for the summertime campaign.

Page 2 line 18: i.e. at least up to 50 nm. This value of critical diameter depends on supersaturation in the parcel as it cools below the dew point temperature by lifting, radiation or mixing. For fog and low level stratus with limited vertical motion the Dcrit may be around 50 nm. For stratocumulus it may be closer to 30 nm. For cumulus, less than 30 nm. Your point about growth by condensation (and some coagulation) determining the relative organic vs. inorganic (with greater vs. lesser water solubility) chemical composition of the CCN is still valid. A volume growth factor of 10^4 to 10^5 is still needed.

Line 20: It should be mentioned that, although particle size is the parameter of primary importance, chemical composition does modify the PNSD-based CCN determination by affecting the hygroscopicity or solubility of the potential CCN particle. But this effect is only significant for particles at or slightly greater than Dcrit . However, if the condensing vapor causing NP growth has a strong surfactant effect that lowers the water vapor accommodation coefficient or diffusion of condensed water during cloud droplet formation from the particle's surface into its volume, then the chemical composition effect on CCN fraction may extend to Dp much larger than Dcrit .

Page 3, line 9: State the particle size range. ... particle size range from xx to xxx nm.

line 12: Was the data during locally influenced time periods eliminated from the analysis? What hours constituted daytime? Does it match the chemical sampling schedule? Was this simply determined by hour of the day or was there meteorological input such as inversion height, thermal stability, wind speed?

Line 15: Does “Inc., Thermo,” refer to the nafion dryer?

Page 4, line 4: What was the particle diameter range of the DMA-CCNC system? Does it match the SMPS system? What was the time resolution of the AR measurement system? Was it operated in a scanning or stepping mode? If the latter, what was the step interval?

Line 11 “The size-resolved particle activation ratio was then inverted ... “ I understand the general idea here but not the details. You have AR for specific SS and Dp values. Eventually you determine the activation ratio curve, as the function AR(Dp,SS) used in Eqn. 2. The inversion operation is not clear; maybe it is not needed if explained in Deng 2011.

Line 14: Was the SS calibration done with monodisperse particles of known chemical composition?

Line 23: Were the TDMA calibration ammonium sulfate particles monodisperse?

Page 5, Figure 2: The details of the PNSD data that are discussed are not clear to this reader even at 300% magnification due to the high time and size variability of the data. This could perhaps improved by smoothing of the contours. The fine structure in the data is not needed to convey the general features such as “nucleation mode did not start at the lower detection limit of our SMPS”, and the beginning and end of particle growth by condensation of vapors. A quantitative label for color scale is needed for panels 1 and 2. The hygroscopic growth at 50 nm is most germane to understanding CCN activation; however κ-PDF at other diameters would be of interest, perhaps as a supplement to the manuscript.

Page 6, line 10: The inference of the chemistry of nuclei mode particles from PM10 chemical analysis leaves a lot to be desired. Is there data from previous experiments in the NCP when mass spectrometric analysis was done to aid in the understanding of what the size dependence of sulfate and organic compounds might have been in this

field study?

Line 17: I don’t understand “production activity”. Do you mean rate of condensation?

Line 24: It would be useful in this figure to identify the two events, the sulfate-dominant NPF event and OM-dominant NPF events, either in the caption or under the dates at the top of panel 1.

Line 25: “And two types of NPF ... “ Does this refer to Yue’s work? If yes, then I suggest, “Furthermore, they observed two types of NPF .... “

Line 31: You present BC mass concentrations. Do you have similar mass concentration data for sulfate and OM? Total sub 800nm and sub 80 nm mass derived from the SMPS volume and an assumed density would be useful as well.

Page 7, line 4, Figure 3A The label on the ordinate should be Dp, particle diameter. The color scale label should be placed next to the color scale bar.

Figure 3 overall: The timing of the appearance of NFP varies depending on the parameter. NFP appear sporadically beginning at 900, Fig 3A. ΔN(40,60) and κ increases sharply at about 1030. Nuclei mode reaches 50nm about 1200LT. The condensational sink does not decrease sharply over time in the morning. Of course there are other parameters not quantified and presented such as advection or mixing from more polluted layers aloft or actinic flux and photochemical precursor gas formation. These are beyond the scope of the observations and discussion. Simply mention that the indicatory parameters for NFP, Dp,nuclei, ΔN(40,60) and κ, increase more or less in coincidence over a three hour period.

Figure 3 D: The legend shows NFH while the right hand label shows NFNH.

Line 27, Figure 3E: The highlighting of the points used for calculating the average size-resolved activation ratio shown in Figure 5 is difficult to see and the change in color is not clear. A larger circle for those points would help the reader at a glance.

Also, a theoretical critical Dp line for ammonium sulfate as a reference for the three SS values would be useful for comparison.

Page 8, line 30, Figure 5: What is the SS for the campaign average curve? It is difficult to follow all the curves and colors on this plot. I suggest breaking the single plot into three panels, one for each SS. The information in Figure 5 is summarized in Figure 3 panels E and F, but, these do not show the OM vs. sulfate differences or that activation ratios remain below 1.0 even at sizes much larger than Dcrit,SS, so figure 5 is of value for showing this result.

This last point, AR < 1 at Dp»Dp,crit, needs explanation. Certainly size plays the dominant role as you point out since approximately 80% of the particles activate at Dp50 plus about 5 nm. However, on average only about 85% activation ratio is reached at twice the Dp50. In two cases the maximum AR is only about 60%. Do you have an explanation, e.g., truly insoluble, non-wettable primary particles, or organic surfactants?

Page 8, line 11, Figure 6: Change caption and legends and plotting in figure 6 as suggested for figure 3. See Word changes in figure 3 caption.

Page 9, line 29: Do you know from chemical measurement that sulfate dominated the particle growth size mode, i.e., nuclei and Aitken modes? From PM10 sulfate analysis alone that cannot be supported. The best evidence you have is for sulfate vs. OM is from your κ and NFNH.

Page 10, lines 1 through 3: It is not clear how the difference ratio plotted in Figure 7 was calculated, what NCCN ref and NCCN Aravg are. The text and figure caption and x-scale label symbols are not consistent. Provide an equation (4) in the text for the bias parameter used in the figure e.g. CCNbias = ...

Line 13, Figure 7: The caption should the time period of average, i.e., afternoons of July 22nd and July 24th. I assume the frequency statistics are number of occurrences per interval of relative ratio, and for the 2 dim, number of occurrences per interval of

relative ratio and time. Mention this in the caption.

Are there significant differences between the two parameters? To me they look very similar other than the left hand tail. You do not mention the chemistry or physics behind this tail. Nor can I imagine any.

In other plots and discussions you have presented and compared data from 22 July vs. 24 July. Were there significant differences in the frequency distribution plots for those two days?

Page 11, line 31: " ... bias of the estimated NCCN ranges from about 0 to 30% ... " From your frequency distribution plots in Figure 7, I would put the biases at $\pm$10%. That is my simple ocular analysis. Better would be the percent bias at $\pm$ one or two standard deviations of the of the data.

Page 12, line 25: I would make a stronger statement. This means that during NPF in the NCP, the CCN activity of newly formed particles was different during these two events; the aerosol present during the organic dominated event was less hygroscopic and less active as CCN for a given diameter and supersaturation.

Line 29: Again your 0 to 30% values could be more accurately presented as I suggested above, page 11, line 31.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-23, 2016.