Cover letter:

We sincerely appreciate your careful inspection of our manuscript; we have taken great care in thoroughly revising the document in line with your invaluable feedback. Additionally, we have further enhanced the quality of this manuscript through using expertise of Elsevier Language Editing Services. We have attached the certificate of language editing for your reference, and you will find our responses to your comments comprehensively addressed below.

In addition, we agree with the editor that we should avoid excessive definition of the same parameter in figure captions. However, one of the reviewers said "In my view it is required to explain those abbreviations, which are not widely known, such as MAF, CCOA, regularly again, also in figure captions", this is why we defined these parameters repeatedly in figure captions. We have refined our approach in the revised version. We now provide the initial definitions of these parameters with their respective abbreviations in Table 1. Furthermore, in the figure captions, we present both the abbreviation and the complete term but have refrained from repetitive definitions, according to the guidance provided by the language editor.

Certificate of Elsevier Language Editing Services

The following article was edited by Elsevier Language Editing Services:

Markedly different impacts of primary emissions and secondary aerosol formation on aerosol mixing states revealed by simultaneous measurements of CCNC, V/HTDMA and SP2

Ordered by:

Jiangchuan Tao

Estimated Delivery date:

2023-08-31

Order reference:

ASLESTD1017819

Suggestions and comments are addressed point-by-point and corresponding responses are listed below.

L135: "different particle groups": particles are internally mixed, so you cannot talk of particle groups

Response: Thanks for your suggestion. We have revised this sentence as:

"Because SAs formed through different mechanisms, have different chemical compositions and add mass to different aerosol populations, …"

L168: "Inlet changes would affect the dry state aerosol sampling": not clear what this means

Response: Thanks for your suggestion. We have revised this part as:

"The inlet was switched among three impactors: TSP (Total Suspended Particles), PM2.5 (Particulate Matter with an aerodynamic diameter of less than 2.5 μm), and PM1 (Particulate Matter with an aerodynamic diameter of less than 1 μm). Inlet changes among impactors affect dry-state aerosol sampling owing to ambient aerosols are enlarged through aerosol hygroscopic growth or activation."

L172: "by two parallelly assembled Nafion": why two?

Response: Thanks for your suggestion. We have revised this part as:

“The sampled aerosol was dried by two parallelly assembled Nafion dryers with a length of 1.2 m, two Nafion driers was used because of the high RH and sample flow rate (~16 L/min) during the campaign to ensure drying efficiency. In addition, during autumn and winter in the NCP, ambient air temperature (<20 °C and sometimes <0 °C) can be significantly lower than the room temperature (~24 °C). Therefore, this dryer system can maintain the RH of sampled aerosols to below 20%.”

L214: “volume concentration derived from AMS and rBC measurements”: which density was used?

Response: Thanks for your suggestion. We have revised this sentence as:

“The average ratio between volume concentration derived from AMS and rBC measurements (densities of compounds are the same as Kuang et al., 2021)”

L245: “without conditioning”: must be dried. At which RH?

Response: Thanks for your suggestion. We have revised this sentence as:

“…selecting dried particles without conditioning (RH ~15%) …”

L259: “measured in the V mode.”: residence time?

Response: Thanks for your suggestion. We have revised this sentence as:

“…were measured in the V-mode (residence time inside the heated tube to be about 1.6 s; Hong et al., 2017).”

L288: “(flow rate range of SP2: 0.03 to 0.18 L/min).”: why this variability?

Response: Thanks for your suggestion. We have revised this sentence as:

“(allowed flow rate range of SP2: 0.03–0.18 L/min from the specification) …”

L366: “SOA, POA and BC mass all reached 10”: unclear: together or individually?

Response: Thanks for your suggestion. We have revised this sentence as:

“…the highest mass concentrations of SOA, POA, and BC reached 10 beyond ug/m^3”

L431: “that some BC-free aerosols were characterized as low volatile and non-negligible fractions of BC-free aerosols dominated within these less volatile aerosol components”: could also contain BC with smaller size than minimum threshold

Response: Thanks for your suggestion. We have revised this sentence as:

“However, during the cleaning period, NF$_V$ was even lower than NF$_{noBC}$, suggesting that some BC-free aerosols were characterized as low volatile, which were likely less volatile organic aerosols (not likely contributed by BC-containing particles with a BC smaller than the SP2 detection limit, because the SF of this type of volatile BC-

containing aerosols has an SF lower than 80/200, which is substantially lower than the threshold SF of 0.85 for NF_V calculation). …"

L440: "As mentioned above that NFH was also lower 441 than MAF during the moderately polluted period, suggesting periods, there may be a significant fraction of volatile BC-free aerosols": not clear

Response: Thanks for your suggestion. We have revised this sentence as:

"As mentioned above, NF_H was also lower than MAF during moderately polluted periods, and there may be a significant fraction of volatile BC-free aerosols with hygroscopicity lower than the critical κ value of 0.07; however, they were still CCN-active and therefore not fully hydrophobic"

L492: "correlation with MFFFOA (-0.45~-0.74) was much weaker compared to MFBBOA. (-0. 10~-0.45).": do not mix up weaker correlation and stronger anticorrelation

Response: Thanks for your suggestion. We have revised this sentence as:

"However, the anticorrelation with MF_{FFOA} (-0.45~-0.74) was much stronger than MF_{BBOA} (-0.10~-0.45)."

L510: "was not contributed by BC-containing aerosols": again, pssibility of BC smaller than lower cut of SP2

Response: Thanks for your suggestion. This is not likely, a BC-containing aerosols of 200 nm with BC core smaller than 80 nm was quite aged in the air. This sentence is revised as:

"was not contributed by BC-containing aerosols (BC-containing aerosols of 200 nm with BC core smaller than 80 nm which is smaller than the detection limit of SP2 likely to be quite aged in the air, thus not possible to be nearly hydrophobic)"

Sincerely Yours

Ye Kuang and Li Liu

Reference:

Kuang, Y., Huang, S., Xue, B., Luo, B., Song, Q., Chen, W., Hu, W., Li, W., Zhao, P., Cai, M., Peng, Y., Qi, J., Li, T., Chen, D., Yue, D., Yuan, B., and Shao, M.: Contrasting effects of secondary organic aerosol formations on organic aerosol hygroscopicity, Atmos. Chem. Phys. Discuss., 2021, 1-27, 10.5194/acp-2021-3, 2021.

Hong, J., Äijälä, M., Häme, S. A. K., Hao, L., Duplissy, J., Heikkinen, L. M., Nie, W.,

Mikkilä, J., Kulmala, M., Prisle, N. L., Virtanen, A., Ehn, M., Paasonen, P., Worsnop, D. R., Riipinen, I., Petäjä, T., and Kerminen, V.-M.: Estimates of the organic aerosol volatility in a boreal forest using two independent methods, Atmos. Chem. Phys., 17, 4387–4399, https://doi.org/10.5194/acp-17-4387-2017, 2017.

Reviewer #1:

General comments:

The presented study investigates the mixing state of aerosol particles using different techniques: H- and V-TDMA, CCNC, and SP2 measurements are available in connection with chemical measurements for a 1-month campaign in the North China plain (NCP). This combination provides a useful data set to investigate the aerosol mixing state. However, this combination of measurements gives a lot of information and in this study many parameters were calculated. To understand the relationships and differences between these parameters, they need to be explained and presented in more detail. I believe, the data itself are worth to be published, but the quality of analysis and publication should be improved. The authors use too many abbreviations that disrupt the flow of reading. Some abbreviations are not explained at all, but I think even those that are well known in a particular community should be written out at least once. Furthermore, the statistical analysis is not convincing. Linear correlations are applied to all data points, but in my view, they do not well describe the data in all cases. A critical analysis is needed here to determine which of these statistical results are meaningful. This is my main criticism of this work.

The quality of the language is not very good and the manuscript is not easy to read. I *recommend a complete check by a native speaker.*

Thus, the paper needs major revision regarding the statistical analysis. After that, the text should be partly rewritten or at least significantly revised before it can be accepted for publication in ACP.

Response: Thanks for your comments. This study provides a first-time intercomparison of aerosol mixing state parameters from the instruments including DMA-SP2, DMA-CCN, HTDMA and VTDMA and offers insights into the interlink among these parameters and potential influencing factors. Aerosol mixing states were usually investigated using one or two of instruments listed above, however, none of them could deliver a full picture of aerosol mixing state variations. The purpose of this paper is to investigate what's the difference among these mixing state parameters and mechanism behind those difference under atmospheric conditions of the campaign, which helps aerosol scientists to understand better aerosol mixing states obtained using different techniques and also design better their future aerosol experiments, because differences among mixing state parameters might deliver important message about physical and chemical properties of primary and secondary aerosols as discussed in this study. Some observed differences can be qualitatively explained based on existing knowledge; however, some differences help us explore possible properties of primary and secondary aerosols and might deliver phenomena that urge explanation in the future. If we go very detail into the variations of each aerosol mixing state parameters, the manuscript would be very long and more difficult for readers because it was very difficult to find readers who understand very well all instruments listed above (DMA-SP2, DMA-CCN, HTDMA, VTDMA) and aerosol primary emissions as well as atmospheric chemistry related with secondary aerosol formations. The authors struggled in writing this manuscript because this is also difficult for us, although the first author has very good records of research using DMA-CCN and HTDMA, and the corresponding author have good records of aerosol physical properties and atmospheric chemistry. We decided to write this paper because we find this might be important and interesting for aerosol community, and also helpful for us and we want to share these insights. Actually, we plan to dig more into these variations based on insights obtained in this research in the our future studies.

We agree with the reviewer that some places should be explained more in detail, and therefore more explanations were added before reaching conclusions in some parts as recommended by the reviewer#2.

In terms of statistical analysis, we use linear correlations to examine whether the primary emissions or the secondary aerosol formations have significant impacts on the aerosol mixing state parameters, rather than getting linear relationships. Linear

fittings in the manuscript delivered false impression thus all linear fittings are removed in related figures and leave only correlation coefficients. We discussed this with authors and believe that there are no explicit relations among these parameters, thus correlation test is the only way we could have now based on our limited measurements to explore potential influencing factors as what was done in most previous papers that discuss possible mechanisms behind variations in mixing state parameters.

In terms of writing, the reviwer#2 have raised a lot of comments to help improve the readability, and we revised the manuscript based on comments of both reviewers which is beneficial for non-expert readers. We have also improved this manuscript through Elsevier Language Editing Services:

ELSEVIER

Certificate of Elsevier Language Editing Services

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Comments in detail:

There are basic criticisms of the manuscript, so I will go into less detail. Most of my comments are more general, only few of them focus on typos and so on, which does not mean, that these are all minor comments. But I would focus on the detail after the rest is done.

Examples for abbreviations, that are never written out:

SOA, POA, SSOA, BBOA, CCOA, FFOA, MAF..

Some of them are well known, others not. I do not know all of them which makes the reading really difficult. Each abbreviation has to be explained once, but I would suggest to use less abbreviations in general. Even if abbreviations are explained in the technical section and used later without explanations does not really help. I prefer written text, it helps a lot to understand the text much better. In my view it is required to explain those abbreviations, which are not widely known, such as MAF, CCOA, regularly again, also in figure captions.

Response: Thanks for your suggestion. We have added a table listing the definition and description of the abbreviations as follow:

Table 1. Definition and description of abbreviations.

Abbreviation	Full name and/or Definition
BBOA	Biomass Burning Organic Aerosol Characterized by obvious m/z 60 (mainly $C_2H_4O_2^+$) and 73 (mainly $C_3H_5O_2^+$), which are two indicators of biomass burning
FFOA	Fossil Fuel Organic Aerosol A mixed factor that comprises traffic emissions and coal combustion, which was characterized by typical hydrocarbon ion series
OOA	Oxygenated Organic Aerosol
OOA1 and OOA2	Two OOA factors resolved from the PMF analysis
SOA	Secondary Organic Aerosol Summation of OOA1 and OOA2
POA	Primary Organic Aerosol Summation of BBOA and FFOA
SIA	Secondary Inorganic Aerosols, including nitrate, sulfate, and ammonium
$PM_{2.5}$	Particulate Matter with an aerodynamic diameter <2.5 µm

PM_1	Particulate Matter with an aerodynamic diameter <1 µm
NR-PM_1	Non-refractory PM_1
MF	Mass Fraction
D_p	Particle diameter after humidification or heating
D_d	Particle diameter under dry conditions without humidification or heating
κ	Hygroscopicity parameter
SS	Supersaturation
SPAR	Size-resolved Particle Activation Ratio Size-dependent CCN activity under a specific SS
MAF	Maximum Activation Fraction An asymptote of the measured SPAR curve at large particle sizes and represents the number fraction of CCNs to total particles
D_a	Midpoint activation diameter Linked to the hygroscopicity of CCNs
GF	Growth factor The ratio between particles with and without humidification and is linked to aerosol hygroscopicity
SF	Shrinkage Factor The ratio between particles with and without heating and is linked to aerosol volatility
PDF	Probability Distribution Function
NF_H	Number Fraction of Hydrophilic aerosol whose hygroscopicity parameter is >~0.07
NF_V	Number Fraction of Volatile aerosol whose Shrinkage

	Factor at 200 °C is <0.85
NF_{noBC}	Number Fraction of black carbon (BC)-free particles
NF_{CBC}	Number Fraction of thickly coated BC particles
R_{exBC}	The number concentration ratio of externally mixed BC particles in total BC-containing particles Externally mixed BC particles are defined as identified bare/thinly coated BC-containing particles
NF_A-NF_B (NF_{noBC}-NF_H, NF_V-NF_H, NF_{noBC}-NF_V, NF_V-MAF, NF_{noBC}-MAF)	The difference between the number fraction of A and B

In addition, we have also added the definition and description of the abbreviations when first introduced in each section and also in the caption of the figures for clarification.

Section 2.2:

Some more technical details about the aerosol measurements would be helpful. What type of inlet was used? Was the measurement flow dried? How was the relative humidity in the inlet flow?

Response: Thanks for your suggestion. We have added technical details about the aerosol measurements in Section 2.1 as follow:

"The inlet was switched among three impactors: TSP (Total Suspended Particles), $PM_{2.5}$ (Particulate Matter with an aerodynamic diameter of less than 2.5 μm), and PM_1 (Particulate Matter with an aerodynamic diameter of less than 1 μm). Inlet changes among impactors affect dry-state aerosol sampling owing to ambient aerosols are enlarged through aerosol hygroscopic growth or activation. However, the aerosol mixing state and aerosol chemical composition measurements were made on submicron aerosols, and the inlet change almost did not affect those measurements under conditions of RH less than 90%. The sampled aerosol was dried by two parallelly assembled Nafion dryers with a length of 1.2 m. Two Nafion driers was used because of the high RH and sample flow rate (~16 L/min) during the campaign to ensure drying efficiency. In addition, during autumn and winter in the NCP, ambient air temperature (<20 °C and sometimes <0 °C) can be significantly lower than the room temperature

(~24 °C). Therefore, this dryer system can maintain the RH of sampled aerosols to below 20%.”

Were losses in inlet line and sampling systems considered?

Response: losses in inlet line and sampling systems are not considered in this study. reasons are listed below: (1) investigated mixing state parameters are represented by number fractions of different diameters which are much less affected by losses in sampling systems compared with absolute umber concentrations; (2) good consistency was achieved between measurements of particle number size distributions (PNSD) and mass concentrations measured by AMS, with the average ratio between volume concentration derived from AMS and rBC measurements and volume concentration derived from PNSD measurements is 0.79 (R=0.97, as shown in the following), which is consistent with previous reports due to that AMS cannot detect aerosol components such as dust (Kuang et al., 2021). This means that almost same aerosol populations were sampled by AMS and instruments of measuring aerosol mixing states.

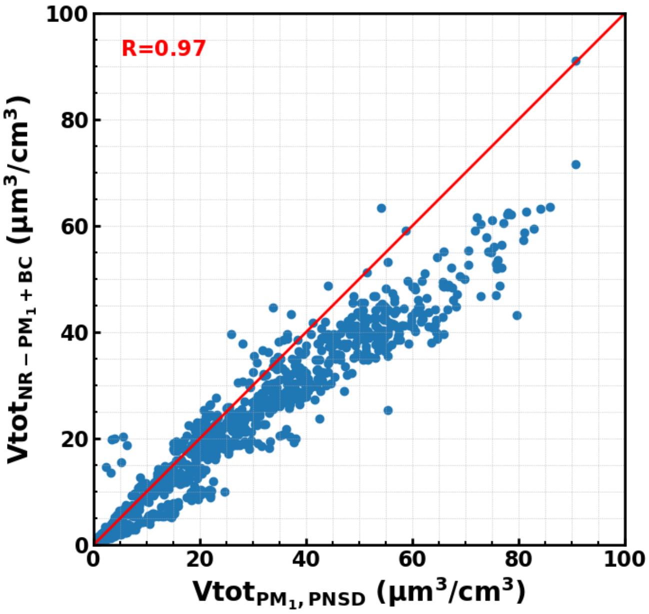


Fig. S3. Comparison between aerosol volume concentration derived from measurements of PNSD and aerosol chemical compositions.

The following sentences are added in the revised manuscript.

“This study did not consider losses in the inlet line and sampling systems for the following reasons: (1) investigated mixing state parameters are represented by number fractions (NFs) of different diameters, which are much less affected by losses

in sampling systems compared with absolute number concentrations; and (2) good consistency was achieved between measurements of particle number size distributions (PNSD) and mass concentrations measured by AMS. The average ratio between volume concentration derived from AMS and rBC measurements (densities of compounds are the same as Kuang et al., 2021) and the volume concentration derived from PNSD measurements was 0.79 (R=0.97, as shown in Fig. S3), consistent with previous reports as AMS cannot detect aerosol components, such as dust (Kuang et al., 2021).

”

Dd is probably the dry diameter?! This is not explained. What means ‘dry’? Just not humidified?

Response: Yes, Dd is the dry diameter particle, which corresponds to particle diameter under dry conditions (RH<20%) and not humidified. For clarification, we have revised the description of Equation (1) as:

“… H/V-TDMA can operate in either H- or V-mode, controlled by a three-way solenoid valve. A Nafion humidifier was used in the H-mode to condition the selected dry particles to 90% RH equilibrium. The number-size distribution of humidified particles (D_p) was measured using DMA2 and CPC (Model 3772, TSI Inc.). The RH-dependent hygroscopic growth factor (GF) at a specific diameter (D_d) was calculated as follows:

$$\mathrm{GF}=\frac{D_p(RH)}{D_d} \qquad (1)$$

where D_p(RH) is the size of particles undergoing humidification. …”

The same diameters Dd and DP are used in the definition for the shrinking factor, what is the meaning here?

Response: Thanks for your suggestion. In the definition for the shrinking factor, Dd is the dry diameter particle, which corresponds to particle diameter under dry conditions and not heated while Dp is the particle diameter after heating. we have revised the description of Equation (2) as:

“The temperature-dependent shrinkage factor (SF), which is the ratio of heated particle size to dry particle size without heating (D_d), is defined as:

$$SF=\frac{D_p(T)}{D_d} \tag{2}$$

where $D_p(T)$ denotes the particle diameter during heating. …”

Section 2.3:

Parameterization of the SPAR function is not easy to understand without knowing how it looks like. Can the authors give an example?

Response: Thanks for your suggestion. As shown in Figure S4, the measured SPAR is generally characterized as a sigmoidal curve (the black line). MAF is the asymptote of the measured SPAR curve at large particle sizes and Da indicates the diameter where SPAR equals the half of the MAF value. The parameter s corresponds to the slope of steep increase of SPAR curves when diameter is close to Da.

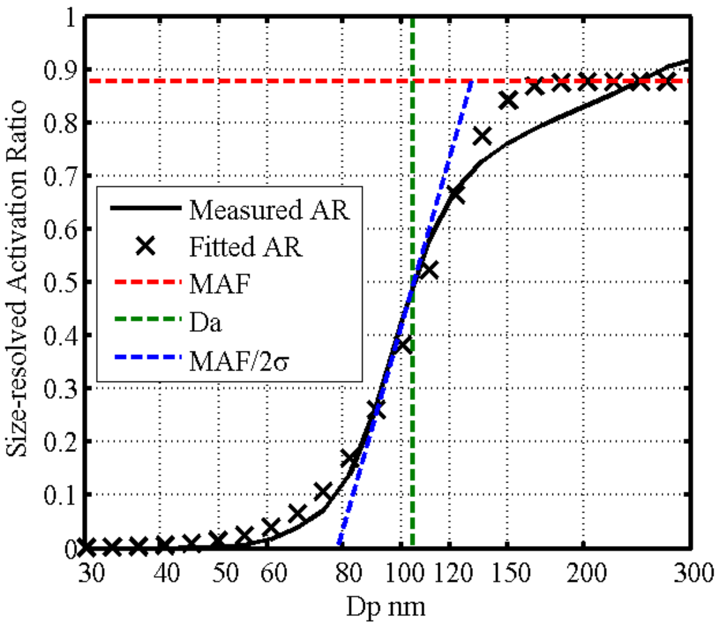


Fig. S4. Schematic of the parameterization scheme of SPAR curves. The black solid curve and the black crossing are the measured SPAR and fitted SPAR with the parameterization scheme. The red, green and blue dashed lines indicate the fitting parameters of Maximum Activation Fraction (MAF), the midpoint activation diameter (Da) and s, respectively.

We have added this figure into the supplement and revised the description of SPAR parameterization scheme as:

"The SPAR curves were parameterized using a sigmoidal function with three parameters. As shown in Fig. S4, a sigmoidal curve generally characterized the measured SPAR. This parameterization assumes that the aerosol is an external mixture of CCN-active hydrophilic and CCN-inactive hydrophobic particles (Rose et al., 2010). The formula used to parameterize the SPAR ($R_a(D_d)$) for a specific SS is as follows (Rose et al., 2008):

$$R_a(D_d)=\frac{MAF}{2}\left(1+\operatorname{erf}\left(\frac{D_d-D_a}{\sqrt{2\pi}\sigma}\right)\right) \tag{7}$$

where erf denotes the error function. The Maximum Activation Fraction (MAF) is an asymptote of the measured SPAR curve for large particles, as shown in Fig. S4, representing the fraction of CCNs relative to the total number of particles. D_a is the midpoint activation diameter, is linked to the hygroscopicity of the CCNs, and indicates the diameter where the SPAR equals half of the MAF value. The σ is the standard deviation of the cumulative Gaussian distribution function and characterizes the heterogeneity of CCN hygroscopicity. In Fig. S4, the σ indicates the slope of the steep increase in the SPAR curves when the diameter is close to Da. …"

People, who are not familiar with the SP2 do not understand the explanation given here. What does the lag time mean? Why is it called lag time? By the way, there are three different ways of writing in the manuscript: lagtime, lag-time and lag time, for consistency one should be chosen. I would take the latter one.

Response: Thanks for your suggestion. The lag time is defined as the time difference between the occurrences of the peaks of the incandescence and scattering signals measured by SP2 (Moteki & Kondo, 2007; Sedlacek et al., 2012; Subramanian et al., 2010), and for coated BC particles, the incandescence signals is generally detected later than the scattering signals. As shown in former studies (Zhang et al., 2018; Zhao et al., 2021), the distribution of the lag time for ambient particles exhibits a clear two-mode distribution and this lag time can be used to indicate the coating thickness of the BC-containing aerosols.

We have revised lagtime and lag-time to lag time, and have revised this paragraph as:

"… For the measurement of coated BC particles at SP2, the incandescence signal is generally detected later than the scattering signals and the time difference between the occurrence of the peaks of the incandescence and scattering signals is defined as the lag time (Moteki & Kondo, 2007; Sedlacek et al., 2012; Subramanian et al., 2010). The coating thickness of BC-containing aerosols in the SP2 measurement can be

indicated by the lag time (Moteki and Kondo, 2007; Schwarz et al., 2006; Sedlacek et al., 2012; Subramanian et al., 2010; Metcalf et al., 2012), which has exhibited a clear two-mode distribution in previous studies (Zhang et al., 2018; Zhao et al., 2021). A critical lag time threshold can be used to differentiate between the different types of BC-containing aerosols and calculate the NF of bare and coated BC particles in the total identified aerosols. …"

"

Section 3:

Figure 1 is very complex. Figures c – e also have a color scale on the right hand side, but this is not explained at all.

Response: Thanks for your suggestion. We have revised the caption of Figure 1 by adding descriptions of each panel and the color scale as:

"Figure 1. Overview of the measurements during the campaign: (a) meteorological parameters: wind speed (dots) and relative humidity (RH) (black line), with colors of dots representing wind direction; (b) mass concentrations of aerosol chemical compositions: secondary inorganic aerosols (SIA, red circle), secondary organic aerosols (SOA, green plus), primary organic aerosols (POA, blue x) and black carbon (BC, black dots); (c) Size-resolved Particle Activation Ratio (SPAR) under supersaturation (SS) of 0.08% observed by the DMA-CCNC, with warmer colors corresponding to higher values; (d) Probability Density Function (PDF) of growth factor (GF-PDF) at 200 nm observed by the HTDMA; (e) PDF of shrinkage factor (SF-PDF) at 200 nm and 200 °C observed by the VTDMA; (f) PDF of lag time at 200 nm observed by the DMA-SP2. The blue, red, and green shaded periods represent the three periods with moderate pollution, heavy pollution, and clean conditions, respectively."

Line 316 ff: '...corresponding fitting parameters, Da...' Da is just one parameter and means probably the mean diameter? How are these diameters obtained? Da should probably be Da?! Other fitting parameters are needed?

Response: Da is the midpoint activation diameter, not the mean diameter. Da is not shown in Figure 2 and may be mistaken as particle size Dp. Here we are referring to Da values during the campaign. It can be found that Da value agree with the particle size where SPAR equals about 0.5. We have revised this sentence as:

"For the three measured SSs, the particle sizes where SPAR equals approximately 0.5

are approximately 90, 120, and 180 nm for the three SSs of 0.08%, 0.14%, and 0.22%, respectively, consistent with the average D_a (see Eq. 7) values of the campaign."

MAF seems to be another fitting parameter, but what does MAF mean?

Response: MAF is Maximum Activation Fraction and an asymptote of the measured SPAR curve at large particle sizes. We have added the description of MAF where MAF is first mentioned in this section as:

"The NF of CCN-active particles in large-diameter ranges (which varies with SS and, for example, is greater than 200 nm for 0.08%) can be indicated by the gradual increase in the SPAR curves and quantified by the fitting parameter, MAF (see Eq. 7)."

There appear again lots of abbreviations, such as RexBC. This is explained once, but since it is not common, I had to look it up again and again. I would prefer reading without so many abbreviations.

Response: Thanks for your suggestion. We added a table listing the description of these abbreviations as mentioned earlier, and have added the explanations of these abbreviations like RexBC where they are first introduced in each section and in caption of each figure.

Line 371, caption figure 4 and others: the word 'composition' is used in the wrong context. The authors mean probably component(s). This appears several times in the text.

Response: Thanks for your suggestion. We have revised it accordingly including:

L47: "BC-containing aerosols emitted from fossil fuel combustion tend to be more externally mixed with other aerosol components …"

L298: "The mass concentrations of different aerosol components …"

L308: "The diurnal variations in mass concentrations of different aerosol chemical components …"

L363: "the mass fractions of aerosol chemical components"

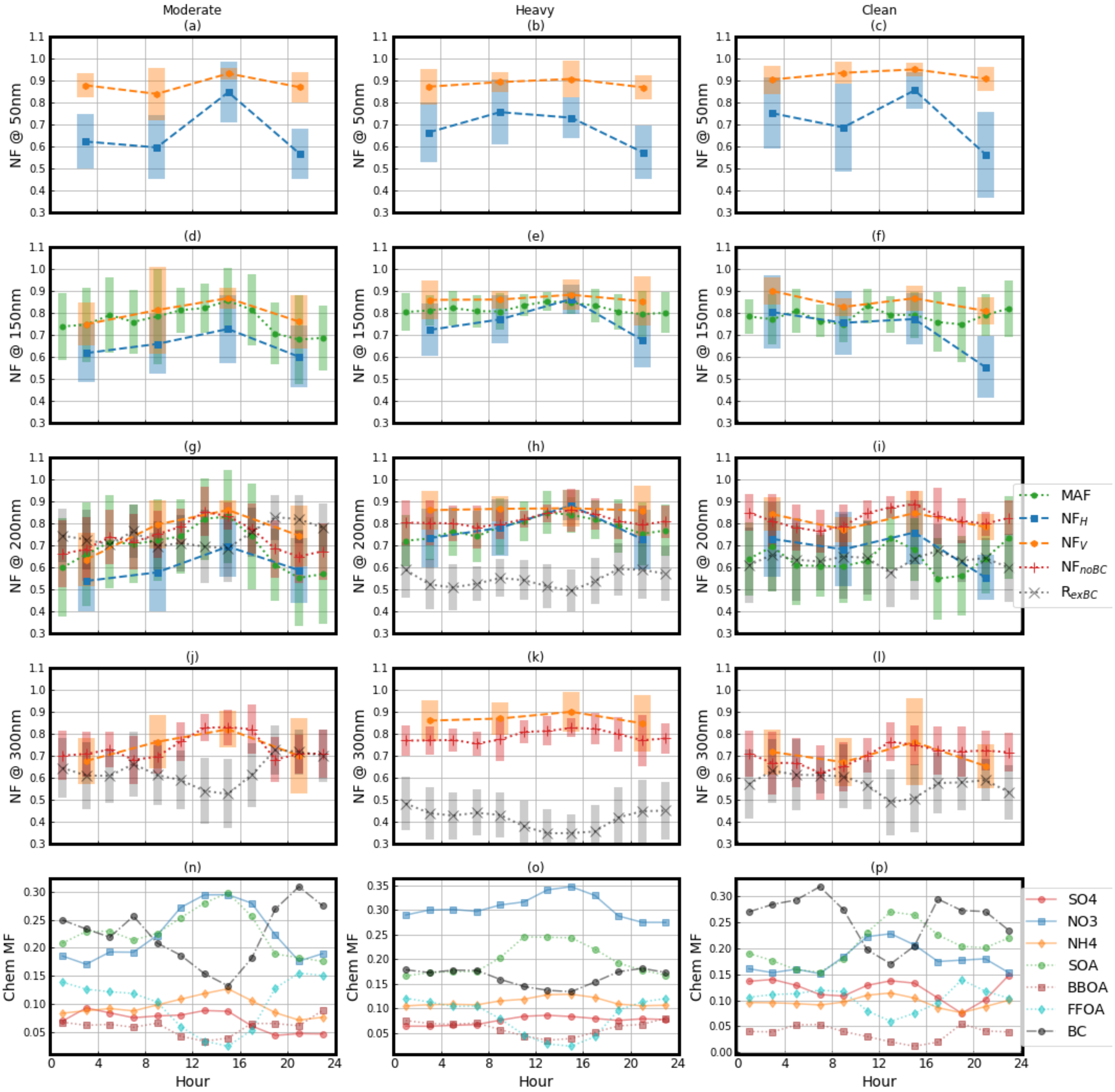
L398 : "the mass fraction of each primary organic aerosol components"

Figure 7, 8 and 9: "the mass fraction of secondary aerosol chemical components"

Figure 4: "mass fraction of aerosol chemical components"

Figure 4: what are the shaded areas? Standard deviations? Uncertainty? This has to be explained in the figure caption! My question is, if the differences e.g., between the different diameters are significant? For me, the shapes of the curves of NF for different diameters look very similar, in particular if the shaded area represents an uncertainty range.

Response: Thanks for your suggestion. The shaded areas indicate the standard deviations, The difference between those of different diameters are not significant, especially for particle diameters larger than 100nm. As the reviewer #2 suggested, we keep the sizes with most concurrent measurements, e.g. 150, 200 and 300 nm and move the rest particle sizes into the supplement. In detail, we have revised Figure 4 and its caption as:

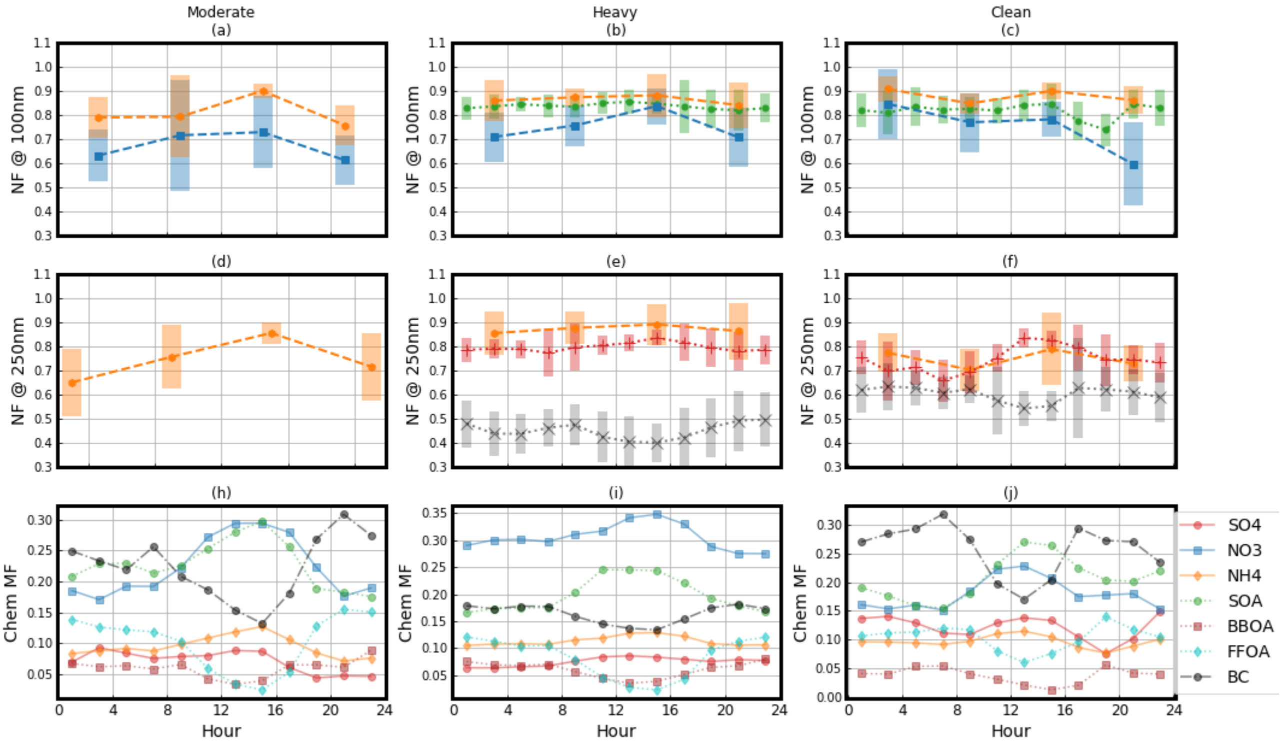


“Figure 4. (a–l) Diurnal variations of aerosol mixing state parameters (identified by color and marker) at different particle sizes (50, 150, 200, and 300 nm) during the three periods. The shaded areas indicate the standard deviations. (m–o) Diurnal variations of mass fractions (MFs) of aerosol chemical compositions, including secondary organic aerosols (SOA), biomass burning organic aerosol (BBOA), fossil fuel organic aerosols (FFOA), and inorganic ions including sulfate (SO_4), nitrate (NO_3), and ammonium (NH_4) (identified by color and marker) during the three periods.”

We have revised the corresponding description of Figure 4 as:

“For particles >100 nm (Fig. 4 and S5), there was a maximum in the afternoon for MAF, NF_H, NF_V, and NF_{noBC}, indicating a peak during this time due to an increase in SA compositions, such as nitrate and SOA, and a decrease in POA and BC.”

We have also added Figure S4 into the supplement as:



“Fig. S5. (a-f) Diurnal variations of aerosol mixing state parameters (identified by color and marker) at different particle sizes (100 and 250 nm) during the three periods. The shaded areas indicate the standard deviations. (g-i) Diurnal variations of mass fraction of aerosol chemical compositions (identified by color and marker) during the three periods.”

In the description of this figure 4 the word ‘peak’ is frequently used, but I see only slight maxima between different times of the day. This has to be checked and needs to be adapted.

Response: Thanks for your suggestion. It should be a maxima between different times of the day and is indicative of a peak in the afternoon. We have revised corresponding descriptions of figure 4 as:

"For particles >100 nm (Fig. 4 and S5), there was a maximum in the afternoon for MAF, NF_H, NF_V, and NF_{noBC}, indicating a peak during this time due to an increase in SA compositions, such as nitrate and SOA, and a decrease in POA and BC."

"In the clean-air period, there was another maximum at midnight for MAF and NF_{noBC}, which may be attributed to the diurnal variations in SA compositions, such as sulfate and SOA, and the decrease in BC and FFOA."

Line 388: What means 'consistency' here? I simply do not understand it.

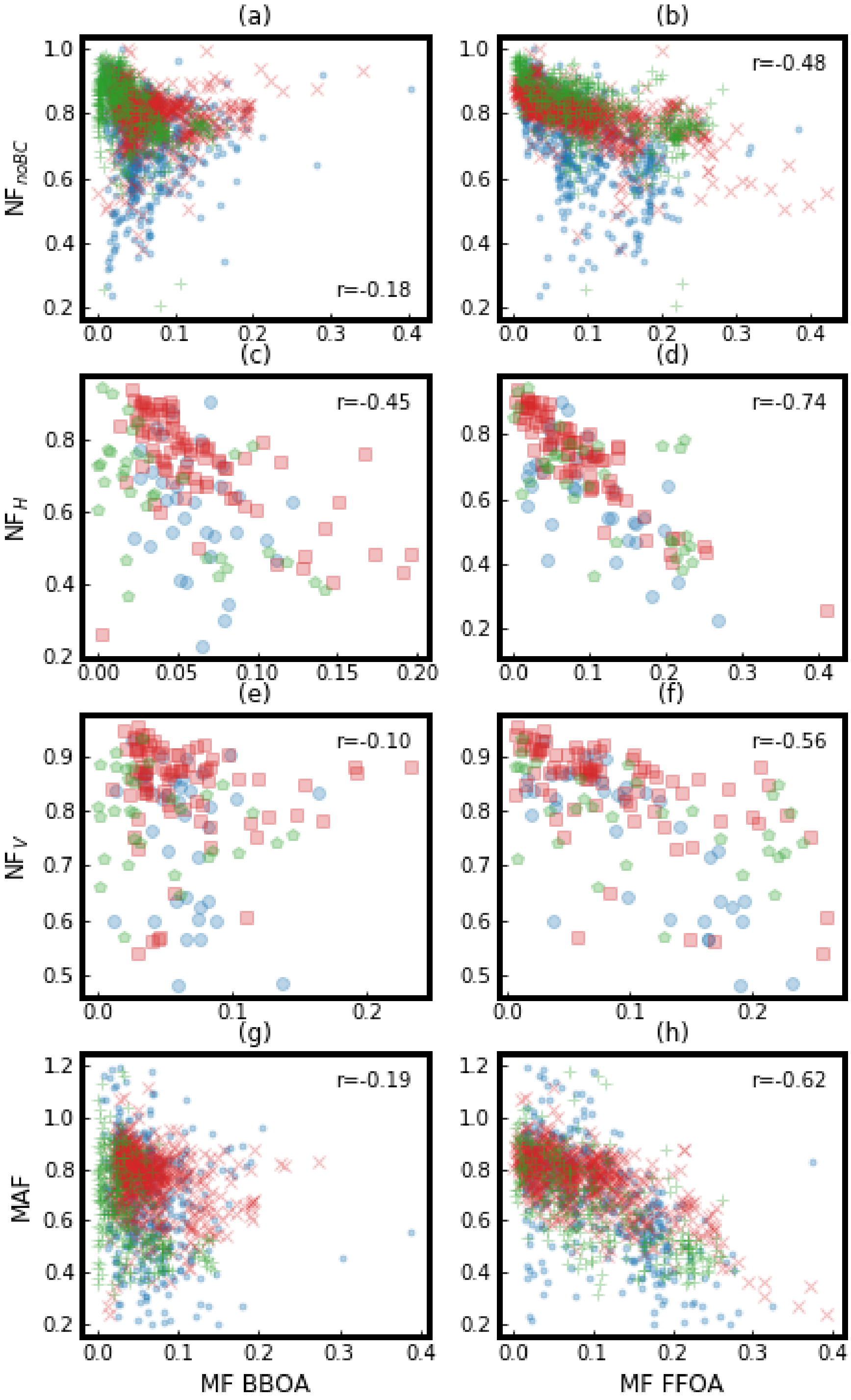
Response: We are referring to the agreement between different aerosol mixing state parameters and we have revised this sentence as:

"The agreement between MAF and NF_V was slightly higher than that between MAF and NF_H or between NF_H and NF_V with similar correlation coefficients (~0.65)."

Figures 5 – 9: linear correlations were fitted here, but the results do not always look convincing. E.g., Figure 7: 2 lowest plots show dots widely distributed and one does not expect a linear correlation. What is the meaning of such a correlation? I strongly suggest to check the quality of these correlations and reduce to number of these plots.

Response: Thanks for your suggestion. In former studies on the aerosol mixing state, it is common to investigate the linear correlations between aerosol mixing state parameters as well as aerosol chemical compositions (Reference listed in the introduction like: Zhang et al., 2014; Hong et al., 2017; Kim et al., 2020; Tao et al., 2021). In this study, the correlation analysis is used to examine whether the primary emissions or the secondary aerosol formations have significant impacts on the aerosol mixing state parameters, and for some cases there was no significant influences which also provide insights into investigating variations of mixing state parameters. In order to avoid misunderstanding and highlight the our findings, we have removed the fit lines. In detail, we have revised Figure 5-9 as:

Figure 5:



(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
r=-0.18
r=-0.48
r=-0.45
r=-0.74
r=-0.10
r=-0.56
r=-0.19
r=-0.62
NF$_{noBC}$
NF$_H$
NF$_V$
MAF
MF BBOA
MF FFOA
0.2
0.4
0.6
0.8
1.0
1.2
0.5
0.7
0.9
0.0
0.1
0.2
0.3
0.4
0.00
0.05
0.10
0.15
0.20

Figure 6:

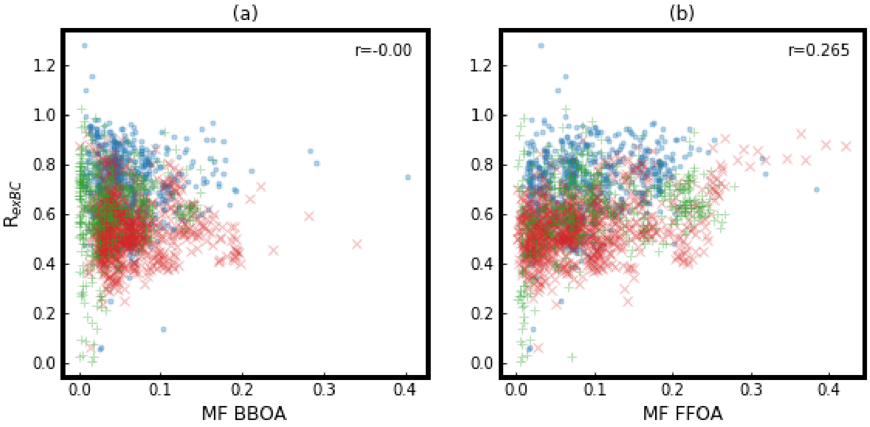


Figure 7:

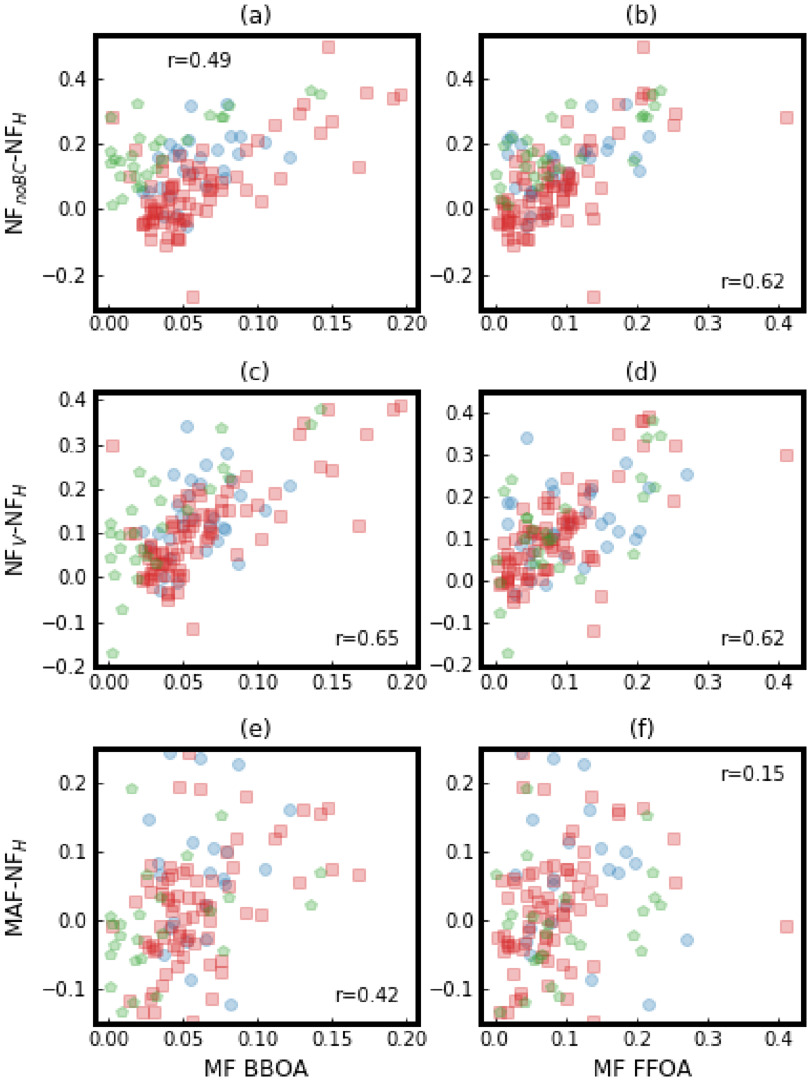


Figure 8:

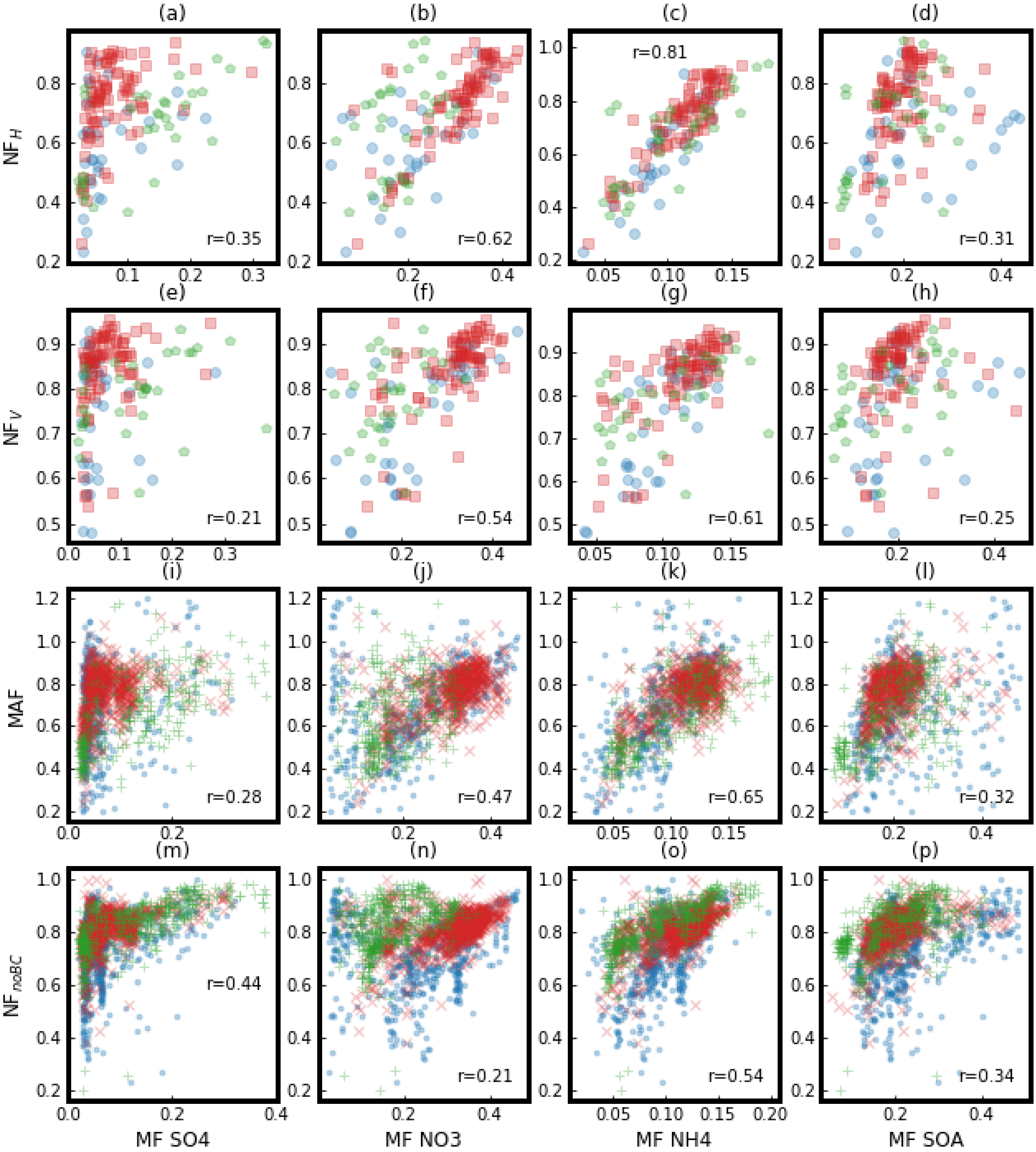

(a)
(b)
(c)
(d)
NF$_H$
r=0.35
r=0.62
r=0.81
r=0.31
(e)
(f)
(g)
(h)
NF$_V$
r=0.21
r=0.54
r=0.61
r=0.25
(i)
(j)
(k)
(l)
MAF
r=0.28
r=0.47
r=0.65
r=0.32
(m)
(n)
(o)
(p)
NF$_{noBC}$
r=0.44
r=0.21
r=0.54
r=0.34
0.0
0.1
0.2
0.3
0.4
0.05
0.10
0.15
0.20
0.5
0.6
0.7
0.8
0.9
1.0
1.2
MF SO4
MF NO3
MF NH4
MF SOA

Figure 9:

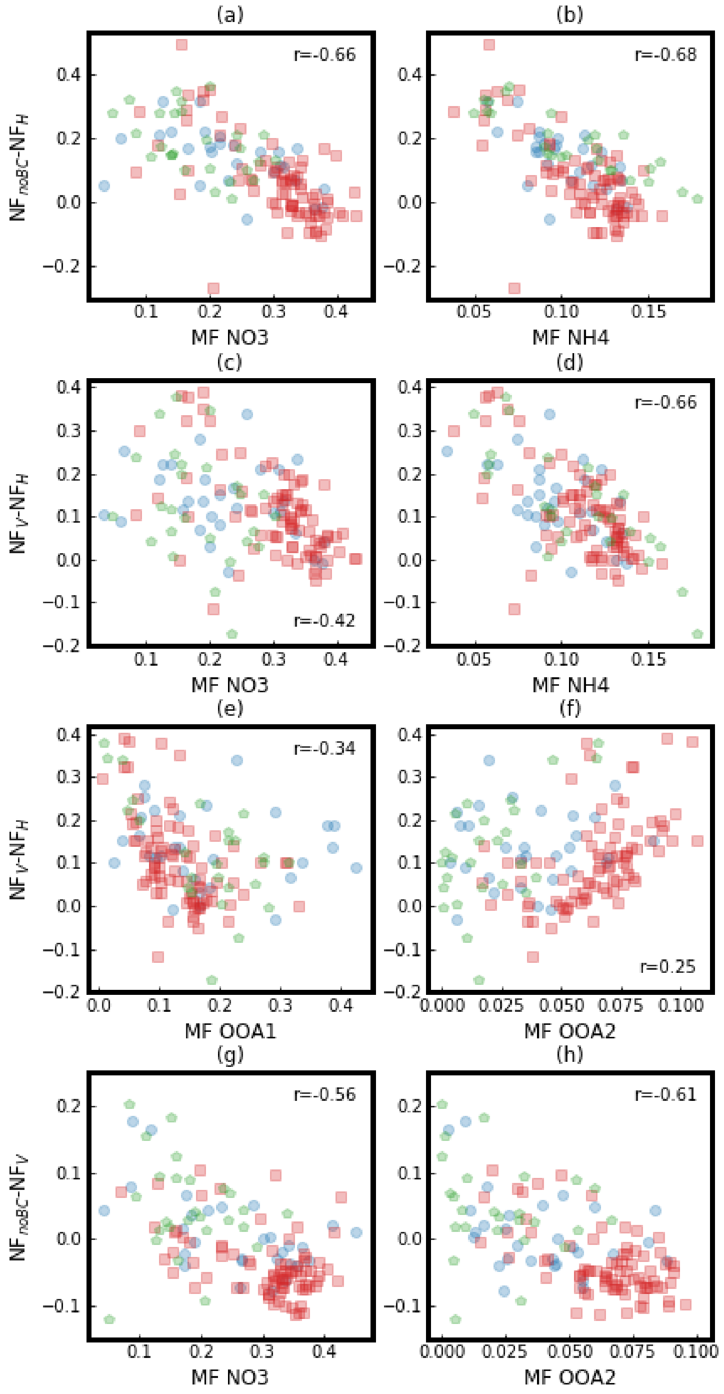


Figure 8: the lower plots seem to follow more an exponential growth, does the linear fit makes sense here?

Response: As we mentioned in the former response, the correlation analysis of this study is used to qualitatively explore whether the primary emissions or the secondary aerosol formations affect significantly on variations of aerosol mixing state

parameters, as commonly applied in former studies on the aerosol mixing state (Reference listed in the introduction like: Hong et al., 2017; Kim et al., 2020; Tao et al., 2021). We have removed the fit lines with correlation coefficient (r) less than 0.5 as shown in the former response.

Figure 9: what means OOA1 and OOA2?

Response: OOA1 and OOA2 are two SOA factors from the PMF analysis of organic aerosol. As mentioned in Section 2.1, these two SOA factors were found to display different spectral patterns, correlations with tracers and diurnal variations, suggesting that they resulted from different chemical processing, however, the formation mechanism and possible precursors are yet to be explored in future. For example, OOA1 had higher CO2+/C2H3O+ (3.9) and O/C (0.91) ratios compared to OOA2 (2.1, 0.78). We have revised this caption as:

"Figure 9. The correlation between the difference among the four aerosol mixing state parameters and mass fraction (MF) of secondary aerosol (SA) chemical components during different periods. OOA1 and OOA2 are two secondary organic aerosol (SOA) factors resolved from aerosol mass spectrometer (AMS) measurements using the Positive Matrix Factorization (PMF) technique. Moderately polluted period: blue circle; heavily polluted period: red square; clean period: green pentagon."

All figure captions need more text to explain the figure. One should understand the general content of a figure without reading the full text around.

Response: Thanks for your suggestion. Besides the captions of Figures 1, 4 and 9 whose revision have been mentioned earlier, the captions of other figures are revised as:

"Figure 2. The campaign average of (a) Size-resolved Particle Activation Ratio (SPAR) curves measured by DMA-CCNC at the three supersaturations (SSs, represented by different colors and markers), (b) Probability Density Function (PDF) of lag time measured by DMA-SP2 at four particle sizes (represented by different colors and markers), (c) PDF of growth factor (GF) measured by HTDMA at four particle sizes (represented by different colors and markers), (d) PDF of shrinkage factor (SF) measured by VTDMA under the temperature of 200 °C at five particle sizes (represented by different colors and markers). The shaded areas indicate the standard deviations."

"Figure 3. (a–c) Size dependence of MAF (green circle), NF_H (blue triangle), NF_V (yellow square), NF_{noBC} (red x), and R_{exBC} (black x) during the three periods. MAF: Maximum Activation Fraction, an asymptote of the measured Size-resolved Particle Activation

Ratio (SPAR) curve at large particle. NF_H: Number Fraction of Hydrophilic aerosol whose hygroscopicity parameter is higher than ~0.07. NF_V: Number Fraction of Volatile aerosol whose Shrink Factor at 200 °C is lower than 0.85. NF_{noBC}: Number Fraction of black carbon (BC)-free particles. R_{exBC}: Number fraction of externally mixed BC particles in total BC-containing particles. (d–f) Corresponding mass fractions (MFs) of aerosol chemical compositions (identified by colors) during the three periods, including secondary organic aerosols (SOA), biomass burning organic aerosol (BBOA), fossil fuel organic aerosols (FFOA), and inorganic ions including sulfate (SO_4), nitrate (NO_3), and ammonium (NH_4)."

"Figure 5. The correlations between aerosol mixing state parameters and mass fractions (MFs) of biomass burning organic aerosol (BBOA) and fossil fuel organic aerosols (FFOA) during different periods (moderately polluted period: blue dot or circle; heavily polluted period: red x or square; clean period: green plus or pentagon), with r representing the correlation coefficient."

"Figure 6. The correlations between the ratio of externally mixed black carbon (BC) in total BC particles (R_{exBC}) and mass fractions (MFs) of biomass-burning organic aerosol (BBOA) and fossil fuel organic aerosols (FFOA) during different periods (moderately polluted period: blue dot; heavily polluted period: red x; clean period: green plus), with r representing correlation coefficient."

"Figure 7. The correlations between the difference among the four aerosol mixing state parameters at particle size 200 nm and mass fractions (MFs) of biomass burning organic aerosol (BBOA) and fossil fuel organic aerosols (FFOA) during different periods (moderately polluted period: blue circle; heavily polluted period: red square; clean period: green pentagon), with r representing correlation coefficient."

"Figure 8. The correlation between the four aerosol mixing state parameters and mass fraction (MF) of secondary aerosol (SA) components during different periods (moderately polluted period: blue dot or circle; heavily polluted period: red x or square; clean period: green plus or pentagon), with r representing correlation coefficient. SA components include secondary organic aerosols (SOA), sulfate (SO_4), nitrate (NO_3), and ammonium (NH_4)."

"Figure 10. Variations of different aerosol mixing state parameters during the pollution accumulation process. (a) The time series of mass concentrations of non-refractory PM_1 (NR-PM_1), secondary aerosols (SAs) (including inorganic ions and secondary organic aerosols (SOA)), primary organic aerosols (POA) and black carbon (BC) (identified by colors and markers). (b and c) The variations of different aerosol mixing state parameters (identified by colors and markers) at particle size 200 nm (b) and 300 nm (c). (d and e) The variations of the difference between NF_V and NF_{noBC} (NF_V-NF_{noBC},

blue large circle) and the difference between NF_V and NF_{noBC}+NF_{CBC} (NF_V-(NF_{noBC}+NF_{CBC}), yellow small circle) with the mass concentration of SA at particle size 200 nm (d) and 300 nm (e) NF_{CBC}: Number Fraction of thickly coated black carbon (BC) particles."

Line 472: exemplarily 'difference between NFV – NFH' means difference between NFV and NFH? This appears several times around this section.

Response: Yes, we have revised it as "difference between NFV and NFH (NFV-NFH)". Similar revisions includes:

L427-434: "The difference between NF_{noBC} and NF_H (NF_{noBC}-NF_H) was significantly positively correlated with MF_{FFOA} and MF_{BBOA} (r>0.5), suggesting that a substantial proportion of POA resided in BC-free aerosols and was volatile, but contributed substantially to nearly hydrophobic aerosols; as did the differences between NF_V and NF_H (NF_V-NF_H). The MFs of BBOA and FFOA were poorly correlated with the differences between the MAF and NF_V (MAF-NF_V), MAF and NF_{noBC} (MAF-NF_{noBC}), and NF_V and NF_{noBC} (NF_V-NF_{noBC}) (Fig. S7). The difference between MAF-NF_H was positively correlated with MF_{BBOA}, further suggesting that BBOA contributed to nearly hydrophobic aerosols under subsaturated conditions; however, their hygroscopicity was enhanced, and they became CCN-active under supersaturated conditions."

L464: "The difference between NF_{noBC} and NF_H (NF_{noBC}-NF_H) showed a strong negative correlation with MF_{NH4} and MF_{NO3} (mainly -0.6), as did the differences between NF_V and NF_H (NF_V-NF_H)."

L483: "The difference between NF_{noBC} and NF_V (NF_{noBC}-NF_V) was negatively correlated with MF_{NO3}, which is consistent with the semi-volatile nature of nitrate."

L555: "… the two resolved SOA factors exhibited different impacts on the differences between NF_V and NF_H (NF_V-NF_H), …"

Figure 10: "… (d and e) The variations of the difference between NF_V and NF_{noBC} (NF_V-NF_{noBC}, blue large circle) and the difference between NF_V and NF_{noBC}+NF_{CBC} (NF_V-(NF_{noBC}+NF_{CBC}), yellow small circle)…"

Minor comments/ typos:

Comment: I did not look explicitly for all typos, because I think, several parts need to be rewritten und after that it should be read again carefully.

Line 293: PA means probably POA

Line 319: in large diameters range~~s~~

Line 334:a dot after ‘size’ is missing

Line 439: ‘are presented’ should be ‘is presented’

Response: Thanks for your suggestion and we have revised them accordingly. We have also checked the manuscript again and improved this manuscript by Elsevier Language Editing Services as mentioned earlier.

Reference:

Hong, J., Äijälä, M., Häme, S. A. K., Hao, L., Duplissy, J., Heikkinen, L. M., Nie, W., Mikkilä, J., Kulmala, M., Prisle, N. L., Virtanen, A., Ehn, M., Paasonen, P., Worsnop, D. R., Riipinen, I., Petäjä, T., and Kerminen, V.-M.: Estimates of the organic aerosol volatility in a boreal forest using two independent methods, Atmos. Chem. Phys., 17, 4387–4399, https://doi.org/10.5194/acp-17-4387-2017, 2017.

Kim, N., Yum, S. S., Park, M., Park, J. S., Shin, H. J., and Ahn, J. Y.: Hygroscopicity of urban aerosols and its link to size-resolved chemical composition during spring and summer in Seoul, Korea, Atmos. Chem. Phys., 20, 11245–11262, https://doi.org/10.5194/acp-20-11245-2020, 2020.

Moteki, N., & Kondo, Y. (2007). Effects of mixing state on black carbon measurements by laser-induced incandescence. Aerosol Science and Technology, 41(4), 398–417. https://doi.org/10.1080/02786820701199728

Sedlacek, A. J., Lewis, E. R., Kleinman, L., Xu, J., & Zhang, Q. (2012). Determination of and evidence for non-core-shell structure of particles containing black carbon using the single-particle soot photometer (SP2). Geophysical Research Letters, 39, L06802. https://doi.org/10.1029/ 2012GL050905

Subramanian, R., Kok, G. L., Baumgardner, D., Clarke, A., Shinozuka, Y., Campos, T. L., et al. (2010). Black carbon over Mexico: The effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios. Atmospheric Chemistry and Physics, 10(1), 219–237. https://doi.org/10.5194/acp-10-219-2010

Tao, J., Kuang, Y., Ma, N., Hong, J., Sun, Y., Xu, W., Zhang, Y., He, Y., Luo, Q., Xie, L., Su, H., and Cheng, Y.: Secondary aerosol formation alters CCN activity in the North China Plain, Atmos. Chem. Phys., 21, 7409–7427, https://doi.org/10.5194/acp-21-7409-2021, 2021.

Zhang, S. L., Ma, N., Kecorius, S., Wang, P. C., Hu, M., Wang, Z. B., Größ, J., Wu, Z. J.,

and Wiedensohler, A.: Mixing state of atmospheric particles over the North China Plain, Atmospheric Environment, 125, 152–164, 2016.

Zhang, Y., Su, H., Ma, N., Li, G., Kecorius, S., Wang, Z., et al. (2018). Sizing of ambient particles from a single-particle soot photometer measurement to retrieve mixing state of black carbon at a regional site of the North China Plain. Journal of Geophysical Research: Atmospheres, 123, 12,778–12,795. https://doi.org/10.1029/ 2018JD028810

Zhao, G., Tan, T., Hu, S., Du, Z., Shang, D., Wu, Z., Guo, S., Zheng, J., Zhu, W., Li, M., Zeng, L., and Hu, M.: Mixing state of black carbon at different atmospheres in north and southwest China, Atmos. Chem. Phys., 22, 10861–10873, https://doi.org/10.5194/acp-22-10861-2022, 2022.

Reviewer #2:

General comments:

The present paper focuses on improving our understanding of the aerosol mixing state in a background site of the North China Plain in China. This is achieved by combining various techniques, including HTDMA, CCN counter, VTDMA, and SP2. The study provides a first-time intercomparison of the four aerosol mixing state parameters from the instruments above and offers insights into the interlink among these parameters and potential sources. I find this research to be important and interesting for aerosol mixing state studies. The manuscript is well-structured and scientifically engaging for the aerosol society. However, in terms of writing, it would be beneficial for non-expert readers if certain sentences were shortened and explanations were provided before reaching conclusions. Please see the detailed comments below. I suggest publishing the manuscript after a minor revision.

Response: Thanks for your comments. Suggestions and comments are addressed point-by-point and corresponding responses are listed below. We have also improved this manuscript through Elsevier Language Editing Services:

ELSEVIER

Certificate of Elsevier Language Editing Services

The following article was edited by Elsevier Language Editing Services:

Markedly different impacts of primary emissions and secondary aerosol formation on aerosol mixing states revealed by simultaneous measurements of CCNC, V/HTDMA and SP2

Ordered by:

Jiangchuan Tao

Estimated Delivery date:

2023-08-31

Order reference:

ASLESTD1017819

Specific comments:

1) Line 70. "..lead to substantial overestimation". Could you provide more details about the magnitude of the substantial overestimation?

Response: Thanks for your suggestion. There can be overestimation of NCCN from 10% to 30%, and we have revised this sentence as:

"Using simple internal mixing state assumptions for aerosol chemical compositions to estimate CCN number concentrations can lead to substantial overestimations (up to 30%; Deng et al., 2013; Farmer et al., 2015; Ren et al., 2018; Ching et al., 2017, 2019; Tao et al., 2021)."

2) Line 94. "highly correlated to those of a VTDMA at high temperature". Which temperature do you refer to and why?

Response: In general, in order to remove most non-refractory materials in aerosol, 300 °C is used in VTDMA measurement (Philippin et al., 2004; Wehner et al., 2009; Zhang et al., 2014; Hong et al., 2017; Wang et al., 2022). But this temperature can be lower to 200 °C depending on the aerosol chemical compositions. We have revised this sentence as:

"Thus, measurements of an SP2 are highly correlated to those of a VTDMA at high temperatures (200 °C–300 °C), with their differences reflecting variations in aerosol density, shape, or volatility (Philippin et al., 2004; Wehner et al., 2009; Adachi et al., 2018, 2019; Wang et al., 2022)."

3) Line 127-129. Please summarize the key messages of the meteorology influences on the aerosol mixing state.

Response: Thanks for your suggestion. As reported by Kuang et al., 2020, the secondary aerosol formations under low RH conditions, mainly taken place in gaseous phase, would change to that mainly taken place in aqueous phase under high RH conditions. As secondary aerosol formed through different mechanism have different chemical compositions and add mass to different particle groups, secondary aerosol formations under different meteorological conditions can affect the aerosol mixing states (Tao et al., 2021). We have revised this sentence as:

"Meteorological conditions can greatly affect SA formation in the NCP and can be significantly exacerbated during severe pollution events. SA formation under low relative humidity (RH) conditions, mainly through the condensation of gaseous-phase oxidation products, would change to that mainly occurring in the aqueous phase

under high RH conditions (Kuang et al., 2020). Because SAs formed through different mechanisms, have different chemical compositions and add mass to different aerosol populations, SA formation under different meteorological conditions can affect the aerosol mixing states differently (Tao et al., 2021)."

4) Line 168 BBOA, line 173 FFOA.., please explain the full name when introducing a new term and check out the remaining of manuscript.

Response: Thanks for your suggestion. The full names of BBOA and FFOA are Biomass Burning Organic Aerosol and Fossil Fuel Organic Aerosol, respectively. We have added a table listing the definition and description of the abbreviations as follow:

Table 1. Definition and description of abbreviations.

Abbreviation	Full name and/or Definition
BBOA	Biomass Burning Organic Aerosol Characterized by obvious m/z 60 (mainly $C_2H_4O_2^+$) and 73 (mainly $C_3H_5O_2^+$), which are two indicators of biomass burning
FFOA	Fossil Fuel Organic Aerosol A mixed factor that comprises traffic emissions and coal combustion, which was characterized by typical hydrocarbon ion series
OOA	Oxygenated Organic Aerosol
OOA1 and OOA2	Two OOA factors resolved from the PMF analysis
SOA	Secondary Organic Aerosol Summation of OOA1 and OOA2
POA	Primary Organic Aerosol Summation of BBOA and FFOA
SIA	Secondary Inorganic Aerosols, including nitrate, sulfate, and ammonium
$PM_{2.5}$	Particulate Matter with an aerodynamic diameter <2.5 μm

PM_1	Particulate Matter with an aerodynamic diameter <1 μm
NR-PM_1	Non-refractory PM_1
MF	Mass Fraction
D_p	Particle diameter after humidification or heating
D_d	Particle diameter under dry conditions without humidification or heating
κ	Hygroscopicity parameter
SS	Supersaturation
SPAR	Size-resolved Particle Activation Ratio Size-dependent CCN activity under a specific SS
MAF	Maximum Activation Fraction An asymptote of the measured SPAR curve at large particle sizes and represents the number fraction of CCNs to total particles
D_a	Midpoint activation diameter Linked to the hygroscopicity of CCNs
GF	Growth factor The ratio between particles with and without humidification and is linked to aerosol hygroscopicity
SF	Shrinkage Factor The ratio between particles with and without heating and is linked to aerosol volatility
PDF	Probability Distribution Function
NF_H	Number Fraction of Hydrophilic aerosol whose hygroscopicity parameter is >~0.07
NF_V	Number Fraction of Volatile aerosol whose Shrinkage Factor at 200 °C is <0.85

NF_{noBC}	**Number Fraction of black carbon (BC)-free particles**
NF_{CBC}	**Number Fraction of thickly coated BC particles**
R_{exBC}	**The number concentration ratio of externally mixed BC particles in total BC-containing particles** **Externally mixed BC particles are defined as identified bare/thinly coated BC-containing particles**

In addition, we have also added the definition and description of the abbreviations when first introduced in each section and also in the caption of the figures for clarification.

5) Line 177, what do you mean by "different chemical process" and could you give more details?

Response: Secondary organic aerosol formations originated from volatile organic compounds precursors could be formed in differ formation pathways such as aqueous phase reactions, heterogeneous reactions or gas phase reactions and also might be oxidized under different conditions, for example oxidized under different nitrogen oxide conditions with different oxidation capacity and oxidants. The following sentences is added in the revised manuscript.

"Secondary organic aerosol formation from volatile organic compound precursors could occur in different formation pathways, such as aqueous-phase, heterogeneous, or gas-phase reactions. It might also be oxidized under different conditions, such as oxidation under different nitrogen oxide conditions with different oxidation capacities and oxidants. The two resolved OOA factors displayed different spectral patterns, correlations with tracers, and diurnal variations, suggesting that they resulted from different chemical processes. However, their formation mechanisms remain to be explored in future studies. In general, the OOA factor 1 (OOA1) has higher $CO_2^+/C_2H_3O^+$ (3.9) and O/C (0.91) ratios than OOA factor 2 (OOA2) with 2.1 and 0.78, respectively."

6) Line 187, why do you choose these three supersaturations for CCN measurements?

Response: As particle size is the most important parameter in determining CCN activity (Duesk et al., 2006), measurement of CCN activity can indicate particle hygroscopicity in different particle size ranges. In general, the three supersaturations indicate the particle hygroscopicity in particle size range from 100 nm to 200 nm.

In order to perform intercomparisons among instruments, three supersaturations (SSs) of 0.08%, 0.14% and 0.22% were applied in a single cycle of about 15 minutes. CCN measurement under these three SSs reveals mainly CCN activity of aerosols reside in accumulation mode aerosol with diameter range of about 100-200 nm, which are close to diameters of HV-TDMA measurements, and higher SSs would reveal CCN activity of smaller aerosol particles (<100 nm) where DMA-SP2 measurement is not available:

"To compare the instruments, three supersaturations (SSs) of 0.08%, 0.14%, and 0.22% were applied in a single cycle of approximately 15 min. CCN measurements under these three SSs revealed that the CCN activity of aerosols resides in the accumulation mode with an aerosol diameter range of approximately 100–200 nm, which is close to the diameters of the HV-TDMA measurements. Higher SSs would reveal CCN activities of smaller aerosol particles (<100 nm), where the DMA-SP2 measurement is unavailable."

7) Line 211, the maximum temperature you chose is 200 degree Celsius, why do you choose this threshold?

Response: The HV-TDMA were scanning at different temperatures and diameters for the HV-TDMA system, to ensure the time duration of one full cycle is about 3 h, we limited the number of temperatures and diameters. Most importantly, results of previous studies in the North China Plain have shown that 200 degree Celsius is enough for removing most non-refractory aerosols (>80%) (Xu et al., 2019).

8) Line 225-229, regarding the chosen size for SP2, which system was conducted for this study, with or without thermodenuder-bypass? Since you are expected to compare with HTDMA and VTDMA, why not choose the same sizes to measure for the three instruments?

Response: The DMA-SP2 system was conducted both with and without thermodenuder-bypass depends on time, and detailed periods are added in the revised manuscript. Compared to HTDMA and VTDMA, more particle sizes are selected in the measurement DMA-SP2 system for obtaining more information of BC mass concentration and mixing states at different particle diameters for other scientific purposes. Because the time needed for a single particle size measurement of DMA-SP2 system is much shorter than that of HTDMA and VTDMA, and one full cycle for H/VTDMA lasts 3 hours. We have added corresponding description into the manuscript as:

“The DMA-SP2 setup was able to measure the mixing states of aerosols with diameters (detection limit of approximately 80 nm based on the calibration) of 100, 120, 160, 200, 235, 270, 300, 335, 370, 400, 435, 470, 500, 535, 570, 600, 635, 670, and 700 nm within 20 min when it was not placed after an denuder-bypass switch system (the 13th to the 24th of October, 09:00 am of the 5th of November to 09:00 am of the 8th of November). However, it only measured mixing states at diameters of 120, 160, 200, 250, 300, 400, and 500 nm when it was placed after a thermodenuder-bypass switch system (11:00 am of the 24th of October to 08:00 am of the 5th of November, and 09:00 am of the 8th of November to 06:00 pm of the 17th of November). Because the HTDMA and VTDMA measurements were conducted solely by a single H/VTDMA system operating in different modes, the time needed for a single particle size measurement of HTDMA and VTDMA was much longer than that of the DMA-SP2 system. Thus, more particle sizes were selected in the DMA-SP2 system for acquiring the BC mass concentration and mixing state at larger diameters than HTDMA and VTDMA.”

9) Line 235, does the flow rate influence the measurements and by how much?

Response: This change satisfied the flowrate requirements of this instrument (0.03 to 0.18 L/min), and 0.12 L/min was typically used. The flow rate change does not affect the measurements when aerosol number concentration is not small. Actually, at the very beginning, 0.1 L/min (less than the typical one 0.12L/min) was usually used because the NCP is generally polluted, and higher flow rate would produce larger data storage, however, does not affect the statistical results. We change to 0.12 L/min is because that we realized that we scan up to 700 nm using the DMA-SP2 which is different with previous studies where aerosol number concentration is much smaller and a larger sample flow rate should be better.

10) Section 2.3.1, the MAF is a fitting parameter from eq.7, what is the physical meaning of this parameter? Is it the maximum activation fraction?

Response: Yes, it’s the maximum activation fraction and we have revised the corresponding description as:

“.. The Maximum Activation Fraction (MAF) is an asymptote of the measured SPAR curve for large particles, as shown in Fig. S4, representing the fraction of CCNs relative

to the total number of particles. …”

To be noted, a schematic of the SPAR parameterization scheme and the corresponding fitting parameters is added into the supplement for clarification as:

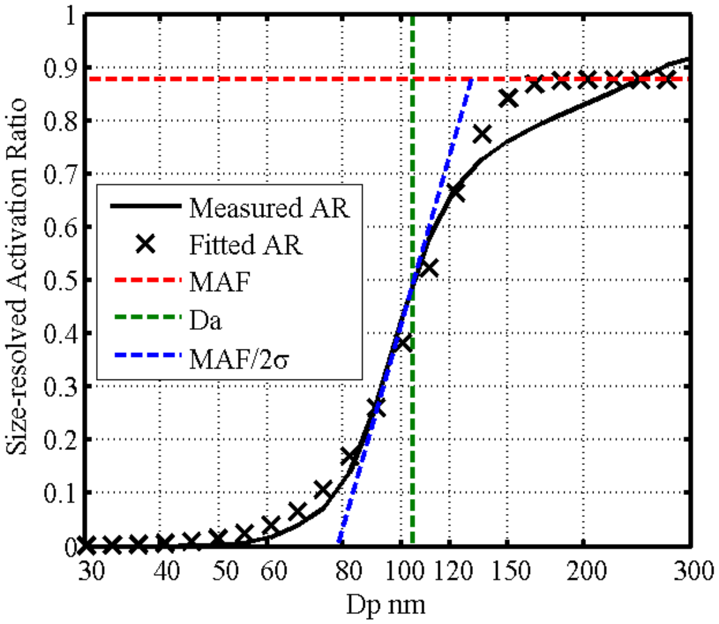


Fig. S4. Schematic of the parameterization scheme of SPAR curves. The black solid curve and the black crossing are the measured SPAR and fitted SPAR with the parameterization scheme. The red, green and blue dashed lines indicate the fitting parameters of Maximum Activation Fraction (MAF), the midpoint activation diameter (Da) and s, respectively.

11) Line 267, add sizes for the GF “The GFC for the four measured particle sizes were 1.1, 1.15, 1.175 and 1.2”.

Response: The GFC for particle size of 50, 100, 150 and 200 nm are 1.1, 1.15, 1.175 and 1.2, respectively. We have revised it as:

“The GF$_C$ for the four measured particle sizes of 50, 100, 150, and 200 nm were 1.1, 1.15, 1.175, and 1.2, respectively,”

12) Section 2.3.3. Here you use the lag time between the peak of the scattering signal and the incandescence signal to classify the bare and coated BC. Is it related to the BC-coating mass ratio? The mass ratio is more commonly used and intuitive to understand.

Response: Thanks for your suggestion. It is related to the coating thickness of the BC-

containing aerosols. The BC-coating mass ratio cannot be directly obtained in SP2 measurement, due to the lack in the accurate density and shape of the BC core. In addition, the lag time is positively correlated to the coating thickness, but their relation cannot be directly quantified and also calibrated. Thus, a critical value of lag time rather than coating thickness or coating mass ratio is used to classify the bare and coated BC. We have revised this sentence as:

"In this study, a two-mode distribution of the lag time (Δt) was observed, and a critical value of 0.8 μs was used to classify the BC-containing particles into thinly coated (or bare) BC ($\Delta t<0.8$ μs) and thickly coated BC ($\Delta t\geq 0.8$ μs)."

13) Line 297-299, please give exact values of PM mass for the heavily polluted and clean period.

Response: Thanks for your suggestion. Non-refractory PM_1 mass for the heavily polluted and clean period are 49.5±22.5 and 5.1±3.3 mg/m^3, respectively. We have revised this sentence as:

"The mass concentrations of different aerosol components increased significantly from the 23rd of October to the 6th of November (heavily polluted period with an average non-refractory PM_1 mass concentration of 49.5±22.5 $\mu g/m^3$) and decreased too much lower levels after the 6th of November (clean period with a non-refractory PM_1 mass concentration of 5.1±3.3 $\mu g/m^3$)."

14) Line 315-316. "At lower SSs, the rapid increases in SPAR curves occur at larger particle sizes and the maximum AR of SPAR curves becomes smaller". Please briefly explain why.

Response: Thanks for your suggestion. For lower SSs, particle size need for CCN activation is larger, thus SPAR curve start to increase from 0 at larger particle size. Because only SPAR in particle size lower than 300 nm is presented and there was less particle to be CCN active under low SSs, the maximum AR of SPAR curves becomes smaller under low SSs. We have revised this sentence as:

"At lower SSs, the particle size required for CCN activation was larger; thus, rapid increases in the SPAR curves occurred at larger particle sizes. In addition, the maximum AR of the SPAR curves decreases as fewer particles are CCN-active under low SSs."

15) Line 318, add SS for the "increases in SPAR curves, are approximately 90 nm, 120 nm and 180 nm"

Response: Thanks for your suggestion. We have revised it as:

"For the three measured SSs, the particle sizes where SPAR equals approximately 0.5 are approximately 90, 120, and 180 nm for the three SSs of 0.08%, 0.14%, and 0.22%, respectively,"

16) Fig 2. Are bars representing the standard deviation of the campaign average?

Response: Yes, and we have added corresponding description in the end of the caption of Figure 2 as:

"The shaded areas indicate the standard deviations."

17) Line 331-333, "In general, the size dependence of MAF, NFH, NFV and NFnoBC were similar to one another, suggesting they were dominated by the same particle group, namely BC-free particles". I think this statement is not well supported, I would suggest weakening it or proving it with more evidence. For example, thickly coated BC particles can be very CCN-activate, hydrophilic and volatile, if mostly contain SIA.

Response: Thanks for your suggestion and we fully agree. We have revised this sentence as:

"In general, the size-dependent characteristics of MAF, NF_H, NF_V, and NF_{noBC} were similar, suggesting that they were likely dominated by the same particle group, namely BC-free particles. "

18) Line 335, please provide exact values of the fraction of BC-containing particles and the applied diameter range, because the terms "higher" or "larger" are not accurate. Check out similar issues for the remaining manuscript too.

Response: Thanks for your suggestion. We have revised this sentence as:

"This suggests that primary emissions tend to have higher fractions of BC-containing particles in larger diameter ranges; for example, the fraction of BC-containing particles increases from ~0.1 to ~0.4 as the particle size increases from 200 to 500 nm during the cleaning period."

We have also checked the manuscript and revised the following:

L333: "This particle group had the highest fraction (>0.7) during the heavily polluted period and the lowest fraction (down to 0.5) during the clean period, with the fraction decreasing with increasing particle size."

L347: **"… when the nitrate fraction was the highest (~30%). The SOA fraction was the lowest (~7%) among all three periods,…"**

L354-355: **"However, they were larger than the NF_H during the moderately and heavily polluted periods (by ~0.2) when the POA/SOA fractions were higher (~40% vs. ~35%)."**

19) Line 342, what do you mean by "the more efficient secondary aerosol formation", increase by secondary aerosol mass or particle size?

Response: Here we are referring to that the formation rate of secondary aerosol mass is more efficient on larger particle, and we have revised this sentence as:

"… while the decrease in R_{exBC} with increasing particle diameter in the polluted period confirmed that SA formation is more efficient for particles with larger diameters."

20) Line 356-357, what is the kappa value for hydrophobic mode aerosol?

Response: The kappa value for hydrophobic mode aerosol is less than 0.07 and we have revised this sentence as:

"The critical k of hydrophilic mode aerosols was 0.07, suggesting that a higher fraction of aerosols had k below 0.07 (i.e., hydrophobic mode aerosols in this study) during the moderately polluted period."

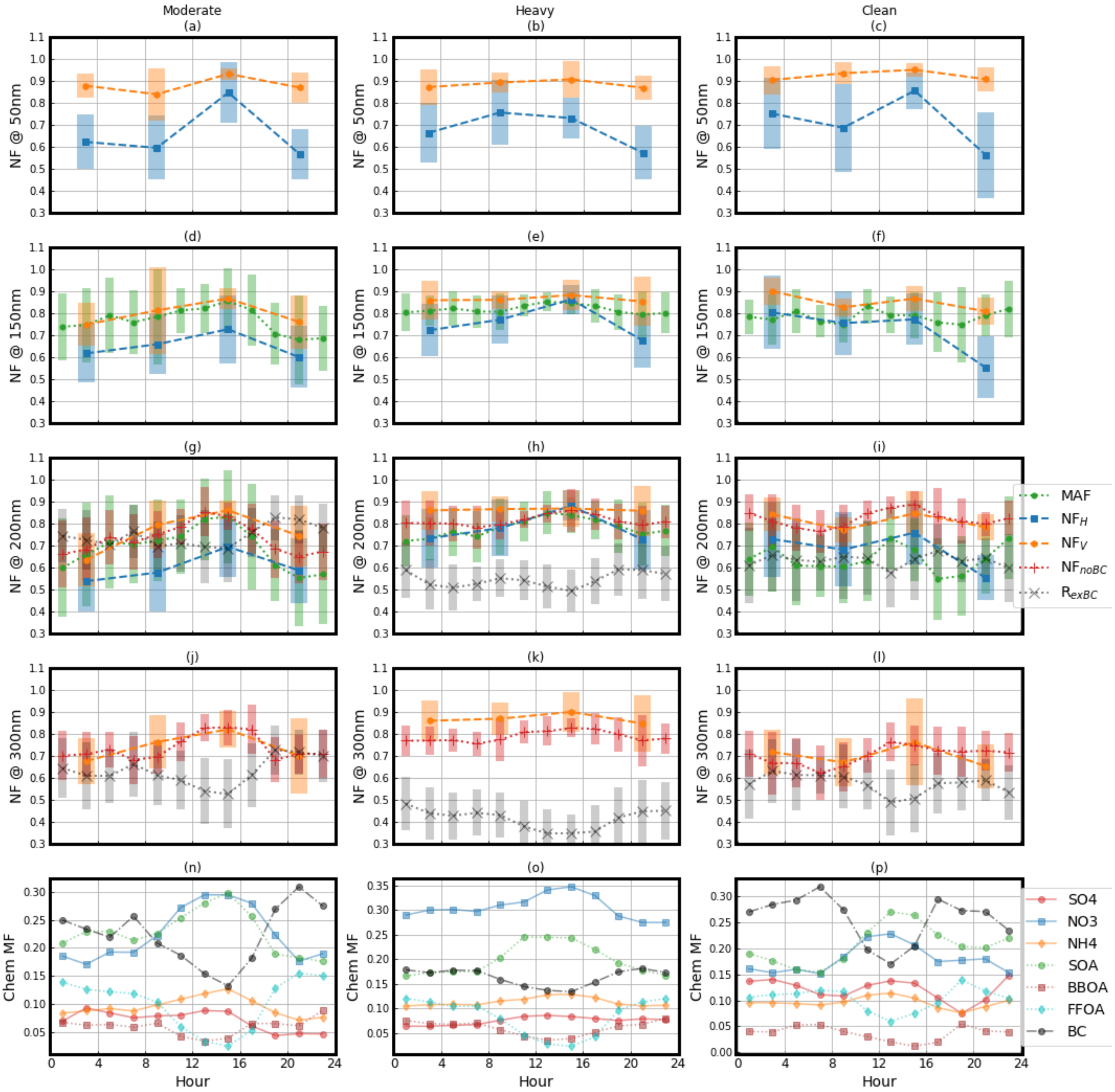
21) Line 361, how do you get this statement with "lower than 0.07 but still CCN active"? please explain in detail.

Response: In this part we are referring to that the difference among MAF, NFV, NFH and NFnoBC and we found that NFH is significantly smaller than the other three parameters. This may indicate that a portion of particles to be CCN active but not hydrophilic, i.e. with κ lower than 0.07. We have revised this sentence as:

"As mentioned above, NF_H was also lower than MAF during moderately polluted periods, and there may be a significant fraction of volatile BC-free aerosols with hygroscopicity lower than the critical κ value of 0.07; however, they were still CCN-active and therefore not fully hydrophobic."

22) Fig4, I would suggest simplifying the plot and keeping the sizes with most concurrent measurements, e.g. 150, 200 and 300 nm. Put other sizes to the supplement.

Response: Thanks for your suggestion. We have revised Figure 4 and its caption as:



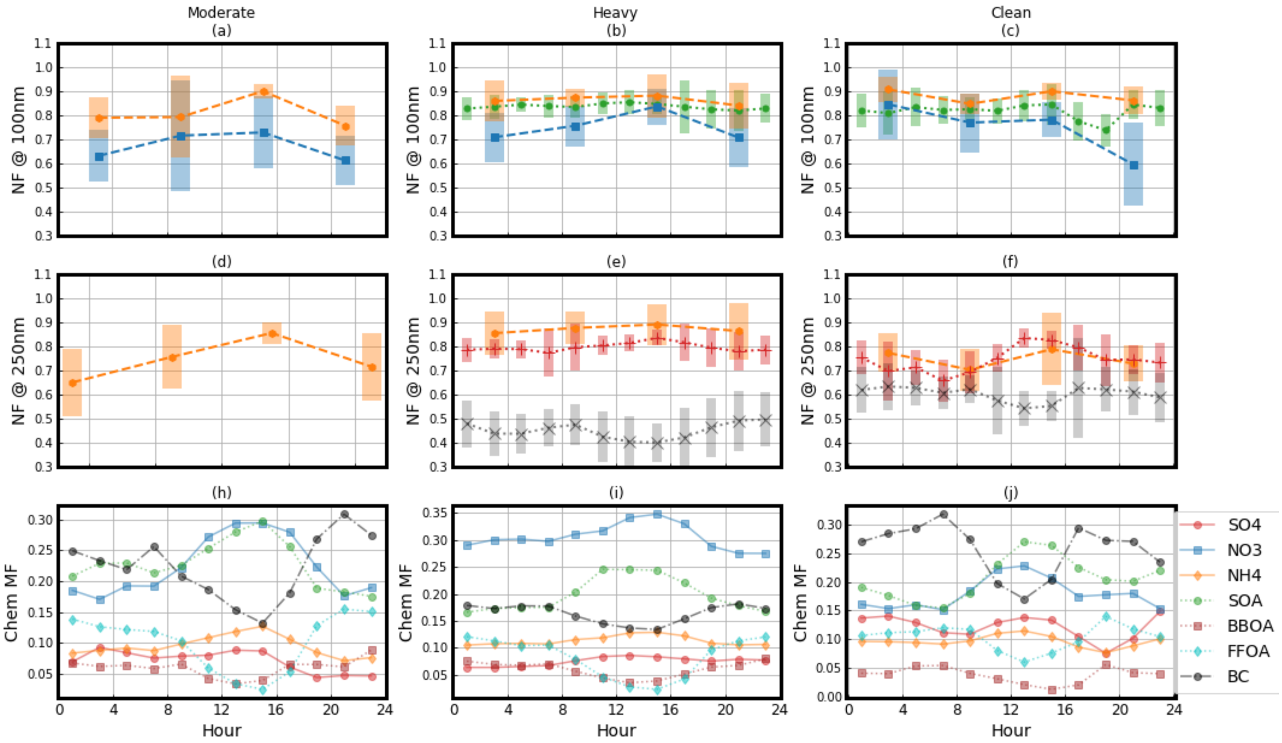
“Figure 4. (a–l) Diurnal variations of aerosol mixing state parameters (identified by color and marker) at different particle sizes (50, 150, 200, and 300 nm) during the three periods. The shaded areas indicate the standard deviations. (m–o) Diurnal variations of mass fractions (MFs) of aerosol chemical compositions, including secondary organic aerosols (SOA), biomass burning organic aerosol (BBOA), fossil fuel organic aerosols (FFOA), and inorganic ions including sulfate (SO_4), nitrate (NO_3), and ammonium (NH_4) (identified by color and marker) during the three periods.”

We have revised the corresponding description of Figure 4 as:

“For particles >100 nm (Fig. 4 and S5), there was a maximum in the afternoon for MAF, NF_H, NF_V, and NF_{noBC}, indicating a peak during this time due to an increase in SA

compositions, such as nitrate and SOA, and a decrease in POA and BC.”

We have also added Figure S4 into the supplement as:



“Fig. S5. (a-l) Diurnal variations of aerosol mixing state parameters (identified by color and marker) at different particle sizes (50, 150, 200 and 300 nm) during the three periods. The shaded areas indicate the standard deviations. (m-o) Diurnal variations of mass fractions of aerosol chemical compositions (identified by color and marker) during the three periods.”

Line 362- 366, the diurnal variations should be described more explicitly as the pattern of RexBC is clearly different from the other three mixing state parameters and explain why.

Response: Thanks for your suggestion. We have added more discussion in the end of this paragraph as:

“R_{exBC} tended to be lower during the daytime, and its diurnal variation was more significant for larger particle sizes. In general, the diurnal variations for R_{exBC} were opposite to those of NF_{noBC} and agreed better with those of the primary aerosol MFs. This is because BC particles originate from primary emissions and are mainly mixed externally. After aging in the atmosphere, BC particles can be coated by SAs, resulting in more coated BC particles and fewer externally mixed BC particles. As SAs tend to form on larger particles, the diurnal variations in SA formation may significantly affect the RexBC of larger particle sizes.”

23) Line 384, table S1 is quite interesting for readers thus I suggest putting it or making a correlation plot into the main context.

Response: Thanks for your suggestion. We agree that useful information is contained in this table, we also struggled before we decided to put it in the supplement. We want readers focus more on key parts of those intercomparison results, however, it was also available in the supplement in case that readers want to know all scenarios.

24) Line 385, why do you choose these three sizes? The critical size for the setting SS?

Response: As shown in Figure 2, the particle size where the rapid increases in SPAR curves are approximately 90 nm, 120 nm and 180 nm for the three SSs of 0.22%, 0.14% and 0.08%, respectively. And the diameter range of rapid increases in SPAR curves are determined by aerosol hygroscopicity in this particle size ranges. Thus, the three particle sizes of 100 nm, 150 nm and 200 nm are chosen in comparison to the MAF at the three SSs of 0.22%, 0.14% and 0.08%, respectively. We have revised this sentence as:

"Note that the MAF at SSs of 0.08%, 0.14%, and 0.22% were used for comparison at 200, 150, and 100 nm particle sizes. This is because the diameter range of rapid increases in the SPAR curves is determined by aerosol hygroscopicity in this particle size range. The midpoints of the rapidly increasing diameter ranges of the SPAR curves at SSs of 0.08%, 0.14%, and 0.22% were approximately 180 nm, 120 nm, and 90 nm, respectively (as shown in Fig. 2). "

25) Line 386. A classification of the correlation should be clarified, such as the r range for the weak, moderate, and strong correlation.

Response: Thanks for your suggestion. The value range of correlation coefficient for weak, moderate and strong was generally less than 0.3, from 0.3 to 0.5 and larger than 0.5. We have added detailed value of correlation coefficient into the manuscript including:

L386: "… moderate correlations (r=~0.5) .."

L392: "… the correlation became weaker (r=~0.4), …"

L421: "…, and weak correlations (r<0.3) …"

L440: "… a strong positive correlation with MF$_{SO4}$ (r>0.5). …"

L445: "… the weaker correlations with SOA (r~0.3) seen in Fig. 8."

L454: **“…, the strong positive correlations between NFV and secondary aerosol formations (r=~0.6) …”**

L457: **“… strong positive correlations (r=~0.5) …”**

L465: **“… a strong negative correlation with MF_{NH4} and MF_{NO3} (mainly -0.6) …”**

26) Line 392, what do you mean by saying “..while the degree was the least for the correlation..”?

Response: We are referring to that the degree of the reduction of correlation was the least for the correlation between MAF and NFV, and we have revised this sentence as:

“For smaller particle sizes, the correlation became weaker (r=~0.4), whereas the degree of reduction was the lowest for the correlation between MAF and NF_V.”

27) Fig. 5, what is the r in the plot? It would be more intuitive to use the same marker to represent different periods in the plot.

Response: The variable r represent the correlation coefficient and we have added corresponding description into the caption as “with r representing the correlation coefficient.” At the request of the Copernicus Publications, the marker used to present different periods are set to be different in order to making this figure friendly to readers with color vision deficiencies.

28) A summary table (or correlation matrix plot) of r in Fig5-7 will be helpful for readers to better understand the interlink between mixing state parameters and chemical composition.

Response: Thanks for your suggestion and the correlation between mixing state parameters and aerosol chemical composition as well as detailed correlation during different pollution periods were summarized in Figures S6 and S8 (Figures S5 and S6 in old version). We have added introduction of these figures into the manuscript as:

In the end of Section 3.3: “The correlations between the mixing-state parameters and primary aerosol composition during the campaign and different pollution periods are summarized in Fig. S7.”

In the end of last second paragraph of Section 3.4: “The correlations between the mixing state parameters and SA composition during the campaign and different pollution periods are summarized in Fig. S9.”

29) Line 400, please give values to the sentence "correlation with MFFFOA was much weaker compared to MFBBOA".

Response: Thanks for your suggestion. We have revised this sentence as:

"However, the anticorrelation with MF_{FFOA} (-0.45~-0.74) was much stronger than MF_{BBOA} (-0.10~-0.45)."

30) Fig.7. Which size of data do you use?

Response: The size is 200 nm and we have added corresponding description into the caption of Figure 7 as "The impact of primary emissions on the differences among the four aerosol mixing state parameters at a particle size of 200 nm was analyzed and is shown in Fig. 7."

31) Line 428, please introduce what the difference (NFnoBC-NFH and NFV-NFH) represents first before jumping to the results.

Response: Thanks for your suggestion. We have added the definition of these abbreviations as:

L427-434: "The difference between NF_{noBC} and NF_H (NF_{noBC}-NF_H) was significantly positively correlated with MF_{FFOA} and MF_{BBOA} (r>0.5), suggesting that a substantial proportion of POA resided in BC-free aerosols and was volatile, but contributed substantially to nearly hydrophobic aerosols; as did the differences between NF_V and NF_H (NF_V-NF_H). The MFs of BBOA and FFOA were poorly correlated with the differences between the MAF and NF_V (MAF-NF_V), MAF and NF_{noBC} (MAF-NF_{noBC}), and NF_V and NF_{noBC} (NF_V-NF_{noBC}) (Fig. S7). The difference between MAF-NF_H was positively correlated with MF_{BBOA}, further suggesting that BBOA contributed to nearly hydrophobic aerosols under subsaturated conditions; however, their hygroscopicity was enhanced, and they became CCN-active under supersaturated conditions."

L464: "The difference between NF_{noBC} and NF_H (NF_{noBC}-NF_H) was significantly positively correlated with MF_{FFOA} and MF_{BBOA} (r>0.5), suggesting that a substantial proportion of POA resided in BC-free aerosols and was volatile, but contributed substantially to nearly hydrophobic aerosols; as did the differences between NF_V and NF_H (NF_V-NF_H)."

L483: "The difference between NF_{noBC} and NF_V (NF_{noBC}-NF_V) was negatively correlated with MF_{NO3}, which is consistent with the semi-volatile nature of nitrate."

L555: "… the two resolved SOA factors exhibited different impacts on the differences between NF_V and NF_H (NF_V-NF_H), …"

Figure 10: **"… (d and e) The variations of the difference between NF_V and NF_{noBC} (NF_V-NF_{noBC}, blue large circle) and the difference between NF_V and NF_{noBC}+NF_{CBC} (NF_V-(NF_{noBC}+NF_{CBC}), yellow small circle) with the mass concentration of SA at particle size 200 nm (d) and 300 nm (e) NF_{CBC}: Number Fraction of thickly coated black carbon (BC) particles. ."**

32) Line 438, why do you choose 200nm?

Response: This is mainly because we focus on the comparison of the four aerosol mixing state as well as their relationship with aerosol chemical compositions, but only in 200 nm were all the four aerosol mixing state parameters measured. We have added corresponding description into the manuscript as:

"The analysis is conducted at only 200 nm, where all four aerosol mixing state parameters were measured to compare the four aerosol mixing state parameters and their relationships with aerosol chemical compositions simultaneously."

33) Line 459-462, out of curiosity, does the transport of ageing aerosols play a role in the increasing fraction of non-BC particles?

Response: The reviewer raised a very interesting topic. Indeed, the transport of aging aerosols could play a role in variations in fraction of non-BC particles, for example, during the clean period. However, for periods of the moderately to heavily polluted, the wind speed generally lower than 2 m/s, with strong local emissions (represented quick increase of rBC and POA in the afternoon) of secondary aerosols formations (represented by quick nitrate and SOA formations), the transport of aging aerosols should play a negligible role.

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