We are thankful to the two reviewers for their thoughtful comments that help improve the manuscript significantly. Following the reviewers' suggestions, we have revised the manuscript accordingly. Listed below are our point-by-point responses in blue to each reviewer's comments.

**Response to reviewer #1**

The authors reported the chemical composition and particle growth event at a downwind ground site in the North China Plain. The results mainly focus on analyzing the aerosol chemical composition measured by aerosol chemical speciation monitor (ACSM) and particle number concentration and size distribution obtained based on scanning mobility particle sizer (SMPS). OA sources (cooking OA, oxygenated OA, and hydrocarbon-like OA) were also resolved by combining source apportionment techniques with ACSM dataset. The species contribution (SO4 and OOA) are the main for particle growth has been analyzed, which is not new since most of the results have already been reported from multiple other field studies in NCP. The CE calculation and the way that the authors analyzed the correlation between chemical component in aerosols and growth rate have their own caveats, as addressed in the comments following. Based on all the major comments as following, I recommend a major revision for this paper.

We thank the reviewer's comments.

Major comments:

1. The detailed operation of AMS and SMPS is totally missed in the paper. No information on how the ACSM were calibrated.

We thank the reviewer's comments. The detailed operations of ACSM and SMPS were now added in the revised manuscript.

"A $PM_{2.5}$ cyclone (Model: URG-2000-30ED) was supplied in front of the sampling inlet to remove coarse particles larger than 2.5 µm. The ambient air was drawn into the container through a 1/2 inch (outer diameter) stainless steel tube at a flow rate of 3 L $min^{-1}$ using an external pump, of which ~0.1 L $min^{-1}$ was sub-sampled into the ACSM. The sampling height was approximately 2 m, which was 1.5 m higher than the roof of container. Thus, the particle residence time in the sampling tube was about 5 s. Aerosol particles were then dried by a silica gel diffusion dryer before sampling into the ACSM. Before the campaign, the ACSM was calibrated with pure ammonium nitrate particles following the standard protocols in Ng et al. (2011b).

"The size-resolved particle number concentration in the size range from 15 to 685 nm was measured in situ by a condensation particle counter (CPC, model 3775, TSI) equipped with a long differential mobility analyser (DMA, model 3081A, TSI). The time resolution is 5 min."

2. The CE needs to be reevaluated. I have already raised this question in the quick review, however, the authors did not revise it. A CE of 0.51 and 0.57 was estimated based on equation in Middlebrook et al. (2012), when the average mass concentration of main components in polluted and clean days in Table 1 were used. The higher CE than default value of 0.5 is mainly due to acidic effect on aerosol bounces in AMS. Thus, the mass concentration of AMS might be overestimated in this study.

Thank the reviewer's comments. Following the reviewer's comments, we recalculated mass concentration of NR-$PM_1$ species using composition-dependent CE (average: 0.5036) as follows (Middlebrook et al., 2012):

$$CE_{dry} = \max\left[0.45, 1.0 - 0.73 \times \left(NH_4/NH_{4,predict}\right)\right]$$

The average mass concentration of Org, $SO_4$, $NO_3$, $NH_4$, Chl were 11.5, 7.4, 4.2, 3.0, and 0.8 μg $m^{-3}$ respectively, which were almost the same as the results calculated by CE = 0.5 (Table R1).

Table R1. The average mass concentration of Org, $SO_4$, $NO_3$, $NH_4$, Chl measured by ACSM using different CE values.

| | CE = 0.5 | CE algorithm |
|---|---|---|
| Org | 11.8 ± 7.3 | 11.5 ± 7.3 |
| $SO_4$ | 7.7 ± 5.1 | 7.4 ± 5.2 |
| $NO_3$ | 4.3 ± 4.3 | 4.2 ± 4.3 |
| $NH_4$ | 3.1 ± 2.3 | 3.0 ± 2.4 |
| Chl | 0.8 ± 1.4 | 0.8 ± 1.2 |

We had carefully considered the reviewer's comments. CE was introduced to correct the incomplete detection of submicron particles by ACSM. It depended on particle acidity, ammonium nitrate fraction and relative humidity. In this study, 1) aerosol particles were not acidic enough to affect the CE substantially. 2) The average mass fraction of $NH_4NO_3$ was 18%, which would not affect CE substantially. 3) A silica gel diffusion dryer was used to dry aerosol particles before sampling into ACSM.

Thus, we kept CE = 0.5, and the results were comparable within the acceptable difference.

3. Line 111: The statement that the calculate SMPS mass is only 75% of the total $PM_1$ cannot not be used a supporting evidence for CE. Multiple other studies show a good

comparison of mass concentration between AMS and integrated SMPS, as examples shown below: Y. Zhang, L. Tang, P. L. Croteau, O. Favez, Y. Sun, M. R. Canagaratna, Z. Wang, F. Couvidat, A. Albinet, H. Zhang, J. Sciare, A. S. H. Prévôt, J. T. Jayne, and D. R. Worsnop: Field characterization of the PM2.5 Aerosol Chemical Speciation Monitor: insights into the composition, sources, and processes of fine particles in eastern China, Atmos. Chem. Phys., 17, 14501-14517, 10.5194/acp-17-14501-2017, 2017. X. F. Huang, L. Y. He, M. Hu, M. R. Canagaratna, Y. Sun, Q. Zhang, T. Zhu, L. Xue, L. W. Zeng, X. G. Liu, Y. H. Zhang, J. T. Jayne, N. L. Ng, and D. R. Worsnop: Highly time–resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos Chem Phys, 10, 8933-8945, DOI 10.5194/acp-10-8933-2010, 2010. P. F. DeCarlo, E. J. Dunlea, J. R. Kimmel, A. C. Aiken, D. Sueper, J. Crounse, P. O. Wennberg, L. Emmons, Y. Shinozuka, A. Clarke, J. Zhou, J. Tomlinson, D. R. Collins, D. Knapp, A. J. Weinheimer, D. D. Montzka, T. Campos, and J. L. Jimenez: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos Chem Phys, 8, 4027-4048, 2008. The authors should look more carefully into their dataset to find out the possible reasons that could cause this difference.

We agree with the reviewer's comments, and modified the inappropriate explanation in the revised manuscript. In fact, such a difference can be caused by (1) measurement uncertainties between different instruments. For example, the SMPS measurement uncertainties can be increased to 30% for particles larger than 200 nm, which dominated the total particle mass (Wiedensohler et al., 2012), while the uncertainties for ACSM measurements varied from 9 – 36% for different aerosol species (Crenn et al., 2015), (2) the effects of particle shape. In this study, we assume spherical particles, and aerodynamic diameter ($D_{va}$) is approximately equal to mobility diameter ($D_m$) times particle density, and (3) the uncertainties in estimating particle density because we didn't the measurements of refractory species, e.g., mineral elements. Similar difference in the comparisons between AMS and SMPS were also observed in many previous studies in China (Zhang et al., 2011; Xu et al., 2014).

4. Line 200-215: The cooking OA (COA) and hydrocarbon-like OA (HOA) have very similar diurnal variations, which show similar peaks in the noon and night time. It indicates that the PMF did not really separate the two factors. A detailed explanation on separating two factors are needed.

Thanks for the reviewer's comments. It is difficult to separate HOA from COA by PMF using quadrupole AMS or ACSM measurements (Sun et al., 2010; Sun et al., 2012). Thus, source apportionment using the bilinear model through a multilinear engine (ME-2) was applied to non-refractory organic aerosol mass spectra collected by ACSM. ME-2 is capable of finding acceptable solutions in accordance with the constraints provided by the user. In this study, we input HOA and COA reference profiles with a-values varying from 0 to 1. The a-value determines the extent to which the output factor profiles is allowed to vary from the input factor profiles. An optimal solution involving three factors with an a-value of 0.2 was accepted at last.

In order to examine the rationality of the solutions, we then tried to use BC as a tracer to separate HOA from COA assuming that BC is dominantly from traffic emissions while the contribution from cooking emissions is minor (Pei et al., 2016). In this study, POA was highly correlated ($r^2 > 0.66$) with BC between 1:00 – 10:00 when cooking emissions are not significant (Figure R1). The ratios of POA/BC were also the lowest during this period, suggesting the dominant contribution of HOA to POA. The average ratio of POA/BC during the period without significant cooking emissions is 0.62. Thus, we estimated the mass concentrations of HOA and COA following the equations below:

(1) $\mathrm{HOA} = (\mathrm{POA/BC})_{nc} \times \mathrm{BC} - \mathrm{COA}_b$

(2) $\mathrm{COA} = \mathrm{POA} - \mathrm{HOA}$

(POA/BC) is the average ratio of POA/BC during the periods without significant cooking emissions, which is 0.62 here, and $COA_b$ is the background concentration of cooking aerosols. According to the diurnal cycles of COA in previous studies in Beijing (Huang et al., 2010; Hu et al., 2016; Hu et al., 2017), we found a background concentration of 1.30 ± 0.39 μg $m^{-3}$. In view of the fact that there are fewer local cooking emissions compared with Beijing, we hypothesized a background concentration of 0.7 μg $m^{-3}$ (half of that in Beijing) for the estimation in this study.

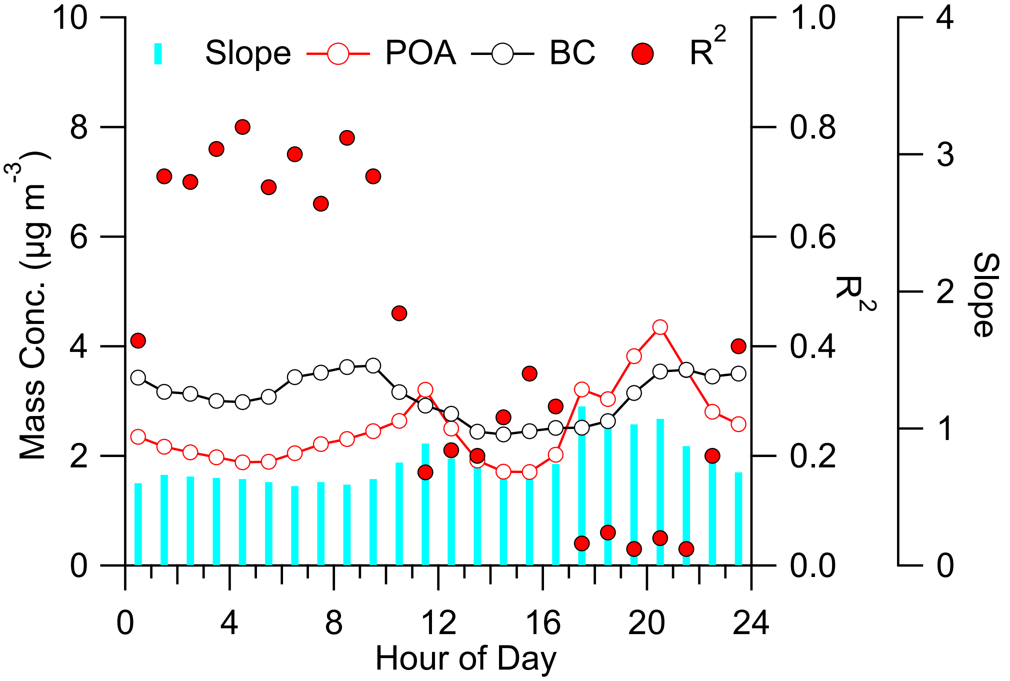


Figure R1. Diurnal variations of POA, BC, correlation coefficients and slopes of POA vs. BC.

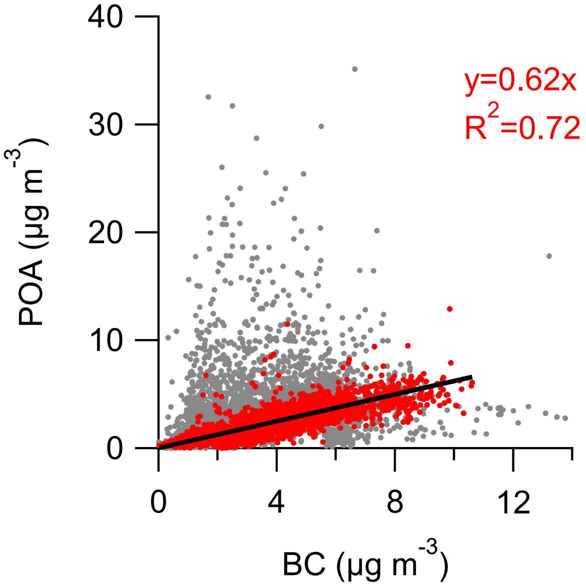


Figure R2. Scatter plot of POA vs. BC, and the red dots are the data between 1:00 – 10:00.

The BC-tracer method has been used in Sun et al. (2018) to response the mix of HOA and COA. The diurnal cycles of estimated COA and is also consistent with the results of ME-2 analysis (Figure R3). The estimated HOA and COA on average contributed both 11% to OA, consistent with the results of ME-2 analysis. This suggested that the results from ME-2 analysis are reasonable.

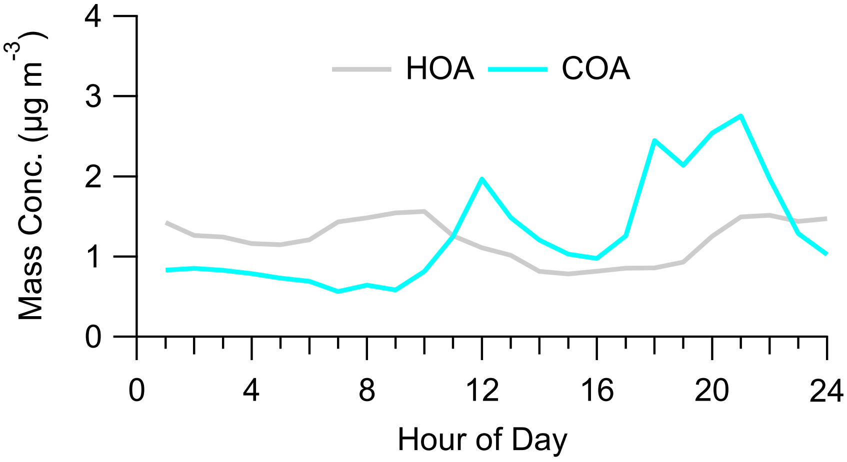


Figure R3. Diurnal cycles of estimated COA and HOA using BC as a tracer.

5. Line 291-292: please give statistic analysis result on correlation of Fig. 10b-c to prove the conclusion stated in this study. I did not see the correlation between growth rate and condensation sink.

Thanks for your comments. We revised this paragraph following the reviewer's comments. The statistic analysis results (value of $r^2$) and plots are also added in Section 3.4 and supplementary materials.

"As indicated in Fig. 10b, GR was positively correlated with CS for most of the time, in particular when the fraction of OOA is higher than 30% (Fig. R4, $r^2$ = 0.61). As CS increased from ~ 0.01 $s^{-1}$ to 0.05 $s^{-1}$, GR increased from 3 nm $h^{-1}$ to 5 nm $h^{-1}$. However, there were some low GRs with high CS, which were characterized by low contributions of OOA. These results show the importance of the involvement of OOA in particle growth. Figure 10c further shows that GR was positively correlated with the concentration of sulfate during periods with low sulfate mass loadings (Fig. R5, < 3 μg $m^{-3}$, $r^2$=0.42), while periods with higher concentrations of sulfate had lower GRs."

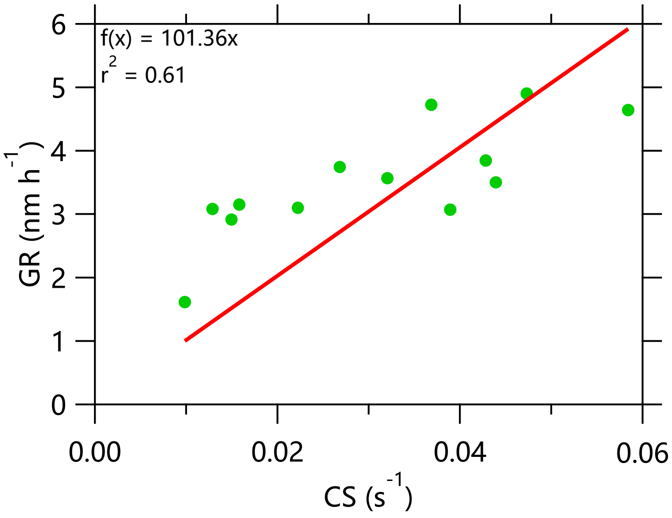


Figure R4. The relationship between GR and CS in the OOA fraction of more than 32% conditions.

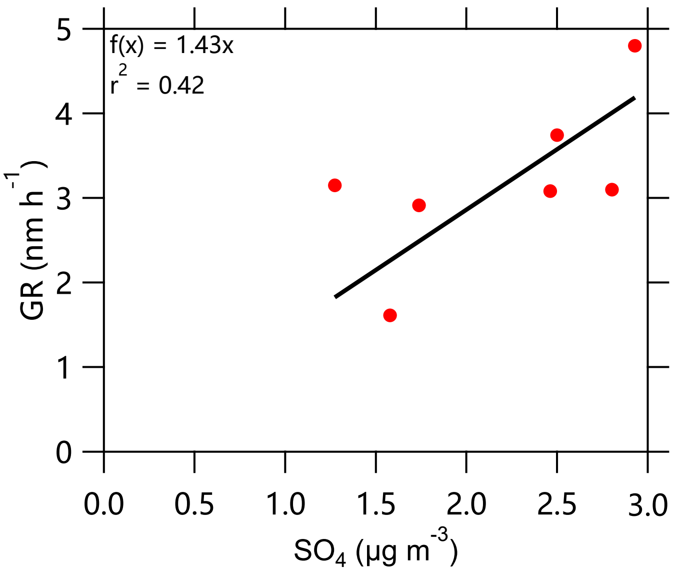


Figure R5. The relationship between GR and sulfate concentration in the sulfate concentration of less than 3 μg $m^{-3}$ conditions.

Minor comments:

1. Line 56-57: Give references. Why did the mass concentration of $PM_1$ in Xingtai (~30 μg $m^{-3}$) is so low compared with the measured annual mass concentration (~90 μg $m^{-3}$) in the past.

Thanks for your comments. The source of data was added in the revised manuscript.

“(the data are from four monitoring sites in urban Xingtai that was released by the China National Environmental Monitoring Centre)”

The mass concentration of $PM_1$ in this study (~30 μg $m^{-3}$) is so low compared with the measured annual mass concentration (~90 μg $m^{-3}$) in the past. This is mainly due to three reasons: (1) In this study, the mass concentration of $PM_1$ was collected by ACSM and AE33 from 30 April to 20 June. The pollution during this period was relatively light compared to that in winter. (2) The results reported in this study are

$PM_1$ and those reported in the past are $PM_{2.5}$. (3) The sample site in this study is a suburban site. The pollution level is lower than those at urban sites where high $PM_{2.5}$ values were observed.

2. Line 108: Have the authors done the RIE calibration of NH4 and SO4. IF so, please specify.

Thanks for your comments. We did the RIE calibration of $SO_4$ using ammonium sulfate, and the RIE of $SO_4$ was 0.98. Such information was now added in the revised manuscript.

"Default relative ionization efficiencies (RIE) were used except ammonium (5.0) and sulphate (0.98) that were determined from pure ammonium nitrate and ammonium sulphate, respectively."

3. Line 129: Please give the range of f55 vs f57 in COA in Mohr et al. 2012.

Thanks for your comments. We added the range of f55 vs f57 in COA in Mohr et al. 2012.

"(~> 1.2)"

4. Line 271: Give detailed evidence for this sentence.

Thanks for your comments. Because the growth sizes of particles in this study (from ~ 25 nm to ~60 nm) are larger than those observed in urban Beijing (from ~22 nm to ~55 nm, Fig.9a), we speculated a stronger aging process (characterized by particle growth) at the suburban site. We revised the sentence as follows:

"Note that the growth sizes of particles were overall larger than those observed in urban Beijing (from ~22 nm to ~55 nm), likely indicating a stronger aging process at the suburban site."

5. Line 277: Please specify if the CO background is offset here. If not, the background of CO should be deducted in the calculation. For an example, J. A. de Gouw, D. Welsh-Bon, C. Warneke, W. C. Kuster, L. Alexander, A. K. Baker, A. J. Beyersdorf, D. R. Blake, M. Canagaratna, A. T. Celada, L. G. Huey, W. Junkermann, T. B. Onasch, A. Salcido, S. J. Sjostedt, A. P. Sullivan, D. J. Tanner, O. Vargas, R. J. Weber, D. R. Worsnop, X. Y. Yu, and R. Zaveri: Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study, Atmos Chem Phys, 9, 3425-3442, 2009.

Thanks for your comments. The CO background was subtracted. We clarified this in the revised manuscript. It now reads: "Note that CO here was subtracted by a background value of 0.068 ppm that was calculated as the average of the lowest 5% data in this study. "

6. Line 290: No information on how the growth rate was calculated.

Thanks for your comments. We added it in the revised manuscript.

"The particle growth rates were calculated using Eq. (1).

$$\mathrm{GR} = \frac{\Delta D\mathrm{m}}{\Delta \mathrm{t}} \tag{1}$$

Where $D_\mathrm{m}$ is the geometric mean diameter from the log-normal fitting of each size distribution and $\Delta D_\mathrm{m}$ is the increase in diameter during the growth period of $\Delta$t."

7. Line 291: What is the GR range in the literatures. How does is compare to the results from Beijing?

Thanks for your comments. We added the GR range from the literatures in the revised manuscript.

“(1-20 nm $h^{-1}$)”

Compared to the results in Beijing (approximate 1.6-6 nm $h^{-1}$), particle growth rates in this study appear to be faster.

**Response to reviewer #2**

The manuscript presented by Zhang et al. proposes an interesting study on the chemical composition and new particle formation in North China Plain. The characterization of PM1 sampled at the field site was performed using an aerosol mass spectrometer. Overall the work performed in this study is good and fall within the scope of the journal. However, the conclusions proposed from the PMF analysis are not always well sustained and more caution should be taken when extrapolating the results. Overall, more information needs to be added to validate PMF analysis and thus the conclusions of this study.

We thank the reviewer's positive comments.

Comments:

1. Line 106-108: The molar ratio is not sufficient to predict aerosol acidity. Please use a thermodynamic model if you want to discuss aerosol acidity (e.g., Weber et al. 2016, Nature Geo.). Presence of organics also impacts CE. Overall the CE correction has to be better constrained/explained. Affct should be affect (line 108).

We agree with your comments. Unfortunately, the measurements of gaseous $HNO_3$, HCl and $NH_3$ were not available in this study. So a thermodynamic model may be not suitable to predict aerosol acidity. And molar ratio can reflect aerosol acidity to some extent, despite the large uncertainties. We just use molar ratio to explain the limited influence on CE from aerosol acidity qualitatively.

Most importantly, Middlebrook et al. (2012) has a full evaluation of AMS CE and found that CE is mainly affected by three factors, i.e., particle acidity (measured $NH_4^+$ vs. predicted $NH_4^+$), RH, and fraction of ammonium nitrate. These three factors were all addressed in our study, and a final of CE of 0.5 is suitable for the entire campaign. Also see our response to reviewer #1.

“Affct “ was corrected as “affect”.

2. Line 113-115: How does the aerosol density compare with other field measurements? How did the authors evaluate that 75% of the mass is within the mass range of 15-685 nm? What is the size cut off of the aethalometer? The authors should better explain how they considered the size ranges and how they compared particle mass between instruments: ACSM mass between 50-1000 nm Aethalometer? SMPS 15-685 nm

We thank the reviewer’s comments. The average aerosol density in this study was 1.5 g $cm^{-3}$, consistent with that in Beijing (1.2-1.6 g $cm^{-3}$, Zhao et al., 2017), Changdao (1.5 g $cm^{-3}$, Hu et al., 2013), Lanzhou (1.61 g $cm^{-3}$, Xu et al., 2014).

A $PM_{2.5}$ cyclone was supplied in front of the Aethalometer sampling inlet to remove coarse particles larger than 2.5 µm. The ratio of the vacuum aerodynamic diameter ($D_{va}$) measured by ACSM/mobility diameter ($D_p$) measured by SMPS is a function of particle shape and density. Assuming spherical particles, $D_{va}$ is approximately equal to $D_p$ × density. Therefore, $D_p$ measured by SMPS is in the range of 22-1027 nm in $D_{va}$, which is similar to that of ACSM. Because the ACSM does not measure BC, Aethalometer was used to measure BC. Although the size cutoff is 2.5 µm, BC from combustion emissions is dominantly in small particles, and the peak diameters are typically 100 – 200 nm.

In fact, such a difference between ACSM and SMPS can be caused by (1) measurement uncertainties between different instruments. For example, the SMPS measurement uncertainties can be increased to 30% for particles larger than 200 nm, which dominated the total particle mass (Wiedensohler et al., 2012), while the uncertainties for ACSM measurements varied from 9 – 36% for different aerosol species (Crenn et al., 2015), (2) the effects of particle shape. In this study, we assume spherical particles, and aerodynamic diameter ($D_{va}$) is approximately equal to mobility diameter ($D_m$) times particle density, and (3) the uncertainties in estimating particle density because we didn't the measurements of refractory species, e.g., mineral elements. Similar differences in the comparisons between AMS and SMPS were also observed in many previous studies in China (Zhang et al., 2011; Xu et al., 2014).

In addition, did the authors correct their data by determining the transmission/losses of the particles into the different instruments?

Thanks for your comments. Ambient air was drawn into the container through a 1/2 inch (outer diameter) stainless steel tube (about 2 m) at a flow rate of 3 L min$^{-1}$. The residence time of aerosol in the sampling tube is approximately 5 seconds. The losses for particles between 20 – 1000 nm are less than 5%.

3. Paragraph 2.3.2. This section should be moved into the "Results and discussion" section as the authors started to discuss the results. In addition, several questions remain in their data analysis and the authors should provide more information (i.e. robust validation).

Thanks for your comments. The content in paragraph 2.3.2 was mainly focused on source apportionment method and its rationality. So we kept it in this section and added more information to validate our results in the response.

"We also noticed that HOA showed similar diurnal cycle as that of COA even though they were separated in ME-2 analysis. To better clarify the uncertainties, we estimated COA concentrations using BC as a tracer for HOA. Indeed, POA was highly correlated ($r^2 > 0.66$) with BC between 1:00 and 10:00 when cooking emissions are little, suggesting the dominant contribution of traffic emissions on BC. The average ratio of POA/BC during this period (0.62) was then used to estimate HOA, and COA was estimated based on the difference between POA and HOA. Our results indicated that COA and HOA concentrations estimated using BC-tracer method on average both contributed 11% to OA which is well consistent with those using ME-2 analysis.

These results together imply that the results of ME-2 analysis are relatively reasonable."

4. Why did the authors directly constrain the PMF? Have they tried to constrain the PMF with biogenic factors (i.e. isoprene and/or monoterpene)? It is unclear why the authors were not able to obtain similar factors as previous studies (e.g. Fig S8). How do the factors correlate with the reference MS? How do the factors correlate throughout the campaign (i.e. event vs non-event)? How do the residuals evolve throughout the campaign and especially during events vs non-events? It is a bit surprising to identify only 3 factors, assuming the complexity of the aerosol formation in such area. Especially when the authors argue that SOA formation is due to different air masses. Therefore the authors should present the time series of the contribution of the factors and Q/Qexp parameter values across different model solutions as functions of the number of factors and constraint parameter (ISO-value).

Thanks for your comments. Quadrupole ACSM is still limited compared with the research-grade AMS, in terms of sensitivity and mass resolution. Also, ACSM introduces more uncertainties because of ion transmission efficiency between m/z 50 – 150. Therefore, PMF analysis of ACSM is very difficult to identify more than three factors. Previous researches using quadrupole ACSM in the NCP only resolved two factors, i.e., POA and SOA (Chen et al., 2015; Sun et al., 2012; Jiang et al., 2013). Because there are restaurants nearby, we are sure that our sampling site has somewhat cooking influences. Thus, we uses ME-2 analysis to separate HOA and COA. The BC-tracer method further showed that the COA results is reasonable, as shown in our response to the fourth comment of reviewer #1. The relationship between factors MS and the reference MS are shown in Fig. R6 and R7. The time series of the contribution of the factors are shown in Fig. R8.

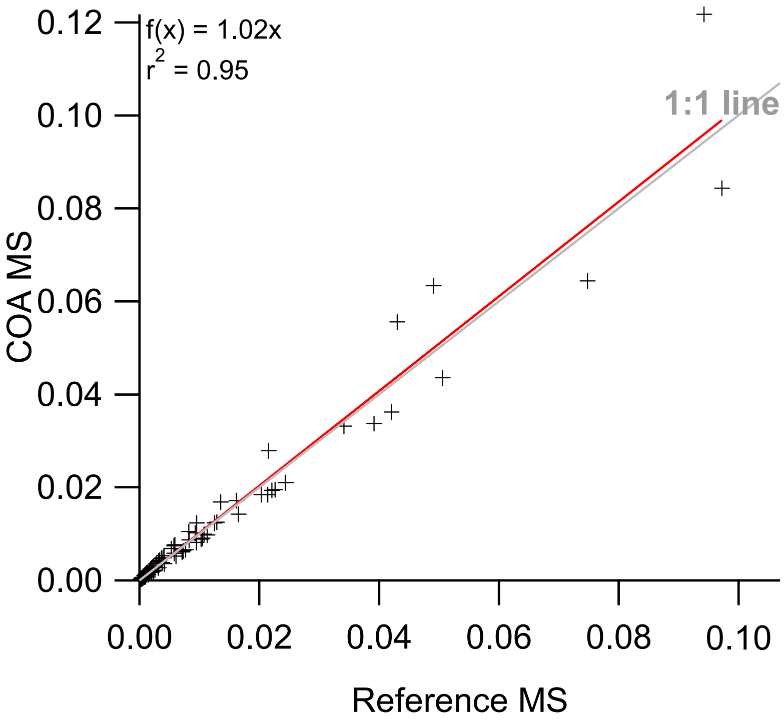


Figure R6. The relationship between COA MS and the reference MS.

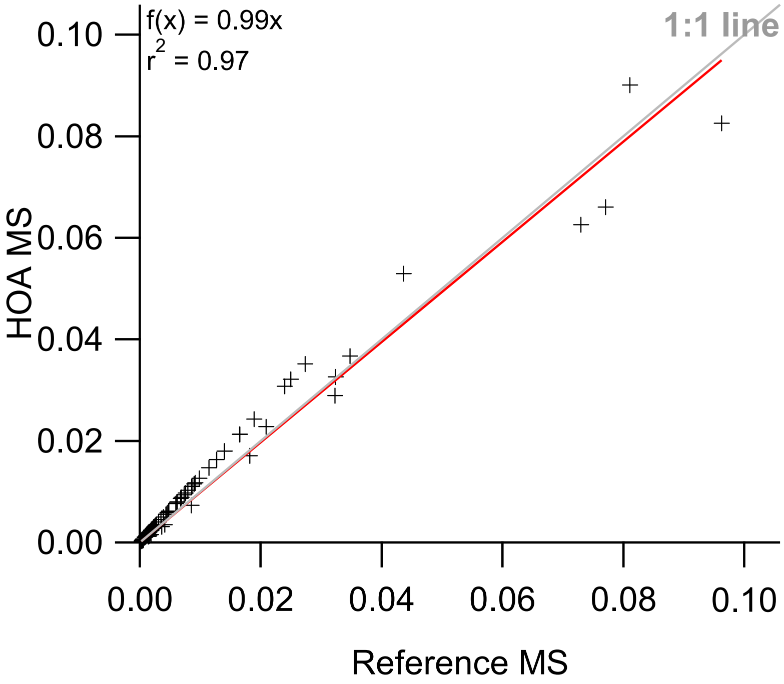


Figure R7. The relationship between HOA MS and the reference MS.

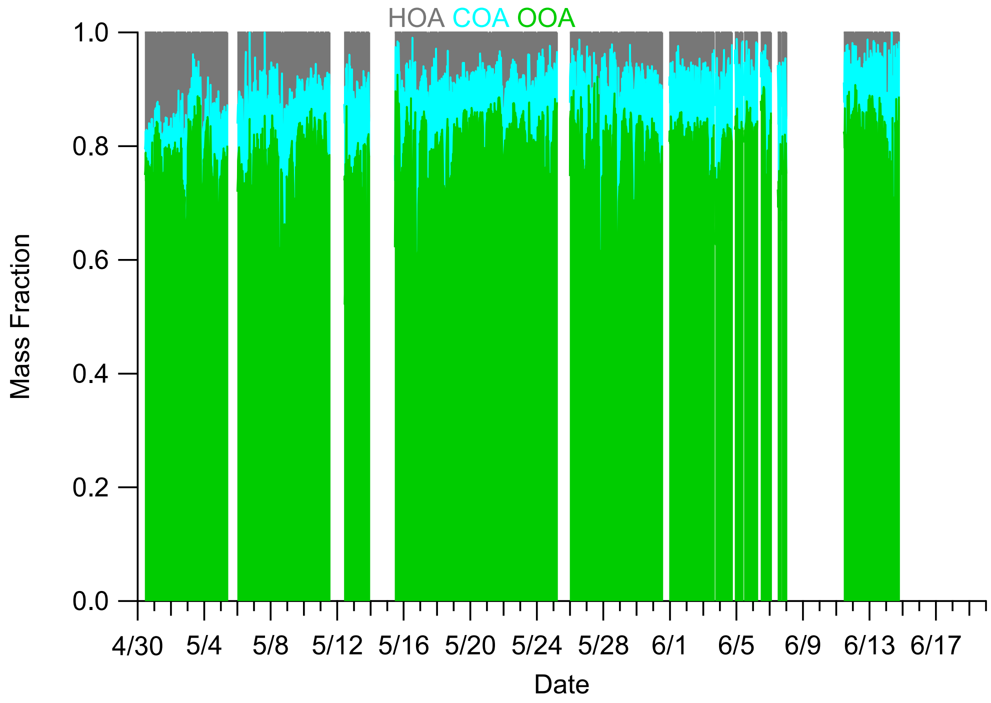


Figure R8. The time series of the contribution of the factors.

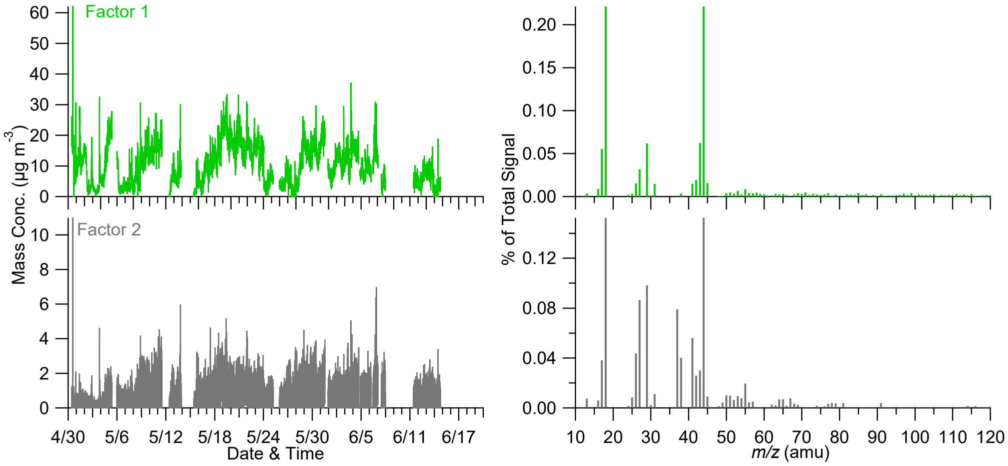
5. Lines 131-132: How is it an evidence that OOA is a surrogate of SOA? In addition, x vs y plot should be proposed for the entire period and not only for a selected period.

Thanks for your comments. The mass spectrum of OOA is characterized by a prominent peak at *m/z* 44. And OOA was highly correlated with SIA, suggesting its secondary source to some extent. Previous studies have shown that OOA was highly correlated with secondary organic carbon everywhere, and OOA is a good surrogate of SOA (Zhang et al., 2007).

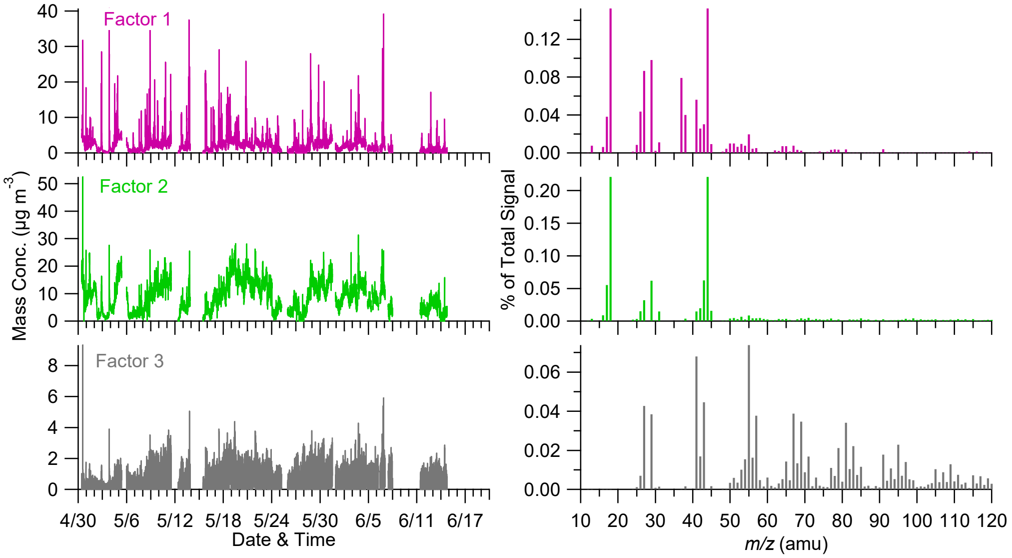
Figure 2 has been proposed for the entire period and the missed data between 14-20, June is due to the malfunction of the instruments.

6. Lines 133-135: Show these results. It would help to understand/validate PMF analysis.

Thanks for your comments. Results of two-factor and three-factor resolved by PMF are shown in Figure R9 and R10. PMF can identify two-factor solution using data from quadrupole ACSM, the solutions with three and more factors show a splitting and mixing of factors.



FigureR9. Mass spectral profiles (on the right) and time series of the mass concentration of two OA factors (on the left).



FigureR10. Mass spectral profiles (on the right) and time series of the mass concentration of three OA factors (on the left).

7. Lines 152-153: Add the concentrations of O3 & NOx to Figure 3.

Thanks for your comments. In the beginning, we prepared to add the time series of gaseous pollutants to Figure 3. But another team in our project who is responsible for gaseous measurement wanted to use them to write another paper. To avoid the conflict, we didn't show time series of gaseous species in Figure 3. We plot Figure S11 to help analyze gaseous pollutants and its impact on PM.

8. Line 155: It is clear for the period early June but it is not obvious for the other periods. RH stays similar and particle scavenging is not showed by the SMPS compared to the beginning of June. Please comment.

Thanks for your comments. We determined wet scavenging through precipitation data, although the RH was not that higher. Particle scavenging is not obvious from the SMPS measurements because of the high concentration of Aitken mode particles. In fact, the number concentration of accumulation mode particles that contributed to particle mass decreased significantly corresponding to particle scavenging (Fig. 6d). To avoid misreading, we revised the sentence as "Several pollution episodes usually lasting ~2–3 days were observed during the study period, e.g., on 9-11, 17–23, 28–31 May, and 2–4 June. These pollution episodes were quickly cleaned mainly by wet scavenging."

9. Line 156-157: The peaks are very sudden and appear suspicious. How long do they last? In addition, those spikes do not show up in the mass fraction plot while they should. What is the reason? In some case, organics should explain 80-90% of the mass (e.g. early May) but the contribution of organics stays ~ constant at 35-40%.

Thanks for your comments. We checked the peaks and found they last only 5-10 min (one or two data points). They may be from instantly local emissions. In these cases, although organics had the highest mass concentration, other species also increased obviously. Thus, the contribution of organics was still lower than 60%.

10. Lines 159-160: How do the diurnal cycles look like for those species? If it is only regional, why does the concentration of sulfate increase continuously? Shouldn't the authors expect to see a stronger diurnal variation if the wind changed?

Good point. Sulfate concentrations obviously increased and remained relatively high concentration during the pollution events. In fact, we also found that the mass concentration of sulfate varied with the change of wind direction. In most cases, it increased when the wind from south while decreased when the wind from north-west. This result also showed in bivariate polar plots of sulfate as a function of wind speed and wind direction (Figure 5c). Thus, we concluded that sulfate was mainly influenced by regional transport although there was other formation mechanism. To avoid misreading, we revised the sentence as "By contrast, sulfate concentrations obviously increased and remained relatively high during the pollution events, suggesting the important role of regional transport at the downwind site of Xingtai."

11. Lines 160-161: It is hard to see as it is. The authors should plot [NO3] vs the temperature.

Thanks for your comments. The diurnal evolution of nitrate showed high concentration at night but low concentration during daytime, which was mainly driven by the gas particle partitioning due to the influence of temperature (Fig. 4d). Because the nitrate formation is also affected by daytime photochemical production (OH + $NO_2$) and nighttime heterogeneous reactions, and also the temperature and precursors varied largely from day to day, you would not expect clear relationship between nitrate and temperature for all data points. The diurnal profile is one of the best ways to show the temperature-influenced gas-particle partitioning.

12. Lines 162-163: The authors indicate that "These results suggest that urban downwind sites in the NCP experience similar PM pollution events as those in urban cities." How do the authors reach this conclusion?

Thanks for your comments. We thought the results of sampling site exceeded the Chinese National Ambient Air Quality Standards by 29%. They also experienced atmospheric pollution. So we reached this conclusion. And we revised improper expression in the revised manuscript.

“The average $PM_{2.5}$ mass concentration was 45.2 μg $m^{-3}$. Although the average $PM_{2.5}$ mass concentration was 15% lower than that (53.3 μg $m^{-3}$) measured at the urban sites in Xingtai, it exceeded the Chinese National Ambient Air Quality Standards by 29%. These results suggest that the urban downwind sites also experience similar PM pollution events as the urban sites.”

13. Lines 184-187 & 189-190: If the authors claim that they observed two different air masses. The PMF should be able to distinguish clean vs haze events and differences should be visible in the MS.

Thanks for your comments. We agreed with the reviewer’s comment. In Table 1, the mass concentrations of HOA, COA, and OOA were 1.66, 1.67, and 12.2 μg $m^{-3}$ during pollution periods, which were much higher than that during clean periods. The use of ME-2 forced the MS to some extent and reduced the differences between clean and haze events in the MS.

14. Lines 240-242: How do the authors define a NPE?

Thanks for your comments. New particle growth events (NPE) occurred in daytime were identified according to four comments: a) outbreak of number concentration of small Aitken mode particles ($N_{20-40}$), b) the number concentration of large Aitken mode and accumulation particles didn’t increased in a consistent manner, c) the particle number size distribution showed a small size mode peaked at ~20 nm in the initial process, d) the geometric mean diameter (GMD) of new particle mode continued to grow more than 3 hours.

15. Line 249: In general, the authors should present the x vs y plots when they want to correlate/demonstrate a correlation between two parameters.

Thanks for your comments. As the reviewer suggested, x vs y plots have been used in the data analysis (Figure R11 and R12).

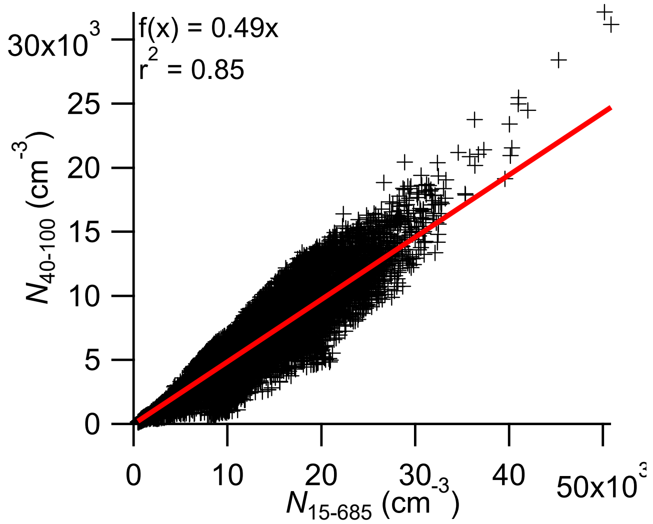


Figure R11. The relationship between $N_{40-100}$ and $N_{15-685}$.

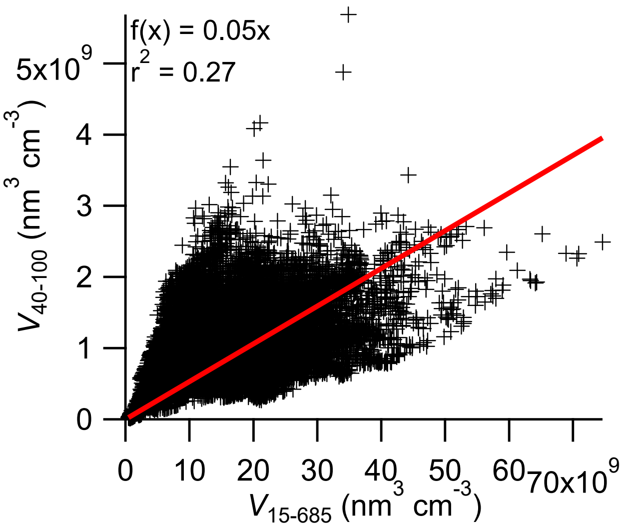


Figure R12. The relationship between $V_{40-100}$ and $V_{15-685}$.

16. Lines 260-265: What is the influence of biogenic-derived SOA during clean periods? Is it possible that biogenic derived SOA contribute more to SOA formation yielding larger NPF? A better comparison of the MS and PMF data is needed to better understand this aspect. In addition, what is the source of the big particles early morning during the polluted events? How do the meteorological conditions impact NPF?

The reviewer suggested an excellent point. Biogenic derived SOA possibly contributes more to SOA formation yielding larger NPF. Unfortunately, it is very difficult to separate biogenic derived SOA from OOA use quadrupole ACSM in summer. The source of the big particles in early morning during the polluted events is the transport of pollutants from urban sites located to the southeast. We checked the dependence of GR on source region to investigate the meteorological conditions impact NPF, but no clear relationship was found (Figure 11). It showed that new particle growth events were observed in different footprints, suggesting that NPF was not limited by meteorological conditions.

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# Aerosol chemistry and particle growth events at an urban downwind site in North China Plain

Yingjie Zhang[1,2,#], Wei Du[1,3,#], Yuying Wang[4], Qingqing Wang[1], Haofei Wang[5], Haitao Zheng[1], Fang Zhang[4], Hongrong Shi[6], Yuxuan Bian[7], Yongxiang Han[2], Pingqing Fu[1], Francesco Canonaco[8], André S. H. Prévôt[8], Tong Zhu[9], Pucai Wang[6], Zhanqing Li[4], and Yele Sun[1,2,3,10]

[1]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[2]Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing University of Information Science & Technology, Nanjing 210044, China

[3]College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

[4]College of Global Change and Earth System Science, Beijing Normal University, Beijing 100875, China

[5]Key Laboratory of 3D Information Acquisition and Application of Ministry of Education, Capital Normal University, Beijing 100048, China

[6]Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[7]State Key Laboratory of Severe Weather, Chinese Academy of Meteorological Sciences, Beijing 100081, China

[8]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI 5232, Switzerland

[9]College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

[10]Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

[#]These authors contributed equally to this work.

*Correspondence to*: Yele Sun (sunyele@mail.iap.ac.cn)

**Abstract.** The North China Plain (NCP) has experienced frequent severe haze pollution events in recent years. While extensive measurements have been made in megacities, aerosol sources, processes, and particle growth at urban downwind sites remain less understood. Here, an Aerosol Chemical Speciation Monitor and a Scanning Mobility Particle Sizer, along with a suite of collocated instruments, were deployed at the downwind site of Xingtai, a highly polluted city in the NCP, for real-time measurements of submicron aerosol ($PM_1$) species and particle number size distributions during May and June 2016. The average mass concentration of $PM_1$ was 30.5 (± 19.4) μg $m^{-3}$, which is significantly lower than that during wintertime. Organic aerosols (OA) constituted the major fraction of $PM_1$ (38%) followed by sulfate (25%) and nitrate (14%). Positive matrix factorization with the Multilinear Engine version 2 showed that oxygenated OA (OOA) was the dominant species in OA throughout the study, on average accounting for 78% of OA, while traffic and cooking emissions both accounted for 11% of OA. Our results highlight that aerosol particles at the urban downwind site were highly aged and mainly from secondary formation. However, the diurnal cycle also illustrated the substantial influence of urban emissions on downwind sites, which are characterized by similar pronounced early morning peaks for most aerosol species. New particle formation and growth events were also frequently observed (58% of the time) on both clean and polluted days. Particle growth rates varying from 1.2 to 4.9 nm $h^{-1}$ were positively related to the condensation sink during periods with high OOA contributions and also to sulfate concentrations during relatively clean periods. Our results showed that sulfate and OOA played important roles in particle growth during clean periods, while OOA was more important than sulfate during polluted events. Further analyses showed that particle growth rates have no clear dependence on air mass trajectories.

## 1 Introduction

Atmospheric aerosols can reduce visibility (Zhang et al., 2010), exert adverse effects on human health (Chen et al., 2013), and also affect radiative forcing directly by absorbing and scattering solar radiation and indirectly by modifying cloud formation and properties (Boucher et al., 2013). According to the latest report on global urban air quality by the World Health Organization (WHO), the top 10 most polluted cities in China are all located on the North China Plain (NCP). The concentration of particulate matter (PM) less than or equal to 2.5 µm in diameter ($PM_{2.5}$) in Xingtai ranked the first in China in 2014 (http://apps.who.int/gho/data/view.main.AMBIENTCITY2016?lang=en). Although extensive studies have characterized the formation mechanisms and evolution processes of haze in the NCP (Quan et al., 2011; Zhao et al., 2013; Yang et al., 2015), high anthropogenic emissions and stagnant meteorological conditions are the major factors leading to severe PM pollution (Zhang et al., 2015a; Fu and Chen, 2017; Guo et al., 2014; Sun et al., 2014). Mitigating air pollution in the NCP remains a challenge. One reason is the complexity of ambient aerosols, which have largely different compositions and that come from different sources from different regions and cities.

Xingtai, one of the most polluted cities in China, had an urgent front-burner environmental problem. PM sources are dynamic and include local emissions, e.g., biomass burning, traffic, and cooking emissions, and the transport of pollutants from upwind (east and south) polluted areas (Fu et al., 2014). As a result, both local and regional sources contribute to high concentrations of PM, leading to certain uncertainties in air quality control. Although the annual average concentration of $PM_{2.5}$ in Xingtai decreased from 160 µg $m^{-3}$ in 2013 to 87 µg $m^{-3}$ in 2016 (the data are from four monitoring sites ~~of~~ in urban Xingtai ~~and~~that was ~~published~~released by the China National Environmental Monitoring Centre), it still far exceeds the Chinese National Air Quality Standard (35 µg $m^{-3}$ for an annual average) and that of the WHO (10 µg $m^{-3}$). In addition, concentrations of $NO_2$ and

CO changed little from 2013–2016 while that of $SO_2$ decreased substantially (Fig. S1). As a response to the changes in precursors, aerosol particle composition may also change significantly. Therefore, characterization of the composition, sources, and processes of PM in regions near Xingtai is important to do so that effective strategies for future air quality improvements can be provided. Previous studies carried out in Xingtai have investigated the frequency of haze events (Fu et al., 2014), ammonia emissions (Zhou et al., 2015), and the sources of $PM_{2.5}$ (Wang et al., 2015a). The results highlighted the importance of both local (especially industrial) and regional sources of air pollution in Xingtai. However, real-time characterizations of aerosol composition and particle number size distributions have not yet been reported. A recent study conducted in a similarly polluted city, Handan, which is approximately ~50 km south of Xingtai, showed significant contributions of coal and biomass combustion to haze formation in winter (Li et al., 2017). However, aerosol characteristics in Xingtai are not well known and the impacts of urban emissions on downwind sites also remain poorly understood.

In this study, an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) along with a suite of collocated instruments was deployed at the downwind site of Xingtai from 30 April to 20 June 2016 to characterize aerosol chemistry and particle growth events in spring and summer. The mass concentrations, chemical composition, and temporal and diurnal variations of submicron aerosol ($PM_1$) species are characterized, and the sources of organic aerosols (OA) are investigated with positive matrix factorization (PMF) and a FLEXible PARTicle dispersion model (FLEXPART) analysis. Also, particle growth events and their relationship to aerosol chemistry are discussed.

## 2 Experimental Methods

### 2.1 Sampling site

Xingtai is located in the central-south part of the Beijing-Tianjin-Hebei region with the Taihang Mountains to the west (Fig. 1a). In this work, all measurements were made at the Xingtai National Meteorological Basic Station (XNMBS), a ~~rural~~suburban site located approximately 17 km northwest of Xingtai City (37.18°N, 114.37°E; 180 m. a. s. l.), from 30 April to 20 June 2016. The sampling site was influenced by mountain-plain winds during the study period. As shown in Fig. 1b, the wind direction showed clear day and night patterns with prevailing south-southeasterly winds in the day and west-northwesterly winds at night. The average wind speed was 4 m $s^{-1}$ and the average temperature was 22.6 °C during the study period.

### 2.2 Measurements

All instruments were placed in a container at the sampling site. The non-refractory $PM_1$ ($NR\text{-}PM_1$) chemical components including sulfate ($SO_4$), nitrate ($NO_3$), ammonium ($NH_4$), chloride (Chl), and organics (Org) were measured in situ by an ACSM at a time resolution of 5 min. The ACSM operated in the same way as in previous studies (Sun et al., 2016b; Zhang et al., 2016). A $PM_{2.5}$ cyclone (Model: URG-2000-30ED) was supplied in front of the sampling inlet to remove coarse particles larger than 2.5 µm. The ambient air was drawn into the container through a 1/2 inch (outer diameter) stainless steel tube at a flow rate of 3 L $min^{-1}$ using an external pump, of which ~0.1 L $min^{-1}$ was sub-sampled into the ACSM. The sampling height was approximately 2 m, which was 1.5 m higher than the roof of container. Thus, the particle residence time in the sampling tube was about 5 s. Aerosol particles were then dried by a silica gel diffusion dryer before sampling into the ACSM. Before the campaign, the ACSM was calibrated with pure ammonium nitrate particles following the standard protocols in Ng et al. (2011b). Because the ACSM does not measure refractory black carbon (BC), a seven-wavelength aethalometer (model AE33, Magee Scientific Corp.; Drinovec et al., 2015) was used to measure BC.

The size-resolved particle number concentration in the size range from 15 to 685 nm was measured in situ by a condensation particle counter (CPC model 3775, TSI) equipped with a long differential mobility analyser (DMA, model 3081A, TSI). The time resolution is 5 min. ~~And t~~The~~ Size-resolved particle number concentrations (15–685 nm) were measured by a Scanning Mobility Particle Sizer (SMPS, model 3938, TSI Inc.) and t~~total number concentrations (7–2000 nm) were measured by a Mixing Condensation Particle Counter (MCPC, model 1720, Brechtel). Other collocated measurements included the light extinction of dry $PM_{2.5}$ at 630 nm measured by a Cavity Attenuated Phase Shift Extinction Monitor (CAPS $PM_{ext}$; Massoli et al., 2010), the mass concentration of $PM_{2.5}$ measured by a 6-channel particle counter (manufactured by Graywolf) and gaseous species of CO, NO, $NO_x$, $SO_2$, and $O_3$ measured by gas analyzers (manufactured by ECOTECH). Meteorological parameters including ambient temperature (*T*), relative humidity (RH), wind speed (WS), wind direction (WD), precipitation, and solar radiation were also measured at the same site by the Xingtai Meteorological Administration.

### 2.3 Data analysis

#### 2.3.1 ACSM data analysis

ACSM data were analyzed using the ACSM standard software (version 1.5.3.0) within the Igor Pro software environment (Wave Metrics, Inc., Oregon, USA). The default relative ionization efficiencies for all species except $NH_4$ were used in the study. That for $NH_4$ was determined from the ionization efficiency calibration. A collection efficiency (CE) of 0.5 was used to account for the incomplete detection of aerosol species, mainly due to particle bounce at the vaporizer (Matthew et al., 2008).

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The CE can be composition dependent and especially sensitive to the fraction of ammonium nitrate ($NH_4NO_3$) as well as affected by particle acidity and RH (Middlebrook et al., 2012). In this study, $SO_4$ dominated inorganic species and the average contribution of $NH_4NO_3$ was 18% (maximum: 38%), which would not affect CE substantially. Aerosol particles were slightly acidic as indicated by the average ratio (~0.7) of measured $NH_4$ to predicted $NH_4$ that is required to fully neutralize $SO_4$, $NO_3$, and Chl (Zhang et al., 2007), which are also not acidic enough to affect the CE. Default relative ionization efficiencies (RIE) were used except ammonium and sulfate that ~~was~~were determined from pure ammonium nitrate and ammonium sulfate, respectively. In addition, to reduce the influence of RH on CE, a silica gel diffusion dryer was deployed to keep the RH in the sampling line below 40%.

Figure S2 shows the comparison between the total $PM_1$ mass (equal to NR-$PM_1$ + BC) and particle volume concentrations measured by the SMPS. Particle volume concentrations were highly correlated with total $PM_1$ mass concentrations ($r^2 = 0.77$, slope = 0.51). We then estimated the particle density using the chemical composition of $PM_1$ (Salcedo et al., 2006). The average density during the study period was 1.5 g $cm^{-3}$. Assuming spherical particles, the calculated SMPS mass reports 75% of the total $PM_1$ mass.~~,~~ Such a difference may be caused by measurement uncertainties between different instruments, the effects of particle shape and the uncertainties in estimating particle density~~suggesting that the chosen value of CE = 0.5 is reasonable~~.

### 2.3.2 Positive Matrix Factorization (PMF) Analysis

To determine the sources of OA, ACSM mass spectra were processed using the Multilinear Engine version 2 (ME-2) algorithm implemented with the toolkit called Source Finder (Canonaco et al., 2013). The so-called *a*-value approach allows the user to introduce a priori information in the form of known factor profiles or time series to obtain a unique solution and thus reduce the rotational ambiguity of the PMF algorithm. The mass spectra and error matrices of OA were prepared according to the procedures detailed by Ulbrich et al. (2009) and Zhang et al. (2011). Given the interference of the internal standard of naphthalene at *m/z* 127–129 and the low signal-to-noise ratios of larger ions, we only considered *m/z* values below 120 in this study. A reference hydrocarbon-like OA (HOA) profile, which is the average of multiple ambient data sets (Ng et al., 2011a), and a reference cooking OA (COA) profile in Beijing (Sun et al., 2013) were introduced to constrain the model performance with *a*-values varying from 0 to 1. Following the guidelines presented by Canonaco et al. (2013) and Crippa et al. (2014), an optimal solution involving three factors with an *a*-value of 0.2 was accepted. Some important criteria for selecting the optimal solution with *a*-value varying from 0 to 1 are shown in Figs. S3-S7. The mass spectra and time series of three OA factors are shown in Fig. 2. The HOA factor has a similar mass spectrum as that of freshly emitted traffic or other fossil-fuel combustion aerosols with major peaks at *m/z* equal to 41, 43, 55, and 57. HOA was moderately correlated with BC ($r^2 = 0.42$). The COA resolved in Xingtai had an *f*55 to *f*57 ratio of 2.3, within the range of values for COA (~ > 1.2)

(Mohr et al., 2011). The mass spectrum of oxygenated OA (OOA) is characterized by a prominent peak at *m/z* 44 (23.6% of the total OOA signal), which has also been reported in previous studies. In addition, OOA was highly correlated with sulfate ($r^2 = 0.75$) and moderately correlated with nitrate ($r^2 = 0.54$), suggesting that OOA is a surrogate of secondary OA (SOA; Fig. 2). We also performed a PMF analysis by applying the PMF2 algorithm to the ACSM-measured OA. Although the two-factor solution identifies a primary OA (POA) and an OOA, solutions with three to five factors show a splitting and mixing of factors. Therefore, the ME-2 algorithm was used in this study.

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### 2.4 Source region analysis

The footprints of the selected episodes were determined using backward simulations from FLEXPART, a Lagrangian transport and dispersion model (Stohl et al., 2005). The model calculated the 36-h backward trajectories of 10,000 particles released every hour from the sampling site at a height of 180 m above sea level. The meteorological data driving the model were simulated by version 3.4 of the Weather Research and Forecasting (WRF) model with a1-h time resolution and a 10-km spatial resolution. The WRF model was driven by initial and boundary conditions from National Centers for Environmental Prediction global reanalysis data.

Seventy-two-hour back trajectories at a height of 500 m were calculated every hour using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015) at the XNMBS. To investigate the chemical characteristics of aerosols from different source regions, a cluster analysis was then performed on the trajectories and three clusters were identified according to their similarities in spatial distributions.

In addition, non-parametric wind regression (NWR; Petit et al., 2017) was performed to evaluate the sources of local emissions and regional transport for $PM_1$ aerosol species and OA factors. The NWR plots represent the probability that a specific compound or source is located in a certain wind direction.

## 3 Results and discussion

### 3.1 Aerosol composition and temporal variations

The temporal variations of $PM_1$ aerosol species and meteorological parameters (RH, *T*, WS, WD, and precipitation) are shown in Fig. 3. The average mass concentration of $PM_1$ (equal to NR-$PM_1$ + BC) was 30.5 μg $m^{-3}$ and ranged from 0.2 to

140.1 μg m$^{-3}$. Several pollution episodes usually lasting ~2–3 days were observed during the study period, e.g., on~~ 9–11,~~ 9-11, 17–23, 28–31 May, and 2–4 June. These pollution episodes were quickly terminated mainly by wet scavenging. The temporal variations varied differently among different chemical species. Organics showed dramatic variations, ranging from 0.01 to 101.5 μg m$^{-3}$, and comprised the major fraction of $PM_1$ for most of the time in this study. High concentration peaks of organics were frequently observed, likely due to the influences of local emissions. By contrast, sulfate concentrations obviously increased and remained relatively high during the pollution events, suggesting the important role of regional transport at the downwind site of Xingtai. ~~The strong variation in nitrate concentration was mainly driven by gas-particle partitioning due to temperature influences.~~ The average $PM_{2.5}$ mass concentration was 45.2 μg m$^{-3}$~~,~~. Although the average $PM_{2.5}$ mass concentration was 15% lower than that (53.3 μg m$^{-3}$) measured at the urban sites in Xingtai, it exceeded the Chinese National Ambient Air Quality Standards by 29%. ~~which is 15% lower than that (53.3 μg m$^{-3}$) measured at the urban site in Xingtai.~~ These results suggest that the urban downwind sites also~~s~~ ~~in the NCP~~ experiences similar PM pollution events as ~~those in~~ the urban sites~~cities~~. For example, the daily $PM_{2.5}$ exceeded the Chinese National Ambient Air Quality Standards 24% of the time during this study. $PM_1$ was highly correlated with $PM_{2.5}$ ($r^2 = 0.95$) and on average, comprised ~64% of $PM_{2.5}$. The average mass concentration of $PM_1$ is close to that measured in Xinzhou (35 μg m$^{-3}$), a city in central China (Wang et al., 2016), but lower than that measured in 2013 in Xianghe (73 μg m$^{-3}$), a rural site near Beijing (Sun et al., 2016a; Fig. S8). One possible explanation is the significant improvement in air quality during the last four years (Fig. S1).

On average, OA was the largest component of $PM_1$, accounting for 38% of the total $PM_1$ mass, followed by sulfate (25%), nitrate (14%), ammonium (10%), and BC (10%; Fig. 1a). POA (equal to HOA + COA) and SOA (OOA) accounted for 22% and 78%, respectively, of the total OA mass. Together, ~18% of $PM_1$ was comprised of primary-related materials (POA + BC) and 82% was from secondary formation ($NO_3$ + $SO_4$ + $NH_4$ + Chl + SOA), indicating that aerosol particles from secondary aerosol formation processes dominated at the downwind site of Xingtai. Compared with aerosol composition in megacities in the NCP, e.g., Beijing (Hu et al., 2016), aerosol composition in this study showed substantially higher contributions of SOA (29%) and BC (10%), while the contributions of $NO_3$ (14%) and COA (4%) were low due to the lesser amount of local traffic and cooking emissions. The nitrate contribution was similar to that observed at a suburban site in Xinzhou (Wang et al., 2016), but the $SO_4$ contribution was relatively low (25% versus 32%). One reason is that the higher RH (70% versus 52%) in Xinzhou facilitated the formation of $SO_4$. The $PM_{2.5}$ concentration during this study period was more than twice lower than that in winter (151 μg m$^{-3}$, Fig. S9), suggesting less dilution in winter but also that PM came from different sources in spring-summer and winter. For example, the winter season has significantly enhanced coal combustion emissions.

We also investigated the compositional differences between clean periods and polluted events (Fig. 3). Secondary inorganic aerosols (SIA) including $SO_4$ (26% versus 21%), $NO_3$ (15% versus 9%), and $NH_4$ (10% versus 7%) showed enhanced contributions to $PM_1$ during polluted events, while a corresponding decrease was found for organics. For example, the contribution of SIA increased by 14% from 37% during clean periods to 51% during polluted events, while organics and BC decreased by 9% and 3%, respectively. Although SOA dominated the OA composition during both polluted events and clean periods, SOA also contributed more to OA during polluted events (78% vs 72%). Comparatively, POA (HOA and COA) was relatively more important than SOA during clean periods. These results suggest that PM at the downwind site of Xingtai was mainly affected by regional transport and secondary formation.

### 3.2 Diurnal patterns

Aerosol species showed distinctly different diurnal patterns in this study (Fig. 4), indicating that the sources and formation processes of PM pollutants were different. The diurnal cycle of $PM_1$ was characterized by peaks at ~1000 and ~2100 local time (LT). The first peak in the late morning was consistent with that of gas pollutants including CO, $SO_2$, and $NO_x$ (Fig. S11). Through comparisons with the diurnal cycle of $PM_{2.5}$ at the urban site in Xingtai (Fig. S12) and daily variations in WD (Fig. 1), the morning peak was mainly associated with the transport of pollutants from urban sites located to the southeast.

The high concentration of $PM_1$ at night was clearly associated with enhanced primary emission concentrations, e.g., HOA and COA, although the shallower boundary layer may have also played a role. It is interesting to note that $b_{ext}$ did not show a pronounced nighttime peak as did $PM_{2.5}$, indicating that the extinction coefficients of primary aerosols were smaller than those of secondary aerosol species (Wang et al., 2015b). The diurnal pattern of $PM_1$ only showed a pronounced peak at night during clean periods, consistent with those of HOA and COA. While the diurnal variations support the enhanced roles of primary emissions for PM during clean periods, they also indicate the lesser influences from urban emissions during daytime.

The diurnal pattern of organics overall resembles that of $PM_1$ and was characterized by two pronounced peaks between 0900–1200 LT and 1900–2100 LT. However, the three OA factors showed different diurnal cycles. The average diurnal cycle of HOA showed a small morning peak and a pronounced nighttime peak. While the two peaks were comparable during polluted periods, only the pronounced nighttime peak was observed during clean periods. As shown in Fig. S10a, winds were dominantly from the south-southeast during polluted periods and mainly from the west-northwest during clean periods. These results suggest that the high morning HOA peak was mainly caused by the transport of pollutants from urban sites, while local traffic emissions became an important source of HOA at night. This is also consistent with what is seen in the corresponding bivariate polar plot (Fig. 5h), which shows high concentrations of HOA in regions to the south-southeast and to the north. The decrease in HOA during the day was mainly associated with the rising planetary boundary layer height.

The diurnal pattern of COA (Fig. 4h) was also similar to that observed in megacities (Sun et al., 2013; Crippa et al., 2013; Elser et al., 2015; Zhang et al., 2015b; Hu et al., 2016; Xu et al., 2016) and was characterized by two peaks around the mealtime hours, reflecting the influence of cooking emissions. However, the COA concentration in this study was much lower than that reported in megacities (e.g., peak concentration: 2.5 μg $m^{-3}$ versus 14 μg $m^{-3}$ in Beijing; Hu et al., 2016), suggesting much less cooking emissions at the ~~rural~~ suburban site. The corresponding bivariate polar plot further shows that the high concentration of COA mainly originated from restaurants and inhabitants' activities to the southeast of the site (Fig. 5i).

Overall, the diurnal cycle of OOA (Fig. 4i) was flat during both clean and polluted periods in this study, reflecting regional characteristics. This is also consistent with the wide distribution of OOA seen in the corresponding bivariate polar plot (Fig. 5j). Secondary inorganic species of nitrate and sulfate had different diurnal profiles. Nitrate had a pronounced diurnal cycle with much higher concentrations at night than during the day. As shown in Fig. 4d, the nitrate concentration decreased from 6.0 μg $m^{-3}$ to 2.6 μg $m^{-3}$ between 1100 LT and 1900 LT, which was mainly due to the evaporative loss of particulate ammonium nitrate particles due to high temperatures. Such diurnal cycles have been observed many times during the summer in megacities, e.g., Beijing (Sun et al., 2012), Nanjing (Ge et al., 2017), Lanzhou (Xu et al., 2016), and also on other continents (e.g., Lanz et al., 2007). Nitrate also showed an increase in the early morning after sunrise (Fig. 4d). While the transport from urban sites played a role, this increase was mainly caused by daytime photochemical production when *T* was not high enough to substantially affect gas partitioning. During daytime clean periods, the diurnal cycle of nitrate was flat with higher concentrations at night. Sulfate showed a much smoother diurnal evolution compared with nitrate (Fig. 4c), reflecting the regional characteristics of sulfate. Two small peaks were observed during the day. While the first peak between 0900–1100 LT was most likely from urban transport, consistent with regional sources from the southeast indicated by the corresponding bivariate polar plot (Fig. 5c), the second one was more likely from daytime photochemical production. Chloride accounted for a small fraction of the $PM_1$ mass, yet it showed a strong diurnal cycle with a pronounced peak in the morning (Fig. 4e). This peak was noticeably similar to those of CO and $SO_2$ (Figs. S11a and S11c), suggesting that the dominant source was from combustion emissions in the southeast.

### 3.3 Particle number size distributions

Figure 6 shows the time series of total number concentration (15–685 nm, $N_{15\text{-}685}$) and three different modes including the small Aitken mode (15–40 nm, $N_{15\text{-}40}$), the large Aitken mode (40–100 nm, $N_{40\text{-}100}$), and the accumulation mode (100–400 nm, $N_{100\text{-}685}$), as well as particles in the range of 7–15 nm ($N_{7\text{-}15}$) that was calculated from the difference between MCPC and SMPS measurements. The corrections for diffusion loss and multiple charge have been applied in SMPS data analysis. The average total number concentration was 11,200 ± 5800 $cm^{-3}$, which is comparable to that measured in Shangdianzi (12,000 cm$^{-3}$; Shen et al., 2011), and Yufa (10200 cm$^{-3}$; Peng et al., 2014), and slightly higher than that observed in Beijing (10100 cm$^{-3}$; Du et al., 2017). $N_{15\text{-}685}$ showed a pronounced diurnal cycle with a clear increase during the day (Fig. 7e). A further analysis highlights that this increase was mainly driven by small and large Aitken mode particles, indicating the impacts of new particle formation and growth on the diurnal variations in particle number (Fig. S13). For example, the small Aitken-mode particles and ultrafine particles showed rapid daytime increases after sunrise by more than a factor of 5 during both polluted events and clean periods. Note that the number concentrations of $N_{7\text{-}15}$ during clean periods was much higher than during polluted events (6600 cm$^{-3}$ versus 3300 cm$^{-3}$, on average), which is comparable to the number concentration of small Aitken-mode particles. These results show that (1) new particle formation was much stronger on clean days than on polluted days, and (2) new particle formation also occurred on polluted days with newly-formed particles growing quickly due to the higher condensation sink (CS; 0.05 s$^{-1}$). About ~~48~~49% of the total particle number was made up of large Aitken-mode particles. However, these particles accounted for a small fraction of the total volume concentration (~~6.3~~5%). We also note that the pronounced nighttime peak in $N_{40\text{-}100}$ coincidently agrees with that of COA during clean periods, suggesting the influence of cooking emissions on large Aitken-mode particles. We calculated the particle number size distribution for two nights that experienced significant cooking emission events, i.e., 2 May and 13 May. Narrow single-mode distributions peaking at ~60 nm were seen (Fig. S14), supporting the influence of cooking emissions on large Aitken-mode particles. The diurnal cycle of $N_{100\text{-}685}$ was relatively flat except for a small morning peak (Fig. 7d). This is also consistent with results from the corresponding bivariate polar plot (Fig. S15d). The number concentration of $N_{100\text{-}685}$ during polluted events was more than a factor of 3–4 times that during clean periods, which contributes toward the major difference in particle number characteristics between polluted events and clean periods. One reason is the higher CS during polluted events, which facilitated the growth of particles.

Figure 8 shows that the average particle number concentration had a bimodal size distribution with the geometric mean diameter (GMD) peaking at 46 nm and 106 nm, respectively. Note that the peak diameter for the entire study was ~62 nm, which is higher than that observed in urban Beijing (45 nm; Du et al., 2017). The higher CS (0.36 s$^{-1}$ versus 0.29 s$^{-1}$) could be one of the reasons leading to more water vapor condensing on preexisting particles at the rural site. This is also consistent with the shift in the peak diameter from 57 nm during clean periods to 88 nm during polluted events. Although similar bimodal size distribution modes peaking at ~46 nm (41 nm) and ~109 nm (106 nm) were observed during clean periods and polluted events, respectively, the relative contributions of the two modes were largely different. While the particle number concentration was dominated by the small mode (56%) during clean periods, the large mode was more important during polluted events, accounting for 73% of the particle number concentration (Table 1). These results confirm the different roles of different mode particles between clean periods and polluted events.

### 3.4 Particle growth events

New particle growth events (NPE) were frequently observed during the study period. As shown in Fig. 9a, particle growth typically started at ~0800 LT and ended at midnight with an increase in GMD from ~25 nm to ~60 nm. This result is consistent with those previously reported for rural sites in the NCP (Wang et al., 2013) and urban sites, e.g., Beijing (Du et al., 2017). Note that the growth sizes of particles were overall larger than those observed in urban Beijing (from ~22 nm to ~55 nm), likely indicating a stronger aging process at the ~~rural~~ suburban site. The growth of particles tracked the diurnal cycle of CS, which showed a continuous increase from early morning to midnight. Though ACSM has a good transmission for only particles within the size range between 70 and 500 nm in diameter(Jayne et al., 2000), some particles from the small Aitken mode might not be detected by the ACSM. Simultaneous comparison between aerosol chemical composition and particle size distribution during the growth period also make some sense. Aerosol composition seemed to significantly change during the growth period. As shown in Fig. 9a, OOA and sulfate were the only two species whose contributions increased, going from 26% to 33% and 27% to 33%, respectively, during the growth period (1000–1800 LT). Although the increases in sulfate and OOA were partly due to the decreases in nitrate and chloride because of the evaporative loss in the afternoon, the CO-normalized sulfate and OOA ($SO_4$/CO and OOA/CO) also showed increases. These results show that both sulfate and OOA played important roles in daytime particle growth. We also examined particle growth events on polluted days and clean days. As shown in Figs. 9b and 9c, the growth process of particles on polluted days started at ~1200 LT with the GMD increasing from ~38 to ~57 nm in six hours. Particle growth started earlier (~1000 LT) on clean days with the GMD increasing from ~27 to ~41 nm. Particle growth on polluted days was faster than on clean days, which was likely due to the higher CS on polluted days. This is also consistent with more significant increases in SOA/CO and sulfate/CO on polluted days. The increase in CS between 0900–1200 LT on polluted days was associated with the corresponding increases in most aerosol species. However, the CO-normalized aerosol species did not show such an increase during this time period, suggesting that aerosol species and gaseous species were from the same air mass, i.e., transported in from urban sites. Such a pattern was not observed on clean days. Particle growth at night was more clearly seen on clean days than on polluted days, consistent with the increase in OOA/CO. However, such an increase was not observed for sulfate/CO on clean days, suggesting that OOA played a more important role than sulfate in particle growth at night.

We further calculated the particle growth rate (GR) of each growth event that lasted more than three hours (Fig. 10a and Table S1). The particle growth rates were calculated using Eq. (1).

$$\mathrm{GR}=\Delta D_{m}/\Delta \mathrm{t}\cancel{,} \qquad (1)$$

Where $D_m$ is the geometric mean diameter from the log-normal fitting of each size distribution and $\Delta D_m$ is the increase in diameter during the growth period of $\Delta t$. The particle GR varied from 1.2 nm $h^{-1}$ to 4.7 nm $h^{-1}$, which generally falls within the range of values (1-20 nm $h^{-1}$) based on observations from around the world (Kulmala et al., 2004). As indicated in Fig. 10b, GR was positively correlated with CS for most of the time, mainly for the fraction of OOA higher than 30% ($r^2 = 0.61$) As CS increased from ~0.01 $s^{-1}$ to 0.05 $s^{-1}$, GR increased from 3 nm $h^{-1}$ to 5 nm $h^{-1}$. However, there were some low GRs with high CS, which were characterized by low contributions of OOA. These results show the importance of the involvement of OOA in particle growth. Figure 10c further shows that GR was positively correlated with the concentration of sulfate during periods with low sulfate mass loadings (< 3 µg $m^{-3}$, $r^2$=0.42), while periods with higher concentrations of sulfate had lower GRs. This is corroborated by Fig. S16, showing that GR decreased as the sulfate contribution increased. By contrast, GR was positively correlated with OOA/$PM_1$ for most of the time. These results highlight that OOA played a more important role in particle growth than sulfate although sulfate was also important during periods with low mass loadings. We further checked the dependence of GR on source region, but no clear relationship was found. For example, GR varied from 1.6–3.2 nm $h^{-1}$ during periods with air masses from the north, 1.8–4.9 nm $h^{-1}$ from the southwest, and 1.8–4.6 nm $h^{-1}$ from the east-southeast (Fig. 11). This shows that GR had no clear dependence on air masses from different regions although sulfate concentrations showed much difference.

### 3.5 Aerosol composition and particle number concentrations from different source regions

Figure 12 shows the average composition and particle number distributions from different source regions. The air masses in cluster 3 (C3, 39% of the time) were mainly from the southeast while the other two clusters were mainly from the northwest. The average $PM_1$ concentration for C3 was 42 µg $m^{-3}$, which is ~ 30% higher than that from the other two source regions. The high mass loadings for this cluster suggest that source regions southeast of the site were responsible for the high PM pollution at the sampling site. This is also supported by the bivariate polar plots of aerosol species with high concentration regions in the southeast (Fig. 5). Among all clusters, the two dominant species in $PM_1$ were SOA (26–28%) and sulfate (26–29%). Overall, the aerosol bulk composition for the three clusters from different source areas was similar. These results suggest that aerosol particles were relatively well mixed over the region around Xingtai. Particle number concentrations showed more differences among the different clusters. The two clusters from the northwest were both dominated by large Aitken-mode particles, on average accounting for 49% and 51% of the particles making up the clusters, respectively. Although large Aitken-mode particles dominated the total particle number for C3, we also observed large increases in accumulation-mode particles (39%) compared with the other two clusters (28–30%). These results suggest that air masses from the northwest were relatively clean, which led to a more frequent occurrence of new particle formation and growth events, while those from the southeast with higher PM loadings tended to form more large particles due to the high CS.

## 4 Conclusions

We presented an analysis of aerosol chemistry and particle growth events at an urban downwind site in the NCP during May and June of 2016 using real-time measurements from an ACSM, an SMPS, and a suite of collocated instruments. Our results showed that the $PM_1$ level in spring and summer (30.5 μg $m^{-3}$) was much lower than that during wintertime when coal combustion emissions were enhanced. Similar to previous studies with a focus on the NCP, aerosol composition at the downwind site of Xingtai was dominated by organics (38%), 78% of which was identified as secondary OA according to the ME-2 analysis. Secondary aerosols (i.e., SNA + SOA) accounted for 78% of $PM_1$, highlighting the major source of secondary formation and regional transport at the downwind site. Local sources of PM from traffic and cooking emissions accounted for less than 10% of the total $PM_1$ mass. We also observed daytime transport from urban sites leading to similar pronounced early morning peaks for most aerosol species. New particle growth events were frequently observed (58% of the time) during the study period. The particle GR was positively correlated with the CS most of the time. By linking the GR with aerosol composition, we found that OOA and sulfate were two major species affecting the growth of particles. In particular, both OOA and sulfate played important roles in particle growth during clean periods, while OOA was more important than sulfate during polluted events. This is also supported by the decrease in GR as the sulfate contribution increased. A further analysis showed that particle growth rates have no clear dependence on air mass trajectories.

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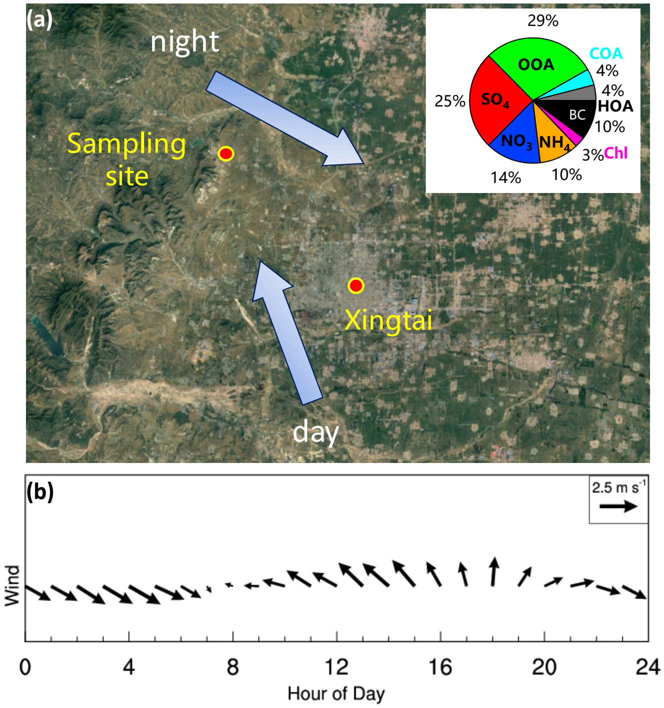

**Figure 1:** (a) Location of the sampling site. (b) average diurnal evolution of wind vector. The pie chart in (a) shows the average aerosol composition for the entire study. The two arrows in (a) show the daytime and nighttime prevailing wind directions.

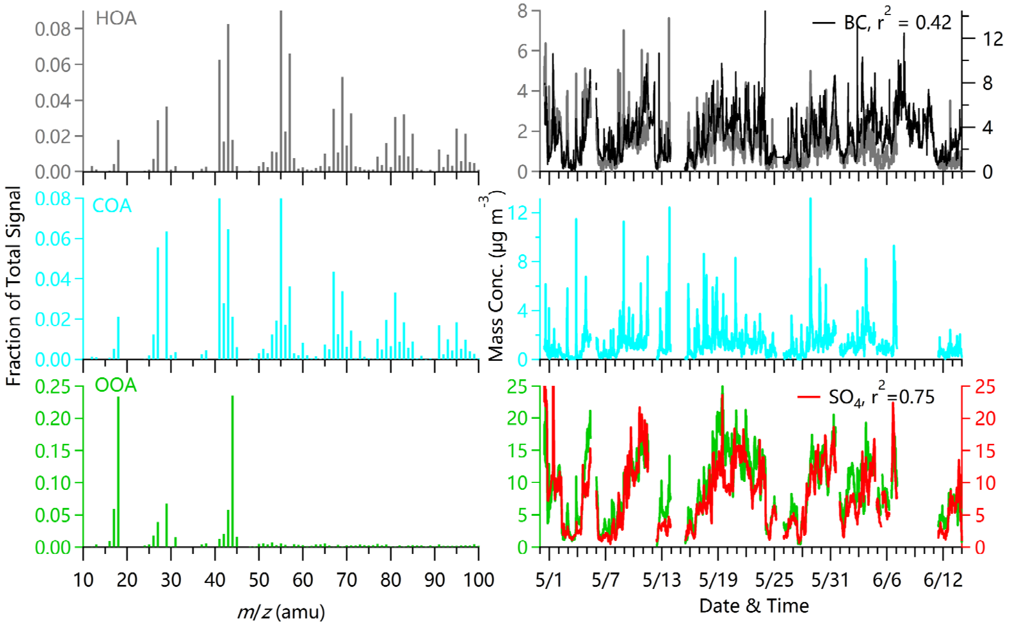

**Figure 2:** Mass spectral profiles (on the left) and time series of the mass concentrations of three OA factors (on the right), i.e., HOA, COA, and OOA. Times series of the mass concentrations of BC and sulfate (right axis) are also shown.

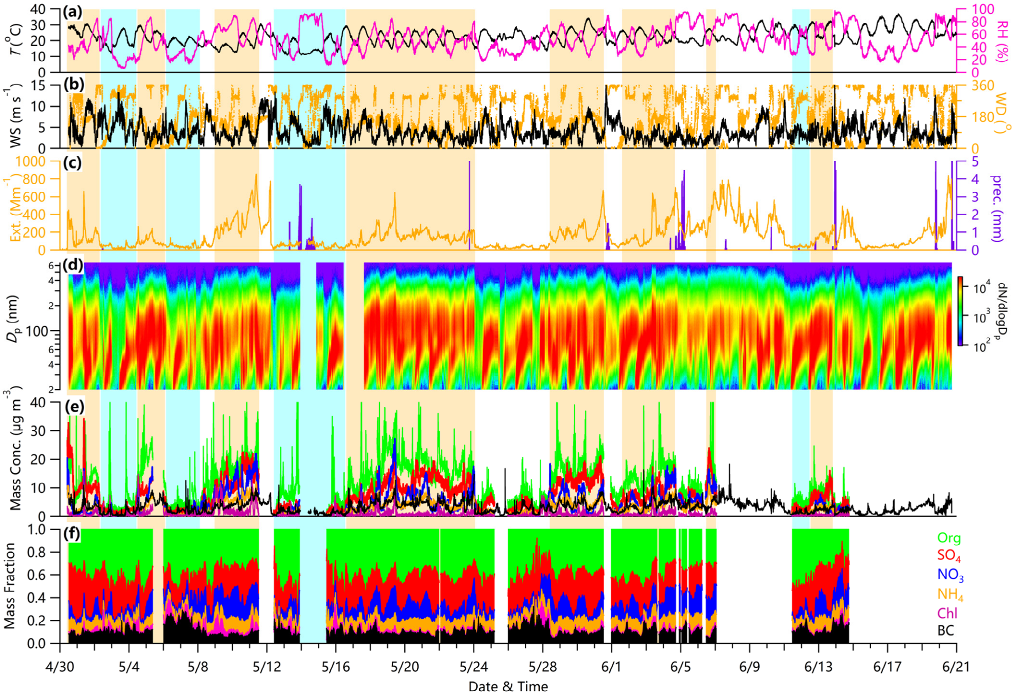

**Figure 3:** Time series of (a) temperature ($T$, in black) and relative humidity (RH, in magenta), (b) wind direction (WD, in orange) and wind speed (WS, in black), (c) particle extinction coefficient (Ext., in orange) and precipitation (Precip., in purple), (d) particle number size distribution, (e) mass concentrations of Org, $NO_3$, $SO_4$, $NH_4$, Chl, and BC, and (f) mass fractional contribution of chemical species to total $PM_1$. Polluted events (PE) and clean periods (CP) are marked as shaded orange and blue areas, respectively.

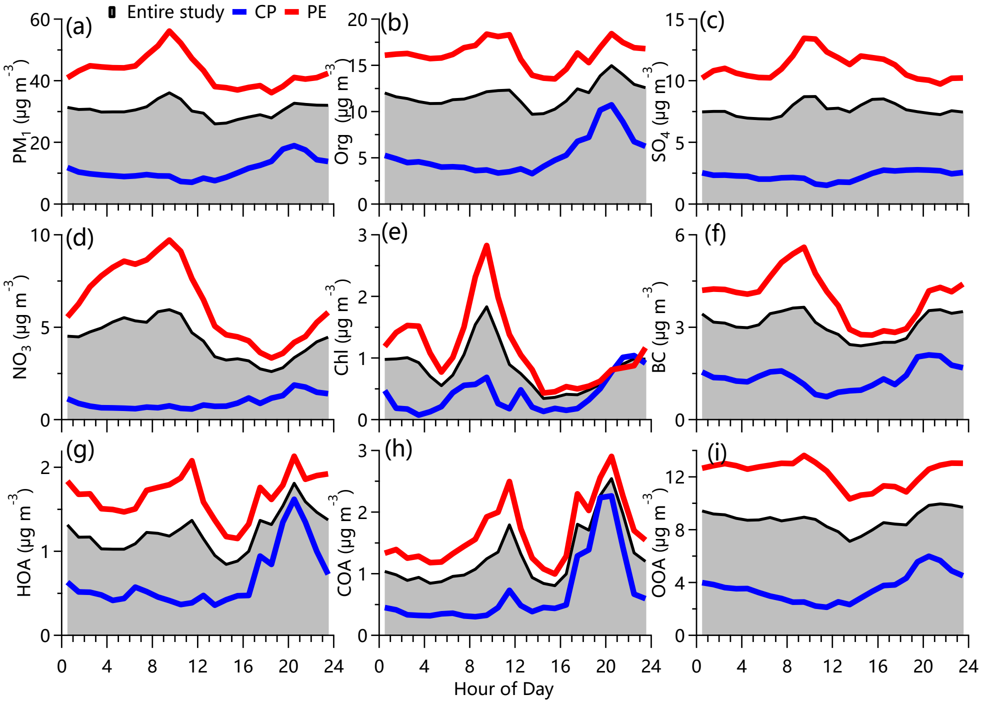

**Figure 4.** Average diurnal cycles of chemical species of PM$_1$ and OA factors during the entire study period, polluted events (PE) and clean periods (CP).

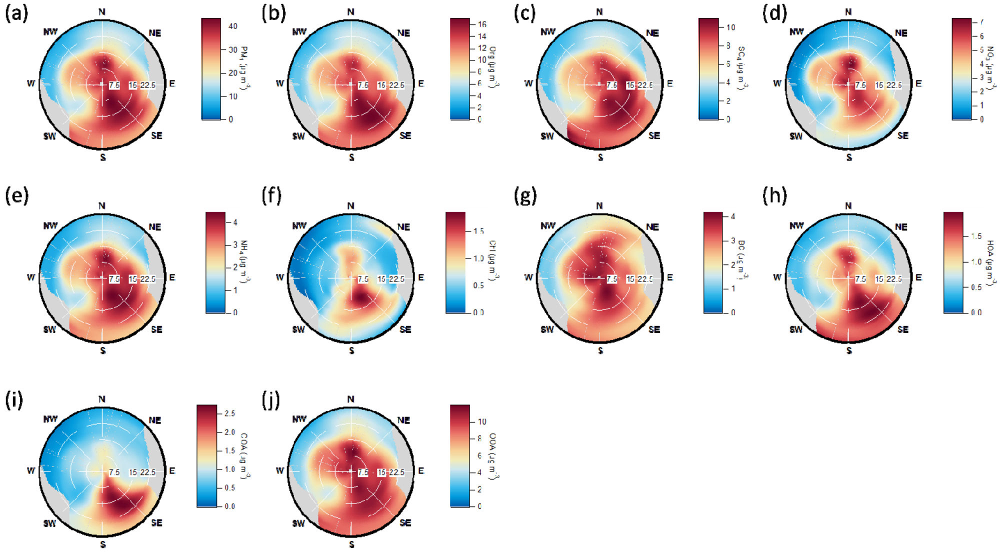

**Figure 5:** Bivariate polar plots of PM$_1$ species as a function of wind speed and wind direction: (a) PM$_1$, (b) Org., (c) SO$_4$, (d) NO$_3$, (e) NH$_4$, (f) Chl, (g) BC, (h) HOA, (i) COA, and (j) OOA.

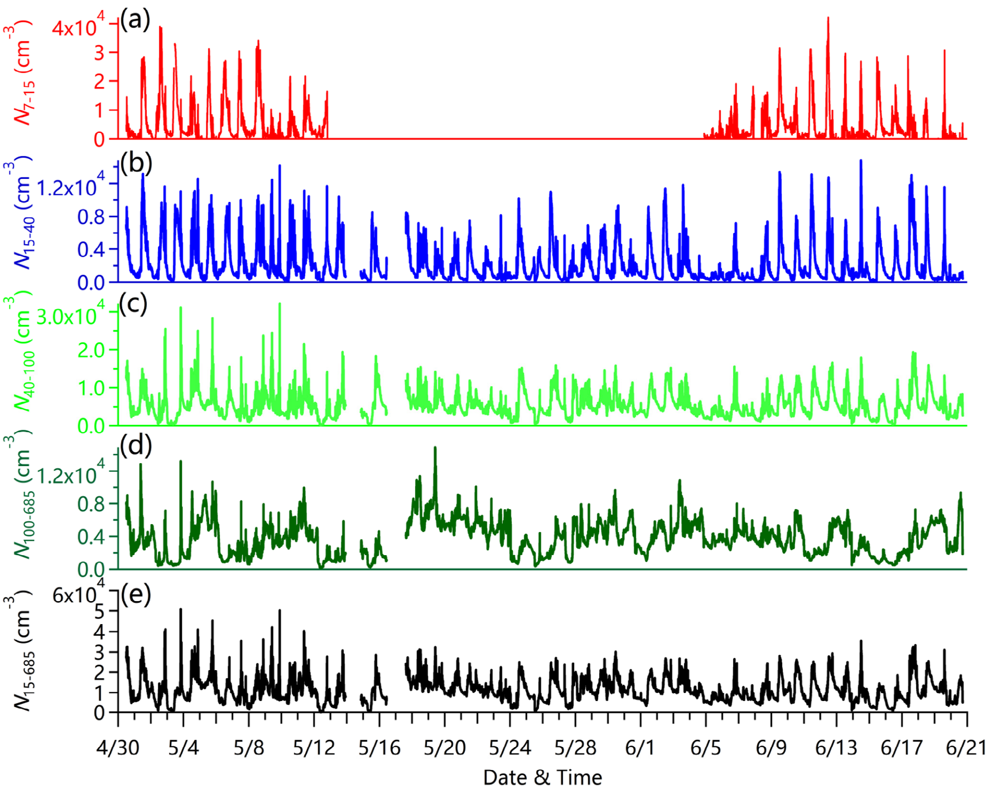

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**Figure 6:** Time series of particle number concentrations for (a) $N_{7\text{-}15}$ calculated from the differences between MCPC and SMPS measurements, (b) $N_{15\text{-}40}$ (15–40 nm), (c) $N_{40\text{-}100}$ (40–100 nm), (d) $N_{100\text{-}685}$ (100–685 nm), and (e) all particles, $N_{15\text{-}685}$ (15–685 nm). The gap in (a) is mainly due to the malfunction of MCPC during this period.

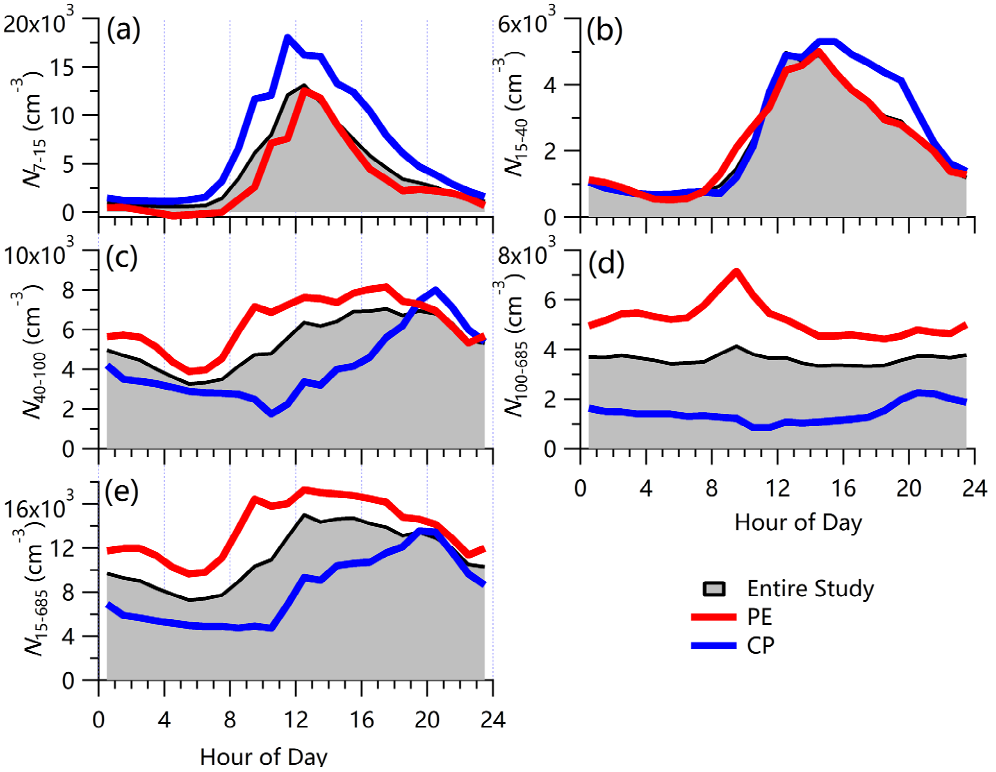


**Figure 7:** Diurnal cycles of particle number concentration for (a) $N_{7\text{-}15}$ calculated from the differences between MCPC and SMPS measurements, (b) $N_{15\text{-}40}$ (15–40 nm), (c) $N_{40\text{-}100}$ (40–100 nm), (d) $N_{100\text{-}685}$ (100–685 nm), and (e) all particles, $N_{15\text{-}685}$ (15–685 nm). Overall mean cycles are shown as black lines. Mean cycles for polluted events (PE) and clear periods (CP) are shown as red and blues lines, respectively.

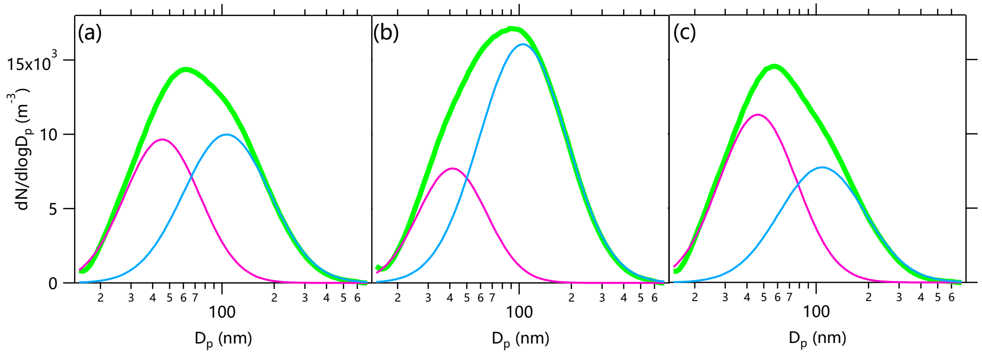


**Figure 8:** Average particle number size distributions during (a) the entire study, (b) polluted events, and (c) clean periods.

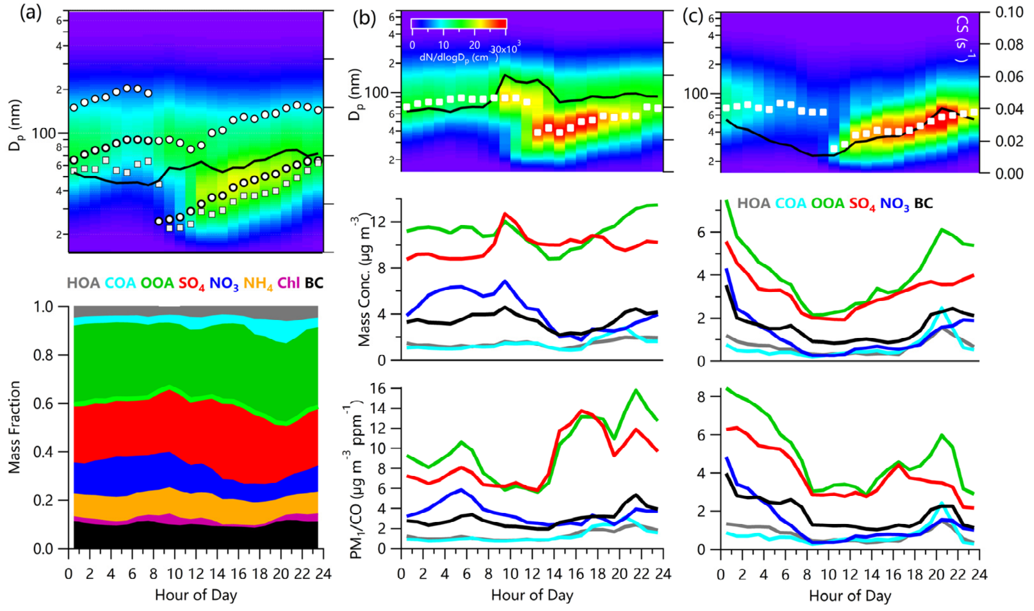


**Figure 9:** Average diurnal evolution of particle number size distributions and aerosol composition for new particle growth events during (a) the entire study, (b) polluted events, and (c) clean periods. The black solid lines in the top three panels show the diurnal cycles of CS. The circles and squares show the GMD from the log-normal fitting from this study and in Beijing (Du et al., 2017), respectively. The average diurnal cycles of aerosol species and CO-normalized aerosol species during polluted events and clean periods are shown in (b) and (c).

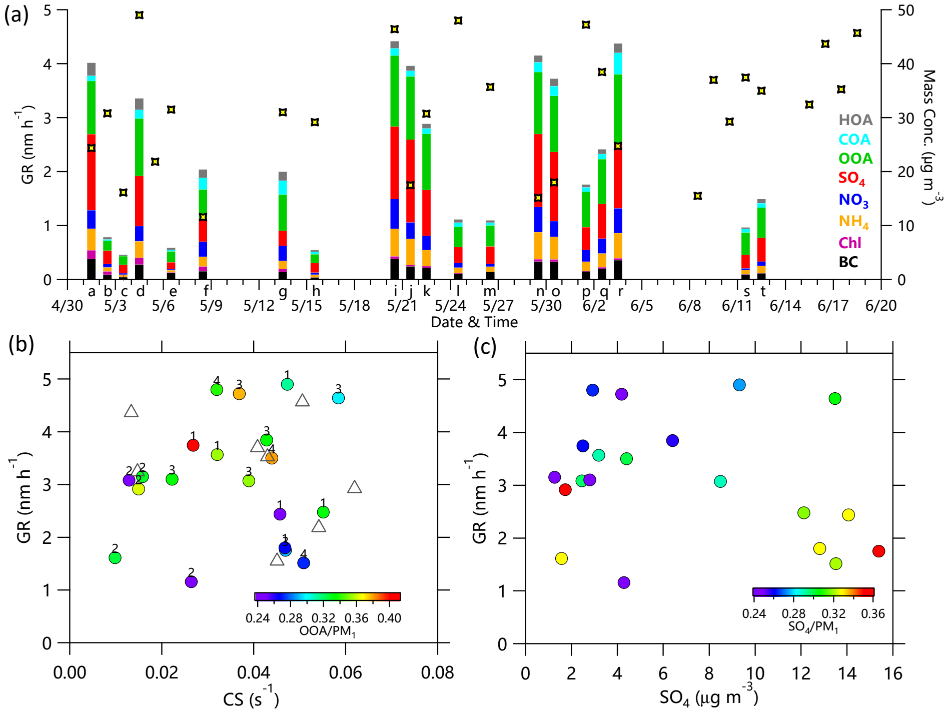
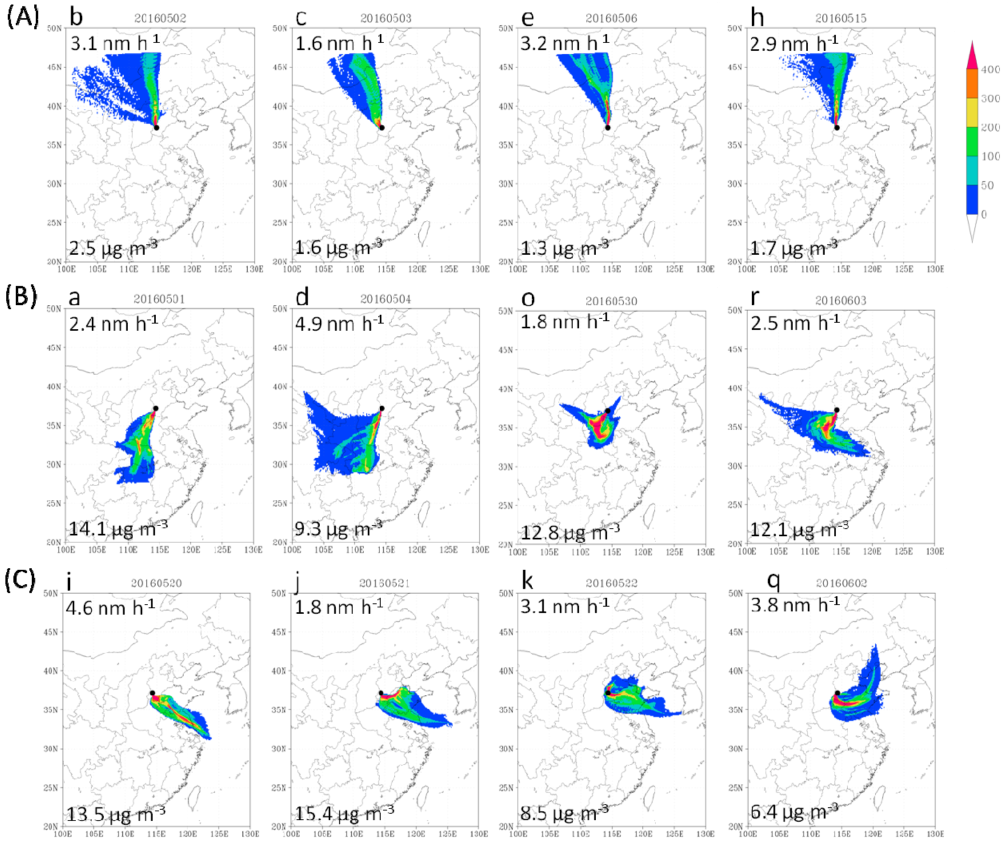


**Figure 10:** (a) Particle growth rates (GR) and the corresponding aerosol composition during the growth period, (b) the relationship between GR and CS, color-coded by OOA/PM$_1$, and (c) the relationship between GR and sulfate concentration, color-coded by SO$_4$/PM$_1$. The numbers over the circles in (b) represent different source regions (Fig. 11) and the triangles represent data without information about composition.



555 **Figure 11:** Particle GR and sulfate concentrations during the days shown in Fig. 10a with different footprints: (A) north, (B) southwest, and (C) east-southeast.

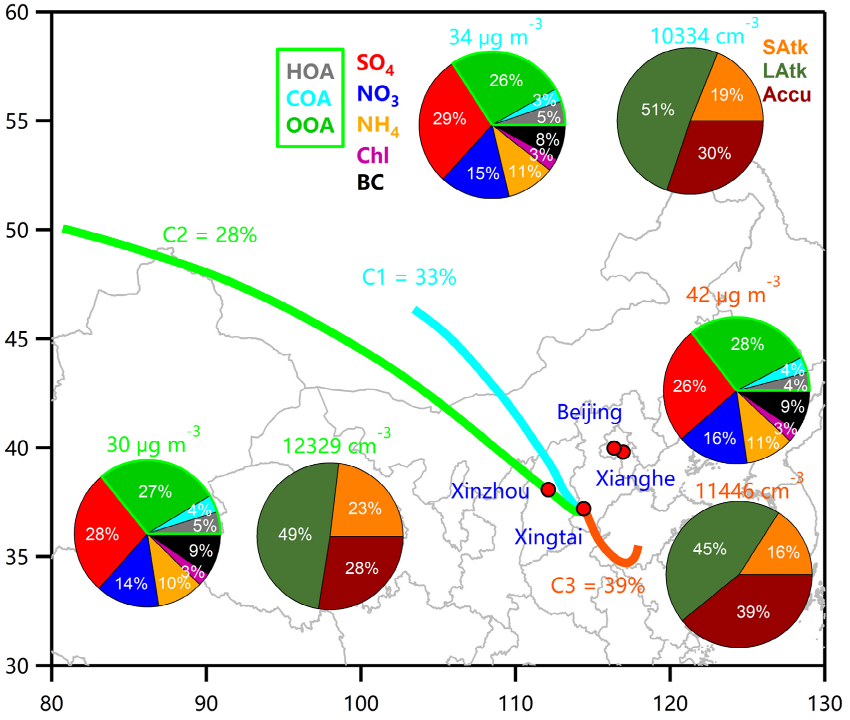


**Figure 12:** Average composition of aerosol particles and particle number concentration for three different clusters.

**Table 1:** Comparison of aerosol properties and meteorological parameters between polluted events and clean periods.

| | Polluted Events | Clean Periods |
|---|---|---|
| Mass concentration (µg $m^{-3}$) | | |
| $SO_4$ | 11.1 | 2.3 |
| $NO_3$ | 6.2 | 1.0 |
| $NH_4$ | 4.4 | 0.8 |
| Chl | 1.1 | 0.4 |
| BC | 4.0 | 1.3 |
| Org | 16.2 | 5.4 |
| HOA | 1.66 | 0.68 |
| COA | 1.67 | 0.73 |
| OOA | 12.2 | 3.6 |
| Particle number concentration ($cm^{-3}$) | | |
| $N_{15-40}$ | 2176 | 2471 |
| $N_{40-100}$ | 6095 | 5308 |
| $N_{100-685}$ | 5424 | 2977 |
| $N_{15-685}$ | 13696 | 10756 |
| Gaseous species | | |
| CO (ppm) | 1.3 | 0.8 |
| $O_3$ (ppb) | 81.2 | 48.9 |
| $NO_x$ (ppb) | 35.0 | 26.2 |
| NO (ppb) | 6.4 | 5.6 |
| $SO_2$ (ppb) | 15.9 | 4.4 |
| Meteorological parameters | | |
| $T$ (°C) | 22.9 | 18.6 |
| RH (%) | 52.7 | 41.3 |