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[1] The introduction needs significant improvement as overall interpretation of PM sources and processes is rather outdated, or straightforward or not consistent with the most recent fundamental papers.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.

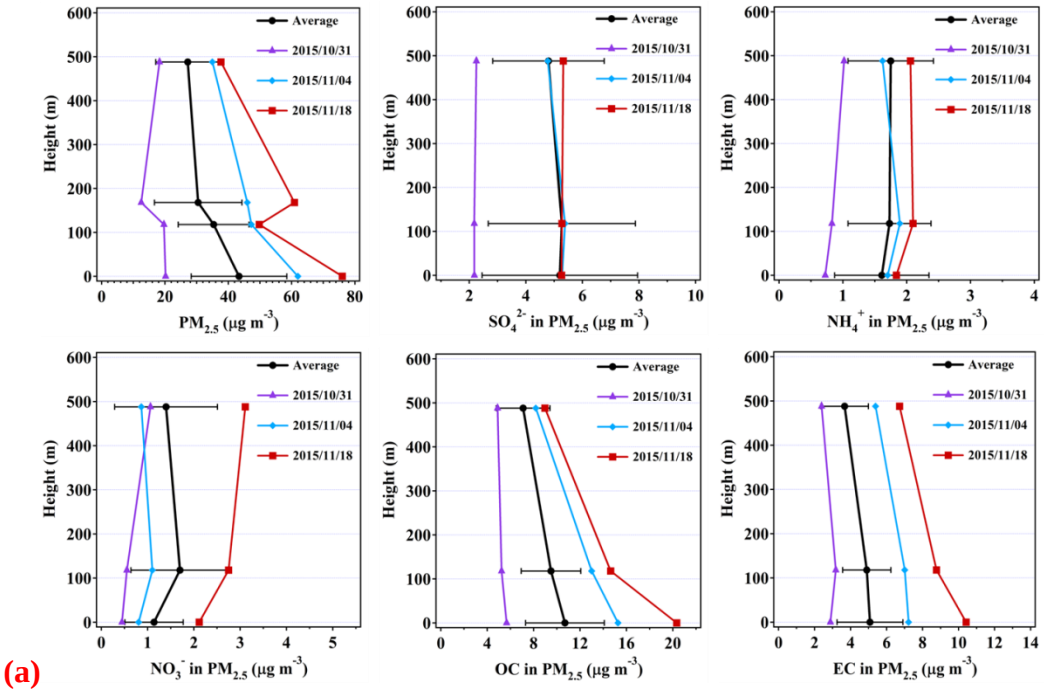
[A]: We thank the reviewer for the valuable comments on the presentation of the paper. In this paper, we analyze the vertical mass size distribution of the PM chemical components and the factors that affect their vertical variations. In addition, we also investigate the roles of in-cloud processes and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

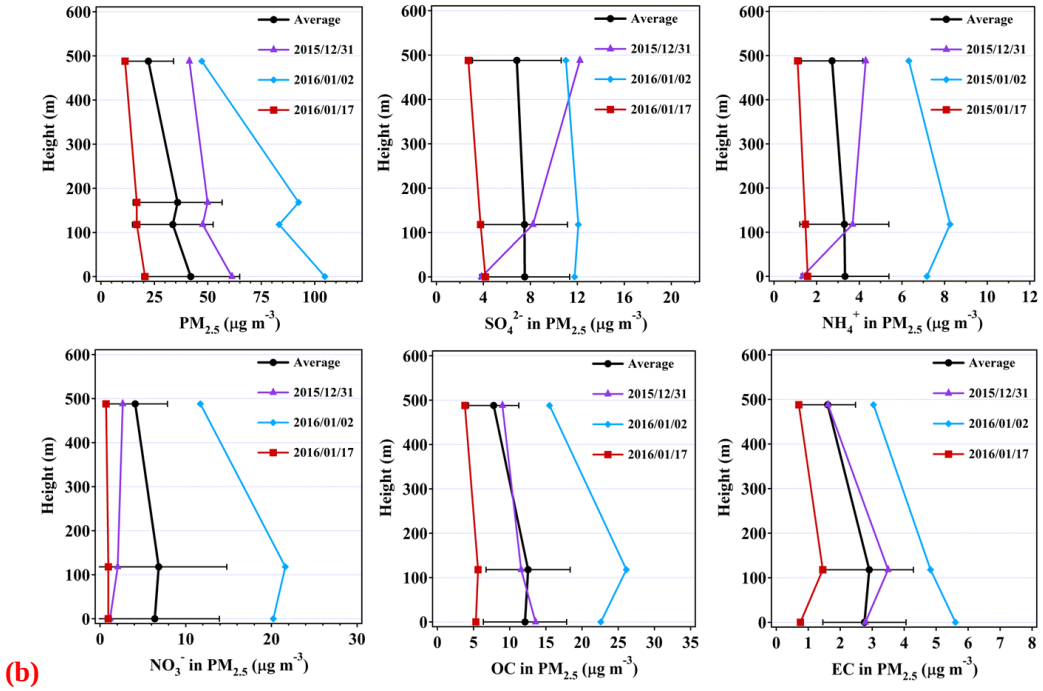
Please see more details in our point-by-point response to your specific comments below. We believe that revised manuscript has been improved in this regard.

[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.



(a)



(b)

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 ^{o}C and 24.1 ^{o}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/m^3. We calculated the flow rate when the temperature was 24.1 ^{o}C and the pressure was 95.72 kPa, i.e. at 488 m, assuming a flow rate of 100 L/m^3 at the ground level (temperature = 301.15K and pressure = 101.15kPa).

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

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

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

(1)/(2) we get:

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

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 likably attributed to the turbulent mixing of air pollutants within the boundary layer (Guinot et al., 2006).

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

source during the sampling time (Fig. S4) and then local chemical formation was likably the source that led to high SNA mass concentrations."

Table S1 and S2 in the supplementary:

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

Date	SO4	NO3	NH4	OC	EC	$PM_{2.5}$
	gradient type	gradient type	gradient type	gradient type	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	gradient type	gradient type	gradient type	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.
$PM_{2.5}$ concentraions 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 SO_2, CO, O_3, 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 μg m^{-3}, 12.3–54.2 μg m^{-3}, and 7.9–44.4 μg m^{-3} in autumn, and in the ranges of 10.2–104.8 μg m^{-3}, 10.7–83.4 μg m^{-3}, and 7.2–47.2 μg m^{-3} in winter. The average $PM_{2.5}$ mass concentrations were 44.1 ± 14.9, 36.0 ± 11.1, and 27.8 ± 10.1 μg 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 ± 11.8 μg 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 μg 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].

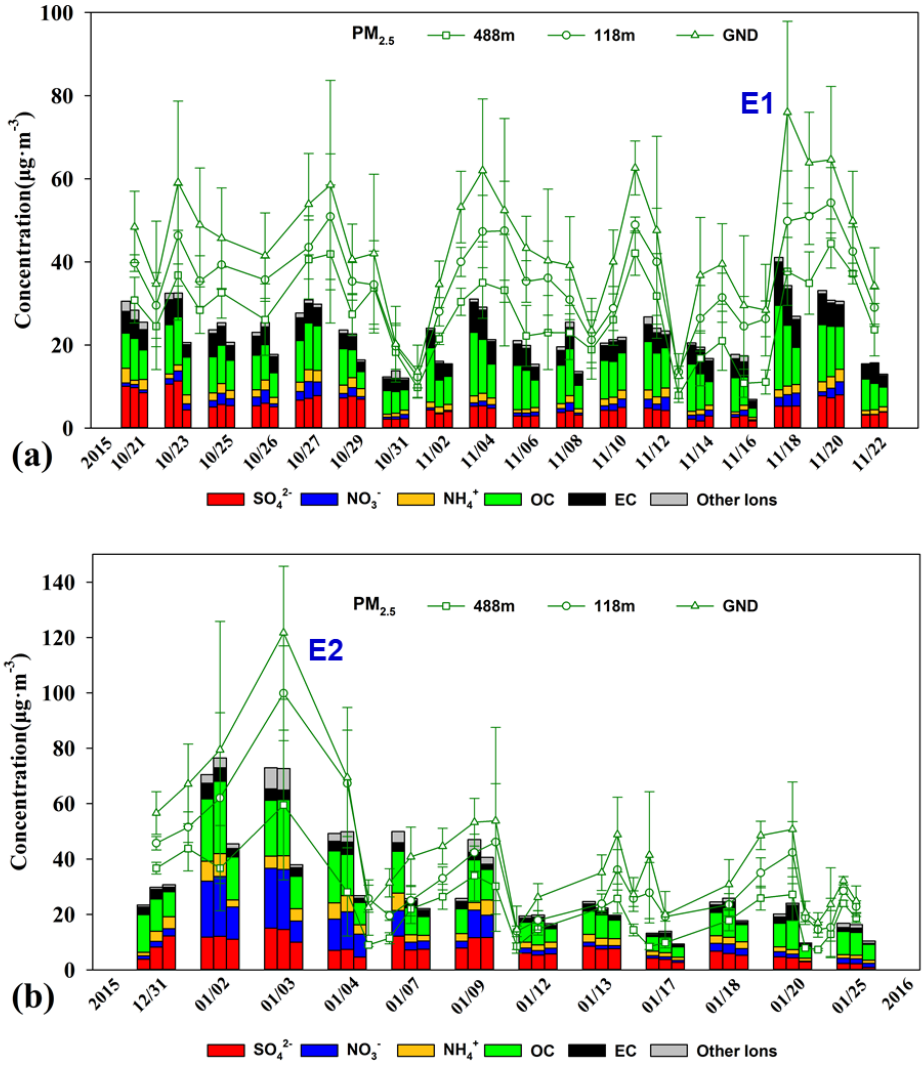


Figure 2. $PM_{2.5}$ mass and chemical components concentrations at ground level (GND), 118 m, and 488 m during the (a) autumn and (b) winter sampling periods. The dates on the x-axis are the sampling days. The stacked bar diagrams for each day represent chemical components at ground level (left), 118 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 μg 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 PM_{10} 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. SO_2, 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: "SO_2 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 SO_2 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.

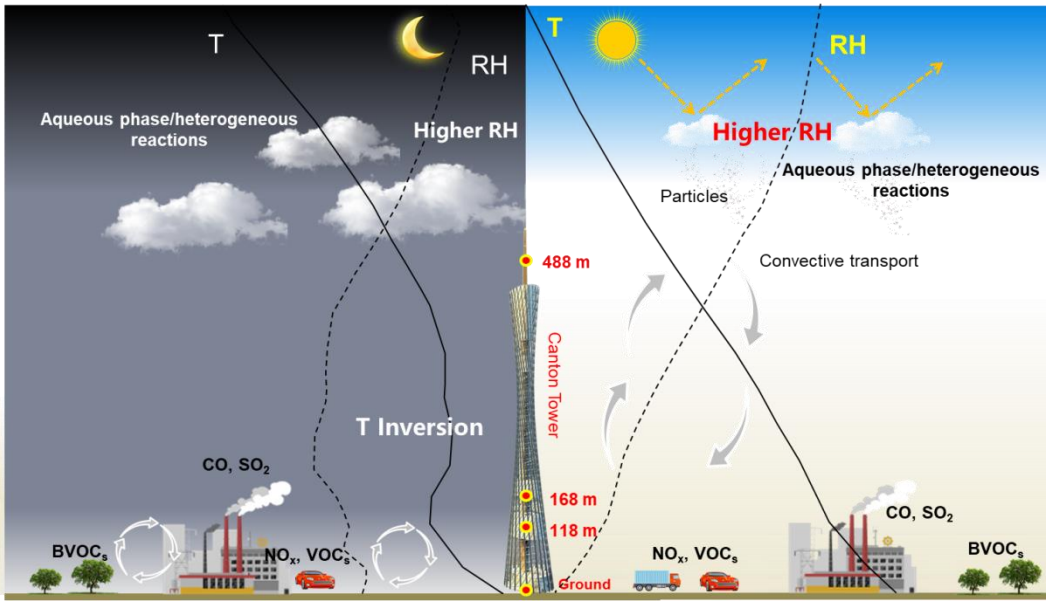


Figure 9. Schematic graph illustrating typical haze formation mechanisms in the PRD region in autumn and winter.

[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].

References:

Ceburnis, D., C. D. O'Dowd, G. S. Jennings, M. C. Facchini, L. Emblico, S. Decesari, S.Fuzzi and J. Sakalys (2008). "Marine aerosol chemistry gradients: Elucidating primary and secondary processes and fluxes." Geophysical Research Letters 35(7): L07804.

Cravigan, L. T., Z. Ristovski, R. L. Modini, M. D. Keywood and J. L. Gras (2015). "Observation of sea-salt fraction in sub-100âA˘ L'nm diameter particles at Cape Grim." Journal of Geophysical Research: Atmospheres 120(5): 1848-1864.

Ovadnevaite, J., A. Manders, G. de Leeuw, D. Ceburnis, C. Monahan, A. I. Partanen, H. Korhonen and C. D. O'Dowd (2014). "A sea spray aerosol flux parameterization encapsulating wave state." Atmospheric Chemistry and Physics 14(4): 1837-1852.

Ovadnevaite, J., A. Zuend, A. Laaksonen, K. J. Sanchez, G. Roberts, D. Ceburnis, S. Decesari, M. Rinaldi, N. Hodas, M. C. Facchini, J. H. Seinfeld and C. O. Dowd (2017). "Surface tension prevails over solute effect in organic-influenced cloud

droplet activation." Nature 546(7660): 637-641.

Valiulis, D., D. Ceburnis, J. Sakalys and K. Kvietkus (2002). "Estimation of atmospheric trace metal emissions in Vilnius City, Lithuania, using vertical concentration gradient and road tunnel measurement data." Atmospheric Environment 36(39-40): 6001-6014.

An Zhisheng, Huang Ru-Jin, Zhang Renyi, Tie Xuexi, Li Guohui, Cao Junji, Zhou Weijian, Shi Zhengguo, Han Yongming, Gu Zhaolin, and Ji Yuemeng (2019). Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes. Proceedings of the National Academy of Sciences, 116 (18): 8657-8666; DOI: 10.1073/pnas.1900125116

Cheng, Y. F., Zheng, G. J., Wei, C., Mu, Q., Zheng, B., Wang, Z. B., Gao, M., Zhang, Q., He, K. B., Carmichael, G., Pöschl, U., and Su, H. (2016): Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Sci. Adv., 2, e1601530, doi: 10.1126/sciadv.1601530.

Ervens, B. (2015). Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. Chemical Reviews 115(10): 4157-4198.

Hinds, W. C. (1999). Aerosol technology: Properties, behavior, and measurement of airborne particles (2nd ed.), New York: Wiley.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R.J., Rautiainen, J., Sun, J.Y., Zhang, Y. M., Worsnop, D. R. (2007). Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically influenced northern hemisphere mid-latitudes. Geophys. Res. Lett., 34, L13801, http://dx.doi.org/10.1029/2007GL029979.

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing (2015). The impact of synoptic

weather, regional transport and heterogeneous reactions, Atmos. Chem. Phys., 15: 2969–2983, https://doi.org/10.5194/acp-15-2969-2015..