

Dear editor,

Thank you very much for your helps to handle this review. I am grateful to you and the reviewers for the valuable comments and suggestions provided. Our manuscript has been carefully revised based on the comments and suggestions. We respond to all comments of the reviewers. A revised manuscript is also prepared with the changes highlighted in red. Below, comments of the reviewers are given in normal font style and our responses are given in blue color. The changes to the manuscript are marked in red and also provided here.

Thank you again and looking forward to hearing from you soon.

Sincerely yours,

Shengzhen Zhou on behalf of the coauthors

Response to the referee comments

Response to Anonymous Referee #1

The study by Zhou et al. is an interesting one considering the fact that very high towers are not readily accessible to researchers. Having said that, similar studies have been performed around the world and despite claiming the uniqueness of the study it is not entirely unique, except for utilising perhaps the highest tower. However, it is not the height of the tower which makes any study unique, but instead scientific insights about the processes drawn from it. The study is not without significant drawbacks and needs significant improvement to warrant publication in the respected journal of Atmospheric Chemistry and Physics. Last but not least, English of the manuscript needs significant improvement as many sentences are unclear or dubious.

[A]: We thank the reviewer for valuable comments and suggestions and we have revised the paper accordingly. The revised manuscript has undergone a professional language editing and we sincerely hope that the English in the revised version could meet the ACP publishing standard.

In this study, size-segregated aerosol samples were concurrently collected at ground level, 118 m and 488 m of Canton tower in autumn and winter. Vertical mass size distributions of the PM chemical components were analyzed and the factors that affect their vertical variations were elucidated. The roles of in-cloud processes and heterogeneous aqueous reactions in haze formation were investigated in this subtropical urban area.

We have made thoroughly revision of introduction part to clarify our motivations and aims of the study. We have reanalyzed the vertical profiles of major PM components. Uncertainties and errors are included in this revised version. The haze formation schematic in the PRD region has been significantly improved and more discussions are added in this part.

Please kindly find our following point-by-point response. The reviewer's comments are in black and the authors' responses are in blue. Any changes made in the revision are highlighted in red.

Major comments

[1] The introduction needs significant improvement as overall interpretation of PM sources and processes is rather outdated, or straightforward or not consistent with the most recent fundamental papers. Very often the authors choose to reference either old papers missing out on recent ones, or choose to reference very recent, neglecting pioneering earlier papers. It is unclear what exactly were the goal and aims of the study other than utilising a very high tower. Those goals should normally arise from the earlier papers by identifying scientific knowledge gaps and which the authors choose to advance upon.

[A]: Thank you the reviewer for thoughtful comments. We have improved the introduction section as suggested. In addition, relevant and pioneering works are summarized in the revised manuscript. Major changes are made below. Please also see our responses to the minor comments [1]-[6].

A new paragraph was added in 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

et al, 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] The paper currently stands more like a report rather than a scientific paper. It presents data, but lacks coherent view. More often than not the authors seek consistency with other studies or providing references which support or fit their data. Taken altogether, the paper is currently a collection of interpretations which are not always consistent with each other and most importantly lacking conclusive findings which would advance rather than confirm already known processes or phenomena.

[A]: We thank the reviewer for the valuable comments on the presentation of the paper. In this paper, we analyze the vertical mass size distribution of the PM chemical components and the factors that affect their vertical variations. In addition, we also investigate the roles of in-cloud processes and heterogeneous aqueous reactions in haze formation in the subtropics urban areas.

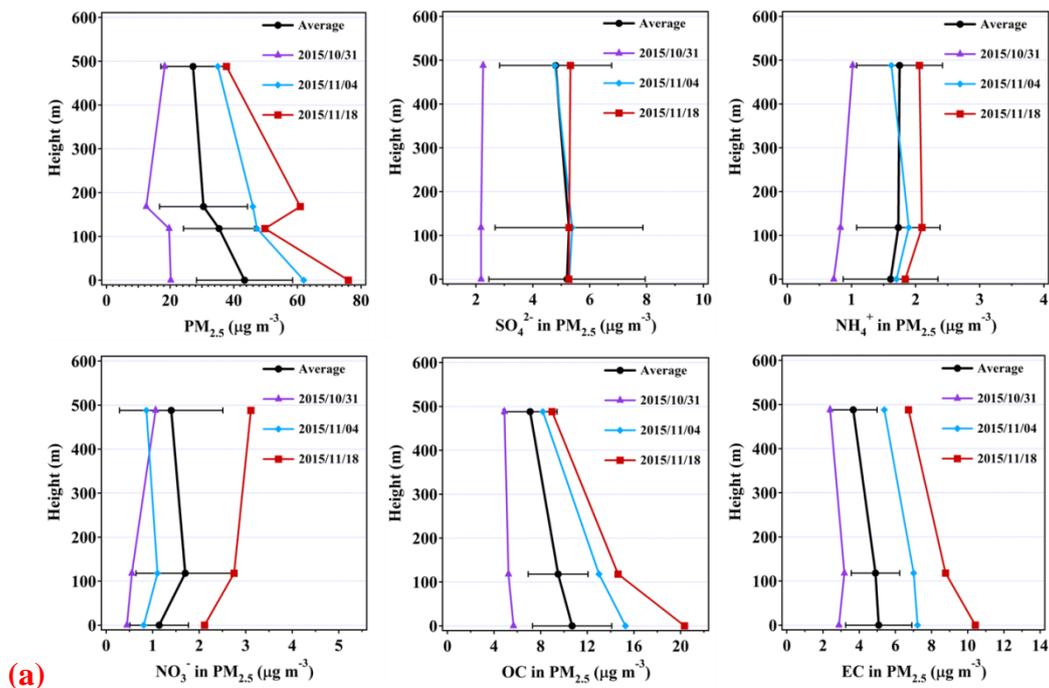
We have carefully addressed the reviewer’s concerns and made a thorough revision in the introduction section. In addition, we have added several discussions about the haze formation mechanisms in section 3.3.

Please see more details in our point-by-point response to your specific comments below. We believe that revised manuscript has been improved in this regard.

[3] The study is lacking an overview of all the profiles, splitting into certain categories and introducing the scope and variability of the data set first. There is a complete lack of uncertainty and error analysis. Analytical and sampling uncertainty would propagate into vertical profile uncertainties which would then make profiles or concentrations at different heights significantly different or not. The authors choose to select specific episodes or profiles which are most obvious or interpretable and neglecting which are not. Selected profiles are certainly insightful, but only when put into overall context.

[A]: We thank the reviewer for the valuable comments. We have added two tables (Tables S1 and S2) in the supplementary to show an overview of all the profiles.

Uncertainties and errors were included in Fig. 3.



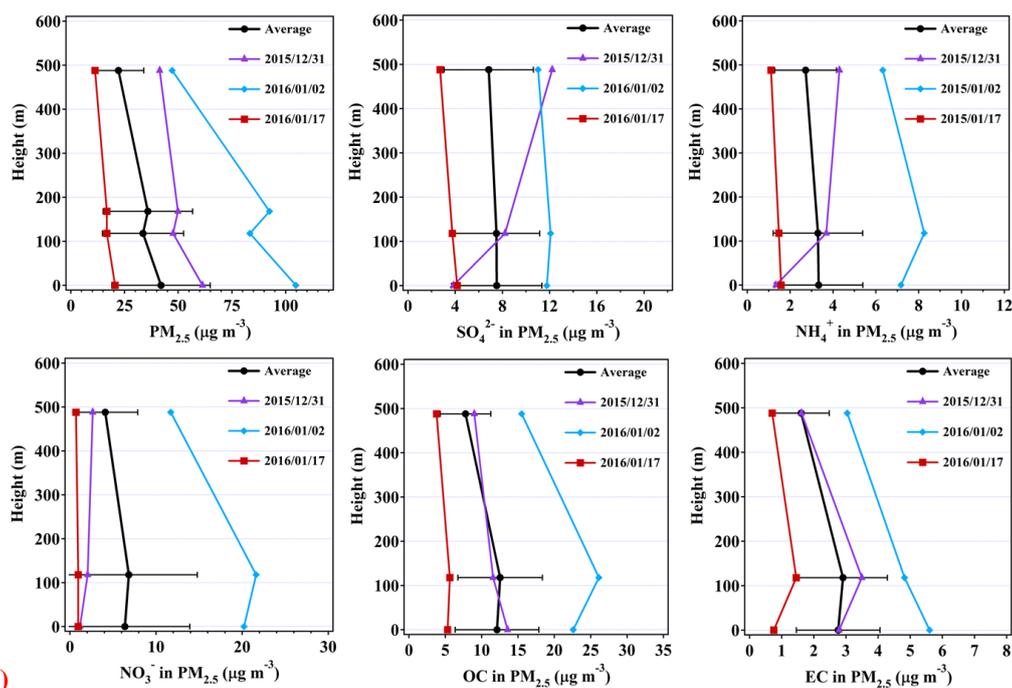


Figure 3. Representative and average vertical profiles of sulfate, ammonium, nitrate, OC, and EC mass concentration at ground level, 118 m and 488 m during (a) autumn; (b) winter. Four layers of PM_{2.5} mass concentrations were shown here with the data measured by Guangzhou EMC. Error bars represent standard deviation of the mean.

✓ The sampling uncertainty may originate from (a) the sampling flow rate, and (b) possibly from the impacts of temperature and pressure due to the sampling heights. We performed a carefully calibration on the sampling flow rate to the impactors before use. Our calibration shows that the uncertainty from sampling flow rate is **less than 5%**. We have added the information 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.”

We calculated the impacts of temperature and pressure on the flow rate due to the sampling heights to estimate this uncertainty. The results showed that impacts of pressure and temperature on the flow rate are **less than 5%**. Here 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 °C and 24.1 °C at the ground level and 488 m, respectively. 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/m³. We calculated the flow rate when the temperature was 24.1 °C and the pressure was 95.72 kPa, i.e. at 488 m, assuming a flow rate of 100 L/m³ at the ground level (temperature = 301.15K and pressure = 101.15kPa).

Assume the ambient air is an ideal gas. At the ground level, $P_1 = 101.15$ kPa, $V_1 = 100$ L/m³, $T_1 = 273.15 + 28 = 301.15$ K. At 488 m, $P_2 = 95.72$ kPa, $V_2 = ?$, $T_2 = 273.15 + 24.1 = 297.25$ K. R is the ideal gas constant. n is the moles of air.

We obtain: $P_1 V_1 = nRT_1$ (1)

$$P_2 V_2 = nRT_2 \quad (2)$$

(1)/(2) we get:

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

Therefore, we think the total uncertainties would be within 10%.

✓ We now rewrote section 3.2.1 (lines 19-28 on page 8 and page 9):

“The profiles of the major PM_{2.5} chemical components can be generally classified into three vertical gradients. The first category represents 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 likely 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 likely the source that led to high SNA mass concentrations.”

Table S1 and S2 in the supplementary:

Table S1 Vertical distributions of major PM_{2.5} components in autumn and winter field studies.

Date	SO4	NO3	NH4	OC	EC	PM _{2.5}
	gradient type	mg/m ³				
2015/10/21	I	I	I	II	I	48.4
2015/10/23	II	II	III	II	I	59.1
2015/10/25	II	II	II	II	I	45.7
2015/10/26	II	II	II	II	I	41.5
2015/10/27	III	II	II	II	I	53.9
2015/10/29	II	II	II	II	I	40.6
2015/10/31	III	III	III	I	II	20.2
2015/11/02	I	I	III	I	I	34.6
2015/11/04	II	II	II	I	I	62.0
2015/11/06	III	III	III	I	I	43.3
2015/11/08	II	II	II	II	II	39.2
2015/11/10	III	III	III	I	II	40.0
2015/11/12	I	III	III	I	II	47.6
2015/11/14	II	II	II	I	II	36.8
2015/11/16	II	II	II	I	I	29.5
2015/11/18	III	III	III	I	I	76.0
2015/11/20	III	III	III	I	I	64.6
2015/11/22	III	I	III	I	II	34.2

Date	SO4	NO3	NH4	OC	EC	PM _{2.5}
	gradient type	mg/m ³				
2015/12/31	III	III	III	I	II	61.3
2016/01/02	II	II	II	II	I	104.8
2016/01/03	I	II	II	II	I	87.2
2016/01/04	II	II	II	I	II	54.4
2016/01/07	I	I	I	I	I	42.6
2016/01/09	II	II	III	I	I	65.8
2016/01/12	I	III	III	I	I	31.7
2016/01/13	I	I	I	I	I	37.3
2016/01/17	I	I	I	I	I	20.6
2016/01/18	I	II	I	II	I	35.2
2016/01/20	I	I	I	II	II	33.9
2016/01/25	I	I	I	I	I	24.5

Type I: represents the highest concentration at the ground level.

Type II: shows the highest concentrations at 118 m.

Type III: shows the highest concentration at 488 m.

PM_{2.5} concentrations were recorded at the ground level.

Table S2 The percentages of the three types in autumn and winter campaigns

	SO4	NO3	NH4	OC	EC
Type I	17%	17%	6%	72%	67%
Type II	44%	50%	44%	28%	33%
Type III	39%	33%	50%	0%	0%

Winter	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	OC	EC
Type I	67%	42%	50%	58%	58%
Type II	25%	42%	25%	42%	42%
Type III	8%	17%	25%	0%	0%

[4] Considering the challenges in organising such a study it is pity that high frequency micrometeorological measurements (including an important vertical wind speed) were not undertaken making it impossible to derive fluxes (refer to papers by (Valiulis, Ceburnis et al. 2002, Ceburnis, O’Dowd et al. 2008).

[A]: We agree with the reviewer that it is impossible to derive fluxes based on the current measurements. We may however expand our measurement capacity and make flux measurements possible in the future study. In this study, we focus on the size-segregated chemical composition and secondary formation through cloud processing and heterogeneous reactions. We are planning involve the high frequency micrometeorological measurements in the future studies, which we added in the manuscript as a future perspective (page 16, lines 21-25):

“However, more studies, such as long-term field measurements, aqueous SOA (aqSOA) formation and high frequency micrometeorological measurements (Valiulis et al., 2002; Ceburnis et al., 2008; Ervens et al., 2015), are warranted to determine the extent of the impacts of meteorology and aqueous and heterogeneous reactions on regional air quality and on the radiation budget of the atmosphere in southern China.”

Minor comments

[1] Page 2, line 27. Outdated literature overview of the processes involved and oversimplifying the system.

[A]: We agree that atmospheric aerosol distribution is a complex system which is controlled by a number of factors, including particle emissions, in situ chemical formation, and atmospheric processes. In this paper, we presented measurement data on mass concentration of aerosol compositions in several size ranges (0.25 - 18.0 μm). We have rearranged relevant sentences in the revised manuscript.

Page 2, lines 27-28 and page 3, lines 1-2: “Atmospheric aerosol number size distribution is characterized by a number of modes, such as the Aitken and nucleation modes (less than 0.1 μm), accumulation mode (~ 0.1 to ~ 2 μm), and coarse mode (~ 2 to ~ 50 μm). However, the mass distribution of airborne particles is typically dominated

by two modes: the accumulation mode and the coarse mode (Seinfeld and Pandis, 2006).”

[2] Page 3, line 5. Old literature support. There is plenty of hard evidence that the first sub-mode can also be formed by cloud processing, e.g. (Ovadnevaite, Zuend et al. 2017).

[A]: To clarify, we added one sentence in the revised manuscript.

Page 3, lines 10-13: “Recently, strong evidences have been shown that the first sub-mode (i.e., condensation mode) can also be formed by cloud processing (Ovadnevaite et al, 2017). However, the contribution of smaller size particles in condensation mode to total aerosol mass concentration was found to be quite small.”

[3] Line 6. Unclear sentence - what was exactly demonstrated worldwide?

[A]: We rephrased this sentence in the revised manuscript.

Page 3, lines 8-9: “Numerous studies have shown that in-cloud processes or heterogeneous aqueous reactions are plausible mechanisms for the formation of droplet-mode particles.”

[4] Line 9. Sea salt can also be submicron down to 20 nm, e.g. (Ovadnevaite, Manders et al. 2014, Cravigan, Ristovski et al. 2015).

[A]: Thank you for pointing out this. We have deleted it.

[5] Line 19. One of the earliest papers published by (Valiulis, Ceburnis et al. 2002) which also estimated emissions from the observed gradients.

[A]: The reference was added in the revised manuscript.

Page 3, lines 20-23: “Valiulis et al. (2002) estimated the trace metal emissions in Vilnius city using a vertical concentration gradient based on a TV tower and road tunnel measurement data and showed that traffic was the main source for airborne trace metals.”

[6] Page 4, line 13. Introduction should only present goals and objectives of the study and not the description of measurements performed unless nobody measured them before which is not the case here.

[A]: We have improved the section of introduction. We removed the original sentence and new ones have been added at the end of the third paragraph of the Introduction section. The objectives and goals of this study were rephrased in the revised version (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.”

[7] Line 26. delete "the other three levels".

[A]: Deleted.

[8] Page 5, line 5. Why 168m level is missing? 168m is often missing in the results section and is not clearly explained why.

[A]: Four levels (the ground level, at 118 m, 168 m, and 488 m) were selected by the Guangzhou Environmental Protection Bureau to create the vertical gradient observation platform at respective heights. Online measurements of pollutants including SO₂, CO, O₃, NO/NO_x, PM_{2.5} and PM_{1.0} were conducted on this four-layer observation platform.

However, size-segregated aerosol samples were only concurrently collected at three of the four levels (i.e., ground level, 118 m and 488 m), given that 118 m is close to 168 m on the tower. We highlighted this in the revised manuscript.

Page 6, line 1: “In this study, size-segregated aerosol samples were concurrently collected at three of the four levels (i.e., ground level, 118 m and 488 m) in autumn (October and November 2015) and winter (December 2015 and January 2016) seasons (Fig. 1)”

[9]: Page 6, line 17. Why the study is focused only in several pollution episodes when an overview of gradient should be presented first including error bars and uncertainties. Selected gradients discussed later become suspicious whether they are representative or just being random.

[A]: We have modified this paragraph accordingly and error bars were added in the Figure 2.

Page 7, lines 25-27 and page 8, lines 1-5: “The daily averaged $PM_{2.5}$ mass concentrations on the three heights varied significantly in the ranges of 12.5–76.0 $\mu\text{g m}^{-3}$, 12.3–54.2 $\mu\text{g m}^{-3}$, and 7.9–44.4 $\mu\text{g m}^{-3}$ in autumn, and in the ranges of 10.2–104.8 $\mu\text{g m}^{-3}$, 10.7–83.4 $\mu\text{g m}^{-3}$, and 7.2–47.2 $\mu\text{g m}^{-3}$ in winter. The average $PM_{2.5}$ mass concentrations were 44.1 ± 14.9 , 36.0 ± 11.1 , and $27.8 \pm 10.1 \mu\text{g m}^{-3}$ at ground level, 118 m and 488 m in autumn, slightly higher than those in winter (42.0 ± 22.9 , 33.6 ± 18.9 , and $22.2 \pm 11.8 \mu\text{g m}^{-3}$). A pollution episode (i.e., E1) in autumn was identified when the $PM_{2.5}$ concentration at ground level exceeded the air quality standard ($75 \mu\text{g m}^{-3}$), and another episode (i.e., E2) was identified in winter when the standard was exceeded continuously over three day period.”

We also rephrased section 3.2.1 (page 8, lines 19-28, and page 9). Please find our response to the major comment [3].

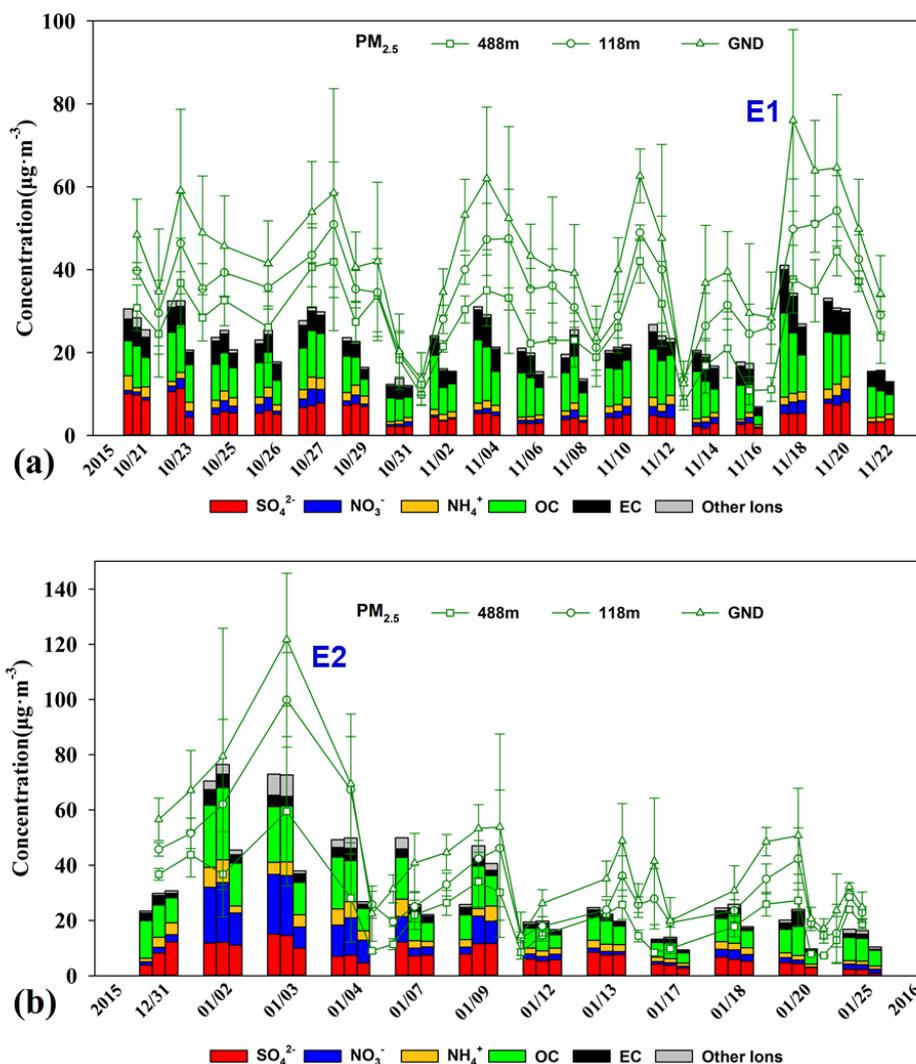


Figure 2. PM_{2.5} mass and chemical components concentrations at ground level (GND), 118 m, and 488 m during the (a) autumn and (b) winter sampling periods. The dates on the x-axis are the sampling days. The stacked bar diagrams for each day represent chemical components at ground level (left), 118 m (middle), and 488 m (right). The green lines represent the daily averaged PM_{2.5} mass concentration. E1 and E2 represent two haze episodes with daily average PM_{2.5} concentrations on the ground site higher than 75 $\mu\text{g m}^{-3}$. Error bars represent the standard deviations of the mean.

[10] Line 23. It is not the consistency with other studies that makes the measurements reliable trusted. Instead, decreasing concentration with height points at the ground/surface sources as opposed to increasing concentration with height pointing at sources aloft (Ceburnis, O’Dowd et al. 2008).

[A] This expression was deleted in the revised manuscript.

[11] Page 7, line 1. This needs to be investigated if not occurring due to temperature

inversions impeding mixing. That can be especially true in winter, but temperature inversions readily forming under clear sky condition due to radiative cooling.

[A]: After reanalyzing the data, we presented average diurnal variations for PM_{2.5} and PM₁₀ during the observation campaign, which showed unimodal distribution for the PM concentrations at 488 m, although some exceptions exist. In addition, we did not find temperature inversion during daytime in our study period.

To clarify, we defined the general day with unimodal distribution as “on normal days” in line 11 on page 8.

[12] Line 6. “Concentration gap” is unclear and unsuitable term.

[A]: We changed “Concentration gaps” to “Concentration differences” in page 8, line 15.

[13] Line 10. Composition cannot be vertically distributed - chemical components are distributed instead.

[A]: Corrected.

[14] Line 16. Repetition.

[A]: We deleted the repetitive sentence.

[15] Line 21. It does not need to be associated to EC as many other species are emitted by sources at the ground.

[A]: We deleted this expression.

[16] Line 24. Please spell acronyms used for the first time.

[A]: The phrase was changed to: “sulfate, nitrate, and ammonium (SNA)”

[17] Line 27. No established vertical gradients...

[A]: Thanks and changed to “established”.

[18] Page 8, line 12. Secondary WSOC formation is the scientific fact - why is it missing from interpretation?

[A]: Thank you for your suggestion. WSOC were not measured in this field study.

[19] Line 21. If distributions were averaged they must be presented with errors bars or ranges.

[A]: The error bars were added in Fig. 5 and Fig. 6.

[20] Line 27. Sulfate having similar formation mechanism to what?

[A]: We changed this sentence to “sulfate may have similar formation mechanisms at these levels”.

[21] Page 9, line 4. Coagulation is negligible at typical ambient number concentrations (refer to e.g. W.C. Hinds Aerosol Technology Textbook). In-cloud coalescence of droplets is more likely or multiple cloud cycles could explain production of several modes.

[A]: We thank the reviewer for valuable suggestions. We have modified accordingly in the revision.

Page 10, lines 25-27: “It is generally recognized that coagulation is negligible at typical ambient particle number concentrations (Hinds, 1999). Therefore, in-cloud coalescence of droplets is more likely or multiple cloud cycles could explain production of several sulfate modes.”

[22] Line 20. Formation of nitrate is not exclusive to sea salt or dust particles, any surface would promote heterogeneous reactions.

[A]: We have modified this in the text.

Page 11, lines 21-23: “It has been proposed that coarse-mode nitrate was formed through the heterogeneous reactions of gaseous nitric acid on the surface including pre-existing sea- and soil-derived coarse particles.”

[23] Page 11, line 5. Chloride particles do not exist and chloride cannot be considered separately from sodium or other balancing ion like ammonium.

[A]: We have modified this in the text.

Page 13, lines 16-17: “Chloride in the coarse-mode particles was thought to originate from marine sources and be associated with sodium.”

[24] Line 13. Incorrect suggestion. That finding is only demonstrating aged aerosol which undergone significant chemical processing during advection to the sampling location.

[A]: We have modified this in the text.

Page 13, lines 25-26: “..., demonstrating more aged aerosol which had undergone significant chemical processing during advection to the 488 m sampling site.”

[25] Line 22. Unclear sentence. Similar origin of OC at three heights? Its unlikely as similar concentrations can be produced by proportional contribution of ground sources versus in-cloud processing.

[A]: It has been reported that secondary organic carbon accounts for the major part of OC in urban, suburban and remote site (Zhang et al., 2007). We have modified this in the text.

Page 14, lines 6-7: “In addition, the size distributions of OC were similar at the three heights, implying that they probably had the same origins at all heights.”

[26] Line 27. That is not a possibility, but rather the only plausible explanation. However, the fact that nearby chimneys may have affected the profiles diminishes the value of this study making the interpretation of profiles very speculative and simply fitting the observations.

[A]: Thank you for the comments. Our sampling site is located at the urban center, which would be likely impacted by the local point sources due to the air mass transportation. SO₂, CO, and EC are typically related to combustion sources such as coal burning. From our observational data, the point sources indeed impacted the

concentration of gas phase pollutants. However, most of the aerosols in this study are not directly emitted from the point sources (primary aerosols, such as EC) but from the atmospheric transformation (secondary aerosols).

[27] Page 12, line 21. Observed, not found.

[A]: Corrected.

[28] Line 28. Why the authors suggest what was already pointed out as contribution from nearby chimneys and stacks?

[A]: We have modified this in the text.

Page 15, lines 10-12: “SO₂ concentration increased with height (12.4 μg m⁻³ at ground level, 16.1 μg m⁻³ at 118 m and 27.0 μg m⁻³ at 488 m), suggesting that SO₂ was impacted by the point sources, as mentioned before.”

[29] Page 13, line 10. ...temperature inversion extending from 118 to 488 meters...

[A]: Changed.

[30] Line 16-23. Schematics is haphazardly constructed and needs much better discussion and reasoning based on observations. 8 lines are absolutely insufficient. This schematics should be significantly improved or removed altogether. Figure 9. Why an upward convective transport missing? Schematics is lacking sampling heights to validate the processes.

[A]: We thank the reviewer for valuable comments. We have modified the schematic and have added several sentences in the revised manuscript in page 16, lines 1-18):

“A calm wind zone was established over the PRD region during the later autumn and winter pollution episodes due to the confrontation of southerly and northerly air masses, which have potential to further transform into strong nocturnal temperature inversions. The stagnant atmospheric conditions inhibited the air pollution dispersion. Low-level cloud cover aggravated the surface aerosol pollution due to in-cloud processing, where secondary aerosols were produced from the intensive

heterogeneous aqueous reactions within the clouds and cloud evaporation and redistributed residual aerosols. Previous studies have shown high mixing ratios of gas phase hydroxyl (OH) and peroxy (HO_2 , RO_2) radicals in the PRD region (Hofzumahaus et al., 2009; Lu et al., 2012). High concentrations of hydrogen peroxide (H_2O_2) and O_3 were also detected in this region (Hua et al., 2008; Wang et al., 2017). We did not measure these oxidants in either gas or aqueous phases. However, it is reasonable to assume that these gas phase oxidants might be scavenged by the clouds which are then transferred into the cloud droplets and facilitated the aqueous phase reactions. In addition, the temperature inversion layer disappeared during daytime and strong downward vertical wind speed was found through the WRF model results (Figure 8), leading to be under favorable meteorological conditions which facilitate the release and downward transport of residual aerosols from evaporating low-level clouds. The aforementioned processes were confirmed in our study which shows that the vertical concentrations of sulfate, nitrate, and ammonium increased with height during pollution episodes.”

We added upward convective transport in the revised figure (Figure 9) and sampling heights were marked on the Canton tower.

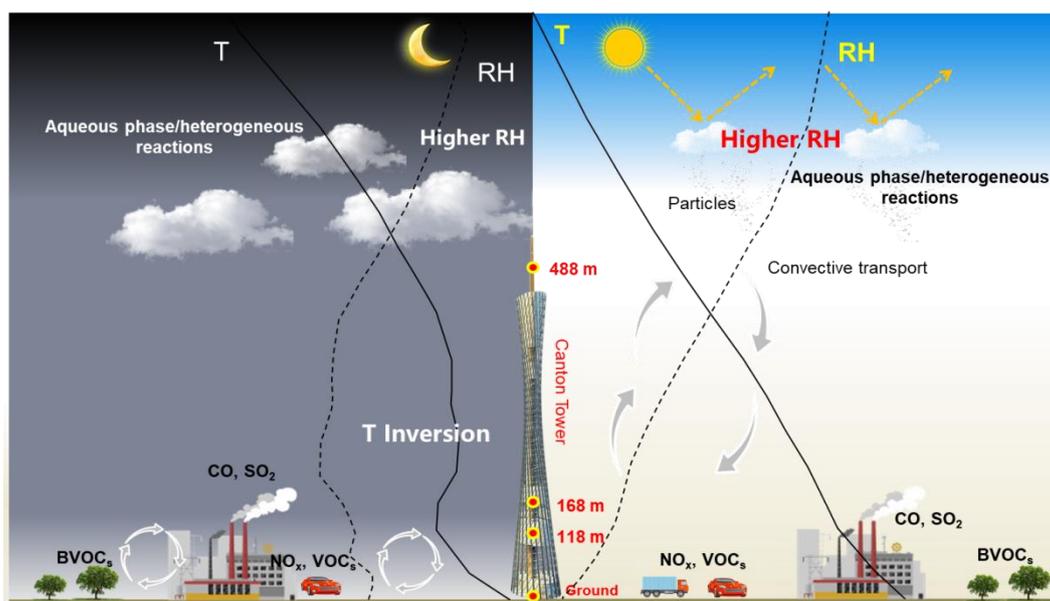


Figure 9. Schematic graph illustrating typical haze formation mechanisms in the PRD region in autumn and winter.

[31] Line 26. "Utilizing the 610m Canton Tower in Guangzhou" has to be moved to the sentence end.

[A]: Changed.

[32] Line 28. Small or smaller? Shallower is perhaps the better word.

[A]: We have changed "Small" to "shallower".

[33] Page 14, line 6. OC missing

[A]: We deleted this sentence.

[34] Line 15. In order for the results of the study helping understanding formation mechanisms, the data interpretation needs considerable improvement.

[A]: We have improved the data interpretation in the section 3.3 (pages 14-16). Please also find our response in minor comment [30].

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2969–2983, <https://doi.org/10.5194/acp-15-2969-2015>..

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 available. 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 quantitatively 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.

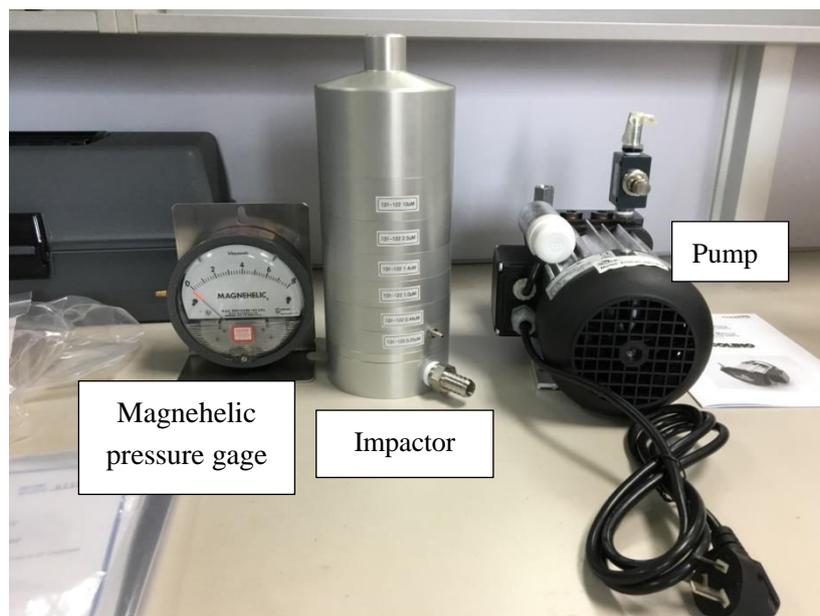


Figure I. Model 131 High-Flow Impactor

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.

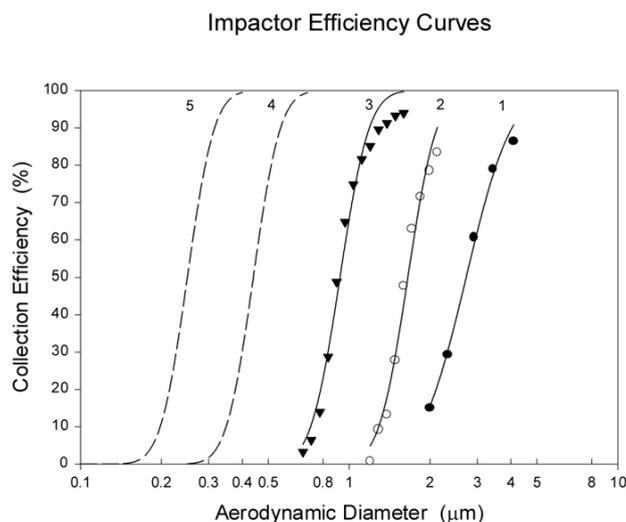


Figure II. High-Flow impactor efficiency curves provided by the manufacture

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%. Below 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 °C and 24.1 °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/m³. We calculated the flow rate when the temperature was 24.1 °C and the pressure was 95.72 kPa, i.e. at 488 m, assuming a flow rate of 100 L/m³ 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, $P_1 = 101.15$ kPa, $V_1 = 100$ L/m³, $T_1 = 273.15 + 28 = 301.15$ K. At 488 m, $P_2 = 95.72$ kPa, $V_2 = ?$, $T_2 = 273.15 + 24.1 = 297.25$ K. R is the ideal gas constant. n is the moles of air.

$$\text{We obtain: } P_1 V_1 = nRT_1 \quad (1)$$

$$P_2 V_2 = nRT_2 \quad (2)$$

(1)/(2) we get:

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

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.”

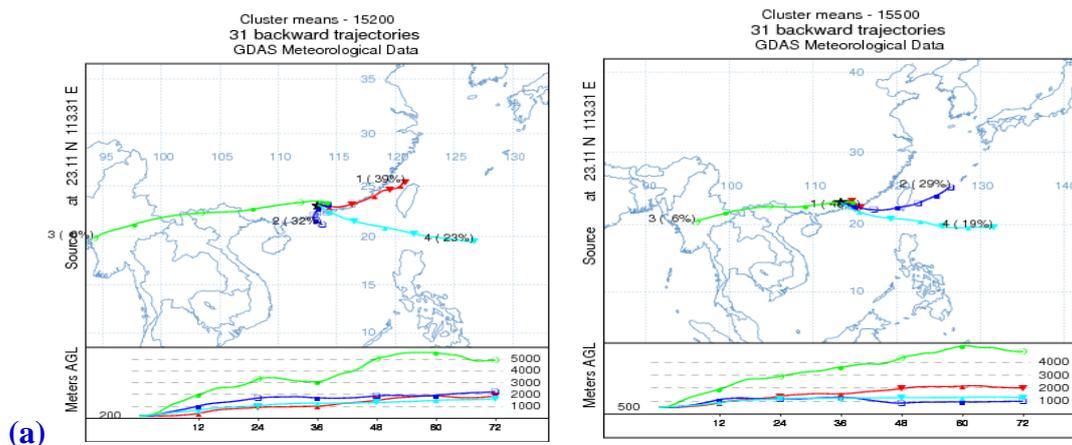
Reference:

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.



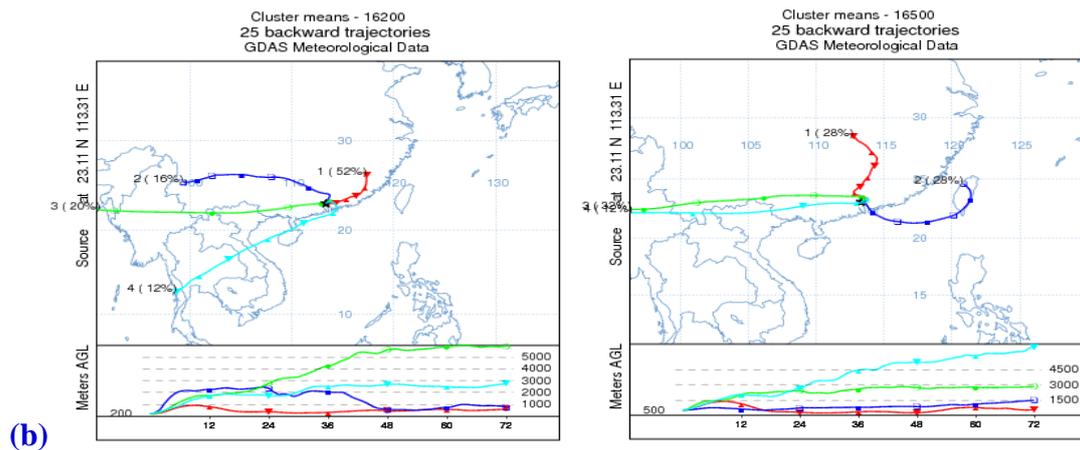


Figure S3. Cluster analysis of the airflow in 200 m and 500 m in (a) autumn and (b) winter campaigns.

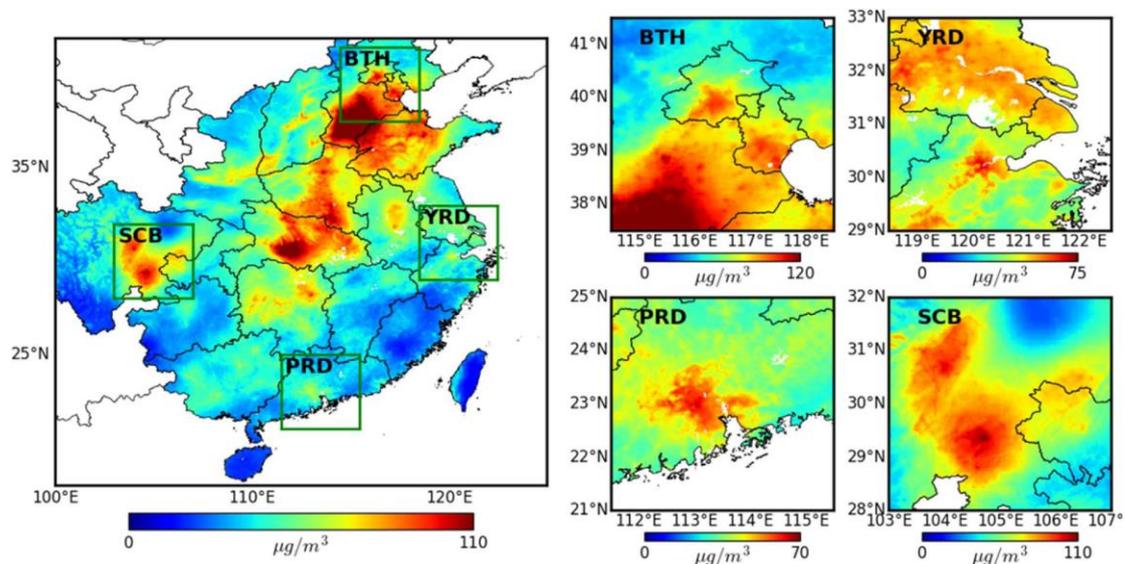


Figure III. Spatial distribution of the 15-year mean of PM_{2.5} concentrations at a resolution of 1 km in the study region (left panel) and in the 4 major city clusters (right panel). Cited from Lin et al (2018).

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

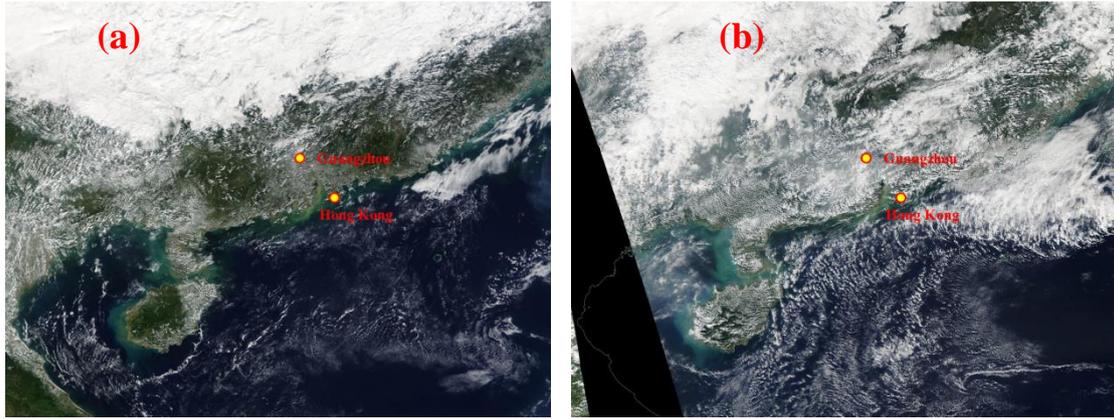
formation or regional transport of particles. However, back trajectory analysis of air masses showed that regional transport was unlikely the important source during the sampling time (Fig. S4) and then local chemical formation was likely the source that led to high SNA mass concentrations.”

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.

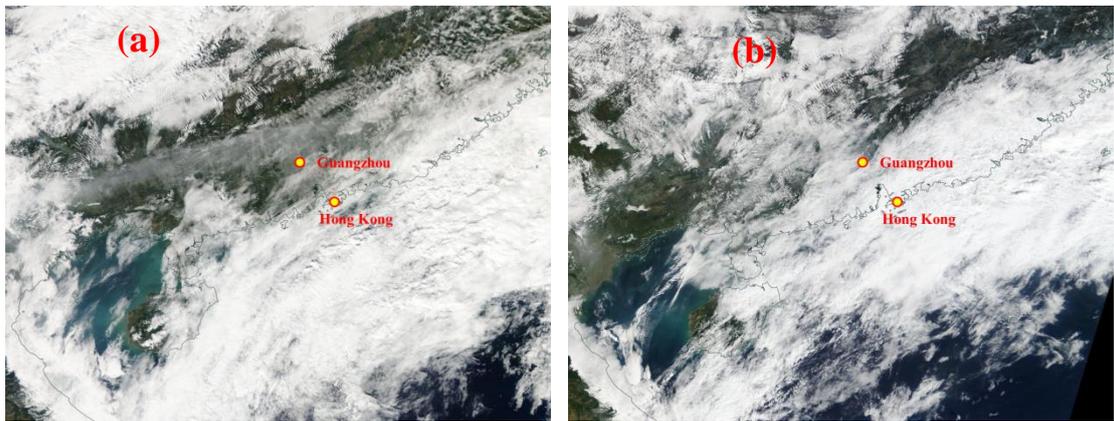
[A]: As suggested, we have now added the MODIS satellite images and ceilometer data in the supplementary of the revised manuscript. The ceilometer was mounted on the roof of South China Institute of Environment Sciences, Ministry of Ecology and Environment, which is about 4 km northeast of the Canton 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,

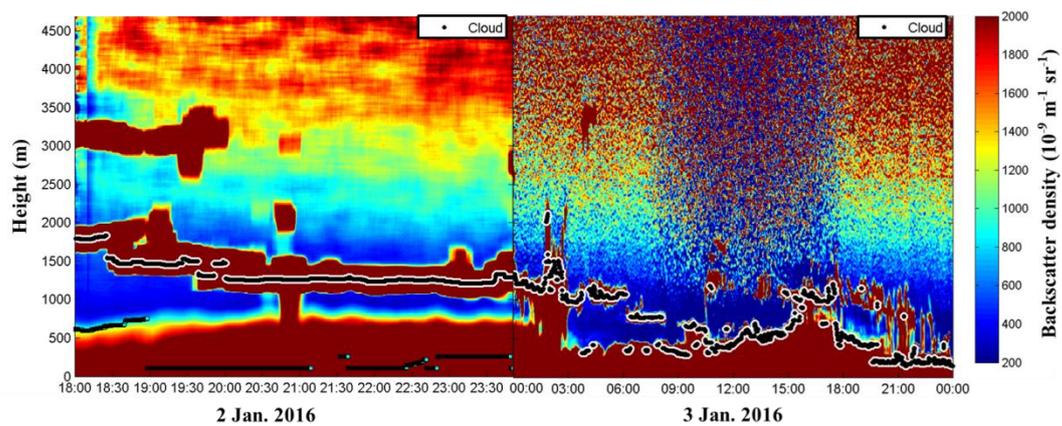
(b) November 19, 2015

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 SO₄ and NO₃ 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 NH₄NO₃ 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](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.

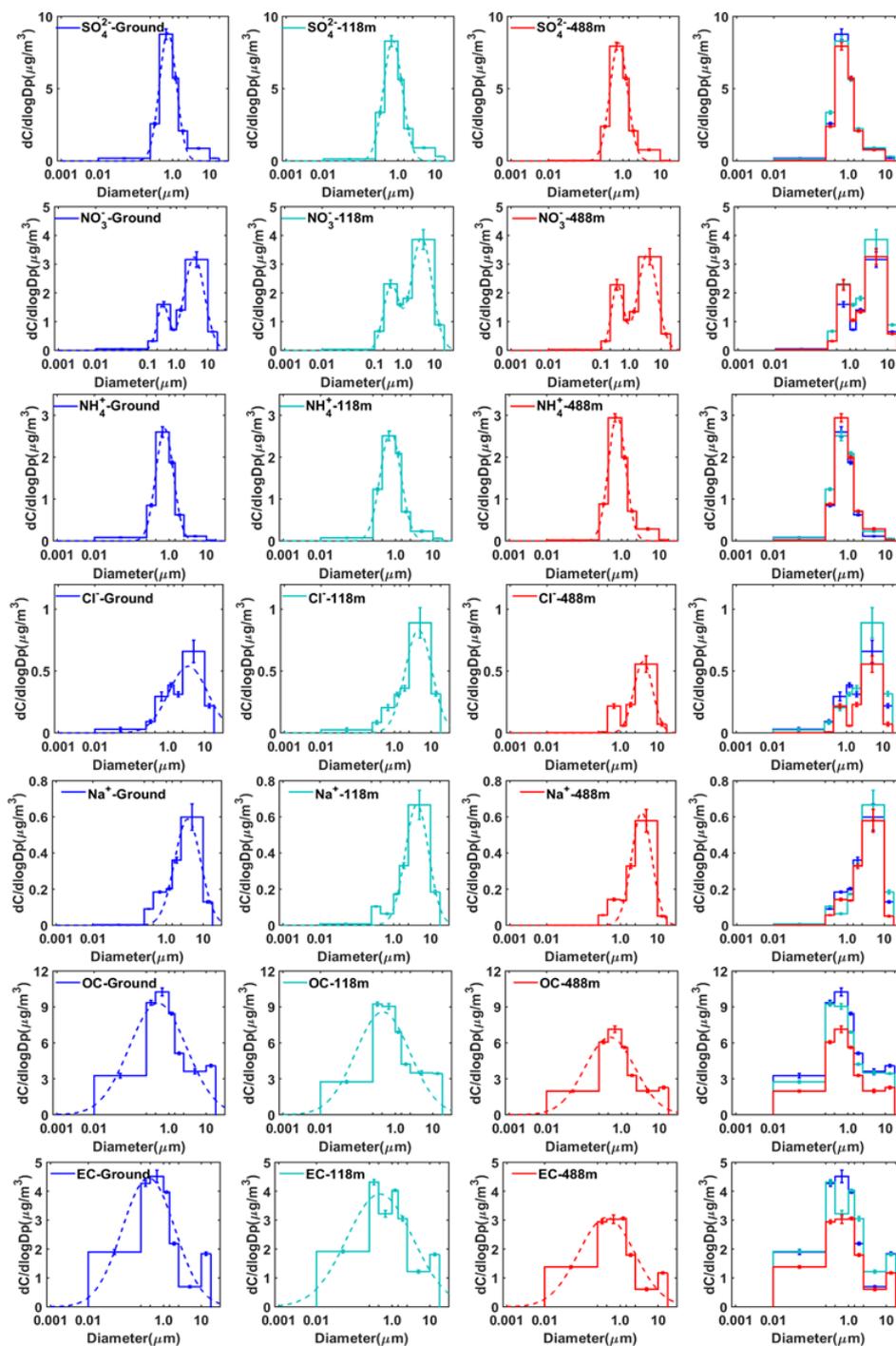


Figure 5. Mass concentration size distributions of the main chemical components measured at ground level, 118 m and 488 m in autumn. The dotted lines represent nonlinear fitting of the measured average size distribution. The error bars represent the sampling and analytical standard errors for each compound.

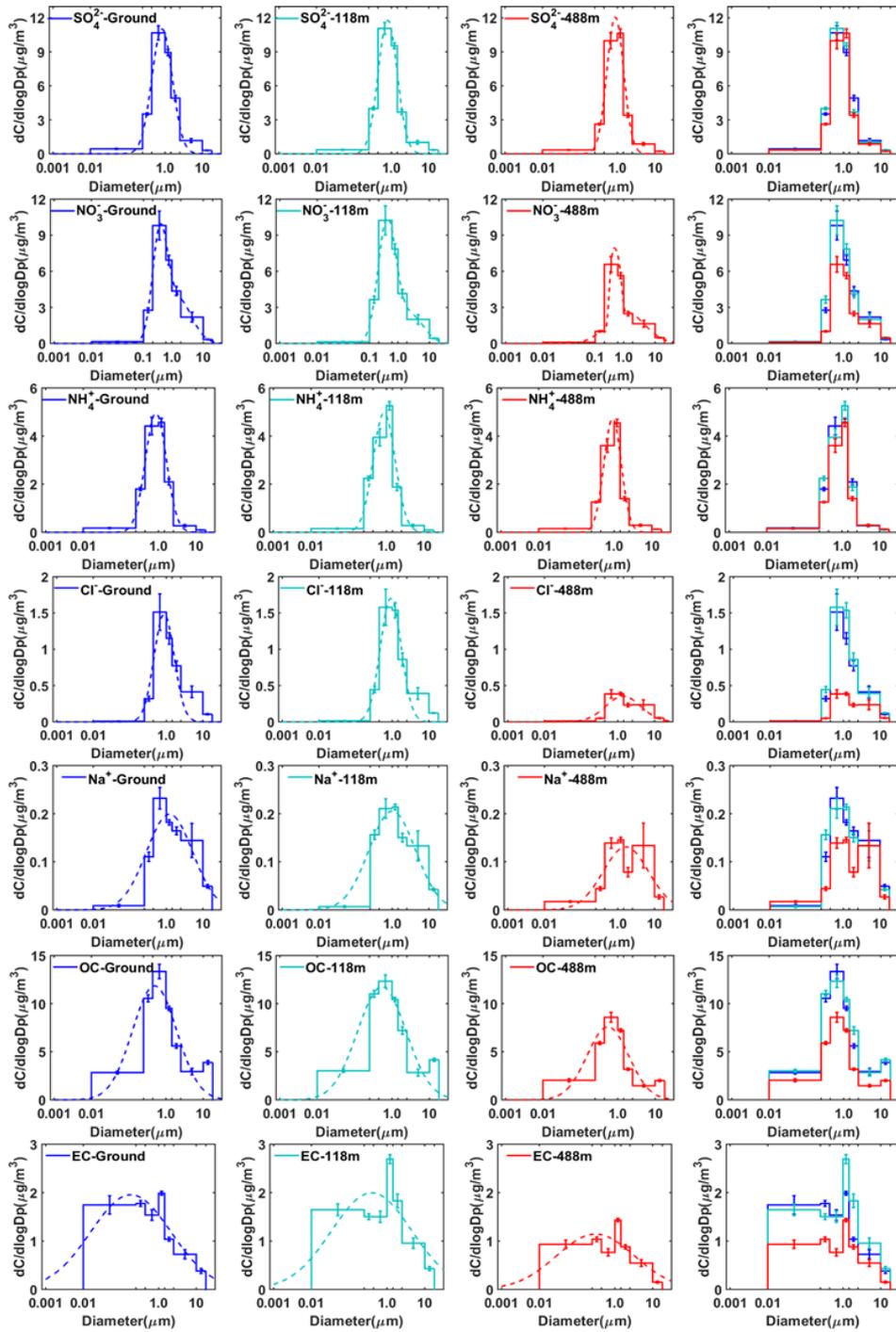


Figure 6. Mass concentration size distributions of the main chemical components measured at ground level, 118 m and 488 m in winter. The dotted lines represent nonlinear fitting of the measured average size distribution. The error bars represent the sampling and analytical standard errors for each compound.

Vertical distribution of atmospheric particulate matters within urban boundary layer in southern China: Size-segregated chemical composition and secondary formation through cloud processing and heterogeneous reactions

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Abstract. Great progress has recently been made in understanding the sources and formation mechanisms of atmospheric aerosols at ground level. However, vertical profiles and sources of size-resolved particulate matter within the urban boundary layer are still lacking. In this study, vertical
25 distribution characteristics of size-segregated particles were investigated at three observation platforms (ground level, 118 m and 488 m) on the 610-meter-high Canton Tower in Guangzhou, China. Size-segregated aerosol samples were simultaneously collected at the three levels in autumn and winter. Major aerosol components, including water-soluble ions, organic carbon and elemental carbon, were measured. The results showed that daily average fine-particle concentrations generally decreased with

height. Concentrations of sulfate and ammonium in fine particles displayed small vertical gradients and nitrate concentrations increased with height in autumn, while the chemical components showed greater variations in winter than in autumn. The size distributions of sulfate and ammonium in both seasons were characterized by dominant unimodal droplet modes with peaks at the size range of 0.44–1.0 μm .
5 In autumn, the nitrate size distribution was bi-modal, peaking at 0.44–1.0 μm and 2.5–10 μm , while in winter it was unimodal, implying that the formation mechanisms for nitrate particles were different in the two seasons. Our results suggest that droplet-mode sulfate and nitrate are probably formed from aqueous-phase reactions and coarse mode nitrate formation can be attributed to the heterogeneous reactions of gaseous nitric acid on existing sea-derived coarse particles in autumn at the measurement
10 site. The results from pollution case studies further showed that atmospheric aqueous-phase and heterogeneous reactions together with adverse weather conditions, such as temperature inversion and calm wind, resulted in the autumn and winter haze pollution in the PRD region.

1 Introduction

15 Air pollution is of serious environmental concern in China and is often characterized by high concentrations of many pollutants, among which fine particulate matter (particles with the aerodynamic diameter of 2.5 μm and smaller or $\text{PM}_{2.5}$) is currently the primary pollutant in most cities. Aerosol particles can profoundly affect public health, visibility, and climate change, and their effects are strongly dependent on size distribution and chemical composition (Pöschl, 2005; Zhang et al., 2015).
20 The chemical constituents of particulate matter (PM) include sulfate, nitrate, ammonium, organic matter, elemental carbon, crustal species, and trace metals, which have a variety of primary and secondary sources in both nature and human activities. Although the sources and formation mechanisms of atmospheric particles have been extensively investigated, they are highly uncertain in the fine size regime (Huang et al., 2014; Sun et al., 2015; Zhang et al., 2015; Liang et al., 2016; Tian et al., 2016).

25 Knowing the size-resolved PM chemical composition is a key factor in understanding the sources, formation, and transformation of atmospheric particles (Cabada et al., 2004; Seinfeld and Pandis, 2006; Wang et al., 2014). **Atmospheric aerosol number size distribution is characterized by a number of modes, such as the Aitken and nucleation modes (less than 0.1 μm), accumulation mode (~0.1 to ~2**

μm), and coarse mode (~ 2 to $\sim 50 \mu\text{m}$). However, the mass distribution of airborne particles is typically dominated by two modes: the accumulation mode and the coarse mode (Seinfeld and Pandis, 2006). In many cases, accumulation mode consists of two overlapping sub-modes: condensation mode and droplet mode. The condensation mode is generally from gas-to-particle conversion or direct emission from combustion, while droplet mode mainly results from cloud processing or coagulation of smaller particles. The two sub-modes were first reported for sulfate particles ($0.2 \pm 0.1 \mu\text{m}$ for the condensation mode and $0.7 \pm 0.2 \mu\text{m}$ for the droplet mode) (Hering and Friedlander, 1982; John et al., 1990). Numerous studies have shown that in-cloud processes or heterogeneous aqueous reactions are plausible mechanisms for the formation of droplet-mode particles (Meng and Seinfeld, 1994; Zhuang et al., 1999a; Yao et al., 2003; Guo et al., 2010; Tian et al., 2016). Recently, strong evidences have been shown that the first sub-mode (i.e., condensation mode) can also be formed by cloud processing (Ovadnevaite et al., 2017). However, the contribution of smaller size particles in condensation mode to total aerosol mass concentration was found to be quite small. Coarse-mode particles with large sizes and irregular shapes, such as dust particles, are usually produced from mechanical processes; however, coarse-mode secondary sulfates and nitrates have also been observed, and their formation has been attributed to heterogeneous and multiphase reaction mechanisms (Pakkanen, 1996; Liu et al., 2008).

Measurements of ambient particles at several heights, rather than at a single ground level, provide unique information about their sources and dynamic transport. In addition, vertical PM distribution can reflect the influences of atmospheric boundary meteorology on aerosol chemistry. Vertical profiles of atmospheric pollutants are frequently measured in tall towers located in urban areas. Valiulis et al. (2002) estimated the trace metal emissions in Vilnius city using a vertical concentration gradient based on a TV tower and road tunnel measurement data and showed that traffic was the main source for airborne trace metals. Harrison et al. (2012) reported a wide measured range of ambient particle physical properties and chemical compositions on the BT Tower 160 m above street level in central London. Oztürk et al. (2013) conducted high-resolution measurements of aerosol particle composition using a compact time-of-flight aerosol mass spectrometer and found considerable variability in the vertical distribution of aerosol mass concentration and composition on a 265-m tall tower near suburban Denver, Colorado. Chan et al. (2005) showed a complex vertical distribution of fine PM and

carbonaceous species over the Beijing city based on measurements from a 325 m meteorological tower. Sun et al. (2015) conducted real-time and simultaneous vertical measurements of aerosol particles at ground level and at 260 m on the same tower, and showed very dynamic vertical profiles of meteorological parameters below 300 m that affected the formation and evolution processes of aerosols during haze episodes (Sun et al., 2015; Wang et al., 2018). A series of vertical measurements of atmospheric particulate matter and meteorological parameters on a 255 m meteorological tower in the Tianjin have been carried out in recent years (Zhang et al., 2011; Shi et al., 2012; Wang et al., 2016). Deng et al. (2014) reported the vertical distribution of PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ mass concentrations measured on Canton Tower at 121 m and 454 m from November 2010 to May 2013. However, measurements of the vertical size-resolved chemical composition within the urban boundary layer are still lacking. Wang et al. (2016) investigated the size distribution of chemical compositions and sources of particulate matter in different modes at ground level and 220 m in Tianjin. They suggested that 220 m is insufficiently high enough to eliminate the influence of local surface emissions and measurements taken at that height do not reflect the background levels of pollutants within urban canopy. 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.

The Pearl River Delta (PRD) region is the low-lying area surrounding the Pearl River Estuary, where the Pearl River flows into the South China Sea. The weather is generally warm and humid all year and is strongly influenced by the Asian monsoon. The PRD region is one of the most densely urbanized regions in the world, and has recently experienced severe PM pollution and photochemical smog events (Zhang et al., 2008; Huang et al., 2014; Zhou et al., 2014). Autumn and winter are typical pollution seasons in this region (Chan et al., 2008). In this study, size-resolved PM samples were collected at three heights (ground level, 118 m, and 488 m) on Canton Tower in Guangzhou, the central city in the PRD region. The main water-soluble ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) and carbonaceous species (organic carbon, OC; elemental carbon, EC) were measured and their chemical characteristics, formation mechanisms and sources were presented. 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 Methodology

2.1 Observational site and sample collection

The sampling site, Canton Tower, is located in central urban Guangzhou and is the second highest TV tower in the world with a total height of 610 m. The main tower is 454 m high and the antenna mast adds another 156 m. Four levels (ground level, 118 m, 168 m, and 488 m) were selected by the Guangzhou Environmental Monitoring Center (EMC) to create a vertical gradient of observation platform. Online measurements of pollutants including SO_2 (model 43i, Thermo), CO (model 48i, Thermo), O_3 (model 49i, Thermo), NO/ NO_x (model 42i, Thermo), PM ($\text{PM}_{2.5}$ and $\text{PM}_{1.0}$, SHARP 5030, Thermo) were conducted on this four-layer observation platform. Meteorological factors (relative humidity, temperature, wind speed and direction) were also recorded on the tower. All these data were applied for the discussions in the following sections.

Size-segregated aerosol samples were concurrently collected at three of the four levels (i.e., ground level, 118 m and 488 m) in autumn (October and November 2015) and winter (December 2015 and January 2016) (Fig. 1). Three six-stage samplers (Model 131 High-Flow Impactor, MSP Corporation) with a sampling flow rate of 100 L min^{-1} were used at the three heights. The 50% cut-point diameters of the six-stage sampler were 0.25, 0.44, 1.0, 1.4, 2.5, 10.0, and 18.0 (inlet) μm . 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. A 24-h sampling resolution was adopted every other day from 10:00 a.m. to 10:00 a.m. the next day (local time, UTC + 8). The collection substrates were 75-mm diameter quartz filters and a final 90-mm quartz filter was applied to collect aerosols with diameters of less than 0.25 μm . To eliminate possible organic contaminants, all of the quartz membrane filters were prebaked at 550 $^{\circ}\text{C}$ for 4 hours before use. In total, 19 and 13 sets of samples, including one set of background samples, were collected at each height in autumn and winter. After collection, the filters were put into Petri dishes, kept in ice boxes during transportation to the laboratory and then stored in a refrigerator at -18 $^{\circ}\text{C}$ prior to analysis.

2.2 Chemical analysis

A quarter of each quartz filter was cut out and dissolved in 15 mL of deionized water (18.2 M Ω , Millipore) for 30 min in an ultrasonic ice water bath. The extracted solution was filtered through a microporous membrane (pore size, 0.2 μm) into a clean polycarbonate bottle, and then analyzed by an ion-chromatograph (ICS-5000, Dionex). The cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+) were separated using a CS12A column (4 \times 250 mm) and eluted with KOH solution. The anions (F^- , Cl^- , NO_3^- , NO_2^- and SO_4^{2-}) were analyzed using an AS23 column (4 \times 250 mm) and eluted with a methane sulfonic acid solution. Multiple points of calibration were used for each batch of ionic analysis. The OC and EC mass concentrations were determined using a thermal optical carbon analyzer (DRI Model 2001A,

Atmospheric Inc., USA). The analytical procedures were described in detail in Chow et al. (2001) and Cao et al. (2004). Due to the non-uniform deposition nature of the size-resolved samplers, charring correction using optical transmittance may introduce uncertainty in determining the OC and EC split point (Huang et al., 2009). The data presented in this paper were all field-blank corrected.

5 2.3 Data analysis

Back-trajectory analysis was performed using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT 4.9) (Draxler and Hess, 1998). The Global Data Assimilation System (GDAS, $1^{\circ} \times 1^{\circ}$) was used for the input meteorological data, and 72-h air mass back-trajectories were calculated at starting times of 02:00, 08:00, 14:00, and 20:00 (UTC), with arrival heights of 200 and 500 m above ground level. Cluster analysis was performed to segregate the calculated trajectories into distinct cluster groups using the HYSPLIT clustering algorithm. Ceilometer (Model CL-31, Vaisala Corp, Finland) was applied to measure the vertical backscatter density 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.

15 To study the effects of meteorology, vertical profiles of wind direction and speed, relative humidity (RH) and temperature (T) were simulated by the Weather Research and Forecasting (WRF) Model (Skamarock et al., 2008). Detailed information on the model setup can be found in the supplementary materials and references (Fan et al., 2015; Chen et al., 2016).

3 Results and discussion

20 3.1 General characteristics

Figure 2 shows the temporal profiles of daily averaged $\text{PM}_{2.5}$ mass concentrations measured at the three heights (i.e., ground level, 118 m and 448 m) during the sampling periods. **The mismatch between the real-time $\text{PM}_{2.5}$ concentrations and the reconstructed $\text{PM}_{2.5}$ mass by combining the main components was likely due to sampling artefacts and lack of comprehensive offline $\text{PM}_{2.5}$ chemical analysis (Chow et al., 2015). The daily averaged $\text{PM}_{2.5}$ mass concentrations on the three heights varied significantly in the ranges of 12.5–76.0 $\mu\text{g m}^{-3}$, 12.3–54.2 $\mu\text{g m}^{-3}$, and 7.9–44.4 $\mu\text{g m}^{-3}$ in autumn, and in the ranges of 10.2–104.8 $\mu\text{g m}^{-3}$, 10.7–83.4 $\mu\text{g m}^{-3}$, and 7.2–47.2 $\mu\text{g m}^{-3}$ in winter. The average $\text{PM}_{2.5}$ mass**

concentrations were 44.1 ± 14.9 , 36.0 ± 11.1 , and $27.8 \pm 10.1 \mu\text{g m}^{-3}$ at ground level, 118 m and 488 m in autumn, slightly higher than those in winter (42.0 ± 22.9 , 33.6 ± 18.9 , and $22.2 \pm 11.8 \mu\text{g m}^{-3}$). A pollution episode (i.e., E1) in autumn was identified when the $\text{PM}_{2.5}$ concentration at ground level exceeded the air quality standard ($75 \mu\text{g m}^{-3}$), and another episode (i.e., E2) was identified in winter when the standard was exceeded continuously over three day period. The diurnal variations of $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ concentrations at the three heights in autumn and winter are shown in Figs. S1 and S2. In general, $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ concentrations at ground level and 118 m showed distinct diurnal cycles with higher concentrations occurring at rush hours in the morning and evening. However, the concentrations at 488 m showed unimodal distribution with higher concentrations observed in the afternoon (12:00-17:00), lagging 3-4 hours behind those at ground level and 118 m. This can be attributed to the fact that the convective boundary layer begins to extend vertically after sunrise on normal days, and particles were transported upward by turbulence. The diurnal variations of CO and NO_x showed similar trends as the PM. The O_3 diurnal cycle showed a single peak pattern at the three levels with the highest values at around 14:00 LST. The O_3 concentrations were higher at 488 m than at the lower levels. The O_3 concentration differences between the lower levels and 448 m were widened at night due to the intensive NO titration loss at lower levels (Figs. S1 and S2).

3.2 Vertical distribution

3.2.1 Vertical distribution of the major chemical components

The profiles of the major $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$, 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 likely 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 likely the source that led to high SNA mass concentrations.

3.2.2 Chemical composition in fine and coarse aerosols

Figure 4 shows the percentages of measured chemical composition in fine ($PM_{2.5}$) and coarse ($PM_{2.5-18}$) particles at the three heights (ground level, 118 m, and 488 m). Sulfate, OC, and EC were the major chemical components of fine particles in autumn. Elevated proportions of nitrate and ammonium were found in winter, possibly related to the equilibrium between gas phase HNO_3 and NH_3 and the

particle phase. During our sampling periods, the average temperature in winter (13.5 °C) was much lower than that in autumn (23.1 °C), resulting in the enhanced production of NH₄NO₃ particles (Bian et al., 2014). There was no significant difference between the relative contributions of the main chemical components of fine particles at ground level and at 118 m. We found that the total contribution of SO₄²⁻, NO₃⁻ and NH₄⁺ at 488 m was higher than the corresponding contributions at the two lower levels, indicating the favorable secondary formation or regional transport of aerosols at the higher altitude. Our results showed that OC, nitrate, crustal (e.g., Ca²⁺, Mg²⁺) and sea salt (e.g., Na⁺ and Cl⁻) were the major components of coarse particles. The percentages for nitrate and sea salts were higher in autumn than in winter, suggesting that sea salt is a nonnegligible source of aerosols in autumn in the PRD region. We also found that the fractions of primary inorganic ions (e.g., Ca²⁺) and EC in coarse particles decreased with height, probably due to their sources (e.g., road dust and traffic emissions) being near the ground.

3.2.3 Mass size distributions

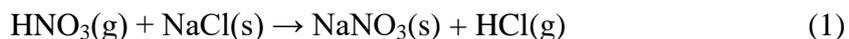
Difference in mass size distributions may be attributed to difference in the sources and formation mechanisms of aerosol chemical components. The average mass size distribution of the ionic compounds, OC and EC at the three heights during autumn and winter are shown in Figs. 5 and 6.

(1) Sulfate, nitrate, and ammonium

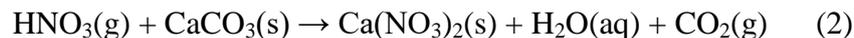
Sulfate did not show obvious seasonal and vertical variations in mass size distribution (Figs. 5 and 6). The average mass size distributions of SO₄²⁻ showed a dominant peak in the range of 0.44–1.0 μm (a typical droplet mode) and a minor coarse mode in the range of 2.5–10 μm. The mass size distributions of sulfate at the three levels were similar, indicating that sulfate may have similar formation mechanisms at these levels. Previous studies showed that droplet mode sulfate could be formed in cloud or fog (Zhuang et al., 1999a; Kerminen and Wexler, 1995; Meng and Seinfeld, 1994). Guo et al. (2010) proposed three possible formation processes for droplet mode sulfate, including condensation and coagulation of smaller particles, in-cloud aqueous processes, and processes in deliquesced aerosol particles. It is generally recognized that coagulation is negligible at typical ambient particle number concentrations (Hinds, 1999). Therefore, in-cloud coalescence of droplets is more likely or multiple cloud cycles could explain production of several sulfate modes. Using a positive matrix factorization

(PMF) method similar to that described in Guo et al. (2010), we obtained three modes (i.e., condensation, droplet, and coarse modes) for the sulfate size distribution. The droplet mode accounted for 79.4%, 78.5%, and 86.9% in autumn, and 78.5%, 78.3%, and 80.4% in winter at ground level, 118 m, and 488 m (Table S3). High relative humidity was measured during the autumn and winter measurement periods (at ~78% and 80% on average) in Guangzhou. The contribution of droplet-mode sulfate was higher at 488 m than that at the two lower levels, suggesting that in-cloud or aerosol droplet processes are likely to be the main formation pathways for sulfate. There is also evidence of frequent cloud coverages at 500-1500 m above the ground in urban Guangzhou measured using a ceilometer during the measurement periods (Figures S9 and S10). **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.**

The mass size distribution for nitrate exhibited two modes with mass median aerodynamic diameters at 0.44–1.0 μm (fine mode) and 2.5–10 μm (coarse mode) in autumn, while the fine mode pattern peak, at around 1.0 μm , was observed in winter. The coarse-mode nitrate in autumn accounted for 63%, 58%, and 58% of the total nitrate measured at ground level, 118 m, and 488 m. **It has been proposed that coarse-mode nitrate was formed through the heterogeneous reactions of gaseous nitric acid on the surface including pre-existing sea- and soil-derived coarse particles** (Anlauf et al., 2006; Pakkanen, 1996; Zhuang et al., 1999a). NaCl particles usually represent sea salt. Shown below is the reaction between nitric acid and sea salt particles (Wall et al., 1988; Pakkanen, 1996; Harrison and Pio, 1983):



Other studies have suggested that gaseous nitric acid may react with soil-derived coarse particles via the following reaction (Wu and Okada, 1994; Harrison and Kitto, 1990; Pakkanen, 1996):



We found that coarse-mode Na^+ , Cl^- , and NO_3^- were at almost the same particle size, while Ca^{2+} peaked at a particle size larger than NO_3^- (Fig. S3). It is thus reasonable to conclude that coarse-mode NO_3^- is probably associated with sea salt rather than Ca^{2+} , which is consistent with the previous work in Hong Kong (Zhuang et al., 1999b). The back-trajectory cluster analysis showed that the sampled air masses were predominantly from the South China Sea and moved toward Guangzhou in autumn (Fig. S4), bringing high concentrations of sea salt particles available for heterogeneous reactions. In addition, sea-salt particles can be activated by cloud or fog droplets under certain supersaturation conditions (Zhuang et al., 1999b). A previous study showed that a substantial amount of nitrates forms when HNO_3 reacts with deliquesced sea-salt as compared to the dry NaCl particles (Brink, 1998). Hence, nitrates were probably formed from the reactive uptake of HNO_3 in the deliquesced sea salt droplets rather than dry particles in Guangzhou. Other factors, such as high relative humidity, fog, and low clouds, could facilitate the formation of deliquesced sea salt particles which then accelerate the heterogeneous formation of coarse-mode nitrates.

In winter, the mass size distribution for nitrate was dominated by the droplet mode (with a size range of 0.44–1.0 μm), in contrast to a relatively small nitrate peak in this mode in autumn (Figs. 5 and 6). Previous studies showed that droplet-mode nitrate could be produced by the condensation of nitric acid onto pre-existing particles and/or heterogeneous reactions of N_2O_5 (Guo et al., 2010, Wang et al., 2012). Yun et al. (2018) pointed out the important contribution of heterogeneous uptake of N_2O_5 to nitrate formation during the winter haze in the PRD region. Based on the mass size distribution for nitrate and high relative humidity, we speculated that hydrolysis of N_2O_5 would also be an important mechanism for nitrate formation in the PRD region in winter. The contribution of heterogeneous reactions between nitric acid and sea salt droplets was minor in winter given that the air masses were predominantly from inland (Fig. S4), bringing a much lower concentration of coarse-mode sea salt aerosols than that in autumn (Figs. 5 and 6). Therefore, the heterogeneous reactions of nitric acid with sea salt droplets were less prominent in winter.

Ammonium commonly appears in the forms of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. Although fine-mode NH_4^+ ions were found to be dominant in the mass size distribution in both autumn and winter, the concentration of fine-mode NH_4^+ ions was strongly correlated with that of the same mode SO_4^{2-} ($R > 0.89$ at three heights), while only moderately correlated with that of fine-mode NO_3^- ions in autumn, 5 implying that fine-mode nitrates exist not only as NH_4NO_3 but also as other forms (i.e., NaNO_3) in autumn. **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** 10 **concentration in fine particles generally increased with height (Figure 3).**

(2) Sodium and chloride

The mass size distributions for Na^+ and Cl^- showed distinctly different patterns in autumn and in winter. Na^+ and Cl^- exhibited unimodal peaking in the range of 2.5–10 μm in autumn. The proportion of Na^+ in coarse mode of the total Na^+ mass was 63%, 71%, and 68%, and the proportion Cl^- ions observed 15 in coarse mode was 59%, 69%, and 70% respective to ground level, 118 m, and 488 m. This indicates that their contributions at the upper levels were higher than those at ground level. **Chloride in the coarse-mode particles was thought to originate from marine sources and be associated with sodium** (Zhao and Gao, 2008; Bian et al., 2014). As discussed above (Fig. S4), ambient air in Guangzhou was strongly influenced by particles from marine sources which were transported from the South China Sea 20 in autumn. We calculated the chloride depletion based on the concentrations of Na^+ and Cl^- (Eq. 3) to estimate the nitrate and sulfate formation rates on the sea-salt particles (Zhuang et al., 1999b):

$$[\text{Cl}_{\text{dep}}] = (1.174[\text{Na}^+] - [\text{Cl}^-])/1.174[\text{Na}^+] \times 100\% \quad (3)$$

where $[\text{Na}^+]$ is the measured concentration and 1.174 is the molar ratio of Cl^- to Na^+ in seawater. Higher chloride depletion (in percentage) was found for larger size of particles ($> 1.0 \mu\text{m}$) at the highest testing 25 level (488m) (Fig. S5), **demonstrating more aged aerosol which had undergone significant chemical processing during advection to the 488 m sampling site.** In comparison, possible sources for fine-mode chloride particles were biomass burning, coal combustion and waste incineration (Fu et al., 2018; Zhao

and Gao, 2008). The origin of fine chloride particles in winter during the measurement periods, however, is difficult to determine based on the broad peaks for Na^+ and Cl^- .

(3) OC and EC

In general, the mass size distributions for OC were unimodal with peaks at 0.44–1.0 μm , in which percentages of 84% and 88% of the total mass were attributed to fine mode in autumn and winter (Figs. 5 and 6). **In addition, the size distributions of OC were similar at the three heights, implying that they probably had the same origins at all heights.** Similarly, EC was mainly in fine mode except that it had a much broader size distribution than that of the OC. Interestingly, there was a sharp peak in the size range (1.0–1.44 μm) in the mass size distribution of the EC at 118 m, suggesting that its source at this level might be different from other levels. In particular, we found that the SO_2 and CO concentrations were highest among the three heights (Fig. S6). One possible reason for the abnormally high concentrations of those species was the influence of the local point sources (i.e., high chimneys from power plants and factory chimneys) around Guangzhou which emitted elevated concentrations of air pollutants.

15 3.3 Case studies of PM vertical profile during pollution episodes

Factors that influence vertical distribution of PM include meteorology, regional transport, source emissions, and chemical reactions. Here we selected two PM pollution episodes (E1 and E2) to investigate the haze formation in autumn and in winter (Fig. 2). The E1 episode which occurred on November 18, 2015 represented a typical pollution scenario in autumn. An anomalous increase in $\text{PM}_{2.5}$ concentration was observed at 168 m, as compared to the concentrations on non-event days. In addition, the average sulfate, nitrate, and ammonium (SNA) concentrations were higher at 488 m and 118 m than those at ground level (Fig. 3a). We employed the WRF model to simulate horizontal and vertical wind, RH, and T. The results showed that horizontal southerly wind was prevalent prior to November 18 with a period of calm wind from around 2:00 LST to 14:00 LST of the day. Subsequently, the wind direction changed predominantly to northerly (Fig. S7a), consistent with back trajectory analysis which showed that air masses firstly came from the south and then changed direction to the north on November 19 (Fig. S8). Low altitude temperature inversion was observed between 118 m and 168 m that night probably

due to the convergence of two different air streams (Fig. S7a). A previous study (Wu et al., 2015) demonstrated that poor air quality is associated with surface and low-altitude inversions in the PRD region. The RH vertical profile decreased from ground level to 168 m and became relatively stable between 168 m and 488 m. Subsequently the RH increased until it reached maximum at around 900 m, followed by a sharp decrease (Fig. 7a). We also observed a large amount of low cloud cover on November 17 and 18 based on WRF model results and MODIS satellite images (Fig. 8a and Fig. S9). The vertical wind blew dominantly upward during nighttime and downward during daytime (Fig. 8a), which facilitated transport of residual particles produced from cloud evaporation to lower altitudes after sunrise. The average sulfur oxidation ratio ($SOR = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} + n\text{-SO}_2)$) during E1 was 0.22, 0.18, and 0.12 at ground level, 118 m, and 488 m, higher than that on non-event days. SO_2 concentration increased with height ($12.4 \mu\text{g m}^{-3}$ at ground level, $16.1 \mu\text{g m}^{-3}$ at 118 m and $27.0 \mu\text{g m}^{-3}$ at 488 m), suggesting that SO_2 was impacted by the point sources, as mentioned before. The corresponding values for nitrogen oxidation ration ($NOR = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2)$) were 0.01, 0.02, and 0.07 at the three levels. A number of previous studies demonstrated that high relative humidity favors the production of secondary aerosols (Sun et al., 2013; Cheng et al., 2016; Zheng et al., 2016). Our results show that aqueous phase and heterogeneous reactions also significantly contribute to sulfate and nitrate aerosol formation in the PRD region.

The E2 episode represented a typical pollution event in winter, showing a similar $\text{PM}_{2.5}$ vertical distribution as E1. The highest sulfate, nitrate, ammonium, and OC concentrations were observed at 118 m (Fig. 3b). Horizontal wind was mainly from the north before noon (January 2) and changed to south in the afternoon (Fig. S7b). Similar temperature and RH profiles were found for E2 to those for E1 which was characterized by low altitude temperature inversion extending from 118 m to 488 m at January 2 and from 50 m to 168 m on January 3, as well as a higher RH at higher levels during the nighttime (Fig. 7b). High amount of low-level cloud cover and strong convection mixing process were observed during this episode (Fig. 8b and Fig. S10). The average SOR in $\text{PM}_{2.5}$ was 0.36, 0.27, and 0.30 at ground level, 118 m, and 488 m, again higher than non-event days. The average NOR was 0.13, 0.14, and 0.21 at ground level, 118 m, and 488 m, twice or three times higher than on non-event days. Based on the above findings, a schematic graph was generated to illustrate one of the typical haze formation

mechanisms in the PRD region in autumn and winter (Fig. 9). A calm wind zone was established over the PRD region during the later autumn and winter pollution episodes due to the confrontation of southerly and northerly air masses, which have potential to further transform into strong nocturnal temperature inversions. The stagnant atmospheric conditions inhibited the air pollution dispersion. Low-level cloud cover aggravated the surface aerosol pollution due to in-cloud processing, where secondary aerosols were produced from the intensive heterogeneous aqueous reactions within the clouds and cloud evaporation and redistributed residual aerosols. Previous studies have shown high mixing ratios of gas phase hydroxyl (OH) and peroxy (HO_2 , RO_2) radicals in the PRD region (Hofzumahaus et al., 2009; Lu et al., 2012). High concentrations of hydrogen peroxide (H_2O_2) and O_3 were also detected in this region (Hua et al., 2008; Wang et al., 2017). We did not measure these oxidants in either gas or aqueous phases. However, it is reasonable to assume that these gas phase oxidants might be scavenged by the clouds which are then transferred into the cloud droplets and facilitated the aqueous phase reactions. In addition, the temperature inversion layer disappeared during daytime and strong downward vertical wind speed was found through the WRF model results (Figure 8), leading to be under favorable meteorological conditions which facilitate the release and downward transport of residual aerosols from evaporating low-level clouds. The aforementioned processes were confirmed in our study which shows that the vertical concentrations of sulfate, nitrate, and ammonium increased with height during pollution episodes. Our results suggested that adverse meteorology (such as nighttime temperature inversion and calm wind) together with aqueous phase (cloud processing) and heterogeneous reactions would significantly contribute to the aerosol formation and haze episodes in the PRD region during the measurement periods. However, more studies, such as long-term field measurements, aqueous SOA (aqSOA) formation and high frequency micrometeorological measurements (Valiulis et al., 2002; Ceburnis et al., 2008; Ervens, 2015), are warranted to determine the extent of the impacts of metrology and aqueous and heterogeneous reactions on regional air quality and on the radiation budget of the atmosphere in southern China.

4 Conclusions

Vertical characteristics and formations of size-resolved aerosols were studied during autumn and winter seasons utilizing the 610 m Canton Tower in Guangzhou. Complex vertical variations in PM

composition were observed. In autumn, sulfate and ammonium had shallower vertical gradients than nitrate, which showed higher concentrations at higher observation levels. OC and EC showed steeper vertical gradients, with concentrations 34.0% and 27.9% lower, at 488 m than at ground level. The chemical components of the fine particles showed more pronounced and complex vertical gradients in winter than in autumn, possibly due to the effects of atmospheric stability, regional transport, and chemical reactions. The percentage of secondary inorganic ions in fine particles generally increased with height. The size distributions of sulfate and ammonium were similar at the three heights during the observation, characterized by a dominant droplet mode. Nitrate showed bi-modal size distributions in autumn and a unimodal pattern in winter, suggesting different nitrate formation mechanisms. Na⁺ and Cl⁻ exhibited dominant unimodal distributions in the range of 2.5–10 μm in autumn, associated with regional transport of sea salt. Na⁺ and Cl⁻ size distributions were dominant in the fine mode in winter. OC and EC were generally observed in the fine mode with a comparatively broad size distribution. Our study indicated that vertical meteorological parameters, such as RH and T, and the aqueous and heterogeneous atmospheric chemical reactions altogether led to the aerosol formation and haze episodes in the PRD region. The results of this study can help improve understanding the formation of atmospheric aerosols in polluted sub-tropical environments and can be used to refine global models that simulate the aerosol properties.

Author contributions.

SZ and XW designed and led the study. SZ, HZ, JPZ, YC, and JK contributed to aerosols measurement. SZ, JG, and WC carried out the data analysis. LW and WC performed the model simulations. JZ, YFC, YS, PF, and SJ discussed the results and commented on the manuscript. SZ wrote the paper with contributions from all co-authors.

Competing interests.

The authors declare that they have no conflict of interest.

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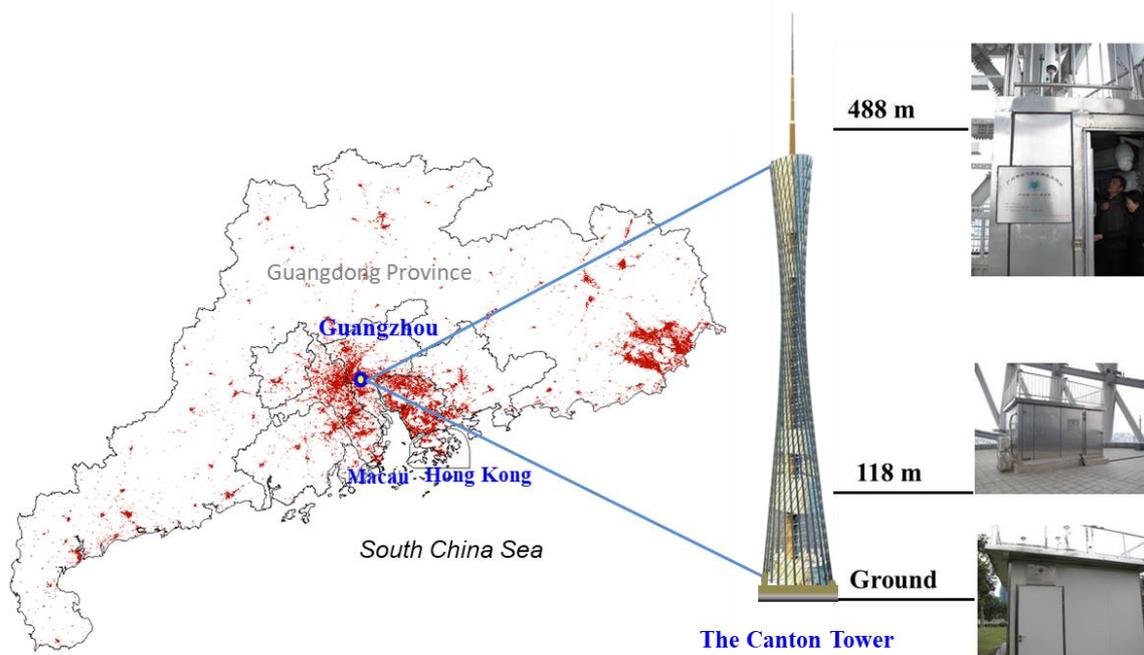


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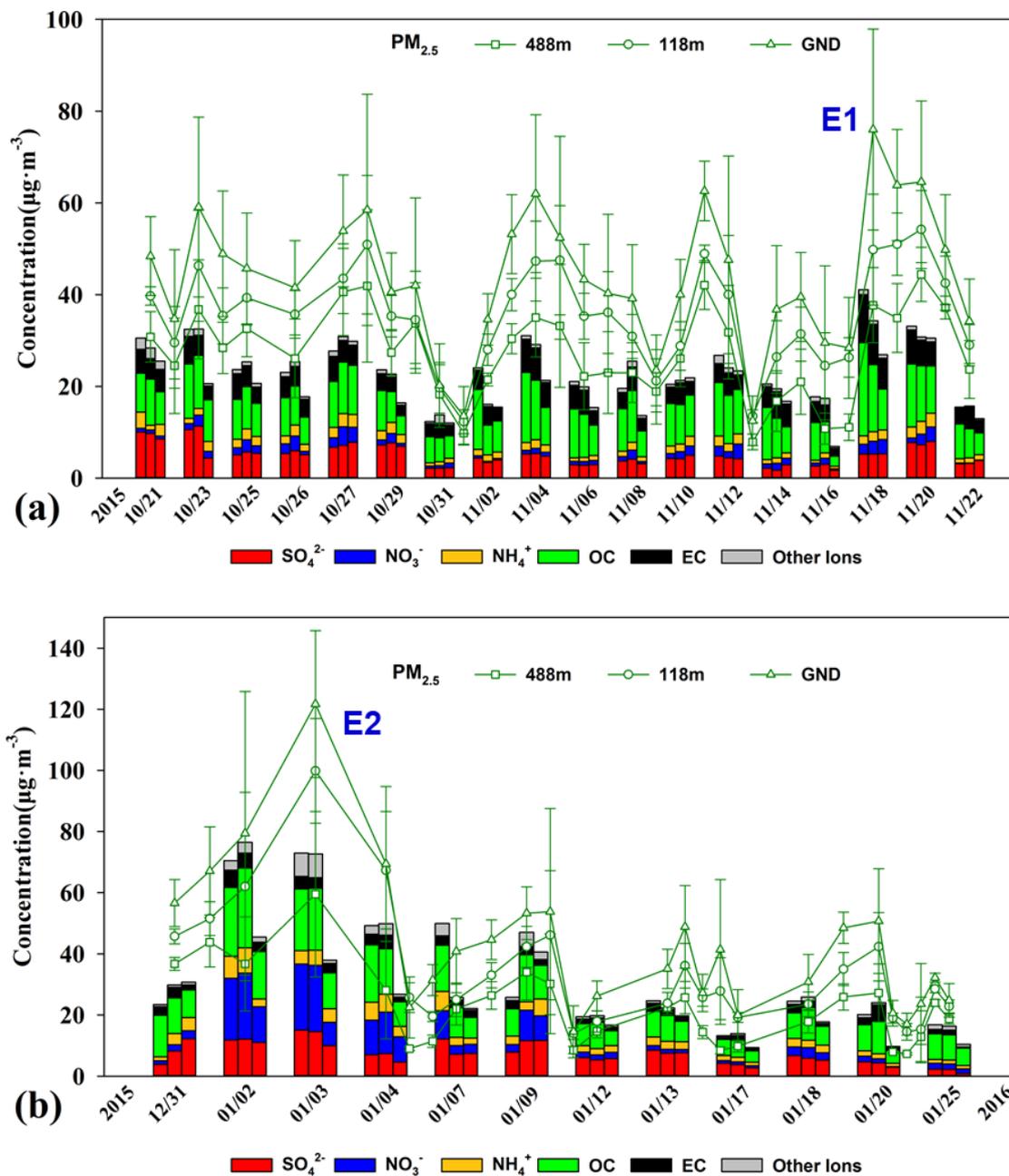


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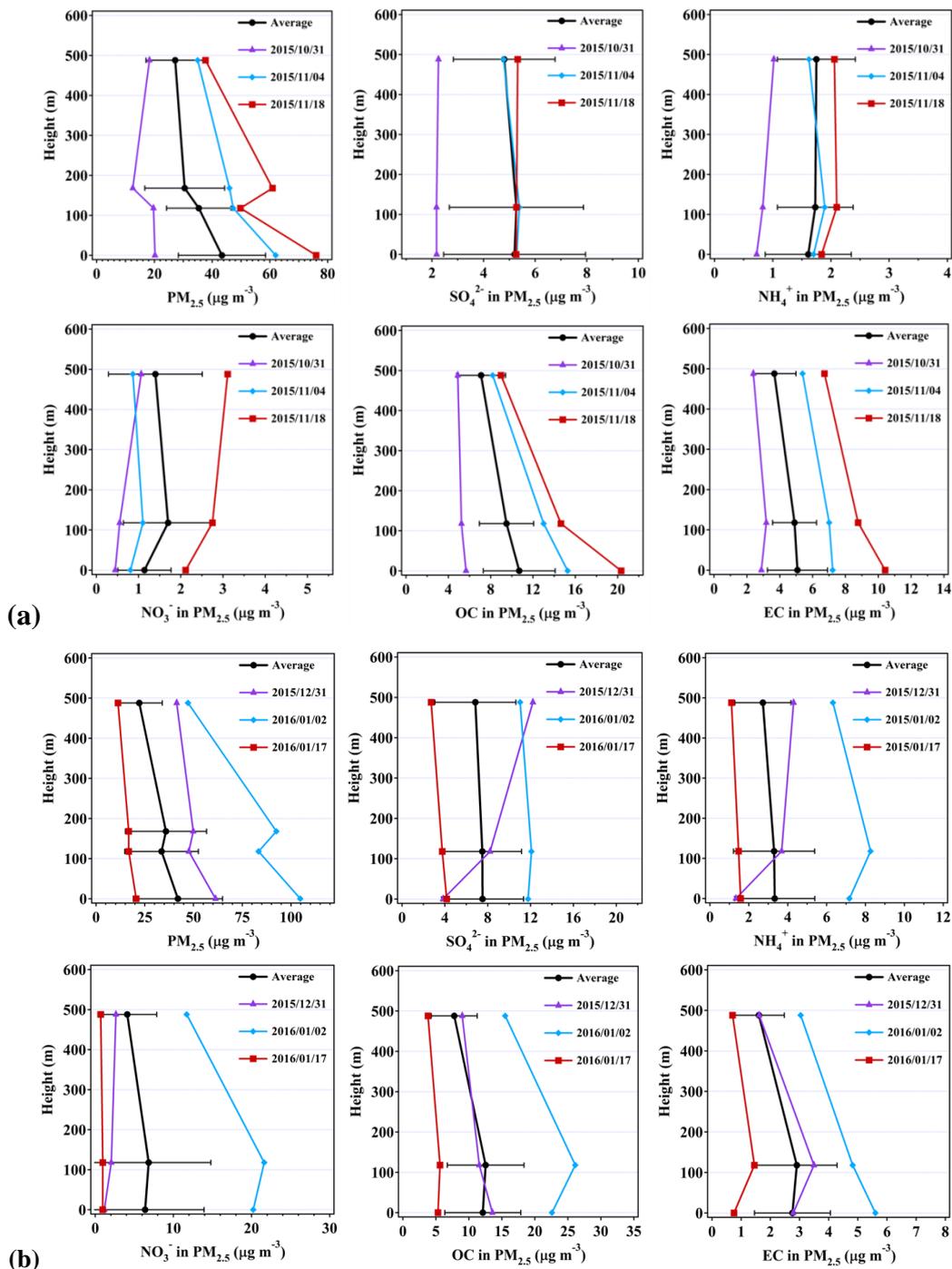


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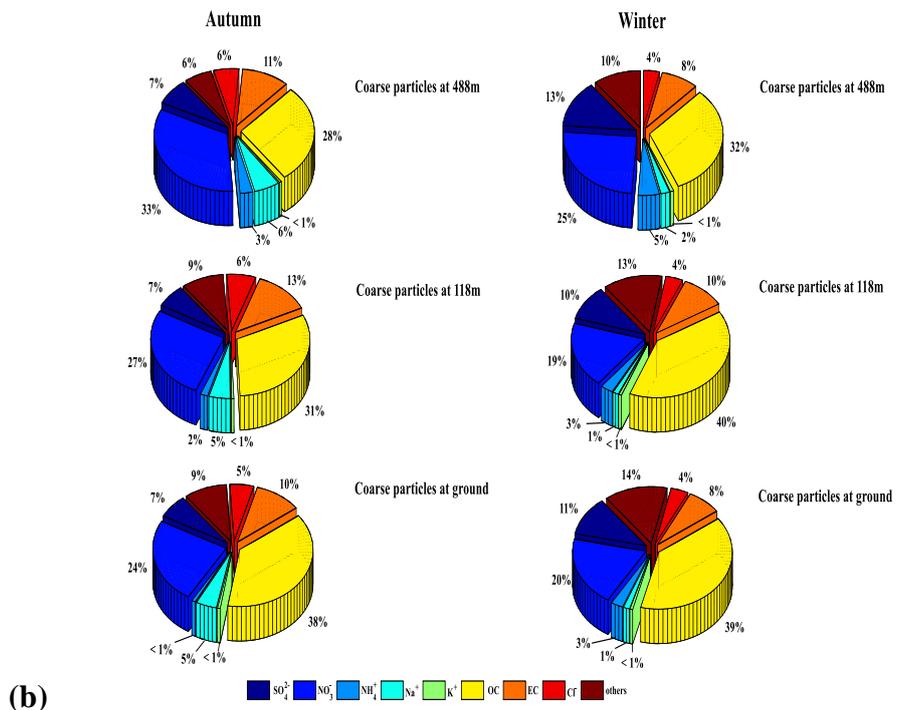
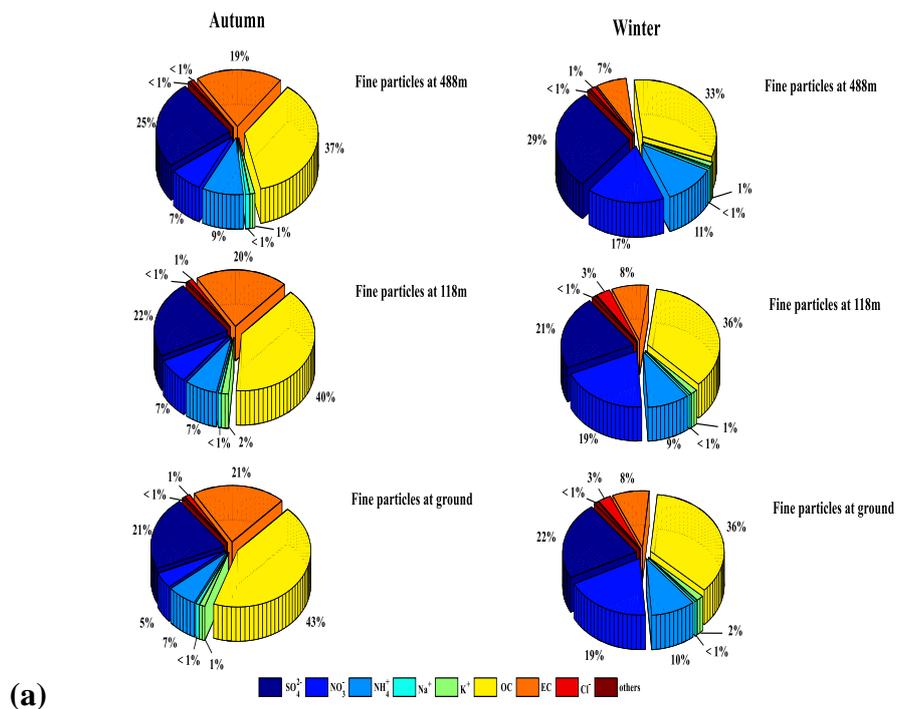


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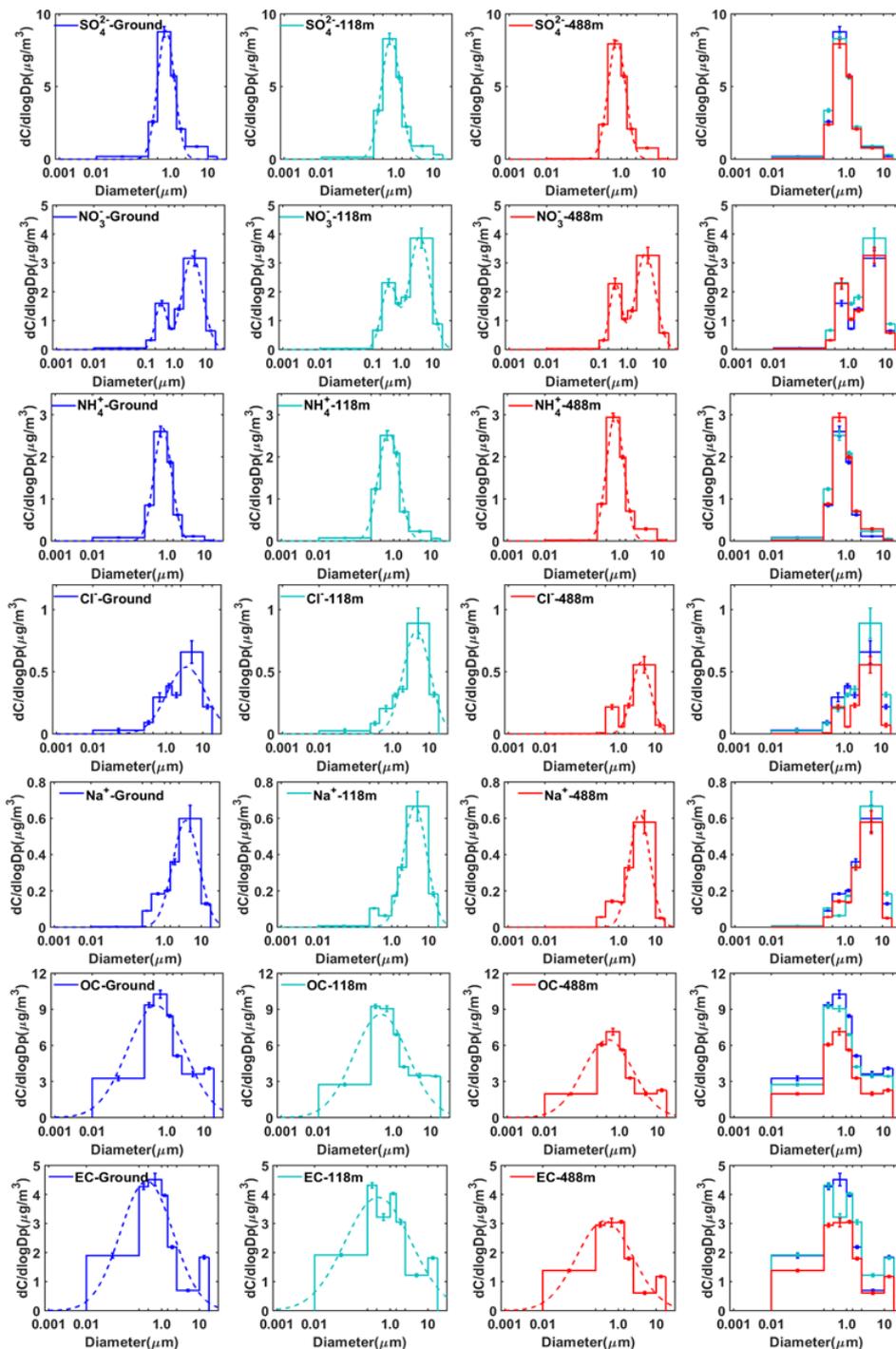


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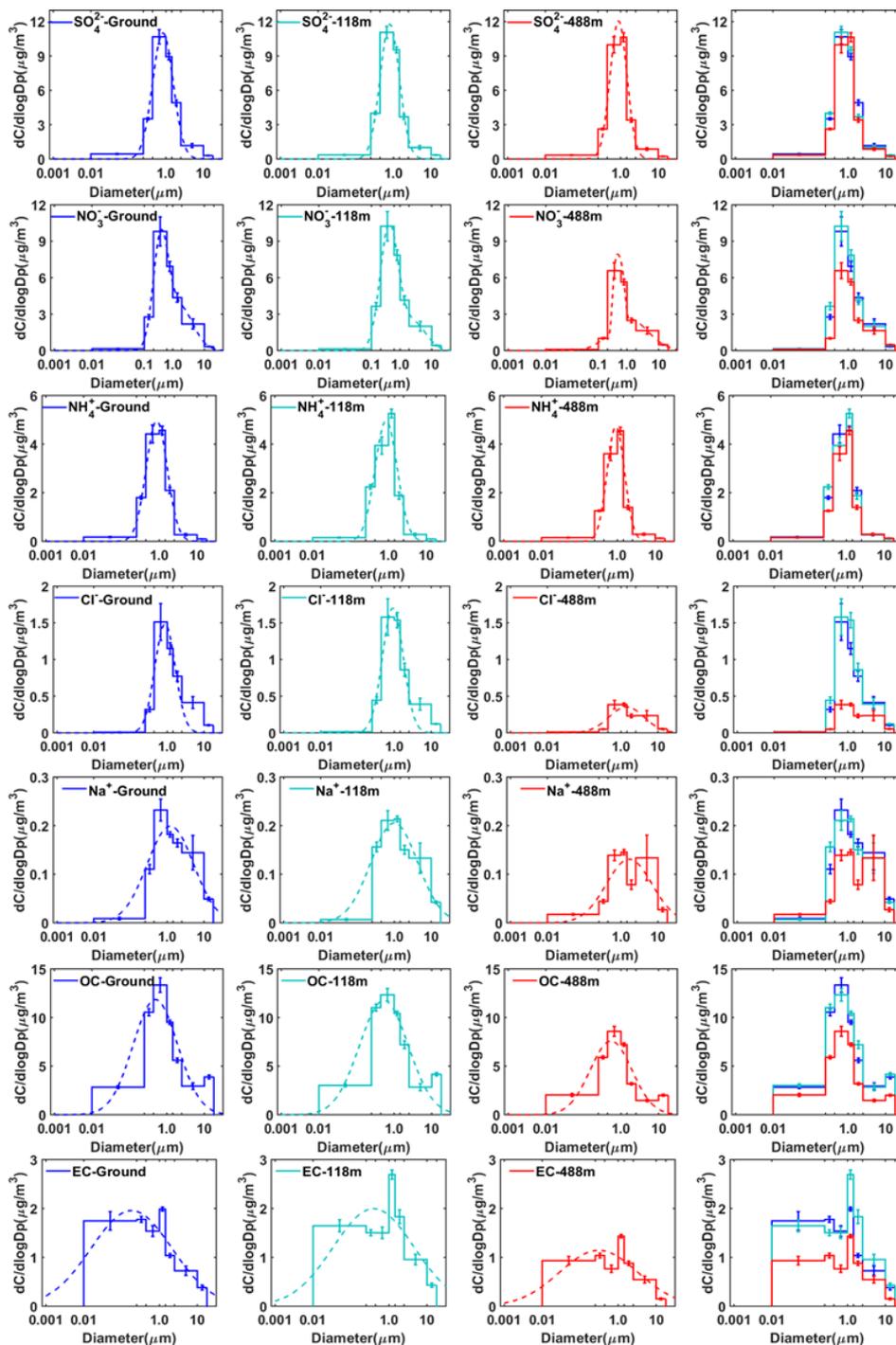
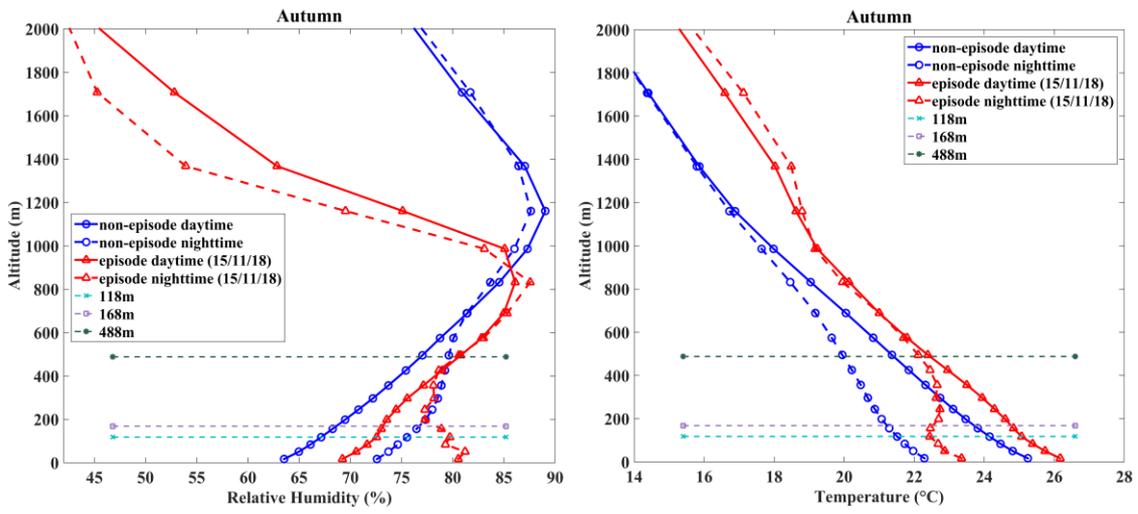
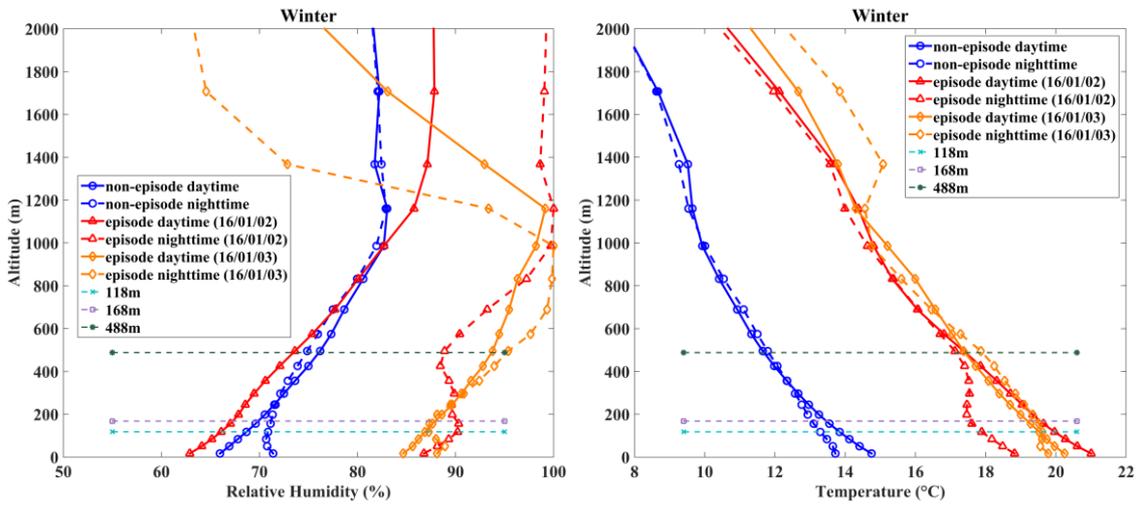


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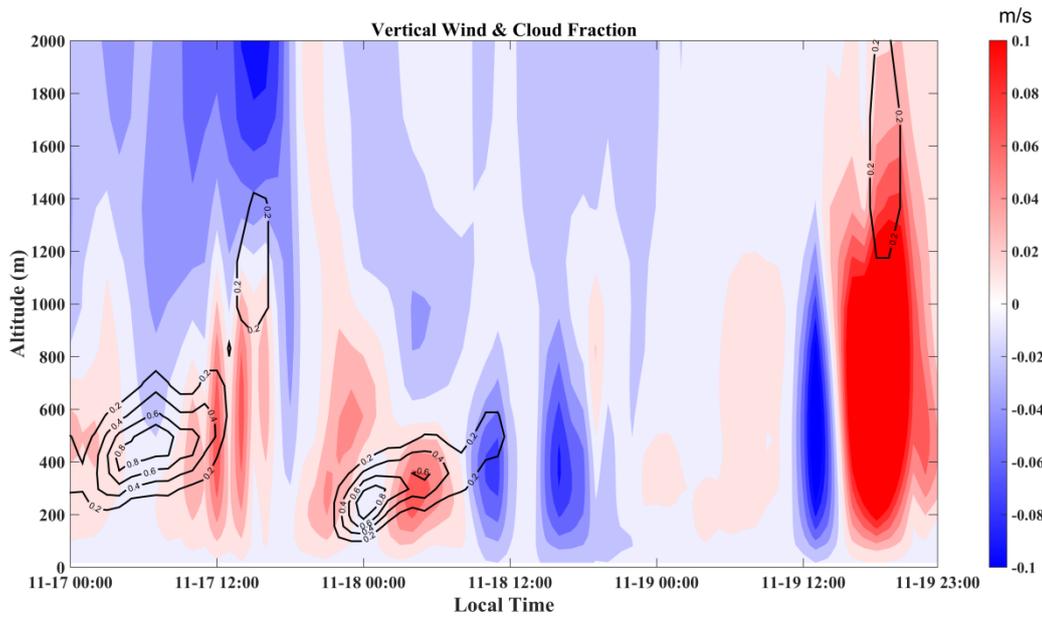


(a)

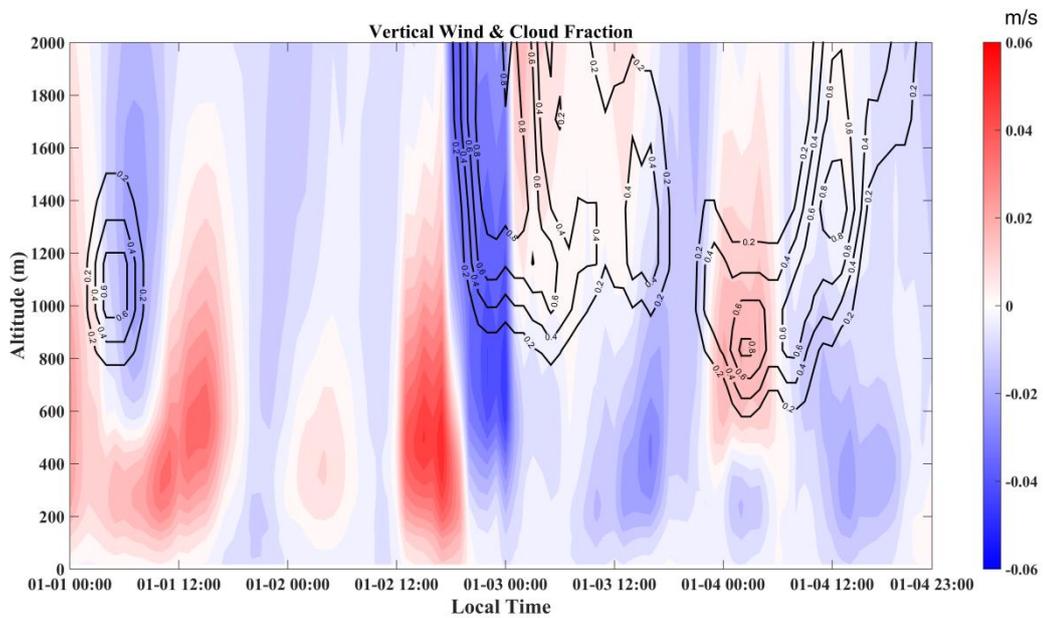


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(a)



(b)

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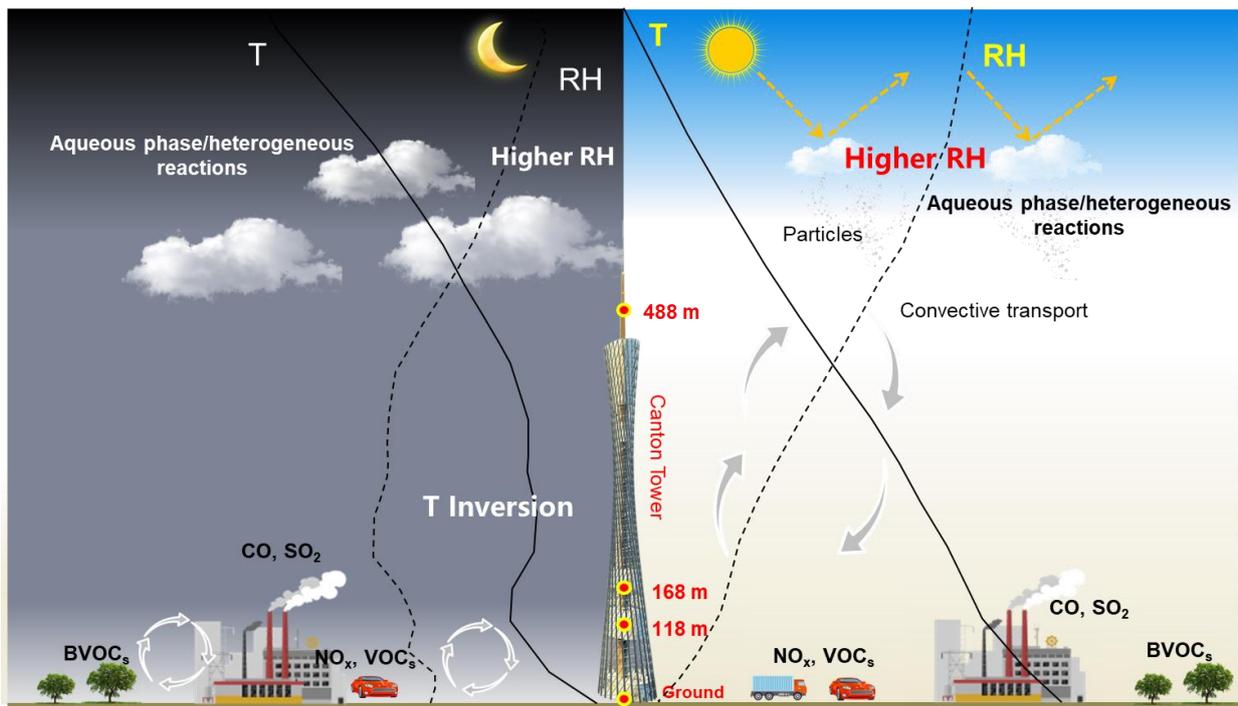


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