Response to the referee comments

Response to Anonymous Referee #2

This manuscript presents measurements of the vertical distribution of aerosol composition in Guangzhou, China and, based on those data, provides insight into the sources and formation mechanisms of the different chemical components. The manuscript is certainly understandable, but would require editing prior to publication. As is noted in the paper, datasets such as these can be very useful and yet there are very few avail-able. Because of that utility I feel that this dataset should be published.

[A]: We would like to express our sincere appreciation for the reviewer's careful reading and invaluable comments to improve the paper. We have revised the manuscript accordingly. Please kindly find our itemized responses to the specific comments below. The reviewer's comments are in black and the authors' responses are in blue. Any changes made in the revision are highlighted in red.

[1] However, I feel that the use of the data to infer aerosol sources is weak and can probably not be refined to the level that would make ACP the appropriate journal for publication.

[A]: We thank the reviewer for valuable suggestions. In this study, we are not aiming at quantitively source apportionment but more to gain insight on the possible processes and mechanisms (e.g., secondary formation through cloud processing and heterogeneous reactions) that could contribute to the particulate matter formation with detailed mass size-resolved chemical components of particulate matters at different vertical levels. To clarify this, we have thoroughly revised the introduction.

Page 4, lines 14-28 and page 5, lines 1-3: "Severe aerosol pollutions frequently occur in China, as exemplified by three cities groups in the Jing-Jin-Ji (Beijing, Tianjin, and Hebei province), the Yangtze River Delta, and the Pearl River Delta regions. State–of–the–art air quality models still often fail to simulate the observed high $PM_{2.5}$ concentrations even after including aerosol-radiation-meteorology feedback, indicating that key atmospheric chemical processes, such as heterogeneous and multiphase reactions, are lacking in models for secondary aerosol formation (Zheng et al., 2015; Cheng et al., 2016). To improve the understanding of haze formation, models will require updated kinetic and mechanistic data of multiphase chemistry and quantification of the aerosol formation through heterogeneous reactions under real atmospheric conditions (Zheng et al., 2015; An et al., 2019). Additionally, more consistent evidences of aerosol formation through heterogeneous reactions are needed from field measurements, laboratory experiments and model simulations. Field studies showed that extremely high $PM_{2.5}$ concentrations usually occurred under high relative humidity conditions (Sun et al., 2014; Wang et al., 2014). Heterogeneous aqueous phase reactions in the cloud liquid water and in aerosol water can promote secondary aerosol formation (Seinfeld et al., 2006; Ervens, 2015; McNeill, 2015; Cheng et al., 2016). It is hence critical to investigate the aerosol sources and formation mechanisms by measuring size-resolved PM components vertically using a tall tower, where they can be strongly influenced by the dynamic variations of atmospheric boundary layer and cloud processing."

In addition, we have clarified the objectives of this study in the revised manuscript. Page 5, lines 13-17: "The objectives of this study are to (1) analyze the vertical mass size distribution of the PM chemical components and the factors that affect their vertical variations; and (2) investigate the roles of in-cloud processes and heterogeneous aqueous reactions in secondary aerosol formation and the implication for haze pollution in subtropical urban areas."

[2] Simultaneous and semi-continuous measurements such as those described here are challenging to make and are more amenable to collection and off-line analysis techniques such as those used here. Nevertheless, interpretation of the data is constrained by the resulting low time (24 h) and size (7 bins) resolution. For example, some of the central conclusions of the manuscript are based on the relative concentrations of species in the droplet mode, but that mode is contained in a very broad 0.44 – 1.0 micron bin. The time resolution also complicates the interpretation, especially when attempting to connect the measurements with meteorology in the case studies.

[A]: We thank the reviewer for valuable comments and suggestions. We agree that our measurements were low in time and size resolution due to the limited instruments and sampling site during the study. It is really difficult to conduct measurements in the vertical direction on Canton tower, and we've done our best so far. However, although size and time resolutions were low, the results from our study can still provide useful aerosol mass size distribution which is complimentary to the number size distribution usually measured in other field studies. Our results can provide a general characteristic of air pollutions in the PRD region, and useful information on the aerosol sources and transformations by the direct aerosol mass size measurements. We will plan to involve high time and size resolution measurements in the future study.

[3] I have questions/concerns about the impactors, in part because I have never used these and am unfamiliar with aspects of their operation. **i)** How were they calibrated? There is no information provided and the calibrated (?) cut sizes just happen to be exactly the same as those reported by the manufacturer. **ii)** How is the flow rate controlled? I ask because any pressure and/or temperature dependence would influence the recorded concentration height dependence. And connected to that, are the reported concentrations at local temperature and pressure or are they adjusted to standard (or other) conditions? **iii)** Is the air dried upstream of the impactors? For such a large flow rate I suspect the answer is no. And if not, this could have important impacts on the relative size distributions of the different chemical species and of the same species at different heights. The size distributions of hygroscopic species such as sulfate and nitrate would be shifted, while those of less- or non-hygroscopic species such as OC and EC would not. I appreciate that such shifts are not solely responsible for the differing size distributions, but they could be a contributor. The size distribution of those hygroscopic species would also vary with height due to variation in RH. This might partly explain the observation that the sulfate size distribution was shifted more into the droplet mode at 488 m, which was argued to be evidence of cloud processing in the manuscript (page 9, line 10). The average RH of between 78% and 80% suggests the bias could be significant.

[A]: We thank the reviewer for insightful comments. We give an overview of the impactor and then address the reviewer's comments point-by-point as shown below. The High-Flow Impactor (Model 131) is a commercial aerosol sampler manufactured by MSP corp. in USA. Its operation principle is inertial impaction using multiple-nozzle stages in series. At each stage, particle-laden air jets impinge upon an impaction plate. Particles larger than the cut-size of that stage cross the flow streamlines and are collected on the impaction plate below the nozzles. Particles smaller than the cut-size can follow the flow streamlines and proceed on to the next stage where the nozzles are smaller, the air velocity through the nozzles is higher and the cut-size is smaller. This continues on through the cascade impactor until the smallest particles which are not able to impact on the last impaction plate are collected by a final filter.

The Model 131 High-Flow Impactor consists of an inlet (which is also a large-particle pre-separator), six impaction stages and a filter holder-base. Stages 1 through 6 and the filter holder-base support the removable 75-mm impaction plates for the pre-separator inlet and stages 1 through 6 respectively. Figure I shows the Model 131 High-Flow Impactor we used in the samples collection.

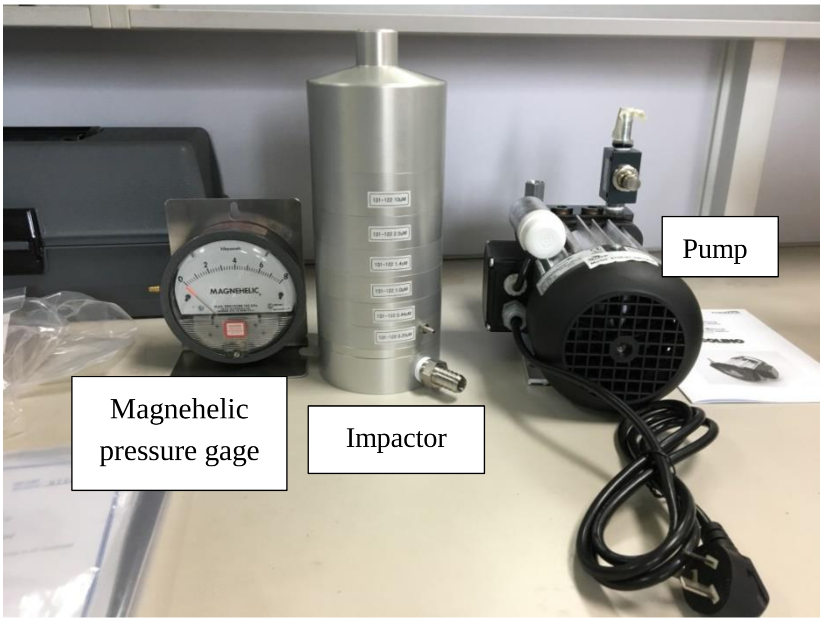


Figure I. Model 131 High-Flow Impactor

i) How were they calibrated? There is no information provided and the calibrated (?) cut sizes just happen to be exactly the same as those reported by the manufacturer.

- We have added more information on the flow rate calibration in the revised manuscript.

Page 6, lines 5-13: “Three impactors (or samplers) were calibrated using mass flow meter (TSI, model 4040) in the laboratory before they were used during the study. The flow rates of the impactors were measured at the beginning of the sampling. At the end of the sampling period, the flow rates were recorded again. If the flow rate of each impactor at the beginning and end of the sampling period differed by more than 10%, the sample was marked as suspect and the data was discarded. The average flow rates at the beginning and end of the sampling time was used as the sampling flow rate. In addition, a magnehelic pressure gauge was used to monitor the inlet flow rate through the impactor. The pressure drop was also recorded at the beginning and end of sampling.”

- These cut-sizes are based on the application of current impactor theoretical predictions (Rader and Marple, 1985). Figure II shows the calibration efficiency curves of the five standard impaction stages by the manufacture. These curves have been fitted with cumulative lognormal distributions to determine the calibration cut-size and geometric standard deviation for each stage. Based on the principle, the cut sizes should be the same as those reported by the manufacturer.

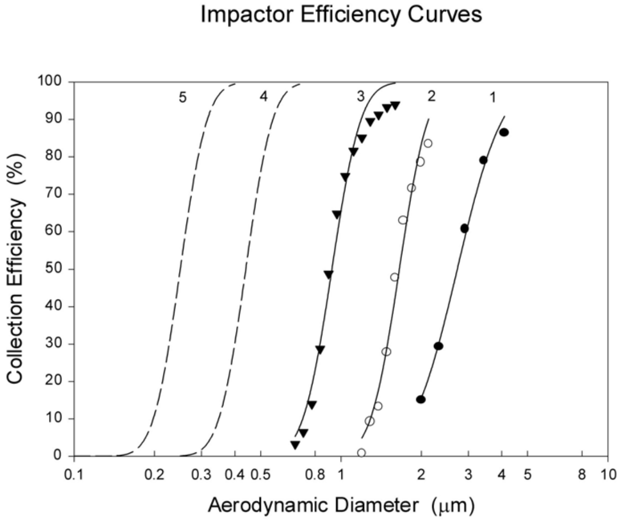


Figure II. High-Flow impactor efficiency curves provided by the manufacture

Reference:

Rader, D. J. and Marple, V. A., “Effect of Ultra-Stokesian Drag and Particle Interception on Impaction Characteristics” Aerosol Science and Technology, 4: 141-156, 1985.

ii) How is the flow rate controlled? I ask because any pressure and/or temperature dependence would influence the recorded concentration height dependence. And connected to that, are the reported concentrations at local temperature and pressure or are they adjusted to standard (or other) conditions?

- The magnehelic pressure gauge can be used to monitor the inlet flow rate through the impactor (each impactor has its own special pressure drop at 100 L/min). The low pressure side of the gauge is connected to the pressure tap on the last impactor stage body. The exhaust port of the impactor is connected to the suction side of a suitable vacuum pump. **A flow control** valve is applied to adjust the impactor inlet flow rate to 100 L/min.

We actually did not adjust to standard conditions given the vertical height is less than 500 m and the impacts are small. To prove this, we calculated the impacts of pressure and temperature on the flow rate, and found that these impacts were less than 5%. Blow are our simple calculations based on the measurements of relevant parameters on the Canton tower on Oct. 23, 2015:

The daily average temperatures were 28.0 ^{o}C and 24.1 ^{o}C at the ground level and 488 m, respectively. And the daily average atmospheric pressures were 101.15 kPa and 95.72 kPa at these two levels. The flow rate at the ground level is 100 L/m^3. We calculated the flow rate when the temperature was 24.1 ^{o}C and the pressure was 95.72 kPa, i.e. at 488 m, assuming a flow rate of 100 L/m^3 at the ground level (temperature = 301.15 K and pressure = 101.15 kPa).

Assume the ambient air is an ideal gas. At the ground level, $\boldsymbol{P_1}$ = 101.15 kPa, $\boldsymbol{V_1}$= 100 L/m^3, $\boldsymbol{T_1}$= 273.15+28=301.15 K. At 488 m, $\boldsymbol{P_2}$ = 95.72 kPa, $\boldsymbol{V_2}$= ?, $\boldsymbol{T_2}$= 273.15+24.1=297.25 K. R is the ideal gas constant. n is the moles of air.

We obtain: $$\boldsymbol{P_1 V_1 = nRT_1} \qquad \textbf{(1)}$$

$$\boldsymbol{P_2 V_2 = nRT_2} \qquad \textbf{(2)}$$

(1)/(2) we get:

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{101.15 \times 100 \times 297.25}{95.72 \times 301.15} = 104.3 L / \mathrm{m}^3$$

We conclude that the impacts of pressure and temperature on the flow rate are less than 5%. **Therefore, we thought that no adjustment of the flow rate was needed.**

iii) Is the air dried upstream of the impactors? For such a large flow rate I suspect the answer is no. And if not, this could have important impacts on the relative size distributions of the different chemical species and of the same species at different heights……

- ➢ We thank the reviewer for the valuable comments. The air was not dried upstream of the impactor in our measurement. We agree that the shifts of the particles sizes would happen due to the increase of relative humidity. However, we think this influence is unlikely to change our conclusion on the droplet mode. Meng and Seinfeld (1994) have proved that water accretion alone cannot account for the growth of droplet-mode particles from the condensation mode. They therefore proposed that activation of condensation mode particles to form fogs or clouds followed by aqueous-phase sulfate formation (also for nitrate and ammonium) and fog evaporation is shown to be a plausible mechanism for formation of the urban and regional aerosol droplet mode. Their findings support our results that in-cloud processing is likely an important source for droplet mode aerosols.

To clarify, we add these discussions into the manuscript as a caveat.

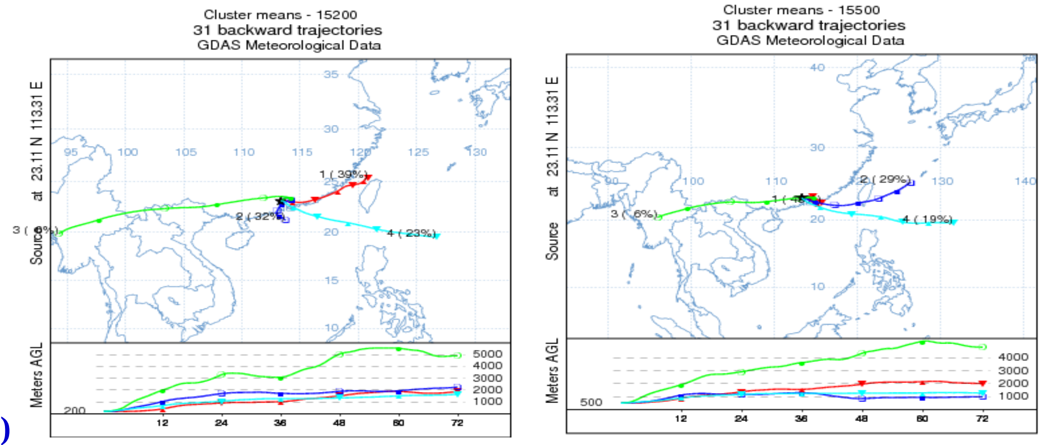
Page 11, lines 9-17: "Relative humidity would influence the relative size distributions of the different chemical species. The air was not dried upstream of the impactor in our measurement. However, we think this influence is unlikely to change our conclusion on the droplet mode. Meng and Seinfeld (1994) have proved that water accretion alone cannot account for the growth of droplet-mode particles from the condensation mode. They proposed that activation of condensation mode particles to form fogs or clouds followed by aqueous-phase sulfate formation (also for nitrate and ammonium) and fog evaporation are shown to be a plausible mechanism for formation of the urban and regional aerosol droplet mode. Their findings support our results that in-cloud processing is likely an important source for droplet mode aerosols.”

Reference:
Meng, Z. and Seinfeld, J.H. On the source of the submicrometer droplet mode of urban and regional aerosols. Aerosol Science and Technology, 20(3): 253-265.

[4] The authors interpret the relatively flat vertical profile of sulfate compared with EC and OC as an indication of the importance of cloud processing. But there is no explanation provided about how that contrast would differ for local emissions of EC and OC and simply regional production of sulfate (gas or aqueous phase). I’m not so sure the difference would be easily discerned.

[A]: We have modified the section “3.2.1 Vertical distribution of the major chemical components.” (page 8, lines 19-28 and page 9).

We performed the 72-h back-trajectory analysis in Figure S3 in the supplementary. We found that the air masses mainly came from either local or from the South China Sea. From the previous study, we know that the PRD region is one of the air pollution hot spot (Figure III). Therefore, local emissions may contribute significantly to the air quality of the PRD region during the sampling periods.



(a)

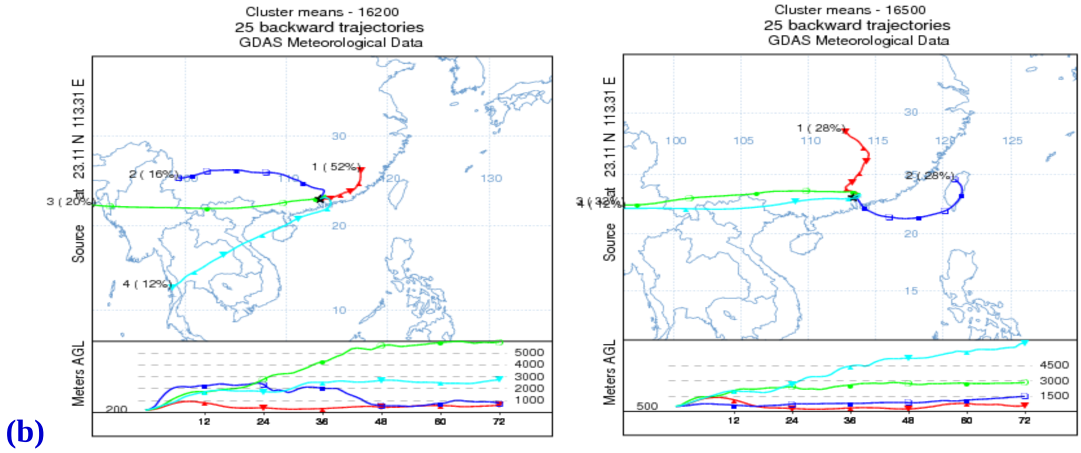


Figure S3. Cluster analysis of the airflow in 200 m and 500 m in (a) autumn and (b) winter campaigns.

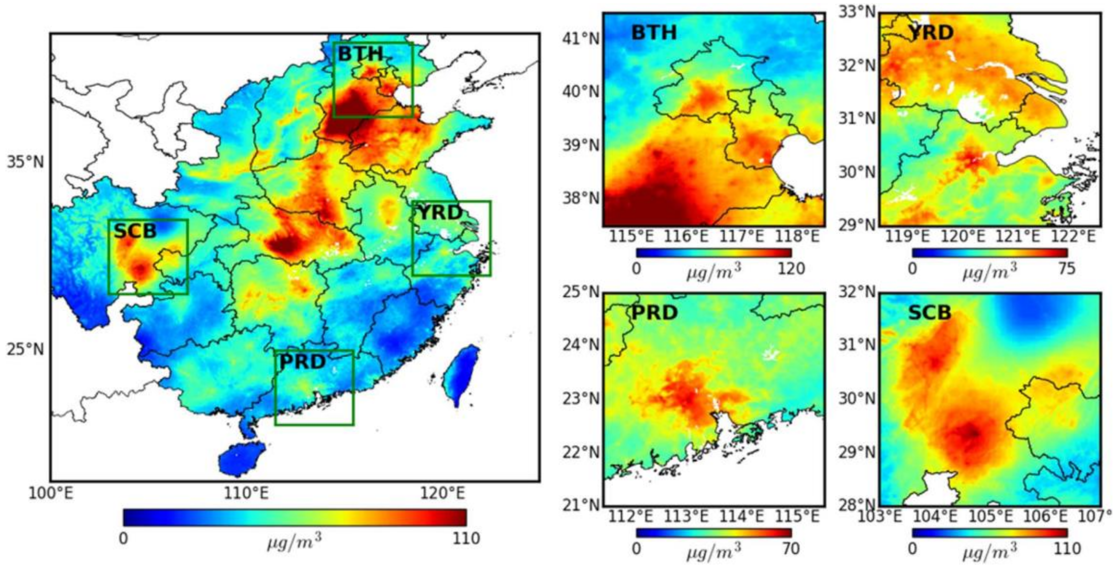


Figure III. Spatial distribution of the 15-year mean of $PM_{2.5}$ concentrations at a resolution of 1 km in the study region (left panel) and in the 4 major city clusters (right panel). Cited from Lin et al (2018).

New discussions are added in the revised manuscript (page 8, lines 19-28, page 9):

“**3.2.1 Vertical distribution of the major chemical components**

The profiles of the major $PM_{2.5}$ chemical components can generally be classified into three vertical gradients. The first category presents the highest concentration at ground level (type I). The second category shows the highest concentrations at 118 m (type II). And, the third category shows the highest concentration at 488 m (type III). The statistics of the three types in autumn and winter are listed in Table S1 and S2. We found that type II and type III were the major categories for sulfate, nitrate and ammonium (SNA) in autumn, while those were most frequently observed in winter belong to type I and type II. Meanwhile, the OC and EC were most frequently seen in type I particles in both seasons.

Figure 3 shows the representative and average vertical profiles of $PM_{2.5}$, sulfate, ammonium, nitrate, OC, and EC mass concentration at the tower. In autumn, the vertical gradients for averaged sulfate, nitrate and ammonium were observed to be shallow, attributed to type II in which sulfate and nitrate concentrations were slightly higher at 118 m (Fig. 3a) while mean ammonium concentrations increased with height, a typical type III profile. Sulfate, nitrate, and ammonium concentrations on the polluted day (i.e., November 18, 2015) all increased with height, a typical type III profile. In particular, nitrate concentration was 1.5 times higher at 488 m than that at ground level, which will be further discussed in case studies. The vertical gradients for OC and EC were found to be much steeper than those for sulfate and ammonium, with the EC concentration 27.9% lower at 488 m than at ground level and OC concentration 34.0% lower at 488 m than at ground level (type I). The decrease in air pollutant concentrations with height is considered to be associated with ground-level sources (Zauli Sajani et al., 2018). No vertical gradients could be established for any of the measured PM components during clean days (e.g., as seen for October 31, 2015), which was likably attributed to the turbulent mixing of air pollutants within the boundary layer (Guinot et al., 2006).

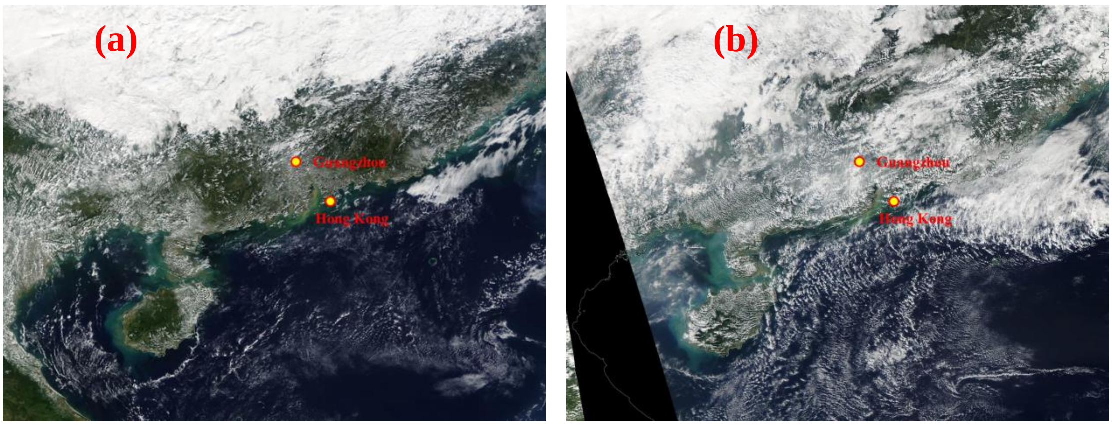
In winter, averaged concentrations of sulfate and ammonium were generally observed to be higher at ground level than in the rest of their vertical gradients (type I) (Fig. 3b). However, concentrations of nitrate, OC and EC were higher at 118 m (type II). On clean days (i.e., Jan. 17, 2016) the vertical gradients for mean $PM_{2.5}$, SNA, OC, and EC mass concentrations were found to be shallow due probably to the well mixed air masses, while on polluted days (i.e., Jan. 2, 2016), the concentrations for sulfate, nitrate, ammonium and OC were higher at 118 m (type II). Our results showed that the vertical gradients for sulfate, nitrate and ammonium concentrations tend to be type II and type III in both autumn and winter seasons when the $PM_{2.5}$ concentrations were high (Table S1). The reasons were currently not clear, but they were probably due to local chemical formation or regional transport of particles. However, back trajectory analysis of air masses showed that regional transport was unlikely the important source during the sampling time (Fig. S4) and then local chemical formation was likably the source that led to high SNA mass concentrations."

Reference:

Lin, C. Q., Liu, G., Lau, A. K. H., Li, Y., Li, C. C., Fung, J. C. H. and Lao, X. Q. High-resolution satellite remote sensing of provincial $PM_{2.5}$ trends in China from 2001 to 2015, Atmos. Environ., 180, 110-116, https://doi.org/10.1016/j.atmosenv.2018.02.045. 2018.

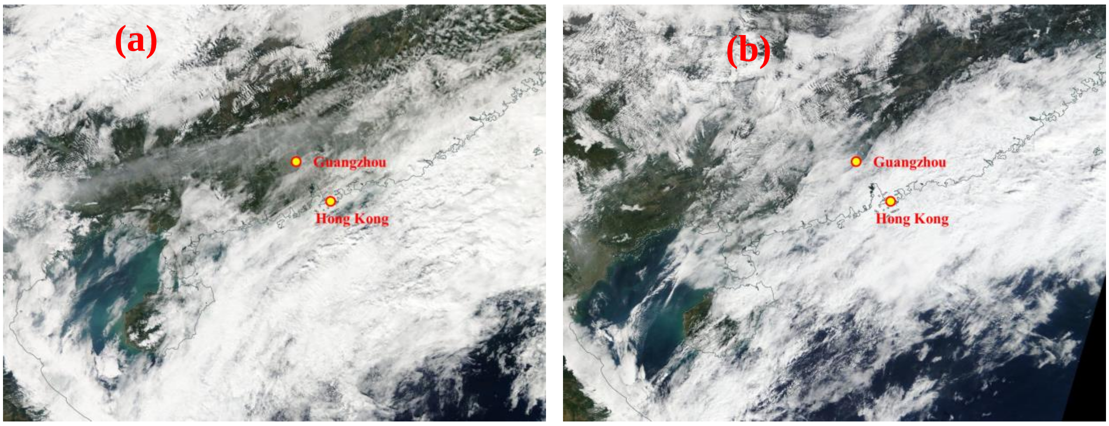
[5] I agree that using meteorology to interpret the aerosol data and to constrain the origin and formation of the different species is logical. But I don't agree that almost exclusively relying on WRF model output is reasonable. Why not at least validate those elements of the model predictions for which surface and/or satellite observations are available. Cloud cover and cloud base height are two that come to mind.

[A]: As suggested, we have now added the MODIS satellite images and ceilometer data in the supplementary of the revised manuscript. The ceilometer was mounted on the roof of South China Institute of Environment Sciences, Ministry of Ecology and Environment, which is about 4 km northeast of the Canton tower. However, we only obtained the winter pollution episode data because the ceilometer did not run during our autumn field study. MODIS satellite remote sensing images showed the cloud covers spreading over the PRD region (Figure S9 and Figure S10).

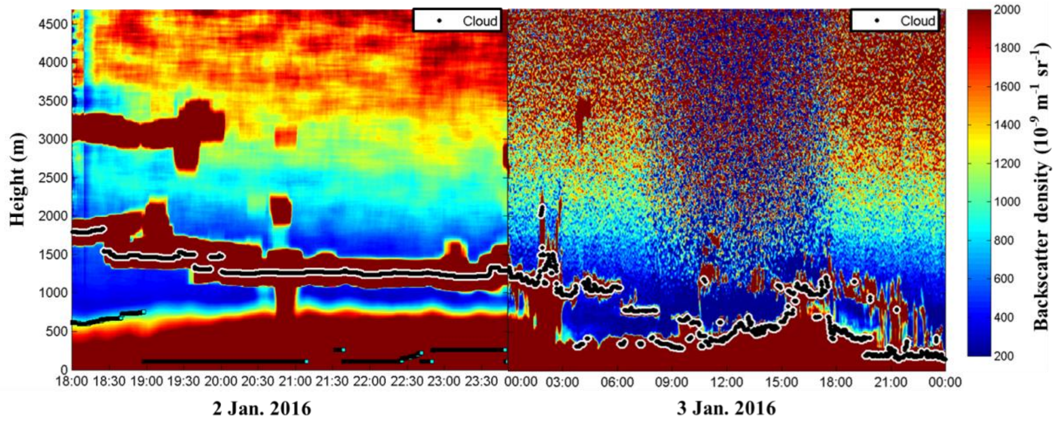


(a) November 18, (b) November 19, 2015

Figure S9. MODIS images show the cloud covers over the PRD region during the autumn pollution episode (https://earthdata.nasa.gov/earth-observation-data/near-real-time/rapid-response)



(a) January 02, 2016 (b) January 03, 2016



(c) Aerosol backscatter densities measured by ceilometer in Jan. 2 and Jan. 3, 2016.

Figure S10. Cloud cover from MODIS satellite (https://earthdata.nasa.gov/earth-observation-data/near-real-time/rapid-response) and cloud heights measured by ceilometer (Model CL-31, Vaisala Corp.) during the winter pollution episode.

We have modified and extended the section 3.3. More discussions have been made in the revised manuscript (see in pages 14-16).

[6] For much of the discussion I believe it would be better to describe variations in absolute rather than relative concentrations. I recognize that for some explanations it is appropriate to describe differences in percent contribution of one or more species to the total concentration. But for other descriptions varying concentrations of other species unnecessarily complicates the results. One example is the conclusion on page 8, line 12 of favorable formation of the inorganic ion species based on relative changes in composition with height. The percentages would of course change in the same way if the concentrations of those species increased or those of other species decreased.

[A]: We appreciate the reviewer for providing valuable comments and suggestions. In fact, we did describe the variations of major $PM_{2.5}$ components using both absolute and relative concentrations. **In section 3.2.1**, we presented the vertical distribution of the major chemical components and discovered some vertical characteristics based on their **absolute** mass concentration profiles. In addition, we showed the **percentages** of different chemical species to fine and coarse particles at the three levels in **section 3.2.2**.

As stated in the paper, we suggested that favorable formation of the inorganic ion species were in the higher levels based on relative changes in composition with height. Our results indicated that cloud processing and heterogeneous aqueous reactions together with unfavorable weather conditions were responsible for this phenomenon.

Minor issues in the order in which they appear in the manuscript:

[1] Page 3, Line 8: What are irregular sizes? And dust is usually used instead of sand.

[A]: We have modified in the text (page 3, line 13):

"Coarse-mode particles with large sizes and irregular shapes, such as dust particles, are usually produced from mechanical processes."

[2] Page 7, Line 24: SNA spelled out only later.

[A]: We changed in the text: "sulfate, nitrate, and ammonium (SNA)"

[3] Figure 2: Some explanation should be provided for the mismatch between the real-time and offline estimates of $PM_{2.5}$.

[A]: Thanks for the referee's suggestion. We added some explanations in the paper.

Page 7, lines 22-25: "The mismatch between the real-time $PM_{2.5}$ concentrations and the reconstructed $PM_{2.5}$ mass by combining the main components was likely due to sampling artefacts and lack of comprehensive offline $PM_{2.5}$ chemical analysis (Chow et al., 2015)."

Reference:

Chow, Judith C., Lowenthal, D. H., Chen, L. W. Antony, Wang, X. L. and Watson, J. G.: Mass reconstruction methods for $PM_{2.5}$: a review, Air Quality, Atmosphere & Health, 8(3), 243-263, https://doi.org/10.1007/s11869-015-0338-3, 2015.

[4] Figure 5: Some explanation should be provided for why the concentration of NH4 is highest at 488 m while that of SO_4 and NO_3 are not.

[A]: We added some explanations for this phenomenon.

Page 13, lines 6-10: "Figure 5 shows ammonium concentration was the highest in 488 m in autumn. The possible reason for this phenomenon might be that temperature (T) was lower and relative humidity (RH) was higher at 488 m, which was favorable for the partitioning of semi-volatile NH_4NO_3 into particle phase (Stelson and Seinfeld, 1982; Wang et al, 2012). This is supported by the evidence that nitrate concentration in fine particles generally increased with height (Figure 3)."

References:

Stelson, A.W., Seinfeld, J.H.: Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. Atmos. Environ., 16(5), 983-992, https://doi.org/10.1016/0004-6981(82)90184-6, 2007.

Wang, X. F., Wang, W. X., Yang, L. X., Gao, X. M., Nie, W., Yu, Y. C., Xu, P. J., Zhou, Y., and Wang, Z.: The secondary formation of inorganic aerosols in the droplet mode through heterogeneous aqueous reactions under haze conditions, Atmos. Environ., 63, 68-76, http://dx.doi.org/10.1016/j.atmosenv.2012.09.029, 2012.

[5] Figures 5 and 6: I believe the 0.1 on all of the x-axes is supposed to be 0.01 and 0.1 is for some reason not shown.

[A]: We have modified these figures in the revised manuscript.

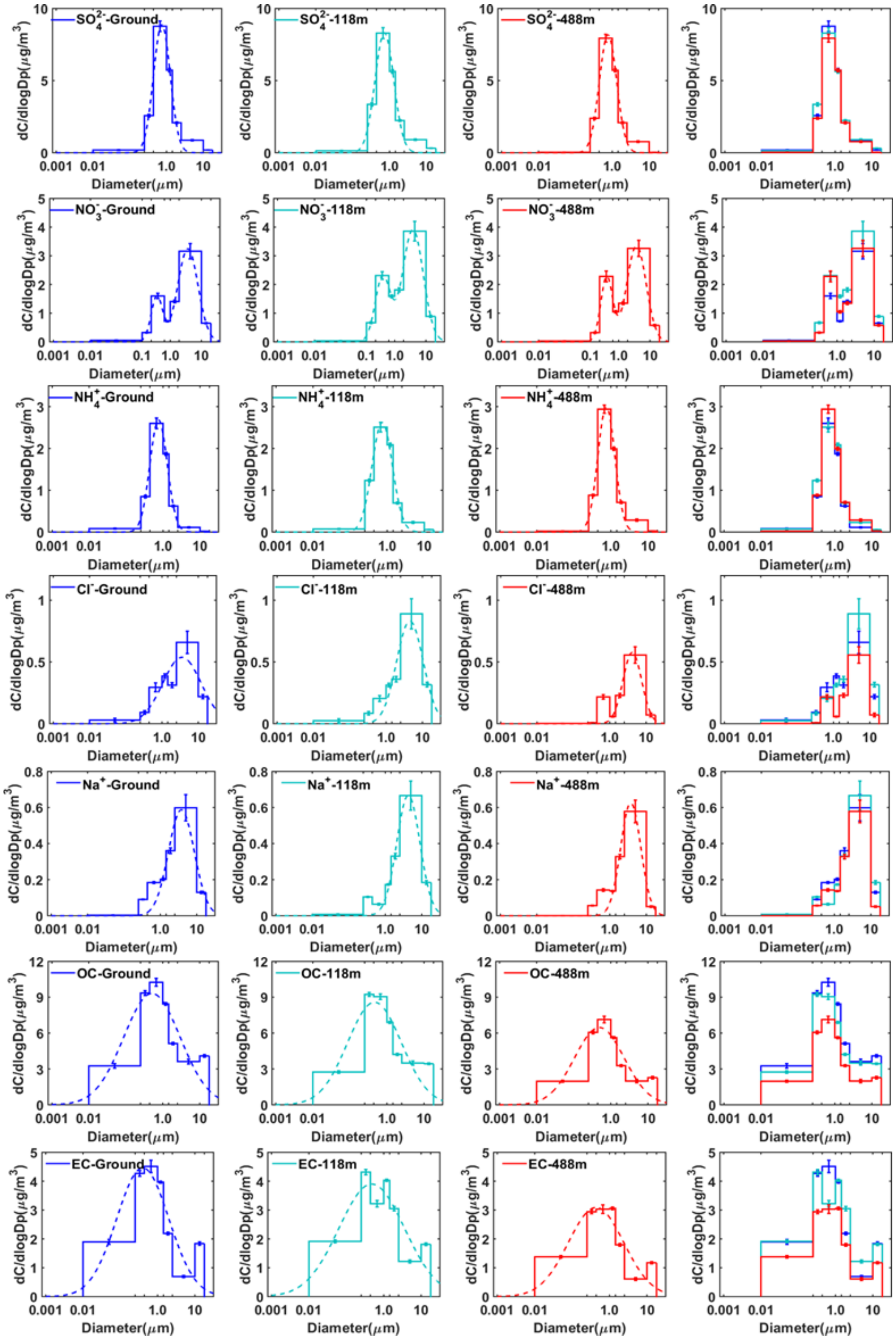


Figure 5. Mass concentration size distributions of the main chemical components measured at ground level, 118 m and 488 m in autumn. The dotted lines represent nonlinear fitting of the measured average size distribution. The error bars represent the sampling and analytical standard errors for each compound.

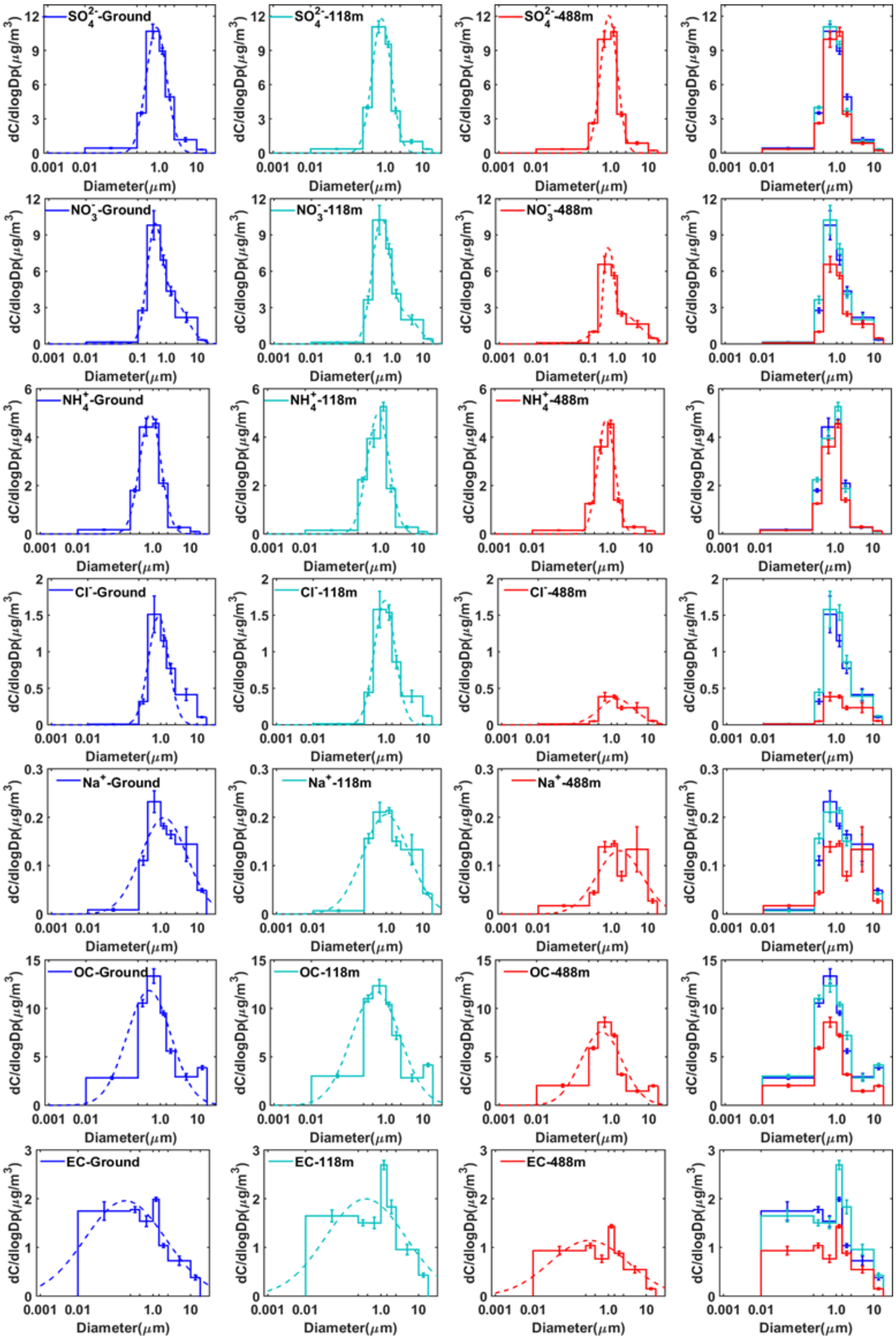


Figure 6. Mass concentration size distributions of the main chemical components measured at ground level, 118 m and 488 m in winter. The dotted lines represent nonlinear fitting of the measured average size distribution. The error bars represent the sampling and analytical standard errors for each compound.