Responses to comments

Dear editor,

We thank the editor and reviewers for their valuable comments and suggestions. We have addressed all raised issues in the revision accordingly. Please kindly find our following point-by-point response. The reviewer's comments are in black and the authors' responses are in blue. Changes that have been made in the revised manuscript are highlighted in red.

Major comments

1) The formation processes of sulfate and nitrate are well known. Thus, the current study does not contribute much to the understanding of the underlying processes that lead to aerosol formation.

In order to make the current study a substantial contribution to our understanding of general implications for atmospheric science rather than being focused on the investigation of local air pollution, the manuscript's focus needs to be expanded.

Referee #4 suggests to apply WRF-Chem not only to predict the meteorological parameters but also to simulate formation of sulfate and nitrate for comparison to measurements. This would provide useful information about model performance and it would broaden the scope of the manuscript as general conclusions on model performance could be drawn using your unique data set of size-segregated vertical aerosol profiles.

[A]: We thank the editor and reviewers for their valuable comments and suggestions.

Vertical profiles of size-segregated aerosol mass and chemical compositions are crucial for elucidating aerosol sources and formation as well as evaluating the performance of atmospheric models. Such data have, however, still scarcely been reported due to the limitations of observational methods and platforms. We agree with the editor and the reviewer that we should provide information about the current model performance by comparison with our measurement data. As suggested, we simulated the vertical concentration profiles of sulfate and nitrate using WRF-Chem model (Weather Research and Forecasting Model coupled with online chemistry model in version 3.7.1).

The results showed that sulfate was generally underestimated in WRF-Chem model at the upper level, while was in relatively good agreement with observation at the surface. Possible reasons for the underestimations of sulfate are: (1) SO_2 precursors were underestimated at the upper levels (by about 45% to 77%, table S6), possibly due to the insufficient upward transport of SO_2 in the current model, especially in urban area where the urban canopy is low in resolution; (2) heterogeneous/multiphase formations of sulfate in droplets or aerosol water have not been considered enough in current model (Chen et al., 2016; Cheng et al. 2016).

The WRF-Chem model overestimated nitrate concentrations in both seasons. We put forward three potential explanations: (1) underestimation of SO_4^{2-}, which consumes less NH_3, facilitates NH_3NO_4 formation in the fine model at the high levels (Tuccella et al., 2012); (2) heterogeneous reaction of HNO_3 on coarse-mode sea salt aerosols, however, will reduce the formation of fine-mode nitrate (Chen et al, 2016). Therefore, sea salt emissions in current model should be evaluated especially over the coastal regions; (3) the cloud fraction and liquid water content may not be well simulated in the model. We added above discussion in the revision.

The model performance and possible implications have now been added in a new section (section 3.4, page 17, lines 20-28 and page 18, lines 1-22) and supplementary.

"3.4 Model simulation and implications

Vertical concentration distributions of sulfate, nitrate and ammonium were further simulated by WRF-Chem model. The description and configuration of the model can be found in the Supplementary. Figures S13 and S14 show the simulated vertical concentration profiles of sulfate, nitrate and ammonium in autumn and winter and their comparisons with observation. Sulfate was generally underestimated in WRF-Chem model at the upper level, while was relatively in good agreement with observation at the surface. Possible reasons for the underestimations of sulfate are: (1) SO_2 precursors were underestimated at the upper levels (by about 45% to 77%, table S6), possibly due to the insufficient upward transport of SO_2 in the current model, especially in urban area where the urban canopy is low in resolution; (2) heterogeneous/multiphase formations of sulfate in droplets or aerosol water have not been considered enough in current model (Chen et al., 2016; Cheng et al. 2016). Nitrate was overestimated by WRF-Chem model. Here three reasons were put forward: (1) the underestimation of SO_4^{2-} at the upper levels, which consumes less NH_3, facilitates the formation of NH_3NO_4 formation in the fine-mode (Tuccella et al., 2012); (2) heterogeneous reaction of HNO_3 on coarse-mode sea salt aerosols, however, will reduce the formation of fine-mode nitrate (Chen et al, 2016). Therefore, sea salt emissions in current model should be evaluated especially over the coastal regions; (3) the cloud fraction and liquid water content may not be well simulated in the model. For ammonium, the simulated concentrations were overall consistent with the measured ones except for being slightly overestimated at ground level. The large discrepancies between observation and simulation on sulfate and nitrate suggested that physical and chemical mechanisms in current WRF-Chem model still need to be improved to better predict aerosol mass and composition. Based on our observation, in-cloud aqueous phase reactions and heterogeneous reactions should play important roles in sulfate and nitrate formation, which need to be refined in the model. Evaluation of WRF-Chem model incorporating the above-mentioned mechanisms is beyond the scope of this study and in-depth investigation needs to be done in future. Hence, more studies, such as long-term aerosols and high frequency micrometeorological measurements (Valiulis et al., 2002; Ceburnis et al., 2008; Ervens, 2015), are needed to identify the key aerosol sources and formation pathways, and to further improve the air quality models."

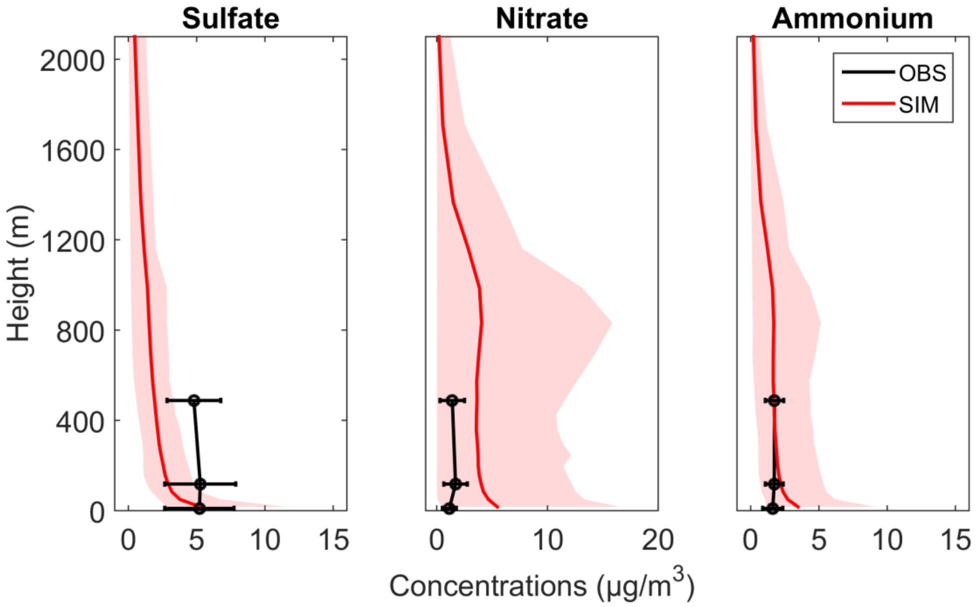

Figure S13. The vertical concentration profiles of sulfate, nitrate, and ammonium in $PM_{2.5}$ during autumn (The red solid lines are the average modeled concentrations and the shaded regions indicate the minimum and maximum values of the simulation; the average measurement data were in black with horizontal error bars).

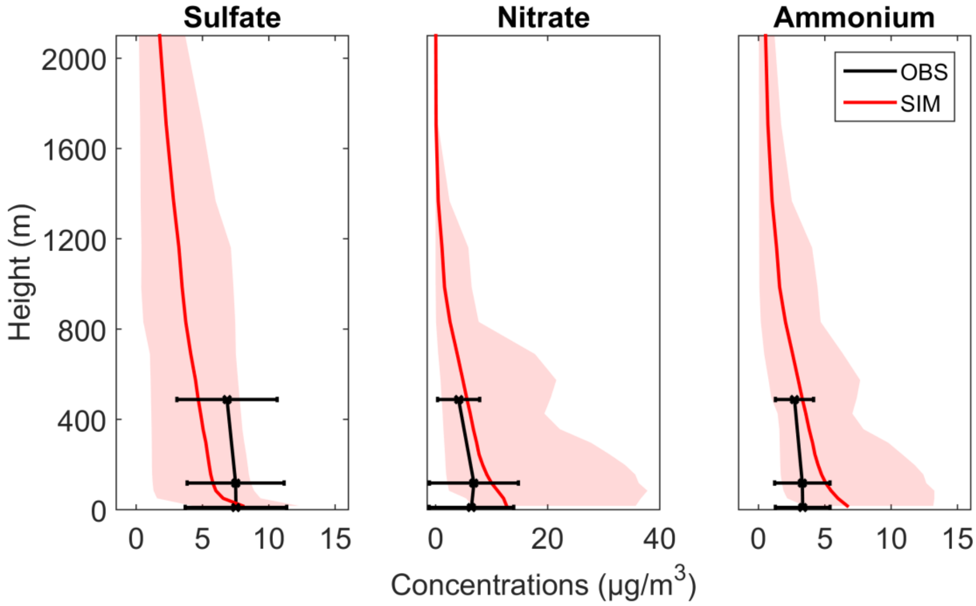

Figure S14. The vertical concentration profiles of sulfate, nitrate, and ammonium in $PM_{2.5}$ during winter (The red solid lines are the average modeled concentrations and the shaded regions indicate the minimum and maximum values of the simulation; the average measurement data were in black with horizontal error bars).

References:

Ceburnis, D., Dowd, C. D. O', Jennings, G. S., Facchini, M. C., Emblico, L., Decesari, S., Fuzzi, S., and Sakalys, J.: Marine aerosol chemistry gradients: Elucidating primary and secondary processes and fluxes, Geophy. Res. Let., 35(7), L07804, https://doi.org/10.1029/2008GL033462, 2008.

Chen, D., Liu, Z., Fast, J. and Ban, J.: Simulations of sulfate-nitrate-ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014, Atmos. Chem. Phys., 16(16), 10707–10724, doi:10.5194/acp-16-10707-2016, 2016.

Chen, Y., Cheng, Y., Ma, N., Wolke, R., Nordmann, S., Schüttauf, S., Ran, L., Wehner, B., Birmili, W., van der Gon, H. A. C. D., Mu, Q., Barthel, S., Spindler, G., Stieger, B., Müller, K., Zheng, G. J., Pöschl, U., Su, H., and Wiedensohler, A.: Sea salt emission, transport and influence on size-segregated nitrate simulation: a case study in northwestern Europe by WRF-Chem, Atmos. Chem. Phys., 16, 12081-12097, 10.5194/acp-16-12081-2016, 2016.

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.: 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, 2016.

Ervens, B.: Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. Chem. Rev., 115(10), 4157-4198, http://dx.doi.org/10.1021/cr5005887, 2015.

Tuccella, P., Curci, G., Visconti, G., Bessagnet, B., Menut, L., and Park, R. J.: Modeling of gas and aerosol with WRF/Chem over Europe: Evaluation and sensitivity study, Journal of Geophysical Research: Atmospheres, 117, 10.1029/2011jd016302, 2012.

Valiulis, D., Ceburnis, D., Sakalys, J., and Kvietkus, K.: Estimation of atmospheric trace metal emissions in Vilnius City, Lithuania, using vertical concentration gradient and road tunnel measurement data, Atmos. Environ., 36(39-40), 6001-6014, https://doi.org/10.1016/S1352-2310(02)00764-1, 2002.

Supplementary materials

"2.1 Description and configurations of WRF–Chem model

The model used in this study is the chemistry version of the WRF model (WRF–Chem v3.7.1). The WRF model is a mesoscale non-hydrostatic meteorological model that includes several options for physical parameterizations of the planetary boundary layer (PBL), cloud processes and land surface (Skamarock et al., 2008). The chemistry version is a version of WRF coupled with an "online" chemistry model, in which meteorological and chemical components of the model are predicted simultaneously (Grell et al., 2005; Fast et al., 2006). Emission, chemical formation and removal, transport and deposition are considered when WRF–Chem predicts the chemical components. In the numerical modeling, a triple-nested grid with 27/9/3 km resolution domain and 39 layers in vertical is set (Figure S12). The chemistry only run in domain d03 (3 km resolution) and MOZART boundary condition is used for the chemistry run. The simulation period is conducted from 0000 UTC 18 October to 0000 UTC 28 November 2015 as the autumn time period and 0000 UTC 25 December 2015 to 0000 UTC 28 January 2016 as the winter time period. The National Center for Environmental Protection (NCEP) 1 ° × 1 °FNL (Final operational global reanalysis) data are applied as the initial and boundary condition in WRF modeling. The physical and chemical parameterization configurations for WRF-Chem model can be found in Table S4. A region local anthropogenic emission inventory is used within the PRD region (Zheng et al., 2009), which is updated to the year of 2015.

For other areas, the Multi-resolution Emission Inventory for China (MEIC, http://meicmodel.org/) is used in this study. MEGAN model version 2.1 is also used for providing the biogenic emissions (Guenther et al., 2006).

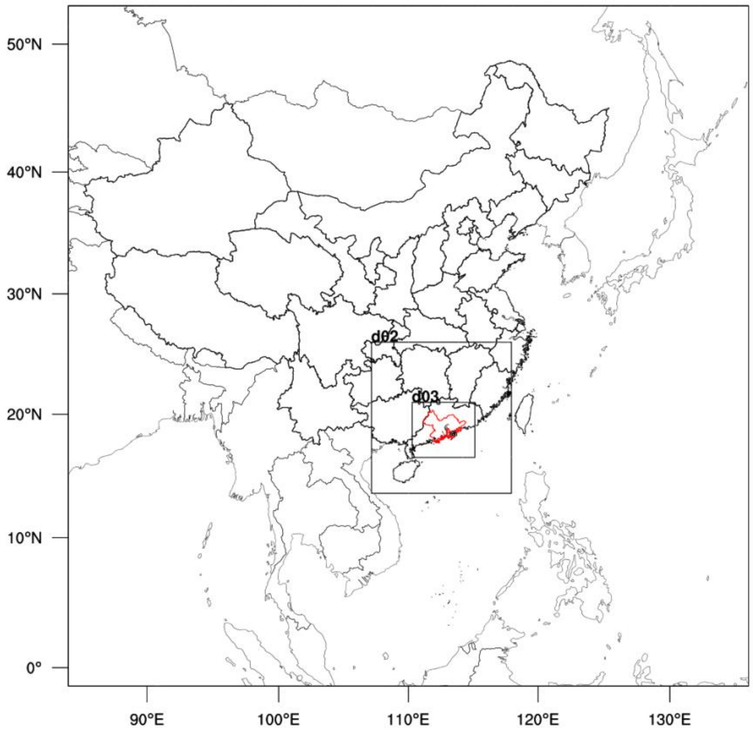

Figure S12. The simulation domain of WRF-Chem model

Table S4. Physical and chemical parameterization configurations for WRF-Chem model

Process	Option
Microphysics scheme	Morrison (2 moments)
Cumulus scheme	Kain-Fristsch
Longwave radiation scheme	RRTM
Shortwave radiation scheme	Dudhia
Boundary-layer scheme	YSU
Land-surface scheme	unified Noah
Urban Surface scheme	UCM
Gas-phase mechanism scheme	CBM-Z
Photolysis scheme	Fast-J
Aerosol scheme	MOSAIC

2) The formation processes and sources of organic aerosol are much more uncertain than those of sulfate and nitrate. Given that a large mass fraction of the aerosol in the study region is composed of organics, some discussion should be dedicated to them. For example, Referee #4 points out that the different vertical gradients of organics compared to inorganics may give evidence of different sources. This idea should be elaborated on and the discussion extended accordingly.

***[A]*:** We agree that the formation processes and sources of organic aerosol are much more uncertain than those of sulfate and nitrate. Current atmospheric models are not able to accurately predict the amount of organic aerosols formed due to these high uncertainties.

The vertical distributions of OC and EC in $PM_{2.5}$ have been discussed and compared with inorganic species in the revision (section 3.2.1, page 9, lines 15-19 and page 10):

"The vertical gradients for OC and EC in autumn were found to be different from those of sulfate and ammonium, with the EC concentration 27.9% lower and the OC concentration 34.0% lower at 488 m than at ground level respectively (type I). The results suggest that the carbonaceous components are likably from local sources and the inorganics (sulfate and nitrate) are transported from some distances.

In winter, averaged concentrations of sulfate and ammonium were generally observed to be higher at ground level than those at higher levels (type I) (Fig. 3b). However, concentrations of nitrate, OC and EC were higher at 118 m (type II). On cleaner 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 are unclear, but they were probably due to local chemical formation or regional transport of particles. However, back trajectory analysis showed that local chemical formation contributed to high SNA mass concentrations rather than regional transport during the sampling time (Fig. S4)."

We also extended our discussion on the mass size distributions of OC and EC in the revision on page 14, lines 20 and below:

"In general, the mass size distributions for OC showed dominant droplet modes in both autumn and winter, with small peaks in coarse mode (Figs. 5 and 6). The size distributions of OC in our work are similar to those in previous studies in Shanghai (Ding et al., 2017) and at Alpine valleys (Jaffrezo et al, 2005), while they are very different from those at rural and remote sites at Tibetan Plateau (Wan et al., 2015) and Xishuangbanna in China (Guo, 2016). The dominant droplet mode for OC is much similar to that of sulfate, suggesting that a large amount of OC may originate from secondary formation processes (Jafferzo et al., 2005). This was further supported by the average OC/EC ratios of larger than 2.0 (Fig. S6), indicating the presence of secondary organic aerosols. In addition, the size distributions of OC were similar at the three heights, implying that they probably had the same origins. The mass size distributions for EC are fairly different between autumn and winter. Huang et al (2006) reported that EC showed a dominant accumulation mode with a mass median aerodynamic diameter of 0.42 μm from vehicle emissions in a tunnel in Guangzhou. However, in this study, the peak concentration for EC in autumn was in the size range of 0.44-1.0 μm, suggesting that EC has been aged after emission. EC showed a general bimodal peak in winter, with a broad EC peak in accumulation mode and a sharp peak (the highest concentration) at around 1.0–1.44 μm at 188 m, suggesting that its source might be different from the other two levels. One possible reason for the abnormally high concentrations of EC was the influence of local point sources (i.e., high chimneys from power plants and industry) around Guangzhou which emitted elevated concentrations of air pollutants from combustion sources. We also found that the concentrations of co-emitted SO_2 and CO were the highest at 188 m among the three heights (Fig. S7).”

References:

Ding, X. X., Kong, L. D., Du, C. T., Zhanzakova, A., Fu, H. B., Tang, X. F., Wang, L., Yang, X., Chen, J. M., and Cheng, T. T.: Characteristics of size-resolved atmospheric inorganic and carbonaceous aerosols in urban Shanghai, Atmospheric Environment, 167, 625-641, https://doi.org/10.1016/j.atmosenv.2017.08.043, 2017.

Guo, Y.: Size distribution characteristics of carbonaceous aerosol in a rural location in northwestern China, Air Quality, Atmosphere & Health, 9, 193-200, 10.1007/s11869-015-0322-y, 2016.

Huang, X. F., Yu, J. Z., He, L.Y., and Hu, M.: Size Distribution Characteristics of Elemental Carbon Emitted from Chinese Vehicles: Results of a Tunnel Study and Atmospheric Implications, Environmental Science & Technology, 40, 5355-5360, 10.1021/es0607281, 2006.

Jaffrezo, J. L., Aymoz, G., and Cozic, J.: Size distribution of EC and OC in the aerosol of Alpine valleys during summer and winter, Atmos. Chem. Phys., 5, 2915-2925, 10.5194/acp-5-2915-2005, 2005.

Wan, X., Kang, S., Wang, Y., Xin, J., Liu, B., Guo, Y., Wen, T., Zhang, G., and Cong, Z.: Size distribution of carbonaceous aerosols at a high-altitude site on the central Tibetan Plateau (Nam Co Station, 4730ma.s.l.), Atmospheric Research, 153, 155-164, https://doi.org/10.1016/j.atmosres.2014.08.008, 2015.

3) Referee #3 suggests improving the structure of your discussion and to more clearly differentiating between hypotheses and clear evidence of aerosol processing based on your observations.

***[A]*:** We have improved the structure of our discussion in revision.

Based on the vertical mass size distribution study, our hypotheses are that in-cloud aqueous reactions and heterogeneous reactions were the important aerosol formation pathways in this coastal urban area under high relative humidity. Then, we carried out aerosol pollution case studies to prove our hypotheses. To make the discussion clear, we have added some sentences in section 3.3:

“In the previous sections, our results revealed that in-cloud aqueous reactions and heterogeneous reactions were important aerosol formation pathways in this coastal urban area under high relative humidity. Here we consider two PM pollution episodes (E1 and E2) to investigate these mechanisms for haze formation in autumn and in winter (Fig. 2).”

We further simulated the vertical concentration profiles of sulfate, nitrate and ammonium using WRF-Chem model, which are compared with the measured values. The model performance was also evaluated. This information was added in a new paragraph (section 3.4).

Your statements should be stronger and more specific; at many places they seem vague, e.g.

***[A]*:** We thank the reviewer for the valuable comments and we have now modified those sentences below for clarification.

p. 1, l. 10: The results from pollution case studies further showed that atmospheric aqueous-phase and 10 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.

***[A]*:** Page 2, lines 10-13: "Case studies further showed that atmospheric aqueous-phase and heterogeneous reactions could be important mechanisms for sulfate and nitrate formation, which, in combination with adverse weather conditions, such as temperature inversion and calm wind, led to haze formation during autumn and winter in the PRD region."

p. 9, l. 21: 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.

***[A]*:** Page 10, lines 1-3: **"**However, back trajectory analysis showed that local chemical formation contributed to high SNA mass concentrations rather than regional transport during the sampling time (Fig. S4)."

p. 10, l. 6: indicating the favorable secondary formation or regional transport of aerosols at the higher altitude.

***[A]*:** Page 10, line 16: **"**indicating more favorable secondary formation and aging processes of aerosols at higher altitudes."

p. 17, l. 9: …. suggesting different nitrate formation mechanisms

***[A]*:** Page 19, lines 5-7: **"**Bi-modal size distributions in autumn and a unimodal mode in winter were observed for nitrate, suggesting different formation pathways for nitrate in different seasons."

Minor comments

[1] - Referee #1 appreciates the detailed uncertainty analysis that you provided in the response to the referee report. It should be included in the manuscript.

[A]: We have added the detailed uncertainty analysis in the text and supplementary.

Page 6, lines 8-15: The three impactors (or samplers) were calibrated using mass flow meter (TSI, model 4040) in laboratory prior to the measurements. The flow rates of the impactors were measured at the beginning of the sampling. At the end of the sampling, the flow rates were recorded again. If the flow rate of each impactor at the beginning and end of the sampling 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 was used to be 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 the sampling.

Page 6, lines 22-25: We estimated the impacts of temperature and pressure on the flow rate due to the sampling heights which are less than 5%. (refer to supplementary).

[2] - Both Referee #2 and #3 pointed out that the hygroscopic growth of particles might lead to a significant shift in diameters which might affect conclusions about aerosol size distributions at different heights. Please take into account the numbers for growth factors etc as suggested by Referee #3 and discuss possible implications for your conclusions on aerosol mass formation vs aerosol growth by water uptake.

***[A]*:** We thank the reviewer for the valuable comments. We agree that the shifts of the particles sizes would happen due to increase of relative humidity. Therefore, we estimated the RH effects on the shift in the size cut-off threshold induced by hygroscopic growth.

In this study, the monthly averaged relative humidity was around 80% in both seasons. We assume that the hygroscopic growth factor, independence of particle size, is about 1.4 and 1.5 respectively for ammonium sulfate and ammonium nitrate at 80% RH (Tang, 1996). A maximum overestimated value of about 10%, 13% and 6% for droplet mode sulfate was obtained at ground level, 118 m and 488 m, respectively. The droplet mode nitrates were overestimated to be about 11%, 16%, and 6% at ground level, 118 m and 488 m, respectively.

Chen et al (2018) explored the influence of cut-off shift on filter-based particle sampling driven by hygroscopic growth. They concluded that the influence is generally negligible (less than 7%) in urban areas, but need to be considered (about 10–20%) in continental background areas in Europe. They also recommended that this influence needs to be assessed individually for each measurement period even at the same location, since it is highly dependent on ambient conditions.

Based on the evaluation, we think the influence of RH on the size shift indeed exists, but is unlikely to change the main conclusion of this paper. Sulfate and nitrate concentrations are still mainly dominant in droplet mode. We have now added the following paragraph as a caveat in the revision.

Page 11, line 22-: The air was not dried upstream of the impactor and therefore relative humidity would influence the size distributions of different chemical species. In this study, the monthly averaged relative humidity was around 80% in both seasons.

We assume that the hygroscopic growth factor is independent of particle size and is about 1.5 for both ammonium sulfate and ammonium nitrate at 80% RH (Tang, 1996). A maximum overestimated value of about 10%, 13% and 6% for droplet mode sulfate was obtained at ground level, 118 m and 488 m, respectively. The droplet mode nitrates were overestimated to be about 11%, 16%, and 6% at ground level, 118 m and 488 m, respectively. Our results are similar to those in Chen el al (2018), which concluded that the influence of cut-off shift on filter-based particle sampling driven by hygroscopic growth is generally negligible (less than 7%) in urban areas, but need to be considered (about 10–20%) in continental background areas in Europe. The influence from relative humidity on the size distribution is indeed present based on the average particle concentrations in the droplet mode in this study; however, it is unlikely to change our conclusion that in-cloud processing contributed to the droplet mode aerosols (Table S3).

References:

Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Größ, J., Wang, L., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmospheric Environment, 195, 141-148, https://doi.org/10.1016/j.atmosenv.2018.09.049, 2018.

Tang, I. N.: Chemical and size effects of hygroscopic aerosols on light scattering coefficients, Journal of Geophysical Research: Atmospheres, 101, 19245-19250, 10.1029/96jd03003, 1996.

[3] - At several places in the manuscript, you use ‘heterogeneous aqueous phase reaction’ or seem to use ‘heterogeneous’ and ‘multiphase’ reactions equivalently. Please check carefully for the correct use of terminology: ‘Heterogeneous processes’ are processes that occur on surfaces (droplet, particles) where the reactants are in two different phases (gas and condensed phase). ‘Multiphase processes’ are processes that occur in the bulk of the aqueous phase into which the reactants might be taken up from or products released to the gas phase (Ravishankara, A. R.: Heterogeneous and Multiphase Chemistry in the Troposphere, Science, 276, 1058–1065, 1997.)

[A]: We thank the reviewer for pointing this out. We have double checked and modified accordingly in the revision.

Page 3, line 13: “heterogeneous aqueous reactions” should be “multiphase reactions”.
Page 5, line 3: “Heterogeneous aqueous phase reactions” should be “Multiphase reactions”.
Page 5, line 19: “heterogeneous aqueous reactions” should be “multiphase reactions”.
Page 17, line 4: “heterogeneous aqueous reactions” changed to “aqueous reactions”.

[4] - Numbers should be rounded to significant digits throughout the manuscript, e.g. 44 ± 14 instead of 44.1 ± 14.9

[A]: All the numbers have been checked and rounded according to the reviewer’s suggestion.

[5] - p. 8, l.11: What are abnormal days, as opposed to 'normal days'?
[A]: As suggested by the reviewer, we changed "normal days" to "typical days".

[6] - Nitrate formation from hydrolysis of N_2O_5 is well known. In the atmosphere, likely no completely dry particles exist as mixed particles have a very low efflorescence relative humidity and continuously undergo efflorescence/deliquescence cycles. The discussion on op. 12 can be shortened.
[A]: We have deleted those sentences associated with hydrolysis of N_2O_5.

[7] - p. 14, l. 10-14: These lines seem out of place in the 'OC and EC' section.
[A]: We rephrased this sentence in the revision. (Page 15, lines 2-9):
"EC showed a general bimodal peak in winter, with a broad EC peak in accumulation mode and a sharp peak at around 1.0–1.44 μm, with the highest concentration in this size range 1.0-1.44 at 188 m, suggesting that its source might be different from the other two levels. One possible reason for the abnormally high concentrations of EC was the influence of local point sources (i.e., high chimneys from power plants and industry) around Guangzhou which emitted elevated concentrations of air pollutants from combustion sources. We also found that the concentrations of co-emitted SO_2 and CO were the highest at 188 m among the three heights (Fig. S7)."

[8] - p. 15, l. 10-12: Was the increase in SO_2 sufficient to lead to the observed decrease in SOR? In other words, does this imply that no sulfate formation occurred?
[A]: We thank the reviewer for pointing this out. It was likely in our study that ambient air at higher elevations was impacted more by emissions from nearby combustion sources, where the air masses were fresh. Therefore, we observed lower SOR (SOR = n-SO_4^{2-} / (n-SO_4^{2-} + n-SO_2) at higher altitudes. That does not mean, however, that no sulfate formation occurred but the new released SO_2 will compensate for part of the sulfate converted from SO_2 at high altitudes, leading to decrease of the SOR.
We have added this discussion in the text (page 16, line 7- 10):
"The concentration of SO_2 increased with height (12.4, 16.1, 27.0 μg m^{-3} at ground, 118 m, and 488 m, respectively), suggesting that it was impacted more by emissions from local sources, where the air masses were fresh. The newly emitted SO_2 at high altitudes compensated for part of the sulfate converted from SO_2, leading to decrease of SOR with heights."

Response to Anonymous Referee #1

The paper improved dramatically and is now suitable for publication. The authors did a great job and their efforts commendable.

Few minor technical comments:

[1]-Use "typical (days", instead of "normal".

[A]: we changed “normal days” to “typical days”.

[2]-I wonder why uncertainty analysis which was well explained to the reviewers did not make into the paper? It can be separated into dedicated chapter.

[A]: We added the detailed uncertainty analysis in the text.

Page 6, lines 8-15: The three impactors (or samplers) were calibrated using mass flow meter (TSI, model 4040) in laboratory prior to the measurements. The flow rates of the impactors were measured at the beginning of the sampling. At the end of the sampling, the flow rates were recorded again. If the flow rate of each impactor at the beginning and end of the sampling 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 was used to be 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 the sampling.

Page 6, lines 22-25: We estimated the impacts of temperature and pressure on the flow rate due to the sampling heights. The results showed that impacts of pressure and temperature on the flow rate are less than 5% (Refer to supplementary).

Response to Anonymous Referee #3

The Authors present original aerosol measurements taken on a tall city tower, including rare observations of size-segregated chemical composition. Measurement periods are short, and the Authors focused on the analysis of specific events. Their results are interesting because they were able to show that aerosol chemical components can be spatially segregated not only horizontally (because of the presence of the buildings and of the heterogeneity of the sources) but also vertically. The analysis of air mass transport and thermodynamics in the lower few hundreds meters above the ground can be blamed for such variability. In spite of such complexity, the Authors' conclusions in the abstract seem very shallow. Just a generic mention to the role of heterogeneous chemistry is given. The quality of presentation is poor, and I struggled to understand what specific day of the campaign some of the figures referred to (e.g. Figure 8) and also why that day and not others? The Authors claim that the presence of low-level clouds was crucial for the production of secondary aerosols on certain days. But they do not discuss the presence/absence of clouds on other days, when concentration vertical profiles are more flat. The full elaboration lacks of a coherent analysis, and sometimes hypotheses and conclusions (e.g., about the importance of aqueous phase chemistry) are mixed up in the discussion.

***[A]*:** We thank the reviewer for the comments. 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 aqueous reactions and heterogeneous reactions in haze formation were investigated in this subtropical urban area. Moreover, vertical distributions of sulfate, nitrate and ammonium were simulated by the WRF-Chem model. The large discrepancies between observation and simulation on sulfate and nitrate suggested that physical and chemical mechanisms in the current model still need to be improved to better predict the aerosols masses and compositions.

In order to make the paper clear and more readable, we adjusted the structure, and a new paragraph on model simulation and implications was added in the revised manuscript.

Specific comments:

The Referee#2's comment on the effect of hygroscopic growth on measured impactor size-distribution, in my view, was only partially addressed by the Authors. In the study of Meng and Seinfeld (1993) quoted by the Authors, the ratio between the diameters of the droplet mode and the condensation mode was 3.5 (= 0.7 vs. 0.2), while here such ratio is only 2.3 for sulphate (= 0.75 vs 0.33; section 1 in the Supplementary). Considering that the hygroscopic growth factor for ammonium sulphate at RH 80% is about 1.4 (and obviously greater at RH values approaching the saturation), I would be more cautious in concluding that ambient RH was irrelevant in contributing to shaping the measured size-distributions.

***[A]*:** We thank the reviewer for the valuable comments. We agree that the shifts of the particles sizes would happen due to the increase of relative humidity. Therefore, we estimated the RH effects on the shift in the size cut-off threshold induced by hygroscopic growth.

In this study, the monthly averaged relative humidity was around 80% in both seasons. We assume that the hygroscopic growth factor, independence of particle size, is about 1.4 and 1.5 respectively for ammonium sulphate and ammonium nitrate at 80% RH (Tang, 1996). A maximum overestimated value of about 10%, 13% and 6% for droplet mode sulphate was obtained at ground level, 118 m and 488 m, respectively. The droplet mode nitrates were overestimated to be about 11%, 16%, and 6% at ground level, 118 m and 488 m, respectively.

Chen et al (2018) explored the influence of cut-off shift on filter-based particle sampling driven by hygroscopic growth. They concluded that the influence is generally negligible (less than 7%) in urban areas, but need to be considered (about 10–20%) in continental background areas in Europe. They also recommended that this influence needs to be assessed individually for each measurement period even at the same location, since it is highly dependent on ambient conditions.

Based on the evaluation, we think the influence of RH on the size shift indeed exists, but is unlikely to change the main conclusion of this paper. Sulfate and nitrate concentrations are still mainly dominant in droplet mode. We have now added the following paragraph as a caveat in the revision.

Page 11, line 25-: “The air was not dried upstream of the impactor and therefore relative humidity would influence the size distributions of different chemical species. In this study, the monthly averaged relative humidity was around 80% in both seasons. We assume that the hygroscopic growth factor is independent of particle size and is about 1.5 for ammonium sulfate and ammonium nitrate at 80% RH (Tang, 1996). A maximum overestimated value of about 10%, 13% and 6% for droplet mode sulfate was obtained at ground level, 118 m and 488 m, respectively. The droplet mode nitrates were overestimated to be about 11%, 16%, and 6% at ground level, 118 m and 488 m, respectively. Our results are similar to those in Chen el al (2018), which concluded that the influence of cut-off shift on filter-based particle sampling driven by hygroscopic growth is generally negligible (less than 7%) in urban areas, but need to be considered (about 10–20%) in continental background areas in Europe. The influence from relative humidity on the size distribution is indeed present based on the average particle concentrations in the droplet mode in this study; however, it is unlikely to change our conclusion that in-cloud processing contributed to the droplet mode aerosols (Table S3).”

References:

Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Größ, J., Wang, L., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmospheric Environment, 195, 141-148, https://doi.org/10.1016/j.atmosenv.2018.09.049, 2018.

Tang, I. N.: Chemical and size effects of hygroscopic aerosols on light scattering coefficients, Journal of Geophysical Research: Atmospheres, 101, 19245-19250, 10.1029/96jd03003, 1996.

Response to Anonymous Referee #4

This paper discusses size segregated measurements of aerosol particle chemistry (major ions, OC and EC) conducted at three vertical levels (ground, 118 m-agl and 488 m-agl) in an urban area of China. In addition to trajectories, the WRF model is used as a representation of low-level vertical profiles of temperature, RH and winds in the area of the measurements.

Overall, I find the presentation and writing of the current version to be clear.

The emphasis of the work appears to be to demonstrate that aqueous-phase production of sulphate plays a significant role in the development of the local aerosol and its vertical gradient. Additionally, it is suggested that nitrate formation is influenced by aqueous-phase processes and the presence of sea salt. In my opinion, the authors have presented fairly convincing arguments that these processes are likely involved in a potentially significant way. However, all of these processes have been known and studied for many years, and, as I understand it, the issue of how they affect local observations is really not in the purview of ACP. Therefore, as the paper now stands, I do not believe it is suitable for publication in ACP.

I have a few suggestions: 1) I think it would be valuable, and something that might have more universal appeal, to test WRF-CHEM against your observations to see how well the model does at reproducing your results. To do this, some local observations of state parameters and winds might be needed. 2) The carbonaceous components of the measurements are really under-emphasized in the paper. More emphasis on the size distributions of EC and OC in a relatively high emissions area, coupled with comparisons for other urban areas, regional and remote results might help. 3) In its current form, the paper might be more suitable for Atmospheric Environment, which has more of a focus on urban issues.

[A]**:** We sincerely thank the reviewer for the valuable comments, which were of great help in revising the manuscript.

In the present study, vertical concentration profiles of aerosol components in different size ranges were studied based on a ~ 610 m tall tower. The vertical concentration profiles of sulfate, nitrate and ammonium and their mass size distribution characteristics suggested that cloud processing and heterogeneous reaction could be important formation pathways for them, which should largely contribute to the aerosols pollution in this coastal urban region. The characteristics of carbonaceous aerosols were also discussed to provide more information on the aerosol sources. Further, we carried out aerosols pollution case studies to prove that cloud processing and heterogeneous reactions played important roles in the aerosols formation and haze pollutions in this area. Although we have already well known about the formation processes of sulfate and nitrate, the dominant formation pathways, and their contribution to haze pollution and climatic effects in different regions may be different and should be considered more in the current models.

As suggested, we simulated the vertical concentration profiles of sulfate and nitrate using WRF-Chem model (Weather Research and Forecasting Model coupled with online chemistry model in version 3.7.1). The results showed that sulfate was generally underestimated in WRF-Chem model at the upper level, while was in relatively good agreement with observation at the surface. Possible reasons for the underestimations of sulfate are: (1) SO_2 precursors were underestimated at the upper levels (by about 45% to 77%, table S6), possibly due to the insufficient upward transport of SO_2 in the current model, especially in urban area where the urban canopy is low in resolution; (2) heterogeneous/multiphase formations of sulfate in droplets or aerosol water have not been considered enough in current model (Chen et al., 2016; Cheng et al. 2016).

The WRF-Chem model overestimated nitrate concentrations in both seasons. We put forward three potential explanations: (1) underestimation of SO_4^{2-}, which consumes less NH_3, facilitates NH_3NO_4 formation in the fine model at the high levels (Tuccella et al., 2012); (2) heterogeneous reaction of HNO_3 on coarse-mode sea salt aerosols, however, will reduce the formation of fine-mode nitrate (Chen et al, 2016). Therefore, sea salt emissions in current model should be evaluated especially over the coastal regions; (3) the cloud fraction and liquid water content may not be well simulated in the model. All these reasons would contribute to the highly varied nitrate concentrations at the upper levels. We added above discussions in the revision (section 3.4).

We also extended our discussions on the mass size distribution of OC and EC. We believe that the paper is now fit into the scope of the journal and can contribute important knowledge to aerosol sources and formation mechanisms in urban atmospheric boundary layer.

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.

Some specific comments:

1) Page 2, lines 22-24 – When you say "highly uncertain", do you mean sources, formation mechanisms or both? I think the formation mechanisms, at least those that you focus on in this paper, are reasonably well known. There may be issues with the carbonaceous components that better fit 'highly uncertain', but you don't discuss those. Sources, because there are so many, may be highly uncertain, but you don't address those either.

***[A]*:** We thank the reviewer for the comments. We have modified this sentence in the text (page 2, lines 23-27).

"Moreover, primary and secondary aerosols undergo chemical and physical processes, for example, transport, cloud processing, and removal from the atmosphere, leading to significantly spatial and temporal variations of the sources and formation mechanisms of atmospheric aerosols (Huang et al., 2014; Sun et al., 2015; Zhang et al., 2015; Liang et al., 2016)."

2) Page 3, lines 4 -6 - Direct emission is not a condensation process. Do you mean that the condensation mode results from condensation of gas-to-particle products condensing on direct emissions?

***[A]*:** We thank the reviewer for the comments. We have modified this sentence in the

text (page 3, lines 8-10).
"The condensation submode originates from primary emissions and growth of smaller particles by coagulation and condensation, while droplet submode mainly results from cloud processing or coagulation of smaller particles (Seinfeld and Pandis, 2006)."

3) Page 3, lines 10 – 11 - There is evidence for this dating back to 1986 (e.g. Hoppel et al., JGR, 1985).
***[A]*:** We thank the reviewer for pointing this out. We have added the reference in the text.
"Hoppel, W. A., Fitzgerald, J. W., and Larson, R. E.: Aerosol size distributions in air masses advecting off the east coast of the United States, J. Geophys. Res.-Atmos., 90, 2365-2379, 10.1029/JD090iD01p02365, 1985."

4) Page 3, line 14 – mechanical processes can also produce particles in the submicron size range.
***[A]*:** We agree with the reviewer that mechanical processes can also produce particles in the submicron size range. We have rephrased this sentence.
"Coarse-mode particles are primarily produced by mechanical processes like sea spay, mineral particles and plant debris."

5) Page 4, line 3 – What are "very dynamic vertical profiles"?
***[A]*:** We have modified "very dynamic vertical profiles" to "very dynamic changes in vertical concentration profiles"

6) Page 4, line 13 – remove "enough"
***[A]*:** It has been removed from the text.

7) Page 4, line 15 – "aerosol pollution frequently occurs"
***[A]*:** Changed.

8) Page 4, line 28 – page 5, line 3 - Instead, maybe say something like "Hence size-resolved vertical profiles of major components of PM can add to important knowledge of aerosol sources and formation mechanisms in the urban atmospheric boundary layer."
***[A]*:** As suggested by the reviewer, we have modified this sentence.
Page 5, line 5-7: "Hence, size-resolved vertical concentration profiles of major components of PM can add to important knowledge of aerosol sources and formation mechanisms in the urban atmospheric boundary layer."

9) Page 5, lines 12-13 – I suggest something like "… were measured, and these observations are used to examine formation mechanisms and sources."
***[A]*:** We thank the reviewer for the suggestion and we have modified the sentence in the manuscript.

10) Page 7, line 4 – reference date?

***[A]*:** We have modified this sentence (Page 7, line 11):

"The principle of this model can be found in Draxler and Hess (1998)."

11) Page 7, line 24 – Please explain: e.g., do you mean things like insoluble components of dust?

***[A]*:** We updated this sentence in the text (page 8, lines 2-4).

"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 analysis of $PM_{2.5}$ chemical components such as H and O associated with OC, geological minerals, and liquid water (Chow et al., 2015)."

12) Page 8, line 6 - Why not show PM_1 in the main text? It seems that PM_1 agrees much better with the sum of your ions, OC and EC, which would imply that much of the difference between your sum and $PM_{2.5}$ is due to water-insoluble material.

***[A]*:** We thank the reviewer for pointing it out. The reasons for including $PM_{1.0}$ are: 1) $PM_{1.0}$ accounts for a large portion of $PM_{2.5}$ in southern China. Therefore, $PM_{1.0}$ agrees much better with the sum of ions, OC and EC. 2) $PM_{1.0}$ is not in the current air quality standard. In order to describe the pollution events, we focused on $PM_{2.5}$ and its components.

13) Page 9, lines 9-10 – They don't appear to be very dissimilar compared with the polluted day profiles.

***[A]*:** The profiles in clean days are similar compared with the polluted day profiles. However, we notice that the concentrations of $PM_{2.5}$ and its components are much lower in the clean days than in the polluted days. In addition, high relative humidity and low clouds were observed in clean days. The main difference between clean days and polluted days in meteorological factors was temperature inversion as shown in Figure 7.

14) Paragraph starting "Figure 3" on pages 8-9 - This paragraph seems to have a take-away message that, in a relative sense, the carbonaceous components are more local and more of the inorganics (sulphate and nitrate) are transported from some distance. This might be a point to summarize.

***[A]*:** A new sentence has been added on page 9, lines 14-16.

"The results suggest that the carbonaceous components are likably from local sources and the inorganics (sulfate and nitrate) are transported from some distances."

15) Page 9, line 14 – "cleanER"

***[A]*:** Changed.

16) Page 9, lines 19-20 – "The reasons are unclear…"

***[A]*:** Changed.

17) Page 10, line 1 – Some mention of RH is relevant here too.

***[A]*:** New information has been added on page 10, lines 9-13:

"Ammonium nitrate is a temperature- and relative humidity-dependent compound, and low temperature and high RH facilitate the gas-to-particle partitioning (Wang et al., 2012; Bian et al., 2014). During the sampling periods, the average temperature in winter (13.5 ℃) was much lower than that in autumn (23.1 ℃) while the RH was vice versa, explaining higher concentration of NH_4NO_3 in winter than in autumn."

18) Page 10, lines 7-8 – If true, I suggest "… were the main components of the measured species, but the comparisons with PM_1 and $PM_{2.5}$ suggest these components were relatively small factors in the coarse particles."

***[A]*:** We thank the reviewer for the suggestion and we have modified this sentence in the page 10, lines 18-19:

"Our results showed that OC, nitrate, crustal (e.g., Ca^{2+}, Mg^{2+}) and sea salt (e.g., Na^+ and Cl^-) were the major components of the measured species, but the comparisons with PM_1 and $PM_{2.5}$ suggest these components were relatively small in the coarse particles."

19) Page 10, lines 25-27 – Coagulation is important for smaller particles. Please clarify. Also, how likely are either in-cloud coalescence or multiple cloud cycles to impact your results. A reference for in-cloud coalescence is appropriate (e.g. Feingold and Kreidenweis).

***[A]*:** Feingold et al. (1996) showed that collision-coalescence and aqueous phase chemistry have great impacts on the mass-mean size particles based on model simulations. We have modified this sentence and added one relevant reference on page 11, lines 10-12:

"It is generally recognized that coagulation is negligible at typical ambient particle number concentrations (Hinds, 1999). Therefore, in-cloud coalescence of droplets or aqueous phase chemistry is responsible for production of several sulfate modes (Feingold et al., 1996)."

Reference:

Feingold, G., Kreidenweis, S. M., Stevens, B., and Cotton, W. R.: Numerical simulations of stratocumulus processing of cloud condensation nuclei through collision-coalescence, J. Geophys. Res.-Atmos., 101, 21391-21402, 10.1029/96jd01552, 1996.

20) Page 11, lines 13-16 - In these conditions of fog or relatively small droplets, it is likely that H_2O_2 would be necessary to support significant aqueous-phase production of sulphate. Later, you mention studies about oxidants and H_2O_2 in particular. It would be useful to mention them at this point.

***[A]*:** We rephrased this sentence on page 12, lines 8-11:

"They proposed that activation of condensation mode particles to form fogs or clouds followed by significant production of sulfate from the SO_2 oxidation within droplets (also for nitrate) and fog evaporation are plausible mechanisms for the formation of urban and regional aerosols in the droplet mode."

21) Page 11, line 23 – replace "on the surface including" with "with"
***[A]*:** Changed.

22) Equations 1 and 2 – I'm not sure either are necessary, but references to these reactions go way back (50+ years).
***[A]*:** Thank you. We deleted equation 2 due to their less importance in our study.

23) Page 14, line 17 – "Here we consider two…"
***[A]*:** Changed.

24) Page 15, line 5 – replace "also observed" with "simulated"
***[A]*:** Replaced.

25) Page 16, line 13 – 0.06 m/s is not strong.
***[A]*:** We have deleted "strong".

26) Page 16, line 18 – remove "adverse"
***[A]*:** Removed.

27) Page 17, lines 15-17 – Apply your results to such a model (WRF-CHEM).
***[A]*:** The model performance and discussions have now been added in section 3.4 (page 17, lines 20-28 and page 18, lines 1-22) and supplementary.

"3.4 Model simulation and implications

Vertical concentration distributions of sulfate, nitrate and ammonium were further simulated by WRF-Chem model. The description and configurations of the model can be found in the Supplementary. Figures S13 and S14 show the simulated vertical concentration profiles of sulfate, nitrate and ammonium in autumn and winter and their comparisons with observation. Sulfate was generally underestimated in WRF-Chem model at the upper level, while was in relatively good agreement with observation at the surface. Possible reasons for the underestimations of sulfate are: (1) SO_2 precursors were underestimated at the upper levels (by about 45% to 77%, table S6), possibly due to the insufficient upward transport of SO_2 in the current model, especially in urban area where the urban canopy is low in resolution; (2) heterogeneous/multiphase formations of sulfate in droplets or aerosol water have not been considered enough in current model (Chen et al., 2016; Cheng et al. 2016). Nitrate was overestimated by WRF-Chem model. Here three reasons were put forward: (1) the underestimation of SO_4^{2-} at the upper levels, which consumes less NH_3, facilitates the formation of NH_3NO_4 formation in the fine-mode (Tuccella et al., 2012); (2) heterogeneous reaction of HNO_3 on coarse-mode sea salt aerosols, however, will reduce the formation of fine-mode nitrate (Chen et al, 2016). Therefore, sea salt emissions in current model should be evaluated especially over the coastal regions; (3) the cloud fraction and liquid water content may not be well simulated in the model.

For ammonium, the simulated concentrations were overall consistent with the measured ones except for being slightly overestimated at ground level. The large discrepancies between observation and simulation on sulfate and nitrate suggested that physical and chemical mechanisms in current WRF-Chem model still need to be improved to better predict aerosol mass and composition. Based on our observation, in-cloud aqueous phase reactions and heterogeneous reactions should play important roles in sulfate and nitrate formation, which need to be refined in the model. Evaluation of WRF-Chem model incorporating the above-mentioned mechanisms is beyond the scope of this study and in-depth investigation needs to be done in future. Hence, more studies, such as long-term aerosols and high frequency micrometeorological measurements (Valiulis et al., 2002; Ceburnis et al., 2008; Ervens, 2015), are needed to identify the key aerosol sources and formation pathways, and to further improve the air quality models."

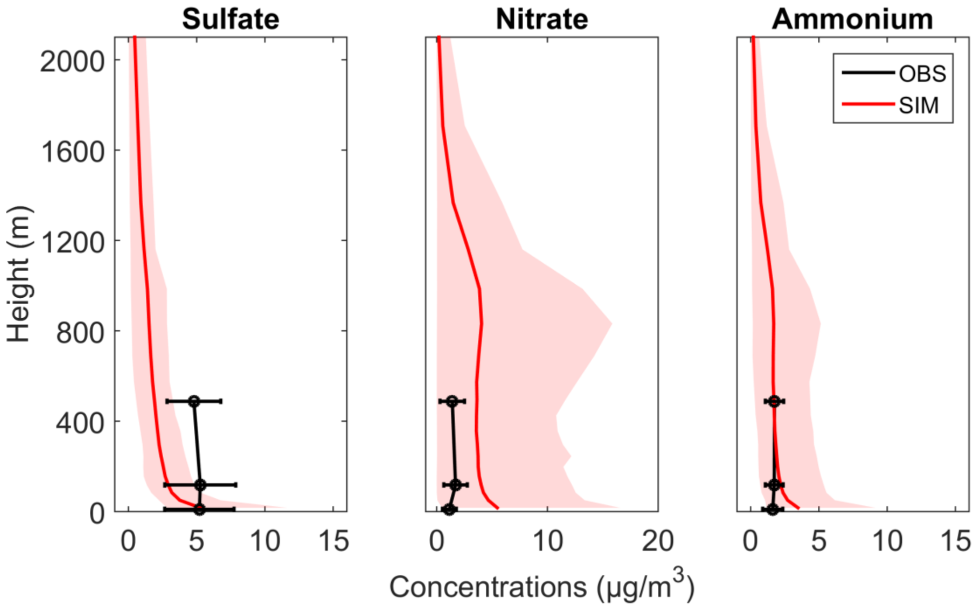

Figure S13. The vertical concentration profiles of sulfate, nitrate, and ammonium in $PM_{2.5}$ during autumn (The red solid lines are the average modeled concentrations and the shaded regions indicate the minimum and maximum values of the simulation; the average measurement data were in black with horizontal error bars).

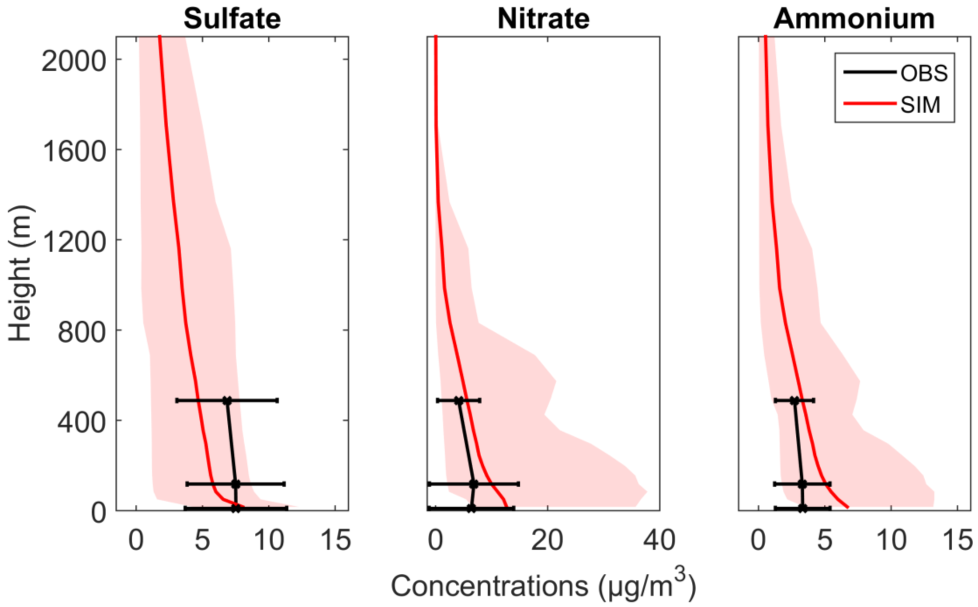

Figure S14. The vertical concentration profiles of sulfate, nitrate, and ammonium in $PM_{2.5}$ during winter (The red solid lines are the average modeled concentrations and the shaded regions indicate the minimum and maximum values of the simulation; the average measurement data were in black with horizontal error bars).

References:

Ceburnis, D., Dowd, C. D. O', Jennings, G. S., Facchini, M. C., Emblico, L., Decesari, S., Fuzzi, S., and Sakalys, J.: Marine aerosol chemistry gradients: Elucidating primary and secondary processes and fluxes, Geophy. Res. Let., 35(7), L07804, https://doi.org/10.1029/2008GL033462, 2008.

Chen, D., Liu, Z., Fast, J. and Ban, J.: Simulations of sulfate-nitrate-ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014, Atmos. Chem. Phys., 16(16), 10707–10724, doi:10.5194/acp-16-10707-2016, 2016.

Chen, Y., Cheng, Y., Ma, N., Wolke, R., Nordmann, S., Schüttauf, S., Ran, L., Wehner, B., Birmili, W., van der Gon, H. A. C. D., Mu, Q., Barthel, S., Spindler, G., Stieger, B., Müller, K., Zheng, G. J., Pöschl, U., Su, H., and Wiedensohler, A.: Sea salt emission, transport and influence on size-segregated nitrate simulation: a case study in northwestern Europe by WRF-Chem, Atmos. Chem. Phys., 16, 12081-12097, 10.5194/acp-16-12081-2016, 2016.

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.: 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, 2016.

Ervens, B.: Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs. Chem. Rev., 115(10), 4157-4198, http://dx.doi.org/10.1021/cr5005887, 2015.

Tuccella, P., Curci, G., Visconti, G., Bessagnet, B., Menut, L., and Park, R. J.: Modeling of gas and aerosol with WRF/Chem over Europe: Evaluation and sensitivity study, Journal of Geophysical Research: Atmospheres, 117, 10.1029/2011jd016302, 2012.

Valiulis, D., Ceburnis, D., Sakalys, J., and Kvietkus, K.: Estimation of atmospheric trace metal emissions in Vilnius City, Lithuania, using vertical concentration gradient and road tunnel measurement data, Atmos. Environ., 36(39-40), 6001-6014, https://doi.org/10.1016/S1352-2310(02)00764-1, 2002.

Supplementary materials

“2.1 Description and configurations of WRF–Chem model

The model used in this study is the chemistry version of the WRF model (WRF–Chem v3.7.1). The WRF model is a mesoscale non-hydrostatic meteorological model that includes several options for physical parameterizations of the planetary boundary layer (PBL), cloud processes and land surface (Skamarock et al., 2008). The chemistry version is a version of WRF coupled with an “online” chemistry model, in which meteorological and chemical components of the model are predicted simultaneously (Grell et al., 2005; Fast et al., 2006). Emission, chemical formation and removal, transport and deposition are considered when WRF–Chem predicts the chemical components. In the numerical modeling, a triple-nested grid with 27/9/3 km resolution domain and 39 layers in vertical is set (Figure S12). The chemistry only run in domain d03 (3 km resolution) and MOZART boundary condition is used for the chemistry run. The simulation period is conducted from 0000 UTC 18 October to 0000 UTC 28 November 2015 as the autumn time period and 0000 UTC 25 December 2015 to 0000 UTC 28 January 2016 as the winter time period. The National Center for Environmental Protection (NCEP) 1 ° × 1 °FNL (Final operational global reanalysis) data are applied as the initial and boundary condition in WRF modeling. The physical and chemical parameterization configurations for WRF-Chem model can be found in Table S4. A region local anthropogenic emission inventory is used within the PRD region (Zheng et al., 2009), which is updated to the year of 2015. For other areas, the Multi-resolution Emission Inventory for China (MEIC, http://meicmodel.org/) is used in this study. MEGAN model version 2.1 is also used for providing the biogenic emissions (Guenther et al., 2006).

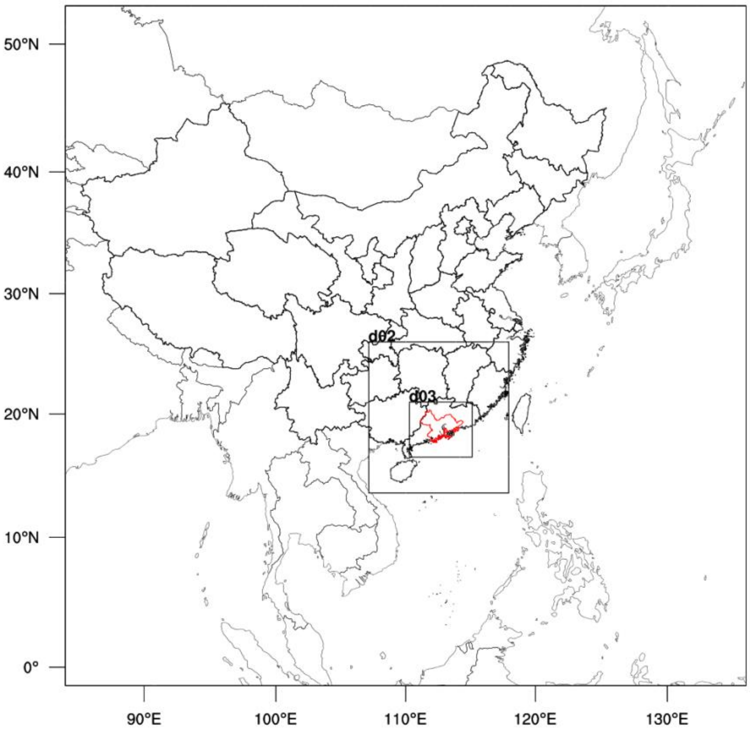

Figure S12. The simulation domain of WRF-Chem model

Table S4. Physical and chemical parameterization configurations for WRF-Chem model

Process	Option
Microphysics scheme	Morrison (2 moments)
Cumulus scheme	Kain-Fristsch
Longwave radiation scheme	RRTM
Shortwave radiation scheme	Dudhia
Boundary-layer scheme	YSU
Land-surface scheme	unified Noah
Urban Surface scheme	UCM
Gas-phase mechanism scheme	CBM-Z
Photolysis scheme	Fast-J
Aerosol scheme	MOSAIC