Please find the following Response to the comments of reviewers.

Reviewers' comments are in plain face.

Authors' responses are in blue color.

Changes in the manuscript are in red color.

Response to the referees' comments

Response to Referee#1:

We would like to thank the reviewer for the careful evaluations and positive comments on our paper, which improved the paper so much. We have revised the manuscript according to the reviewer's detailed comments. Please find the responses to the reviewers.

Comments to the Author:

It is a pleasure to review the manuscript "Properties of aerosols and formation mechanisms over southern China during the monsoon season" by Chen et al. This manuscript addresses an important science question: what are the characteristics of size distribution and formation of atmospheric aerosols in southern China and how they are affected by local and long-range transport? Given the heavy PM concentrations in that region, answering this question has practical implications for public health. This study makes diligent use of a unique in-situ dataset, modeling, and remote-sensing products, investigates various physical and chemical mechanisms of aerosol (including secondary) formation and evolution, and provides some new insights into this scientific issue. The paper is comprehensive in its scope, well organized and well written, and the research quality is high. I suggest to accepting this manuscript after the authors clarify the following points, which are mostly minor concerns and editorial changes:

- Line 150, the model required the use of measured: did you have all those measurements from your site observations?

Response:

Yes, all of these required parameters were observed at these three sites, including ambient temperature, relative humidity, and the concentration of sulfate, nitrate and ammonium. We have added more information about chemical analysis in line 151-156:

'The mass concentrations of six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) were analyzed using an ion chromatography (ICS-3000, DIONEX). Thermal Optical Transmittance (TOT) technique was employed to analyze the quartz filter samples to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) by the use of Sunset Laboratory OCEC Carbon Aerosol Analyzer.'

- Line 180, use of GDAS: why did you use higher resolution WRF/Chem meteorological fields in place of GDAS?

Response:

WRF model could provide higher resolution meteorological data, further to improve the dispersion simulations and lead to an overall better simulation (Stohl, 1998). In addition, a novel convective scheme has been added in the FLEXPART –WRF (Brioude et al., 2013), which also could improve the model simulation, especially for finer scale applications. So meteorological fields provided by WRF instead of GDAS were used in this study. We have added an explanation in line 205-209:

' The application of FLEXPART –WRF with a novel convective scheme being added improves the dispersion simulations and results in an overall better simulation, especially for finer scale applications (Brioude et al., 2013; Stohl, 1998). In this case, the region was modeled with a spatial resolution of 27×27 km and a temporal resolution of 1 hour.'

 - Line 187: the sentence is confusing. It looks like you use WRF simulated fields as input to FLEXPART, which contradicts with the previous statement of using GDAS?

Response:

Just as the reviewer said, WRF simulation provided meteorological fields for ELEXPAET, while GDAS was applied by HYSPLIT. So we have deleted this sentence and just kept the previous statement in line 201-205:

'HYSPLIT uses single air parcels to compute trajectories with the use of Global Data Assimilation System (GDAS, 1°×1°) as input data. FLEXPART, on the other hand, uses a larger number of air parcels to compute trajectories based on the meteorological predictions provided by mesoscale model WRF.'

 - Line 200: Which two sites are referring to here? There are three sites listed in Table 1.

Response:

We are sorry for our imprecise statement. Actually the range of [0.52, 0.55] and [0.72, 0.76] is the range for three sites not only for two sites. We have re-written this part to avoid confusion in line 226-228:

'In terms of the mass size distribution, the percentage of $PM_{1.0}$ to PM_{10} was 60.2%, 66.3% and 75.0%, and $PM_{2.5}$ to PM_{10} was 88.0%, 92.6%, 91.7% in GZ, ZH and JFM, respectively.'

 - Line 203-208: very nice analysis!

Response: Thanks so much for the review's acceptance.

- Line 287: something is missing the sentence "far-upwind urbanization and biomass burning". Urbanization cannot be transported.

Response:

Thanks for the reviewer's reminder, we have added more information in line 316-319:

'We investigated these days and find that emissions that long-range transported from far-upwind areas with highly urbanization or with the existence of biomass burning are responsible, as discussed later in this paper.'

- Line 304,"the sites":which sites? - The quality of some figures are acceptable but not very good. For instance: o Figs 3c&d: the figure labels need to be improved. It is hard to read. o Fig 4:again the x-axis label is hard to read. o Fig 6 labels need to be improved.

Response:

Thanks for pointing out this issue. The sites represent the three sites. We have clarified it in line 339-341:

'Additionally, it was determined that during these times at the three sites there was an abnormally high amount of low cloud cover 60-70% and a relatively higher relative humidity (75~83%) (Table 2).'

Thanks so much for the review's suggestion, we have improved and re-plotted the figures in the main text.

- Line 417:a nice example of using backward trajectories to test your hypothesis!

Response: Thanks so much for the review's acceptance.

- Section 3.6: can authors elaborate on the MODIS Fire products? Are these daily products or twice a day or 8-day?

Response:

Thanks for the reviewer's suggestion, the MODIS fire products are daily products, we have provided some information about MODIS Fire products in the section *2 Measurements and methodology* in line 184-193:

'Aerosol optical depth (AOD), fire products including Fire Radiative Power (FRP), and Fire Quality Assurance [QA] data, were obtained from the MODIS sensors aboard both the AQUA and TERRA satellites. Specifically, we obtained the Collection 6, 3km Level 2 swath product for AOD (Remer et al., 2013), and Collection 5.1, 1km Level 2 swath products for FRP and QA (Giglio et al., 2006). The Collection 5.1 active fire products are daily products and have been improved based on the previous collection 5.0 products. All of the data are cloud-screened, with AOD data being computed using different algorithms over land and water, and the fire data using 19 different channels for quality assurance. We only accept values for FRP and Fire Count where the QA is at least 90%.'

And in line 550-555:

'MODIS fire hotspots are not very useful in wet and tropical regions. Since MODIS fire hotspots are obstructed by both clouds and high levels of aerosols in the atmosphere, both of which are found associated with tropical forest fires. Additionally, due to the highly wet ground surface, a significant amount of the fires may low temperature and therefore not observable using the MODIS sensors (Cohen, 2014, Giglio et al., 2006; Yu et al., 2015).'

Editorial suggestions:

- Line 92: replace "The data is" by "those data were"

Response:

Thanks and we have modified it.

- Line 94: insert "of size distribution" between "characteristics" and "in"

Response:

Thanks and we have added it

- Lin 98-99: something is missing in "and the impacts mixing sea-salt and urban pollutants"

Response:

Thanks for reminding and we have added more information in line 106-107.

'and the impacts mixing sea-salt and urban pollutants on the characteristics of aerosol size distributioin .'

- Line 103: it would be good to show photos of these sites to give an idea of site environments

Response:

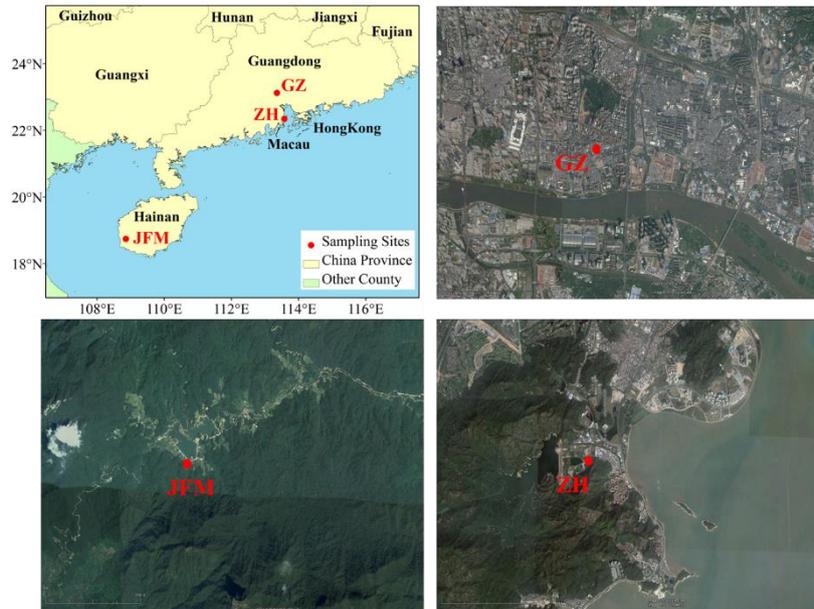Thanks for the suggestion, we have added photos of these sites in Figure 1

Figure 1. Location of sampling sites in Southern China: GZ (Guangzhou), ZH (Zhuhai), and JFM (Jianfeng Mountain) and their surrounding environments

- Line 110: replace "The first site was set at (23.12N, 113.36E), on" by "The first site (23.12N, 113.36E), is located on"

Response:

Thanks and we have modified it.

- Line 111: replace "an urban mega-city" by "a mega-city"

Response:

Thanks and we have modified it.

- Line 149: delete "to"

Response:

Thanks and we have modified it.

- Line 170: replace "All of the data is" by "All data are"

Response:

Thanks and we have modified it.

- Line 194: delete "mass"

Response:

- Line 212-213: replace "no matter what the particle size was" by "irrespective of particle size"

Response:

Thanks and we have modified it.

- Line 217: should "formed" be "from"

Response:

Thanks and we have modified it.

- Line 219: delete "with"

Response:

Thanks and we have modified it.

– Line 226: delete "of"

Response:

Thanks and we have modified it.

 - Line 242: replace "showing" by "shows"

Response:

Thanks and we have modified it.

- Line 281: replace "high levels" by "high-level"

Response:

Thanks and we have modified it.

- Line 288: replace "as talked about later" by "as discussed later in this paper"

Response:

Thanks and we have modified it.

- Line 303: replace "show" by "shown"

Response:

Thanks and we have modified it.

- Line 312: replace "evidence" by "evidenced"

Response:

Thanks and we have modified it.

- Line 323: replace "of the" by "shows that"

Response:

Thanks and we have modified it.

- Line 489: delete the second "instead"

Response:

Thanks and we have modified it.

- Line 527-529: replace "Based on specific case studies, some models of the air flow, and remote sensing, the impacts of chemistry and atmospheric transport were investigated" by "These site observations, together with model simulations and Remote-sensing data, were used to investigate impacts of chemistry and atmospheric transport".

Response:

Thanks and we have modified it.

- Line 547: delete "further"

Response:

Thanks and we have modified it.

- Line 554: be specific on "they". What are they?

Response:

Thanks and 'they' represent 'OC and EC', we have clarified it.

Reference:

Brioude, J., Arnold, D., Stohl, A., Cassiani, M., Morton, D., Seibert, P., Angevine, W.,

Evan, S., Dingwell, A., Fast, J.D., Easter, R.C., Pisso, I., Burkhart, J. and Wotawa, G.: The Lagrangian particle dispersion model FLEXPART-WRF version 3.1, Geoscientific Model Development, 6, 1889-1904, doi:10.5194/gmd-6-1889-2013, 2013.

Stohl, A.: Validation of the lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data, Atmospheric Environment, 32, 4245-4264, doi:10.1016/S1352-2310(98)00184-8, 1998.

Yu, C., Chen, L.F., Li, S.S., Tao, J.H. and Su, L.: Estimating Biomass Burned Areas from Multispectral Dataset Detected by Multiple-Satellite, Spectroscopy and Spectral Analysis, 35, 739-745, doi:10.3964/j.issn.1000-0593(2015)03-0739-07, 2015.

Response to Referee#2:

We would like to thank the reviewer for the careful evaluations and positive comments on our paper, which improved the paper so much. We have revised the manuscript according to the reviewer's detailed comments. Please find the responses to the reviewers.

Comments to the Author:

In this study, size distributions of chemical components of aerosols were observed at three stations located in urban, suburban, and background areas. Results were thoroughly discussed from various aspects. I think this is a nice paper, but I feel the explanations are not enough or not adequate. They should be modified before this paper is accepted for publication.

A lot of previous studies are adequately referred. But, what are new findings of this study? Results of this study may be easily imaginable based on previous studies referred in this paper. The importance and significance, and the differences from previous studies should be made insisted in the introduction.

I think one problem of this manuscript is that the overall observed data are not shown and not discussed. Are all the data obtained for the target two months those shown in Figure S1? If so, this figure should be shown in the main text and overall explanation for them are necessary at first. If it is missing, I have an impression that only the day which are easy to add explanations are picked up for analyses.

Response:

(1). A series of studies about the mass size distribution of aerosol chemical components have conducted at a specific site over Southern China during the past decade (Lan et al., 2011; Liu et al., 2008; Yang and Wenig, 2009; Zhang et al., 2015). Compared with the previous studies, this paper presents a unique combination of analytical and measurement techniques. We use measurements of chemical properties and size distribution conducted at three different functional sites, coupled with multiple modeling results, and reprocess remote sensing products using statistical methods, all in tandem with each other, which is not commonly found in other studies. Furthermore, we test our approach in Southern China, which is one of the regions of the world with the most complex meteorology, coming under the influence of the Monsoon, with shifting winds from Continental and Oceanic sources. Additionally, the season tested is a transition period, during which there were significant meteorological contributions from both remote Continental sources as well as oceanic sources. On top of this, Southern China has a combination of high temperature and relative humidity, strong radiative flux, and high oxidative capacity, leading to the promotion of significant secondary aerosol formation.This paper will provide detailed information on size-resolved aerosol chemical components and discussion on the formation mechanism in a typical region and period. We have emphasized the importance and significance in the introduction in line 84-99:

'A series of studies about the mass size distribution of aerosol chemical components have conducted at a specific site over Southern China during the past decade (Lan et al., 2011; Liu et al., 2008; Yang and Wenig, 2009; Zhang et al., 2015). Compared with the previous studies, this paper presents a unique combination of analytical and measurement techniques. We use measurements of chemical properties and size distribution conducted at three different functional sites, coupled with multiple modeling results, and reprocess remote sensing products using statistical methods, all in tandem with each other, which is not commonly found in other studies. Furthermore, we test our approach in Southern China, which is one of the regions of the world with the most complex meteorology, coming under the influence of the Monsoon, with shifting winds from continental and oceanic sources. Additionally, the season tested is a transition period, during which there were significant meteorological contributions from both remote continental sources as well as oceanic sources. On top of this, Southern China has a combination of high temperature and relative humidity, strong radiative flux, and high oxidative capacity, leading to the promotion of significant secondary aerosol formation.'

(2). The overall observed data for the target two months were shown in Figure S1, which has now been moved into the paper as Figure 2. Additionally, all of the data obtained for the target months is displayed in line 145-150:' A total of 10, 8 and 20 sets of size-segregated particle samples were collected in GZ, ZH and JFM, respectively during the periods of May and June in 2010 (shown in Figure 2). A single set of sample collection lasted for approximately 24h in GZ and ZH, and 48h in JFM. Since the aerosol concentration was relatively low in remote JFM site, we extended the sampling time as long as 48h to allow the chemical components to be detected.'and line 217-223:' The time series of PM_{18} chemical compositions at the three sites during the sampling period were shown in Figure 2. The average concentration and standard deviation of PM_{18} was 47.8±20.8, 24.3±12.1 and 8.1±2.7 µg m^{-3} in GZ, ZH and JFM, respectively. The mean and range of PM_{18} in highly urban GZ was both higher and wider than in suburban ZH and rural JFM, with the respective ranges being 23.3~93.7, 13.3~35.1, 4.7~14.3µg m^{-3} in the three sites. Maximum concentration was found both on 12th Jun. in GZ and ZH, while it was on 3rd Jun. in JFM (to be discussed later).'

Specific comments are as follows:

-Line 58-60 Cohen and Wang (2013) appear twice.

Response:

Thanks for pointing out that and we have deleted the repeated reference.

-Line 60-62 It may be difficult for some readers to understand modes listed here. It is better to briefly explain their definitions. Actually, this sentence is obvious because the four modes listed here (Aitken, condensation, droplet, and coarse modes) cover

almost entire aerosols.

Response:

Thanks for the suggestion and we have provided the definition for the four modes in line 59-61:

'In the environment, the most important aerosol processes occur over the Aitken (<0.1 μm), condensation (~0.1-0.5 μm), droplet (~0.5-2.0μm), and coarse (>2.0 μm) size modes (Seinfeld and Pandis, 2006)'

Just as the reviewer mentioned, the sentence is obvious because the four modes cover almost entire aerosols, what we want to emphasize is the different processes occurred on different modes as shown in line 61-63:

'new particles are formed in the Aitken mode via condensational growth and coagulation of nucleation mode particles, and droplet mode particles are produced by in-cloud processing or aqueous reactions.'

Line 61-62 I suppose that new particles via the nucleation form in the Aitken mode, and not in the condensation mode. Do "new particles" mean those form on existing aerosols via condensation of gases?

Response:

Thanks for pointing out this issue. Just as the reviewer suggested, the new particles are formed in the Aitken mode via nucleation formation. Here, new particles mean that condensational growth and coagulation of nucleation mode particles. We have modified it in line 61-62:

'new particles are formed in the Aitken mode via condensational growth and coagulation of nucleation mode particles'

Line 65 "Different" source types from what? What are differences?

Response:

Coarse mode aerosols usually originate from natural or mechanically produced anthropogenic sources, for example, sea spray, soil dust, dust storm, active biological aerosol (pollen, spores), etc. We have clarified this sentence in line 65-68:

'On the other hand, coarse mode aerosols usually come from very different sources than smaller aerosols. For example, natural sources such as sea spray, dust, soil, and active biological aerosols are unique and therefore provide further information about the aerosol distribution at a given location'

Line 75-76 Pierson and Brachaczek should be (1998), not (1988).

Response:

Thanks for pointing out this mistake and we have amended it.

Line 138 What do "6 sets" correspond to? There are 7 cut-off diameters.

Response:

Thanks for pointing out this clerical error and it should be 7 sets. We have corrected it in the paper.

Line 142-143 I could not understand why number of samples becomes these number. The sampling campaign was performed for two months. 24h sampling was performed every other day in GZ and ZH. So maximum number of samples is around 30, isn't it? 48h sampling was conducted every day in JFM. Does it mean two sampling instruments were used to obtain a sample for 48h every day? How the total number of samples in JFM becomes 140 only for two months? How many days the samples were properly collected and missing? Please add more explanations to understand overall pictures of the samples used in this study.

Response:

We are sorry for our imprecise statement. The sampling was performed on a specific day, but not every other day, the specific date was shown in Figure 2. Only one instrument was operated in JFM since the concentration of aerosol was relatively lower, so we extended the sampling time as long as 48h to allow for sufficient connection of the chemical components so that they could be detected. We have clarified it in line 143-150:

'To attain size-segregated particle samples, a 6-stage High Flow Impactor (MSP) with an airflow rate of 100 L min^{-1} was employed, with cutoff diameters (D_p) of 18 (inlet), 10, 2.5, 1.4, 1.0, 0.44 and 0.25 μm. A total of 10, 8 and 20 sets of size-segregated particle samples were collected in GZ, ZH and JFM, respectively, during the periods of May to June in 2010 (shown in Figure 2). A single set of sample collection lasted for approximately 24h in GZ and ZH, and 48h in JFM. Since the aerosol concentration was relatively low in JFM, we extended the sampling time as long as 48h to make the chemical components detected.'

Line 144 Detailed information of the in-lab chemical analytical techniques is described in Zhang et al. (2013a), but at least it is necessary to mention also here which species were analyzed in this study.

Response:

We agree with the comment and we have added more information about chemical analysis in line 151-156:

'The mass concentrations of six cations (Na$^+$, NH$_4^+$, K$^+$, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and seven anions (F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, SO$_4^{2-}$, NO$_3^-$ and PO$_4^-$) were analyzed using an ion

chromatography (ICS-3000, DIONEX). Thermal Optical Transmittance (TOT) technique was employed to analyze the quartz filter samples to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) by the use of Sunset Laboratory OCEC Carbon Aerosol Analyzer.'

Line 145-147 The background literatures should be explicitly shown here, especially for the definition of droplet particles.

Response:

Thanks for the suggestion and we have added more information in line 159-163:

'To be consistent with the background literature (4 modes include Aitken (<0.1 μm), condensation (~0.1-0.5 μm), droplet (~0.5-2.0 μm), and coarse (>2.0 μm)) (Seinfeld and Pandis, 2006), and the constraints of the size bins measured in this study, we implement 2.5 μm as the cut-off size to separate fine and coarse particles, and the size bins from 0.44-1.4 μm was defined as droplet particles in this study.'

Line 155 Is it possible to ignore effects of other ions? Is it just because only these three ions were detected? Weren't other ions used in AIM-II model, either?

Response:

Actually, the mass concentrations of six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) were analyzed in this study, as we have added the chemical analysis in section *2 Measurements and methodology*. The possible error would be introduced due to the excluding of other ions (e.g. K^+, Na^+, Cl^-), but which exerted only a minor influence on the estimation of aerosol acidity due to their lower concentration. And, Yao et al. (2006) found that AIM provides the most accurate prediction compared with other models, like ISORROPIA and SCAPE2.We have added an explanation in line 163-169:'Although we were not able to directly measure aerosol water content, given its importance for the study here, we instead estimated the amount by the use of E-AIM model II (Clegg et al., 1998), as it provides the most accurate prediction compared with other models, like ISORROPIA and SCAPE2 (Yao et al., 2006). The input parameters of the E-AIM model II are tempreture, relative humidity, strong acidity (H^+), molar contentrations of NH_4^+, SO_4^{2-} and NO_3^- ions (Clegg et al., 1998)' and in line 172-174:'The calculation of strong acidity would introduce possible errors due to the exclusion of other ions(e.g. K^+, Na^+, Cl^-), but which only exerted a minor influence on the estimation of aerosol acidity due to their lower concentration (Yao et al., 2006).'

Line 176-183 Differences between HYSPLIT and FLEXPART are described, but what is a specific reason why these two models were used in this study? What are expectations from these two models in the context of this study?

Response:

HYSPLIT and FLEXPART were applied to determine the origin of air masses. Furthermore, FLEXPART could identify the relative importance of source region that affected the receptor visually. We have added some information to illustrate our expectation in line 196-201:

'Two Lagrangian particle dispersion models, the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hes, 1998) and FLEXPART coupled with The Weather and Research and Forecasting (WRF) model (FLEXPART –WRF) (Stohl et al., 1998; Brioude et al., 2013) were applied to determine the origin of air masses in this study, Compared with HYSPLIT, FLEXPART can identify the relative importance of source region that affected the receptor visually.'

Line 198-200 Does it mean that the percentages of all the samples collected at all the locations fall within such the narrow range? That is kind of incredible. Or just the averaged values shown in Table 1 fall within this range? That is nonsense. The percentages calculated for each sample should be discussed here.

Response:

Thanks for the comment. The percentage is the averaged values at the three sites shown in Table 1. We have re-written this part to avoid confusion in line 224-229:

'Table 1 listed the average concentration of chemical components in the given size-resolved particle ($PM_{1.0}$, $PM_{2.5}$ and PM_{10}) and their percentage of PM_{10} at the three sites. In terms of the mass size distribution, the percentage of $PM_{1.0}$ to PM_{10} was 60.2%, 66.3% and 75.0%, and $PM_{2.5}$ to PM_{10} was 88.0%, 92.6%, 91.7% in GZ, ZH and JFM, respectively. When considered as a whole, it is the smaller sized particles that dominate the aerosol loading at all three of these sites.'

Line 203 What does "the majority of individual chemical species" mean? A reason of this question is because it is unclear which species were detected in this study.

Response:

Thanks for pointing out this issue. We have added more information on aerosol chemical components in line 151-156:'The mass concentrations of six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) were analyzed using an ion chromatography (ICS-3000, DIONEX). Thermal Optical Transmittance (TOT) technique was employed to analyze the quartz filter samples to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) by the use of Sunset Laboratory OCEC Carbon Aerosol Analyzer.' and we have clarified it in line 229-231:'Looking at the data on a species-by-species level, most of chemical components were concentrated in fine mode particles, which contributed at least 57% to $PM_{2.5}$'

Line 207-208 Again, which are "detected chemical components"?

Response:

Thanks for pointing out this issue. The detected chemical components including six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}), seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) and carbonaceous aerosol (OC and EC). We have added more information on aerosol chemical components in line 151-156:

'The mass concentrations of six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) were analyzed using an ion chromatography (ICS-3000, DIONEX). Thermal Optical Transmittance (TOT) technique was employed to analyze the quartz filter samples to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) by the use of Sunset Laboratory OCEC Carbon Aerosol Analyzer.'

Line 215-216 References of "the nature of the sources" should be shown here, especially for shipping sources. Are there any references showing shipping sources are dominant around this region?

Response:

Thanks for pointing out this issue and we have added the related references in line 241-245:

'These findings are consistent with the nature of the sources of sulfur from industrial and power plant (Zheng et al., 2009). In addition, shipping source was becoming increasingly vital for SO_2 emission with an increment of 12% per year in this region (Lu et al., 2013; Zhou et al, 2016)'

Line 217-218 I suppose mobile vehicles are not main sources for sulfate. What is "high temperature industry"?

Response:

We agree with the comment that mobile vehicle are not the main sources of sulfate. High temperature industry reprensent industry and power plant. So we have re-written this sentence to avoid confusion in line 246-247:

'Nitrate, mainly formed from the oxidation of NOx emitted by mobile vehicles and power plants, showed a remarkable difference between urban and background site'

Line 220-221 How can rapid oxidation of precursor species be a reason of differences between urban and background sites? I suppose the phase equilibrium should be also one of important reasons of differences because nitrates would move to gas phase while transported to background areas.

Response:

We agree with that phase equilibrium is one of the important reasons in background areas.However, rapid oxidation of precursors is the main source for nirate in urban area. So we have changed the expression in line 249-253:

 'This is consistent with its more rapid oxidation of its abundant precursor species, especially so in the urban atmosphere (Cohen et al., 2011). In addition, phase equilibrium was another important reason for the discrepancy since nitrate would tend to exist as gas phase while transported to background areas (Seinfeld and Pandis, 2006).'

Line 263-265 The percentages shown here are against what?

Response:

Thanks for pointing out this issue. We have deleted this sentence.

Line 265-266 Droplet mode nitrate is formed similarly to sulfate. Does it mean that nitrate is also formed via aqueous reactions? If so, what kind of aqueous reactions? If not, why nitrate is included in the droplet mode?

Response:

Thanks for pointing out this issue. The formation of droplet mode nitrate is unlike sulfate. Droplet mode nitrate was dominated by the heterogeneous aqueous reaction of gaseous nitric acid (HNO_3) and ammonia (NH_3) on the wet surfaces of pre-existing aerosols with ammonia-rich environment, otherwise by heterogeneous hydrolysis of N_2O_5 on the pre-existing aerosols with ammonia-poor conditions. The dissociation equilibrium of NH_4NO_3 highly depends on temperature and humidity (Stelson and Seinfeld, 1982). We have re-written these sentences in line 293-298:

'Droplet mode nitrate was dominated by the heterogeneous aqueous reaction of gaseous nitric acid (HNO_3) and ammonia (NH_3) on the wet surfaces of pre-existing aerosols within ammonia-rich environment, otherwise by heterogeneous hydrolysis of N_2O_5 on the pre-existing aerosols within ammonia-poor conditions. The dissociation equilibrium of NH_4NO_3 highly depends on temperature and humidity (Stelson and Seinfeld, 1982)'

Line 289 What is coarse OC with a possible source of biological aerosol? Any references?

Response:

The possible source for coarse OC would be active biological aerosol, for example, pollen, spores, plant fragment. We have added more information in line 319-323:

'Additionally, there is some coarse mode OC present in JFM, suggesting a possible source of biological aerosol (e.g. pollen, spores and plant fragment) (Heald and

Spracklen, 2009; Seinfeld and Pandis, 2006; Zhang et al., 2015), which is consistent with the large amounts of vegetation present in that region (Zhang et al., 2015).'

Line 298-301 I could not understand this sentence. How the author judged the average size was small, the particles were relatively young, and indicative of new particle formation? Are all of these coming from the fact that droplet mode sulfate accounted for about two thirds of the total mass concentration of sulfate? More detailed explanations are necessary to reinforce this discussion.

Response:

Thank you for your suggestion. After careful analysis, we admit that we could not draw this conclusion just based on the fact that droplet mode sulfate accounted for about two thirds of the total mass concentration of sulfate. Therefore, we have deleted this sentence to avoid the confusion.

Line 306-308 That is true for selected days. But, how about for days not selected? Low cloud cover 60-70% and higher relative humidity were observed only for the days selected here?

Response:

Thanks for pointing out this issue. In order to study the aqueous-phase reaction of droplet mode sulfate, cases with the air masses came from continent were excluded to avoid the effect of transported pollutants on the concentration of sulfate. Then two cases with a concentration of droplet sulfate above the mean plus one standard deviation were selected as typical cases in each site. It was found that the selected cases happened under the conditions of higher relative humidity and low cloud cover. Lower cloud cover (60-70%) and higher relative humidity were also observed for other non-selected days, which also shared with higher percentage (60% above) of sulfate in droplet mode sulfate to total sulfate but with relatively lower absolute concentrations. Therefore cased with extremely high droplet mode sulfate were selected to study, which were more obvious to observe. We have added more description in line 327-334:

'In order to study the aqueous-phase reaction of droplet mode sulfate, cases with the air masses came from continent were excluded to avoid the effect of transported pollutants on the concentration of sulfate. Then two cases with a concentration of droplet sulfate above the mean plus one standard deviation were selected as typical cases in each site (8th and 12th May in GZ, 12th May and 1st Jun. in ZH, and 4th and 13th May 2010 in JFM), which were more obvious to observe to investigate the effect of aqueous-phase reaction in the formation of droplet mode sulfate (blue shade in Figure 2).'

Line 335 Are the words "Accumulation mode" and "condensation mode" used for the

same meaning?

Response:

The diameter for accumulation mode particles was ~0.1-1μm as for WRF/Chem model, while the diameter for condensation and droplet mode was ~0.1-0.5 and ~0.5-2.0μm. So accumulation mode and condensation mode are not exactly the same, but the diameter for accumulation mode is between the range for condensation and droplet mode.We have clarified it in line 370-372:

'Simulation of these conditions using WRF/Chem indicates that the rapid growth of both Aitken and accumulation (~0.1-1μm) mode sulfate started at 07:00 LT and peaked at 08:00-09:00 LT'

Line 352 Is it possible to judge that fine mode chloride and sodium are coming from sea salts? Are there any anthropogenic sources of chloride and sodium in the fine mode? If chloride and sodium in the fine mode are emitted separately from difference sources from sea salts, discussions on chloride depletion in the fine mode in this paragraph is not appropriate.

Response:

Thanks so much for pointing out this issue. Fine mode Na^+ and Cl^- probably came from combustion sources, e.g. biomass burning and coal combustion (Wang et al., 2005), but the contributions were insignificant since the magnitude of Na^+ and Cl^- from combustion sources is many orders of magnitude smaller than oceanic sources. Furthermore, if the biomass burning source were significant, it would clearly also show up in terms of the K^+ and BC/OC ratio, as explained later in the section *3.6 Quantifying the impacts of fires*.

We totally agree with the reviewer's comment that the anthropogenic emissions would also affect chloride depletion in fine mode particles. So in the revised version, we introduced an indicator, concentration of chloride depletion ($[Cl_{dep}]$), to simply remove the possible effect of non-sea salt emissions. Therefore, samples with possible non-sea salt sources were excluded from analysis to avoid the effect of non-sea salt emission on chloride depletion in fine mode particles. We have clarified it in line 379-399:

'The mass size distribution of Cl^- and Na^+ showed a similar pattern to nitrate at the three sites, peaking in coarse mode particles (Figure 5 (a-c)) with an average percentage of 43%, 62% and 43% for coarse mode Na^+, 53%, 76% and 74% for coarse mode Cl^- in GZ, ZH and JFM, respectively, suggesting the main sea salt sources. Na^+ and Cl^- shown a bi-modal distribution in GZ, illustrating the combustion emissions, e.g. biomass burning or coal combustion for fine mode Na^+ and Cl^- (Wang et al., 2005), but the contributions were insignificant since the magnitude of Na^+ and Cl^- from combustion sources is many orders of magnitude smaller than oceanic sources. Furthermore, if the biomass burning source were significant, it would clearly

also show up in terms of the K^+ and BC/OC ratio, as explained later in the section **3.6 Quantifying the impacts of fires**.

The concentration and percentage of chloride depletion ($[Cl_{dep}]$ and $\%Cl_{dep}$) were calculated using Eq. (2-3), where $[Cl_{meas}^-]$ and $[Na_{meas}^+]$ are the measured molar concentrations of Cl^- and Na^+, respectively; 1.174 was the molar ratio of Cl^- to Na^+ in sea water (Yao et al., 2003b).

$$[Cl_{dep}]=1.174[Na_{meas}^+]\text{-}[Cl_{meas}] \tag{2}$$

$$\%Cl_{dep}=\frac{1.174[Na_{meas}^+]\text{-}[Cl_{meas}]}{1.174[Na_{meas}^+]}*100\% \tag{3}$$

The positive value of $[Cl_{dep}]$ represents chloride depletion, otherwise means the chloride enrichment, suggesting additional sources was existed for Cl^- excluding sea salt. Therefore, samples with negative $[Cl_{dep}]$ were excluded from analysis to avoid the effect of non-sea salt emission on chloride depletion.'

Line 362 What does "calculated ammonium" mean? How was it calculated?

Response:

Calculated ammonium was equal to $2*[nss\text{-}SO_4^{2-}]+[NO_3^-]$, where $[nss\text{-}SO_4^{2-}]$ and $[NO_3^-]$ reprents the molar concentarion of non-sea-salt SO_4^{2-} (i.e., $[nss\text{-}SO_4^{2-}]=[SO_4^{2-}]-0.14\times[Cl^-]$) and NO_3^-. We have added related information in line 413-416:

'Calculated ammonium was equal to $2*[nss\text{-}SO_4^{2-}]+[NO_3^-]$, where $[nss\text{-}SO_4^{2-}]$ and $[NO_3^-]$ reprents the molar concentarion of non-sea-salt SO_4^{2-} (i.e., $[nss\text{-}SO_4^{2-}]=[SO_4^{2-}]-0.14\times[Cl^-]$) and NO_3^- (Huang et al., 2004)'

Line 381 What is another important non-linear effect? It is unreasonable to discuss reasons of percentage differences only based on humidity. A lot of other factors like emission sources on pathways should be considered.

Response:

Thanks for pointing out this issue. There are indeed three important sources of non-linearity, but we do not mention them all. First, chemical/aqueous phase non-linearity. Second, meteorological non-linearity. When the wind direction changes from ocean, to land, or to long-range transport, that the chemical compositions are different, as well as the time under which in-situ chemistry could occur. Third, emissions non-linearity. When there are fire sources, the emissions are significantly different from when there are non-fire sources, and this extends to the NO_2 emissions (and hence NOx).

We estimated the chloride depletion in ZH and JFM when the air masses came from the ocean or continent. Actually, it didn't show much difference for %Cl$_{dep}$ no matter where the air masses came from. We agree with the reviewer's comment that antoher factors like emission sources also need to be considered. So drawing the conclusion that 'suggesting another important non-linear effect between maritime aerosols and anthropogenic NOx' just based on the percentage difference would be inadiquate. Therefore we have deleted this paragraph to make the paper more robust.

Line 403 Please add the definitions of Sulfur Oxidation Ratio and Nitrogen Oxidation Ratio, and their importance in the context of this study.

Response:

The Sulfur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR), which were used to indicate the degree of transformation of secondary aerosol (Wang *et al.,* 2005). We have added related information in line 454-461:
'The Sulfur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) are applied to indicate the degree of oxidation of SO$_2$ and NO$_2$ precursor gases (Wang *et al.,* 2005). The equations for SOR and NOR are calculated as SOR=n-SO$_4^{2-}$/(n-SO$_4^{2-}$+n-SO$_2$) andNOR=n-NO$_3^-$/(n-NO$_3^-$+n-NO$_2$, where n-SO$_4^{2-}$and n-NO$_3^-$are the molar concentrations of particulate SO$_4^{2-}$ and NO$_3^-$ and n-SO$_2$ and n-NO$_2$ are the molar concentrations of the precursor gases SO$_2$ and NO$_2$. SOR and NOR was also the highest On 12th June at the range of 0.44-1.0 μm in GZ with the value of 0.20 and 0.17, respectively'

Line 439 I cannot understand discussions around here. Why can discussions in this paragraph be a reason of long-range transport? As mentioned in the line 425-426, wind speed was very low. Isn't it possible to explain high concentrations and aging under stagnant air around urban area? Do the discussions in this paragraph enable to clearly distinguish effects of stable air and long-range transport?

Response:

Thanks for pointing out this issue. Discussion in this paragraph was only one aspect of long-range transport, the following discussions were additional evidences to support this conclusion. We clearly explain this more precisely as follows:
First, HYSPLIT and FLEXPART-WRF showed that the air flow was mostly from Southeast Asia at levels over the boundary layer, and hence had undergone long-range transport. Second, the windspeed near the surface suddenly became very low. Therefore, there had been a rapid change in the windspeed. Based on conservation laws for air mass, it would be excepted for there to be some reasonable amount of mixing of the air vertically. This was consistent with the finding that some of the air which had undergone long-range transport would have mixed into the surface region. Third, the chemical concentrations of BC, OC, and K$^+$ were all elevated, Na$^+$ and Cl$^-$ size distribution were peaked in the 1.0-1.44 μm size range, and they were bi-modal distribution in ZH, which were also consistent with a significant fire contribution.

Fourth, the time-gap between when the air parcels left Southeast Asia and arrived in Guangzhou and Zhuhai, correspond very well with times during which the EOFs over Southeast Asia showed a significantly large amount of smoke (Figure 10), which would be discussed in section **3.6. *Quantifying the impacts of fires***.

We make clear this in the text in line 495-515:

'Except for in-situ formation, long-range transport was another impact factor. First, HYSPLIT (Take GZ for example, Figure S1(a)) and FLEXPART-WRF (Figure 6(f)) showed that the air flow was mostly from Southeast Asia at levels over the boundary layer ((Figure 6(f)), and hence had undergone long-range transport. Second, the windspeed near the surface suddenly became very low. Therefore, there had been a rapid change in the windspeed. Based on conservation laws for air mass, it would be excepted for there to be some reasonable amount of mixing of the air vertically. This was consistent with the finding that some of the air which has undergone long-range transport would have mixed into the surface region. Furthermore, the ratio of OC to EC concentrations was the minimum measured values on 12th June, with a mean ratio of 1.32 and 2.39 in GZ and ZH, respectively. Also, OC showed a bi-modal distribution, although predominantly in the fine mode while EC mostly peaked at fine mode particles (Take GZ for example, Figure S1 (g-h)), indicating that the organic aerosol was mostly primary, as would be expected from large fire sources. Additionally, the K^+ concentration on 12th June was about 2-3 times higher than that of mean value measured in GZ and ZH (Take GZ for example, Figure 10(a-b), and Figure S1(i)). Na^+ and Cl^- size distribution were found to be uni-modal distribution in GZ, where they peaked in the 1.0-1.44μm size range. Na^+ and Cl^- were bi-modal distribution in ZH on 12th Jun. (figures not showed here). All of these findings above, including the time of the year and the location, are consistent with the long-range transported biomass burning from Southeast Asia (Cohen, 2014).'

Line 485 Is this paragraph saying that MODIS fire hotspots are not useful to see effects of biomass burning?

Response:

We do not state that in general MODIS fire hotspots are not useful. In fact, they have been shown to be very useful in many dry areas and in many temperate and arctic areas. This is why they are commonly used. However, our results show that MODIS fire hotspots are not very useful in wet and tropical regions. This has been published before, such as Cohen, 2014, Giglio et al., 2006 and Yu et al., 2015. MODIS fire hotspots are obstructed by both clouds and high levels of aerosols in the atmosphere, both of which are found associated with tropical forest fires. Additionally, due to the highly wet ground surface, a significant amount of the fires may low temperature and therefore not observable using the MODIS sensors.We make clear this in the text in line 550-555:

'This result showed that the MODIS fire hotspots are not very useful in wet and tropical regions. MODIS fire hotspots are obstructed by both clouds and high levels of aerosols in the atmosphere, both of which are found associated with tropical forest

fires. Additionally, due to the highly wet ground surface, a significant amount of the fires may low temperature and therefore not observable using the MODIS sensors (Cohen, 2014, Giglio et al., 2006; Yu et al., 2015)'

Line 494 The EOF technique may be useful, but it means that it is better than the MODIS fire hotspots discussed in the previous paragraph? What is a specific reason?

Response:

There are some physical and mathematical reasons for this. First of all, observing aerosols is significantly easier and more precise. Since they are measured using variables in the visible and infrared, their measurement is more robust than the hotspot products, which are only in the infrared. There are many articles which show that the aerosol errors are roughly 10% of their total value, whereas for fires, they are significantly higher (Morisette et al., 2005a, 2005b; Levy et al., 2007, 2010; Remer et al., 2007).

From a mathematical sense, we are interested in looking at contributions which are significant. Fire hotspots are effectively point measurements, and as such are not spatially robust. Therefore, it is hard to tell what type of significant impact they have on the atmosphere in general. Given the uncertainties in such precise meteorology, it is highly probable that a point measurement may not convert precisely into an inverse method of atmospheric transport. Whereas AOD is an area measurement, and is a continuous measurement, since the aerosols transport and spread. Therefore, if a significant signal exists, it is far easier to track and transport, at the scale of the inverse meteorological methods used here.

We have added more information in line 558-563:

'Since MODIS fire hotspots are effectively point measurements, and as such are not spatially robust, while AOD are continuous and more easier to be observed, and provides more precise and robust spatial information (Morisette et al., 2005a, 2005b; Levy et al., 2007, 2010; Remer et al., 2005). Therefore, if a significant signal exists, it is far easier to track and transport, at the scale of the inverse meteorological methods used here.'

Figure 2 Please specify which species use the left and right Y-Axes.

Response:

Thanks for the comment. The right Y-Axes was only used for sulfate and the left Y-Axes was for nitrate, ammonium, OC and EC. We have clarified it in line 976-977:

'The mass size distribution of major compositions (SO_4^{2-}, NO_3^-, NH_4^+, OC and EC) at the three sites during the study period (SO_4^{2-} is plotted against the right Y-Axes)'

Figure 4 Why do these figures look different from other species shown in other

figures? They should be consistent.

Response:

Thanks for the suggestion and we have re-plotted the Figure 5 to make all the figures consistent.
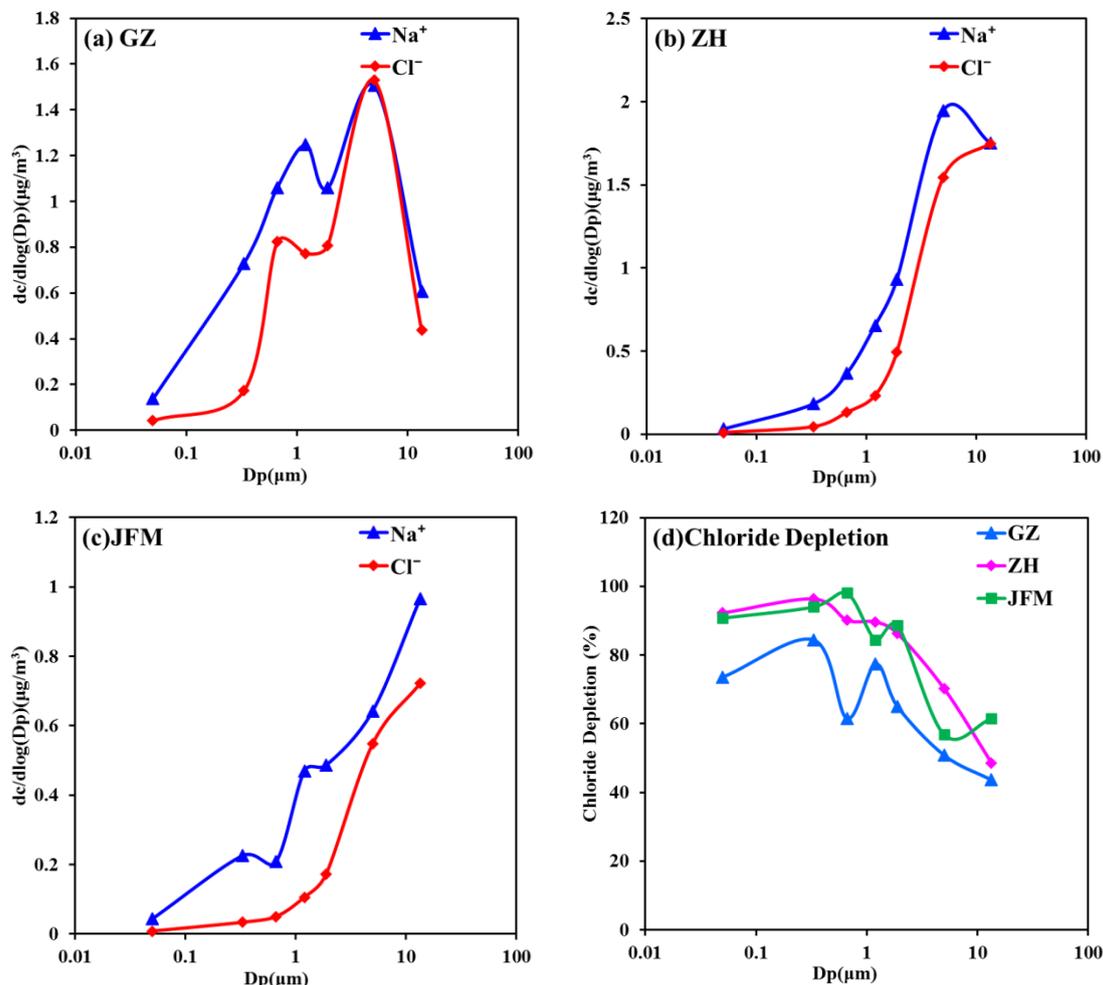

Figure 5. The mass size distribution of (a-c) Na^+ and Cl^- and (d) percentage of chloride depletion at the three sites

Reference:

Heald, C.L. and Spracklen, D.V.: Atmospheric budget of primary biological aerosol particles from fungal spores, Geophysical Research Letters, 36, L09806, doi:10.1029/2009GL037493, 2009.

Huang, Z.E., Harrision, R.M., Allen, A.G., James, J.D., Tilling, R.M. and Yin, J.X.: Field intercomparison of filter pack and impactor sampling for aerosol nitrate, ammonium, and sulphate at coastal and inland sites, Atmospheric Research, 71, 215-232, doi:10.1016/j.atmosres.2004.05.002, 2004.

Levy, R., Remer, L., and Dubovik, O.: Global aerosol optical properties and application to Moderate Resolution Imaging Spectroradiometer aerosol retrieval over land, Journal of Geophysical Research, 112, 1-15, doi:

10.1029/2006JD007815, 2007.

Levy, R., Remer, L., Kleidman, R., et al.: Global evaluation of the Collection 5 MODIS darktarget aerosol products over land, Atmospheric Chemistry and Physics, 10, 10399-10420, doi:10.5194/acp-10-10399-2010, 2010.

Liu, S., Hu, M., Slanina, S., He, L.Y., Niu, Y.W., Bruegemann, E., Gnauk, T. and Herrmann, H.: Size distribution and source analysis of ionic compositions of aerosols in polluted periods at Xinken in Pearl River Delta (PRD) of China, Atmospheric Environment, 42, 6284-6295, doi:http://dx.doi.org/10.1016/j.atmosenv.2007.12.035, 2008.

Lu, Q., Zheng, J.Y., Ye, S.Q., Shen, X.L., Yuan, Z.B. and Yin, S.S.: Emission trends and source characteristics of SO_2, NOx, PM_{10} and VOCs in the Pearl River Delta region from 2000 to 2009, Atmospheric Environment, 76, 11-20, doi: http://dx.doi.org/10.1016/j.atmosenv.2012.10.062, 2013.

Morisette, J.T., Giglio, L., Csiszar, I. and Justice, C.O.: Validation of the MODIS active fire product over Southern Africa with ASTER data, International Journal of Remote Sensing, 26, 4239-4264, doi: 10.1080/01431160500113526, 2005a.

Morisette, J.T., Giglio, L., Csiszar, I., Setzer, A., Schroeder, W., Morton, D. and Justice, C.O.: Validation of MODIS active fire dectection productes derived from two algorithms, Earth Interaction, 9, 1-23, doi: http://dx.doi.org/10.1175/EI141.1, 2005b.

Remer, L., Kaufman, Y., Tanre, D., Mattoo, S., Chu, D.A., Martins, J.V., Li, R.R., Ichoku, C., Levy, R.C., Kleidman, R.G., Eck, T.F, Vermote, E. and Holben, B.N.: The MODIS Aerosol Algorithms, Products, and Validation, Jouranl of Atmospheric Science, 62, 947-973, doi: 10.1175/JAS3385.1, 2005.

Stelson, A.W. and Seinfeld, J.H.: Relative humidity and temperature dependence of the ammonium nitrate dissociation constant, Atmospheric Environment, 16, 983-992, doi:10.1016/0004-6981(82)90184-6, 1982.

Wang, Y., Zhuang, G.S., Tang, A.H., Yuan, H., Sun, Y.L., Chen, S. and Zheng, A.H.: The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing, Atmospheric Enviornment, 39, 3771-3784, doi:10.1016/j.atmosenv.2005.03.013, 2005.

Yang, X. and Wenig, M.: Study of columnar aerosol size distribution in Hong Kong, Atmospheric Chemistry and Physics, 9, 6175-6189, doi:10.5194/acp-9-6175-2009, 2009.

Yao, X.H., Ling, T.Y., Fang, M. and Chan, C.K.: Comparison of thermodynamic predictions for in situ pH in $PM_{2.5}$, Atmospheric Environment, 40, 2835-2844, doi:10.1016/j.atmosenv.2006.01.006, 2006.

Yu, C., Chen, L.F., Li, S.S., Tao, J.H. and Su, L.: Estimating Biomass Burned Areas from Multispectral Dataset Detected by Multiple-Satellite, Spectroscopy and Spectral Analysis, 35, 739-745, doi:10.3964/j.issn.1000-0593(2015)03-0739-07, 2015.

Zhang, Z.S., Engling, G., Zhang, L.M., Kawamura, K., Yang, Y.H., Tao, J., Zhang, R.J., Chan, C.Y. and Li, Y.D.: Significant influence of fungi on coarse carbonaceous and potassium aerosols in a tropical rainforest, Environmental Research Letters, 10,034015, doi:10.1088/1748-9326/10/3/034015, 2015.

Zheng, J.Y., Zhang, L.J., Che, W.W., Zheng, Z.Y. and Yin, S.S.: A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment, Atmospheric Environment, 43, 5112-5122, doi: http://dx.doi.org/10.1016/j.atmosenv.2009.04.060, 2009.

Zhou, S.Z., Davy, P.K., Wang, X.M., Cohen, J.B., Liang, J.Q., Huang, M.J., Fan, Q., Chen, W.H. Chang, M., Ancelet, T. and Trompetter, W.J.: High time-resolved elemental components infine and coarse particles in the Pearl River Delta region of Southern China: Dynamic variations and effects of meteorology, Science of the Total Environment, doi: 10.1016/j.scitotenv.2016.05.194, 2016 (in press).

Properties of aerosols and formation mechanisms over southern China during the monsoon season

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Abstract

Measurements of size-resolved aerosols from 0.25 to 18 μm were conducted at three sites (urban, suburban and background sites) and used in tandem with an atmospheric transport model to study the size distribution and formation of atmospheric aerosols in southern China during the monsoon season (May-June) in 2010. The mass distribution showed the majority of chemical components were found in the smaller size bins (<2.5 μm). Sulfate, was found to be strongly correlated with aerosol water, and anti-correlated with atmospheric SO_2, hinting at aqueous-phase reactions being the main formation pathway. Nitrate was the only major species that showed a bi-modal distribution at the urban site, and was dominated by the coarse mode in the other two sites, suggesting that an important component of nitrate formation is chloride depletion of sea salt transported from the South China Sea. In addition to these aqueous-phase reactions and interactions with sea salt aerosols, new particle formation, chemical aging, and long-range transport from upwind urban or biomass burning regions were also found to be important in at least some of the sights on some of the days. This work therefore summarizes the different mechanisms that significantly impact the aerosol chemical composition during the Monsoon over southern China.

Keywords: chemical component, mass size distribution, aqueous-phase reaction chloride depletion

1. Introduction

Atmospheric aerosols are solid and liquid substances ubiquitously suspended in the Earth's atmosphere, that impair visibility, negatively affect human health, and directly and indirectly impact regional and global climate (Burnett et al., 2014; Chen et al., 2013a; Chung and Seinfeld, 2005; Cohen et al., 2011; Huang et al., 2014; Jacobson, 2001; Kim et al., 2008; Liu et al., 2011; Ramanathan and Carmichael, 2008; Rosenfeld et al., 2014; Tao et al., 2009). The size distributions and chemical composition of aerosols play essential roles on their transport, transformation, removal mechanisms (Cohen and Prinn, 2011; Cohen and Wang, 2013; Delene and Ogren, 2002; Dubovik et al., 2000; Giglio et al., 2003, 2006; Petrenko, et al., 2012; Seinfeld and Pandis, 2006; Zhao and Gao, 2008a). And also, to some extent, they provide useful information to validate and improve model performance (Cohen and Wang, 2013; Cohen, 2014; Cohen and Lecoeur, 2015; Myhre et al., 2013; Pillai and Moorthy, 2001; Schuster et al., 2006; Tsigaridis et al., 2014). In the environment, the most important aerosol processes occur over the Aitken (<0.1 μm), condensation (~0.1-0.5 μm), droplet (~0.5-2.0 μm), and coarse (>2.0 μm) size modes (Seinfeld and Pandis, 2006), where new particles are formed in the Aitken mode via condensational growth and coagulation of nucleation mode particles, and droplet mode particles are produced by in-cloud processing or aqueous reactions (Ervens et al., 2011; Lim et al., 2010; Meng and Seinfeld, 1994; Volkamer et al., 2009; Wang et al., 2012; Yao et al, 2003a). On the other hand, coarse mode aerosols usually come from very different sources than smaller aerosols. For example, natural sources such as sea spray, dust,

67   soil, and active biological aerosols are unique and therefore provide further

68   information about the aerosol distribution at a given location.

69   Previous research suggests that sulfate is mostly contained in the non-coarse

70   modes, with the conversion of SO_2 occurring mostly via gas-phase oxidation followed

71   by condensation, or through droplet mode sulfate produced from fog/cloud process

72   (Barth et al., 1992; Meng and Seinfeld, 1994). On the other hand, nitrate usually has a

73   bi-modal distribution with peaks in both the fine and coarse modes. Fine mode nitrate

74   is formed mainly by oxidation of NO_2 to HNO_3 and subsequent condensation, or from

75   the heterogeneous hydrolysis of N_2O_5, while coarse mode nitrate is often observed

76   due to the effect of chloride depletion of sea salt aerosols (Harrison and Pio, 1983;

77   Pierson and Brachaczek, 1998). Ammonium is mostly found in the fine mode and is

78   chemically associated with sulfate and nitrate. Carbonaceous materials, organic

79   carbon (OC) and elemental carbon (EC), are both found primarily in the non-coarse

80   mode. While both OC and EC are impacted by differing emissions sources and wet

81   deposition, there are other significant differences: EC is hydrophobic and radiatively

82   active, while OC is hydrophylic and further has significant source terms from

83   condensation and secondary particle formation (Lan et al., 2011).

84   A series of studies about the mass size distribution of aerosol chemical

85   components have conducted at a specific site over Southern China during the past

86   decade (Lan et al., 2011; Liu et al., 2008; Yang and Wenig, 2009; Zhang et al., 2015).

87   Compared with the previous studies, this paper presents a unique combination of

88   analytical and measurement techniques. We use measurements of chemical properties

and size distribution conducted at three different functional sites, coupled with multiple modeling results, and reprocess remote sensing products using statistical methods, all in tandem with each other, which is not commonly found in other studies. Furthermore, we test our approach in Southern China, which is one of the regions of the world with the most complex meteorology, coming under the influence of the Monsoon, with shifting winds from continental and oceanic sources. Additionally, the season tested is a transition period, during which there were significant meteorological contributions from both remote continental sources as well as oceanic sources. On top of this, Southern China has a combination of high temperature and relative humidity, strong radiative flux, and high oxidative capacity, leading to the promotion of significant secondary aerosol formation.

In this paper, we present a unique database of the size-different mass distribution of aerosol chemical components during the Monsoon Season over southern China. The data were sampled from a combination of three different sites, one in an urban area, one in a suburban area, and one in a remote area, providing further insights into the characteristics of size distribution in each of these regions, and discussion on the secondary aerosol formation mechanisms, the identification and impacts of long-range transport of biomass and urban sources, and the impacts of mixing sea-salt and urban pollutants on the characteristics of aerosol size distribution.

2. Measurements and methodology

2.1. Description of the sampling sites

The field study was conducted at three sites in southern China (Figure 1), two of which were situated in Guangdong and the other in Hainan. Guangdong is located in a subtropical monsoon climate, primarily influenced by cold and dry air masses from the North in December to February, and warm and wet air masses from the South China Sea in May to August. It has a single annual local rainy season extending from April to September. Hainan is located further to the south, and has year-round warm to hot weather and a distinct rainy season from May to October.

The first site (23.12°N, 113.36°E), is located on the rooftop of a building in the South China Institute of Environmental Sciences, Guangzhou (GZ), a mega-city containing more than 13 million people. The site was located about 50m above ground, in an area surrounded by residential and commercial buildings, with the nearest arterial roads located about 200m away. There were no significant industrial emission sources found around the site. This site was chosen since it is highly representative of a typical megacity.

The second site was located at (22.34°N, 113.58°E), on the rooftop of the library at Sun Yat-Sen University, in the city of Zhuhai (ZH), a medium sized city of about 1.6 million people located in Southern Guangdong adjacent to Macau. The site was located about 60m above the ground, in an area surrounded by mountains on three sides and the estuary where the Pearl River meets the South China Sea about 500m away on the fourth side. There are no significant industrial or major transportation emissions sources nearby. This site was chosen since it is highly representative of a coastal partially urbanized area.

133   The third site was located at Jianfeng Mountain (JFM, 18.74°N, 108.86°E), in a

134   tropical rainforest situated in the Southwest corner of Hainan. This site is distant from

135   the major cities of Hainan province and is further located about 5km away from the

136   coast. JFM is not directly influenced by anthropogenic emissions and is generally

137   regarded as a background site to investigate the long-range transport (Zhang et al.,

138   2013a). This site was chosen both because it is representative of a remote site and

139   because it receives air masses from three different directions: continental East Asia to

140   the North, the South China Sea to the South, and Southeast Asia to the West.

141

142   **2.2 Sampling of aerosol**

143   To attain size-segregated particle samples, a 6-stage High Flow Impactor (MSP)

144   with an airflow rate of 100 L min^{-1} was employed, with cutoff diameters (D_p) of 18

145   (inlet), 10, 2.5, 1.4, 1.0, 0.44 and 0.25 μm. A total of 10, 8 and 20 sets of

146   size-segregated particle samples were collected in GZ, ZH and JFM, respectively

147   during the periods of May and June in 2010 (shown in Figure 2). A single set of

148   sample collection lasted for approximately 24h in GZ and ZH, and 48h in JFM. Since

149   the aerosol concentration was relatively low in remote JFM site, we extended the

150   sampling time as long as 48h to allow the chemical components to be detected.

151   The mass concentrations of six cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Ca^{2+}) and

152   seven anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^- and PO_4^-) were analyzed using an ion

153   chromatography (ICS-3000, DIONEX). Thermal Optical Transmittance (TOT)

154   technique was employed to analyze the quartz filter samples to determine the mass

155 concentrations of organic carbon (OC) and elemental carbon (EC) by the use of

156 Sunset Laboratory OCEC Carbon Aerosol Analyzer. Detailed information of the

157 aerosol sampling and in-lab chemical analytical techniques can be found in Zhang et

158 al. (2013a).

159   To be consistent with the background literature (4 modes include Aitken (<0.1

160 μm), condensation (~0.1-0.5 μm), droplet (~0.5-2.0 μm), and coarse (>2.0 μm))

161 (Seinfeld and Pandis, 2006), and the constraints of the size bins measured in this study,

162 we implement 2.5 μm as the cut-off size to separate fine and coarse particles, and the

163 size bins from 0.44-1.4 μm was defined as droplet particles in this study. Although we

164 were not able to directly measure aerosol water content, given its importance for the

165 study here, we instead estimate the amount by the use of E-AIM model II (Clegg et al.,

166 1998), as it provides the most accurate prediction compared with other models, like

167 ISORROPIA and SCAPE2 (Yao et al., 2006). The input parameters of the E-AIM

168 model II are tempreture, relative humidity, strong acidity (H^+), molar contentrations of

169 NH_4^+, SO_4^{2-} and NO_3^- ions (Clegg et al., 1998). Further, an approximation of the

170 particle strong acidity $[H^+]_s$ was calculated using Eq. (1):

171 $$\left[H^+ \right]_s = 2\left[SO4^{2-} \right] + \left[NO_3^- \right] - \left[NH_4^+ \right] \tag{1}$$

172   The calculation of strong acidity would introduce possible errors due to the

173 exclusion of other ions (e.g. K^+, Na^+, Cl^-), but which only exerted a minor influence

174 on the estimation of aerosol acidity due to their lower concentration (Yao et al., 2006).

175 **2.3 Meteorological data**

176   Meteorological parameters, including wind speed (WS), wind direction (WD),

temperature (T), relative humidity (RH), pressure (P), and precipitation were simultaneously monitored in GZ and JFM sites with a time resolution of 30 minutes. The same meteorological parameters in ZH, as well as the daily low-level cloud cover data at all three sites, were obtained from the China Meteorological Data Sharing Service System (http://data.cma.cn/site/index.html).

2.4 Remotely sensed measurements

Aerosol optical depth (AOD), fire products including Fire Radiative Power (FRP), and Fire Quality Assurance [QA] data, were obtained from the MODIS sensors aboard both the AQUA and TERRA satellites. Specifically, we obtained the Collection 6, 3km Level 2 swath product for AOD (Remer et al., 2013), and Collection 5.1, 1km Level 2 swath products for FRP and QA (Giglio et al., 2006). The Collection 5.1 active fire products are daily products and have been improved based on the previous collection 5.0 products. All of the data are cloud-screened, with AOD data being computed using different algorithms over land and water, and the fire data using 19 different channels for quality assurance. We only accept values for FRP and Fire Count where the QA is at least 90%.

2.5 Atmospheric transport model

Two Lagrangian particle dispersion models, the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hes, 1998) and FLEXPART coupled with The Weather and Research and Forecasting (WRF) model (FLEXPART –WRF)

(Stohl et al., 1998; Brioude et al., 2013) were applied to determine the origin of air masses in this study, Compared with HYSPLIT, FLEXPART can identify the relative importance of source region that affected the receptor visually. HYSPLIT uses single air parcels to compute trajectories with the use of Global Data Assimilation System (GDAS, $1°\times1°$) as input data. FLEXPART, on the other hand, uses a larger number of air parcels to compute trajectories based on the higher resolution meteorological predictions provided by mesoscale model WRF. The application of FLEXPART – WRF with a novel convective scheme being added improves the dispersion simulations and results in an overall better simulation, especially for finer scale applications (Brioude et al., 2013; Stohl, 1998). In this case, the region was modeled with a spatial resolution of 27×27 km and a temporal resolution of 1 hour.

An Eulerian model, WRF/Chem V3.4.1 was used in this study to simulate the fog process. For this model, the target region was modeled at a spatial resolution of 3×3km and a temporal resolution of 1 hour. Detail information about the WRF/Chem model set-up refers to Situ et al. (2013).

3. Results and discussion

3.1. Overall aerosol characteristics

The time series of PM_{18} chemical compositions at the three sites during the sampling period were shown in Figure 2. The average concentration and standard deviation of PM_{18} was 47.8 ± 20.8, 24.3 ± 12.1 and 8.1 ± 2.7 μg m^{-3} in GZ, ZH and JFM, respectively. The mean and range of PM_{18} in highly urban GZ was both higher and

wider than in suburban ZH and rural JFM, with the respective ranges being 23.3~93.7,

13.3~35.1, 4.7~14.3μg m^{-3} in the three sites. Maximum concentration was found both

on 12th Jun. in GZ and ZH, while it was on 3rd Jun. in JFM (to be discussed later).

Table 1 listed the average concentration of chemical components in the given

size-resolved particle (PM$_{1.0}$, PM$_{2.5}$ and PM$_{10}$) and their percentage of PM$_{10}$ at the

three sites. In terms of the mass size distribution, the percentage of PM$_{1.0}$ to PM$_{10}$ was

60.2%, 66.3% and 75.0%, and PM$_{2.5}$ to PM$_{10}$ was 88.0%, 92.6%, 91.7% in GZ, ZH

and JFM, respectively. When considered as a whole, it is the smaller sized particles

that dominate the aerosol loading at all three of these sites. Looking at the data on a

species-by-species level, most of chemical components were concentrated in fine

mode particles, which contribute at least 57% to PM$_{2.5}$. The sole exception is nitrate at

ZH and JFM, which were mainly concentrated in the coarse mode with a percentage

of above 90%. Overall, the sum of five major chemical components (i.e. sulfate,

nitrate, ammonium, OC, and EC) accounted for about 90% of the total mass

concentration of detected chemical components across all three sites.

Two of the species, sulfate and OC, were found to dominate the particle

composition, with concentration of 11.7 ± 5.2, 8.8 ± 3.2, 2.2 ± 1.5 μg m^{-3} for sulfate

and 7.2 ± 2.7, 3.0 ± 1.5, 1.8 ± 0.8 μg m^{-3} for OC in GZ, ZH and JFM, respectively.

Sulfate concentration was much higher than that of OC in urban and suburban

locations irrespective of particle size, while OC concentration was similar to that of

sulfate in fine particles and slightly higher in coarse particles at the remote site. These

findings are consistent with the nature of the sources of sulfur from industrial and

243 power plant (Zheng et al., 2009). In addition, shipping source was becoming

244 increasingly vital for SO_2 emission with an increment of 12% per year in this region

245 (Lu et al., 2013; Zhou et al, 2016)

246 Nitrate, mainly formed from the oxidation of NOx emitted by mobile vehicles

247 and power plants, showed a remarkable difference between urban and background site,

248 ranging from fourteen to thirty times higher in GZ than in the other sites, especially

249 for fine mode nitrate. This is consistent with its more rapid oxidation of its abundant

250 precursor species, especially so in the urban atmosphere (Cohen et al., 2011). In

251 addition, phase equilibrium was another important reason for the discrepancy in urban

252 and background site since nitrate would tend to exist as gas phase while transported to

253 background areas (Seinfeld and Pandis, 2006). A relatively insignificant concentration

254 of NO_3^- in ZH and JFM indicated far less anthropogenic emission of the precursor

255 over these two sites.

256 The values of OC and EC in $PM_{2.5}$ were 7.2 ± 2.7 and 3.4 ± 3.2 μg m^{-3} in GZ,

257 3.0 ± 1.5 and 1.5 ± 0.9 μg m^{-3} in ZH. These values were lower than that found in

258 previous studies done in GZ and ZH during the wet season: OC and EC were 13.1 and

259 4.6 μg·m^3 in GZ in 2007, 14.8 and 8.1 μg m^{-3} in GZ in 2002, and 5.4 and 1.9 μg m^{-3} in

260 ZH in 2002 (Cao et al., 2004; Tao et al., 2009). Furthermore, OC and EC

261 concentrations in JFM were found to be lower than that at other forest sites in China,

262 such as Hengshan: 3.01 and 0.54 μg m^{-3} in 2009 (Zhou et al., 2012), Daihai: 8.1 and

263 1.81 μg m^{-3} in 2007 (Han et al., 2008), and Taishan: 6.07 and 1.77 μg m^{-3} in 2007

264 (Wang et al., 2011). However, the EC and OC in JFM were similar to some

265   background sites in other countries, such as Puy De Dome in France: 2.4 and 0.26 μg

266   m^{-3} in 2004 (Pio et al., 2007) and Sonnblick in Austria: 1.38 and 0.23 μg m^{-3} in 2003

267   (Pio et al., 2007). This finding is not unexpected, since there are very few urban

268   sources near the site. It is therefore relatively representative of a remote background

269   site, and will be treated as such subsequently in this paper.

270

271   **3.2. Size distribution by chemical composition**

272   The mass size distribution of major compositions at the three sites during the

273   study period, shows that sulfate had a single-peaked distribution, with the maximum

274   value found in the 0.44-1.0 μm size over all sites and under all different

275   meteorological conditions examined in this study. The droplet mode sulfate was about

276   56.0 ± 8.0 %, 63.5 ± 5.1 % and 58.8 ± 9.4 % of the total sulfate mass in GZ, ZH and

277   JFM, respectively (Figure 3). This confirms that secondary processing is essential,

278   with aqueous-phase reactions playing a crucial role on the formation and/or growth of

279   droplet sulfate, throughout all of these different regions. It is interesting to note that

280   ZH had the highest relative concentration of droplet model sulfate, which although it

281   is less urban than GZ, is consistent with the fact that it is located very close to large

282   amounts of sulfur emissions from the shipping traffic at the massive nearby ports of

283   Hong Kong and Shenzhen (Lu et al., 2013).

284   Droplet mode ammonium was mainly due to ammonia vapor that reacted with or

285   condensed on an acidic particle surface. Ammonia was observed to highly correlate

286   with sulfate at the three sites (R>0.81, P<0.01), particularly so in the size range of

0.44-1.0 μm. This is consistent with the fact that sulfuric acid preferentially reacts with ammonia (Zhuang et al., 1999), and that most of sulfate in the atmosphere is generally found as ammonium sulfate in the droplet mode (Liu et al., 2008; Zhuang et al., 1999).

The nitrate size distribution was found to be bi-modal in GZ, with the peaks occurring in the 0.44-1.0 μm and 2.5-10 μm size ranges. This is consistent with the fact that Droplet mode nitrate was dominated by the heterogeneous aqueous reaction of gaseous nitric acid (HNO_3) and ammonia (NH_3) on the wet surfaces of pre-existing aerosols within ammonia-rich environment, otherwise by heterogeneous hydrolysis of N_2O_5 on the pre-existing aerosols within ammonia-poor conditions. The dissociation equilibrium of NH_4NO_3 highly depends on temperature and humidity (Stelson and Seinfeld, 1982). On the other hand, this result is consistent with the fact that nitrate was found mostly in the coarse mode in ZH and JFM, where it accounted for up to 60% of total particulate mass. A higher relative humidity, consistent with the warm and wet atmosphere over the South China Sea, makes gaseous nitric acid more likely to be absorbed by coarse particles in the atmosphere (Anlauf et al., 2006), resulting in a higher relative concentration of nitrate in the coarse mode in ZH and JFM (where the relative humidity averaged 80 and 91% respectively, as compared to only 73% in GZ). Further, the presence of coarse mode nitrate is consistent with chlorine reduction, as talked about later.

OC and EC showed a similar mono-modal distribution in GZ and ZH, with a dominant and a broad peak over the range from 0.25-1.4 μm. On the other hand, a

14

bi-modal distribution was found in JFM. In urban and suburban areas, there are significant primary sources from traffic and industry in the e.g. Huang et al. (2006) and Cao et al. (2004). It is also consistent with the high-level emissions due to the ship traffic to Shenzhen and Hong Kong, both of which are located near ZH, which in turn would compensate for the otherwise reduced industrial and traffic sources (Zheng et al., 2012). OC has both primary sources, which are similar to those for EC as well as secondary formation. There were a few days in which the ratios of OC to EC are not consistent, indicating a large secondary source of OC. We investigated these days and find that emissions that long-range transported from far-upwind areas with highly urbanization or with the existence of biomass burning are responsible, as discussed later in this paper. Additionally, there is some coarse mode OC present in JFM, suggesting a possible source of biological aerosol (e.g. pollen, spores and plant fragment) (Heald and Spracklen, 2009; Seinfeld and Pandis, 2006; Zhang et al., 2015), which is consistent with the large amounts of vegetation present in that region (Zhang et al., 2015).

3.3. Observed Aqueous-phase reaction of droplet mode sulfate

The daily droplet mode sulfate ranged from 3.0-13.6, 1.6-9.5 and 0.5-4.9 $\mu g\ m^{-3}$ in GZ, ZH and JFM respectively. In order to study the aqueous-phase reaction of droplet mode sulfate, cases with the air masses came from continent were excluded to avoid the effect of transported pollutants on the concentration of sulfate. Then two cases with a concentration of droplet sulfate above the mean plus one standard

331 deviation were selected as typical cases in each site (8th and 12th May in GZ, 12th May

332 and 1st Jun. in ZH, and 4th and 13th May 2010 in JFM), which were more obvious to

333 observe to investigate the effect of aqueous-phase reaction in the formation of droplet

334 mode sulfate (blue shade in Figure 2). In each of these cases, it was found that droplet

335 mode sulfate accounted for about two thirds of the total mass concentration of sulfate

336 at the three sites.

337   A backward trajectory analysis found that during these events, the air masses at

338 these sites mainly originated over the South China Sea (figures not shown here).

339 Additionally, it was determined that during these times at the three sites, there was an

340 abnormally high amount of low cloud cover 60-70% and a relatively higher relative

341 humidity (75~83%) (Table 2). This combination is consistent with moist air being

342 transported over land where the ship and industrial SO_2 emissions can undergo

343 chemistry in the presence of large amounts of liquid cloud water, to form

344 droplet-model sulfate.

345   We estimated the liquid water content using the AIM-II model (Equation 1). The

346 results showed a significant positive correlation with droplet mode sulfate in GZ

347 (R=0.98, P<0.05), ZH (R=0.53, P<0.05) and JFM (R=0.80, P<0.05), indicating that

348 water content correlated closely with the sulfate aerosol loadings. This is further

349 evidenced that aqueous formation was likely an important contributing factor.

350   We further investigated the aqueous-phase reaction of particles due to the fog

351 process for the data from 8th May in GZ. This is because the measured visibility met

352 the World Meteorological Organization cutoff value of less than 1 km due to water

droplets, in the early morning (05:00-07:00 LT) (Figure 4(c)). Consistently, during this time, it was found that the relative humidity was quite high (RH>90%) and the wind was quite low (wind speeds<1.0 m s^{-1}). Also during this time, the cloud fraction and simulated 2m relative humidity were up to 90% over Southern China (Figure 4(a-b)). Furthermore, the depression dew point (ΔT=T-Td, while Td denotes dew point temperature) was lower than 1 (Figure 4(c)), which indicating that vapor pressure was saturated. An accompanying analysis using WRF/Chem shows that simulated cloud water mixing ratio was the highest during this period over the GZ area and higher value was found around 06:00 LT (Figure 4(e-f)). This combination promoted the existence of fog/low cloud.

Further analysis was done by looking at measurements of SO$_2$ (data from Guangzhou Environmental Protection Bureau, http://www.gzepb.gov.cn/). The diurnal variation on 8th May showed a unique pattern compared with the mean diurnal pattern as measured during 2009-2011 (Figure 4(d)). On this day, the SO$_2$ concentration has decreased dramatically since 05:00-07:00 LT, which is consistent with SO$_2$ transferred from the gas to aqueous phase due to the high solubility of SO$_2$ in fog water droplets (Zhang et al., 2013b).

Simulation of these conditions using WRF/Chem indicates that the rapid growth of both Aitken and accumulation (~0.1-1 μm) mode sulfate started at 07:00 LT and peaked at 08:00-09:00 LT (Figure 4(g-h)). This further supports the conclusion of fresh sulfate production, in this case through both the aqueous and potential initial gas to particle formation, followed by condensation/coagulation and uptake into the liquid

375 droplets present. All of this is consistent with generalized urban modeling studies

376 performed under similar conditions (e.g. Cohen and Prinn, 2011).

377

378 **3.4. Observed interactions between nitrate and chloride depletion**

379 The mass size distribution of Cl^- and Na^+ showed a similar pattern to nitrate at the

380 three sites, peaking in coarse mode particles (Figure 5(a-c)) with an average

381 percentage of 43%, 62% and 43% for coarse mode Na^+, 53%, 76% and 74% for

382 coarse mode Cl^- in GZ, ZH and JFM, respectively, suggesting the main sea salt

383 sources. Na^+ and Cl^- shown a bi-modal distribution in GZ, illustrating the combustion

384 emissions, e.g. biomass burning or coal combustion for fine mode Na^+ and Cl^- (Wang

385 et al., 2005), but the contributions were insignificant since the magnitude of Na^+ and

386 Cl^- from combustion sources is many orders of magnitude smaller than oceanic

387 sources. Furthermore, if the biomass burning source were significant, it would clearly

388 also show up in terms of the K^+ and BC/OC ratio, as explained later in the section *3.6*

389 *Quantifying the impacts of fires*.

390 The concentration and percentage of chloride depletion ($[Cl_{dep}]$ and %Cl_{dep})

391 were calculated using Eq. (2-3), where $[Cl_{meas}^-]$ and $[Na_{meas}^+]$ are the measured molar

392 concentrations of chloride and sodium respectively, 1.174 was the molar ratio of Cl^- to

393 Na^+ in sea water (Yao et al., 2003b).

394 $$[Cl_{dep}]=1.174[Na_{meas}^+]-[Cl_{meas}] \tag{2}$$

395 $$\%Cl_{dep}=\frac{1.174[Na_{meas}^+]-[Cl_{meas}]}{1.174[Na_{meas}^+]}*100\% \tag{3}$$

396 The positive value of $[Cl_{dep}]$ represents chloride depletion, otherwise means the

397 chloride enrichment, suggesting additional sources was existed for Cl⁻ excluding sea

398 salt. Therefore, samples with negative $[Cl_{dep}]$ were excluded from analysis to avoid

399 the effect of non-sea salt emission on chloride depletion.

400   In general, the %Cl$_{dep}$ decreased as the aerosol mass increased (Figure 5(d)).

401 Chloride had been almost entirely depleted in fine mode particles with the value of

402 91%, while the value was 60% in coarse mode particles in ZH and JFM. The chloride

403 depletion was relatively weaker in GZ with a value of 72% and 47% in fine and

404 coarse mode particle, which was in consistent with that the urban area was less

405 affected by ocean emission. The result was consistent with a study conducted in South

406 China Sea in 2004 as well as the theory that reaction between sulfuric acid and nitric

407 acid with sea salt (sodium chloride) is facilitated in fine particles due to their larger

408 surface areas to volume ratio and longer atmospheric residence time (Chatterjee et al.,

409 2010; Hsu et al., 2007).

410   The ratio of calculated ammonium to measured ammonium was used to explain

411 the presence of sulfuric acid and nitric acid in the aerosol, with a value larger than 1

412 indicating there was insufficient ammonium to neutralize nitric acidic NO_3^- (since

413 ammonium first consumes sulfuric acid). Calculated ammonium was equal to

414 $2*[nss\text{-}SO_4^{2-}]+[NO_3^-]$, where[nss-$SO_4^{2-}$] and [$NO_3^-$] reprents the molar concentarion

415 of non-sea-salt SO_4^{2-} (i.e., $[nss\text{-}SO_4^{2-}]=[SO_4^{2-}]-0.14\times[Cl^-]$) and NO_3^- (Huang et al.,

416 2004). The calculated ratio was much higher than 1 in ZH and JFM suggesting that

417 nitrate plays a role in Cl depletion. The ratio of nitrate to percent chloride depletion

418 can then be used to calculate the contribution of coarse nitrate to chloride depletion

419 (Zhuang et al., 1999; Zhao and Gao, 2008b). This result showed that nitrate was

420 responsible for the depletion of 54% and 17% of coarse chloride in ZH and JFM

421 respectively. This suggests that the interaction of sea salt particles with anthropogenic

422 pollutants is an important pathway for the generation of aerosol species in coastal

423 suburban regions like ZH, which have sizable amounts of both sea salt and NO_x

424 emissions (Chatterjee et al., 2010; Liu et al., 2008).

425   Relative humidity exceeded 80% during the whole sampling time in ZH except

426 for 24th May, which was 64% and the air massed mainly came from northern

427 continental areas. The only other day that had a significant continental wind source at

428 ZH with a higher relative humidity (80%) was found on 7th June. The percentage of

429 chloride depletion was 95% and 69% for fine and coarse particles on 24th May and the

430 value was 78% and 64% on 7th Jun. There was no distinct difference found in coarse

431 particles for the two cases, there was a considerable difference in fine particles with

432 higher chloride depletion happened on 24th May. The meteorological conditions were

433 similar on these two days excluding humidity, moreover, the aerosol water content in

434 fine mode particles was about 8 times higher on 7th Jun. (3.6 µg m^{-3}) than that on 24th

435 May (0.45 µg m^{-3}). This finding suggested that humidity or aerosol water content

436 would be an important factor that affected the chloride depletion, which is consistent

437 with our understanding of the release of hydrochloric acid under the known high nitric

438 acid conditions, especially when there is less aerosol water (at relatively lower

439 humidity) to dissolve all of the volatiles, which would shift HNO_3 from gas- to

440 particle-phase and further to reinforce the release of hydrochloric acid (Chen et al.,

441   2013b; Dasgupta et al., 2007). In addition, the concentration of coarse mode nitrate

442   was similar for these two days with a value of 1.3~1.4 µg m^{-3}, but the concentration of

443   fine mode nitrate was bout 4 times higher on 24th May (0.18 µg m^{-3}) than that on 7th

444   Jun. (0.04 µg m^{-3}), further suggesting the relative lower humidity favor the particle

445   phase nitrate over chloride.

446

447   **3.5. The effects of long-range transport, and in-situ chemistry**

448   There were four days that the amounts and properties of the aerosols were

449   significantly impacted by long range transport and unique formation and alteration

450   mechanisms: one in each GZ and ZH (both occurring on 12th June) and three in JFM

451   (1st, 3rd, and 5th June).

452   On 12th June in both GZ and ZH, the total aerosol concentration was the highest

453   measured, at respectively 93.7 and 35.1 µg·m^3 in GZ and ZH (Figure 2). Secondly,

454   the concentration of secondary soluble ions was the highest measured. The Sulfur

455   Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) are applied   to indicate

456   the degree of oxidation of SO$_2$ and NO$_2$ precursor gases (Wang *et al.,* 2005). The

457   equations for SOR and NOR are calculated as SOR=n-SO$_4^{2-}$/(n-SO$_4^{2-}$+n-SO$_2$) and

458   NOR=n-NO$_3^-$/(n-NO$_3^-$+n-NO$_2$, where n-SO$_4^{2-}$ and n-NO$_3^-$ are the molar concentrations

459   of particulate SO$_4^{2-}$ and NO$_3^-$ and n-SO$_2$ and n-NO$_2$ are the molar concentrations of

460   the precursor gases SO$_2$ and NO$_2$. SOR and NOR was also the highest On 12th June at

461   the range of 0.44-1.0 µm in GZ with the value of 0.20 and 0.17, respectively (Figure 6

462   (a-b)) (no supported data to estimate SOR and NOR in ZH on this day). Thirdly, this

463 was the only day in GZ that the nitrate size distribution was found to be uni-modal,

464 where it peaked in the 1.0-1.44μm size range (Figure 6 (d)), which was the largest of

465 any mean size nitrate in GZ measured. Meanwhile, the nitrate size distribution

466 changed from coarse mode to bi-modal and peaked in 0.25-0.44 μm size range in ZH

467 measured on this day (Figure S1(j)). Fourthly, the peak of sulfate and ammonia

468 shifted from typical values in the 0.44-1.0 μm size range to the 1.0-1.44 μm size range

469 (Take GZ for example, Figure 6(c) and Figure S1(f)). All of these are consistent with

470 enhanced secondary production. Such a statistically enhanced amount of secondary

471 production requires the aerosols to have had considerably more time in the

472 atmosphere to have aged as they have, and therefore is consistent with them having

473 undergone considerable long range transport (Cohen et al., 2011).

474 To provide further evidence, 3-day air mass backward trajectories were conducted

475 at each of the three sites. The parcels were released at initial heights of 100, 500,

476 1000 and 2000m, hourly, as a means of robustly sampling the boundary layer

477 throughout the day. The results showed that air masses winded up over GZ and ZH

478 in the lower free troposphere or near the top of the boundary layer had mostly

479 originated over continental Southeast Asia, while those winding up near the surface,

480 had mostly come from Northern China (Take GZ for example, Figure S1(a)).

481 Furthermore, since the air masses came from opposite directions at nearly the same

482 time, the end result was observed to be a stable meteorological condition over GZ

483 (very low wind 0.1 m s^{-1}) and ZH (wind speed was 1m/s which was the lowest

484 during the sampling times). In fact, it seems from the back trajectory analysis that

there was descending air in and around GZ and ZH on this day, which implies that air transported from far away in the lower free-troposphere would have been transported back near the surface (Take GZ for example, Figure S1 (b-c)). FLEXPART-WRF was next applied to address the issue of the air residence time through the column over GZ and ZH for that day. Take GZ for example, as can be shown in Figure 6 (e-f), there was a strong influence from the local region of GZ and surrounding adjoining cities, at a lower altitude (500m and lower) (Figure 6(e) and Figure S1 (d-e)). All of these results were further consistent with the high levels of aerosols measured as well as additional secondary processing having had time to occur.

Except for in-situ formation, long-range transport was another impact factor. First, HYSPLIT (Take GZ for example, Figure S1(a)) and FLEXPART-WRF (Figure 6(f)) showed that the air flow was mostly from Southeast Asia at levels over the boundary layer ((Figure 6(f)), and hence had undergone long-range transport. Second, the windspeed near the surface suddenly became very low. Therefore, there had been a rapid change in the windspeed. Based on conservation laws for air mass, it would be excepted for there to be some reasonable amount of mixing of the air vertically. This was consistent with the finding that some of the air which has undergone long-range transport would have mixed into the surface region. Furthermore, the ratio of OC to EC concentrations was the minimum measured values on 12th June, with a mean ratio of 1.32 and 2.39 in GZ and ZH, respectively. Also, OC showed a bi-modal distribution, although predominantly in the fine mode while EC mostly peaked at

507 fine mode particles (Take GZ for example, Figure S1 (g-h)), indicating that the

508 organic aerosol was mostly primary, as would be expected from large fire sources.

509 Additionally, the K^+ concentration on 12th June was about 2-3 times higher than that

510 of mean value measured in GZ and ZH (Take GZ for example, Figure 10(a-b), and

511 Figure S1(i)). Na$^+$ and Cl$^-$ size distribution were found to be uni-modal distribution

512 in GZ, where they peaked in the 1.0-1.44μm size range. Na$^+$ and Cl$^-$ were bi-modal

513 distribution in ZH on 12th Jun. (figures not showed here). All of these findings above,

514 including the time of the year and the location, are consistent with the long-range

515 transported biomass burning from Southeast Asia (Cohen, 2014).

516 At JFM the total aerosol concentration was highest on the 1st, 3rd, and 5th June. In

517 particular, the levels of EC and potassium were elevated on all three days, and the

518 ratio of OC to EC was depressed (Figure S2 (c-e)). However, in addition to these

519 clues, there were some differences: the levels of sulfate and ammonia were

520 remarkably elevated on the 3rd and 5th June (Figure 7(g) and Figure S2 (b)), likely due

521 to a mixing of urban sources with the fire sources. On the other hand, on the 1st June,

522 the sulfate was lower, but the nitrate was considerably higher, peaking in the coarse

523 mode (Figure 7 (h)), likely due to mixing of South China Sea air with the fire sources.

524 HYSPLIT results showed that on all three of these days, the great majority of air

525 masses arriving at JFM originated from continental Southeast Asia (Figure S2(a).

526 However, all of these parcels of air arrived in the upper boundary layer or the lower

527 free troposphere. By analyzing the FLEXPART-WRF runs at higher resolution, it was

528 demonstrated that there was a strong influence of air from ocean on 1st June (Figure 7

(a-b)) at the lower parts of the boundary layer. This is consistent with the observed

non–elevated sulfate and elevated coarse nitrate on that day. Furthermore, the

FLEXPART-WRF runs at higher resolution demonstrated a considerable influence of

air from Southern China (urban and semi-urban Guangdong Province, including many

major shipping lanes) on the 3rd and 5th June, again in the lower parts of the boundary

layer (Figure 7(c-f)). This is again consistent with the observed elevated levels of

sulfate, due to the in-situ processing of urban emissions as the air was transported to

JFM, and then mixing with the fire emissions transported from the other direction at

height. Additionally, there was some amount of fine mode nitrate found on the 3rd Jun.,

further consistent with the in-situ processing of NO_2 emitted along with biomass

combustion, and therefore further evidence that mixing occurred between the two

different source regions.

3.6. Quantifying the impacts of fires

 Taking a first look at the possibility that fires are responsible, as described above,

we look at a summary of the statistics of the MODIS Fire Hotspots (Figure 8). As we

observe, while the total number of fire hotspots occurring throughout Southeast Asia

is moderate in early May, the number reduces to the extent that there are effectively

almost no burning parcels. Furthermore, those few square kilometers that are burning

are of low radiative intensity, under 200W/m^2, and hence only moderately or lowly

emitting, with the exception of a single day in late June, after the period of interest

has ended. This result showed that the MODIS fire hotspots are not very useful in wet

and tropical regions. Since MODIS fire hotspots are obstructed by both clouds and high levels of aerosols in the atmosphere, both of which are found associated with tropical forest fires. Additionally, due to the highly wet ground surface, a significant amount of the fires may low temperature and therefore not observable using the MODIS sensors (Cohen, 2014, Giglio et al., 2006; Yu et al., 2015).

Instead, we follow the approach of Cohen (2014) and look at the once to twice daily measured AOD data (Figure 9), in the context of the Empirical Orthogonal Functions approach (EOF). Since MODIS fire hotspots are effectively point measurements, and as such are not spatially robust, while AOD are continuous and more easier to be observed, and provides more precise and robust spatial information (Morisette et al., 2005a, 2005b; Levy et al., 2007, 2010; Remer et al., 2005). Therefore, if a significant signal exists, it is far easier to track and transport, at the scale of the inverse meteorological methods used here. The rationale is that over Southeast Asia there are only a few known large urban centers (Hanoi, Ho Chi Minh City, and Bangkok). Therefore, any other significant contribution to the variance of measured AOD must be from fires. The EOF technique has been shown to be an optimal manner by which to reproduce both the spatial extent and magnitude of the smoke over Continental Southeast Asia (Cohen, 2014; Cohen and Leocure, 2015).

As observed, the major regions of high AOD (average AOD > 0.4) are found over Southeast Asia as described above, with most of the sources coming from fires found in two arcs: one from Eastern Thailand, through Laos, and ending in Central Vietnam; and the other in the forests of Myanmar. The region around Hanoi is hard to decipher,

as it could be an urban expansion or fire. Additionally, there are regions found in urban East Asia, including the region between Hong Kong and Guangzhou and urbanization along the Yangtze River, however, all of these are known regions of urbanization and are not regions where fire is important.

An EOF Analysis concludes that in fact these are the only two statistically significant EOFs (Figure 10). The measured AOD over both of these regions is clearly elevated compared with the region as a whole throughout the entire time. Furthermore, there is an especially large contribution from these two EOFs compared with the background over Southeast Asia only (excluding AOD measured over China, which is downwind and hence not a fire source region) from May 31st to June 6th. Given the rapid transport time from Southeast Asia to JFM, the fact that these peaks occur within 1 day of the peaks in the fires is reasonable. Additionally, while the overall Southeast Asian AOD drops from the 8th onwards, there is a very significant difference (difference in AOD more than 0.5) between the overall AOD and that over the two source regions again from June 8th to June 13th. Given that there are markers of fires in GZ and ZH on June 12th, including high potassium and a low OC/EC ratio, and that a significant portion of the airflow over these regions originated from Southeast Asia within the past 72 hours, these results are consistent with high fires originating from Southeast Asia, then being transported over the next 72 hours to GZ and ZH. The fact that only one day has such measured conditions at the surface is likely due to the fact that the smoke is mostly concentrated near the boundary layer and hence local vertical mixing was most prevalent on or around June 12th.

4. Conclusion

Aerosol samples were collected at three sites using a 6-stage sampler during the local wet season in Southern China (May – Jun.) in 2010, to jointly study the mass and size distributions of aerosol chemical components. These site observations, together with model simulations and remote-sensing data, were used to investigate impacts of chemistry and atmospheric transport on the aerosol formation mechanisms at the three sites over Southern China. These were chosen such that they spanned different source and meteorological regions, at urban site GZ, a suburban site ZH, and a remote and forested site at JFM.

Sulfate and Ammonium were found to have a single peaked distribution from 0.44-1.0μm at all sites over the entire sampling period in this study, and accounted for 57.5-99 % of the daily-average total aerosol mass. Aqueous-phase reactions were found to be an essential factor to the formation of droplet sulfate. In addition, we found significant secondary processing and enhancement due to meteorological drivers which were wetter or allowed for a longer residence time.

A bi-modal distribution was found for nitrate, with a droplet mode in 0.44-1.0μm, indicating that it was formed under heavily polluted conditions or through similar secondary aerosol processing. On the other hand, nitrate had a significant fraction in the coarse mode in ZH and JFM during the wet season, where it accounted for about 40% of total mass. In this case, we found that the mass size distribution of nitrate was likely attributed to chloride depletion, with almost complete chloride depletion found

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in ZH and JFM during the wet season. Additionally, relative humidity was an important consideration in chloride depletion under relatively lower relative humidity, conditions, leading to the increase of coarse mode nitrate.

OC and EC showed a broad peak at 0.25-1.0μm in GZ and ZH, consistent with significant local sources, from urbanization, transport, residential, and shipping sources. Furthermore, under less heavily polluted conditions, OC was found to have a bi-modal distribution in JFM, with important contributions from secondary particle formation in the fine mode and potential biological aerosol in the coarse mode particles.

Additionally, OC and EC were shown to have broad peaks, and a significantly different ratio, raising the likelihood of a mixing of the local emissions with emissions transported long-range from biomass burning in Southeast Asia. These conditions were further supported by a large amount of potassium found jointly with the aerosol. An in-depth analysis of the meteorology, and remotely sensed Fire and AOD properties, in conjunction with a variance maximizing technique, provided further evidence to help us validate this assumption. It is clear that there was a significant impact on GZ and ZH from fire sources from Thailand, Laos, and Vietnam, as well as possible long-range transport of urban emissions from the urban megacity of Hanoi in Vietnam. The combination of local formation and long-range transport played a significant role on the variation of particle chemical compositions.

Overall, we found that the size distribution and formation of aerosols greatly depend on emissions, location, and in-situ processing, especially aqueous-phase

639 reactions. Strong local formation and long-range-transport of both urban pollution

640 from GZ and of biomass burning from Southeast Asia all were observed to influence

641 the size distribution of chemical components across all of the area studies. On the

642 other hand, the interaction between sea salt aerosols and anthropogenic pollutants

643 showed significant effects at coastal locations and play an important role in the

644 deterioration of the air quality in Southern China under high relative humidity

645 conditions during the wet season.

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656 **References**

657 Anlauf, K., Li, S.M., Leaitch, R., Brook, J., Hayden, K., Toom-Sauntry D., and Wiebe,

658   A.: Ionic composition and size characteristics of particles in the Lower Fraser

659   Valley: Pacific 2001 field study, Atmospheric Environment, 40, 2662- 2675, doi:

660   10.1016 /j.atmosenv. 2005.12.027, 2006.

661 Barth, M.C., Hegg, D.A., and Hobbs, P.V.: Numerical modeling of cloud and

662   precipitation chemistry associated with two rainbands and some comparisons with

663   observations, Journal of Geophysical Research, 97, 5825- 5845, doi:

664   10.1029/92JD00464, 1992.

665 Brioude, J., Arnold, D., Stohl, A., Gassiani, M., Morton, D., Seibert, P., Angevine, W.,

666   Evan, S., Dingwell, A., Fast, J.D., Easter, R.C., Pisso, I., Burkhart, J., and

667   Wotawo, G.: The Lagrangian particle disperation model FLEXPART-WRF

668   version 3.1, Geoscientific Model Development, 6, 1889-1904, doi: 10.5194/

669   gmd-6-1889-2013, 2013.

670 Burnett, R.T., et al.: An integrated risk function for estimating the global burden of

671   disease attributable to ambient fine particulate matter exposure, Environmental

672   Health Perspectives, 122, 397, doi:10.1289/ehp.1307049, 2014.

673 Cao, J.J., Lee, S.C., Ho, K.F., Zou, S.C., Fung, K., Li, Y., Watson, J.G., and Chow, J.

674   C.: Spatial and seasonal variations of atmospheric organic carbon and elemental

675   carbon in Pearl River Delta Region, China, Atmospheric Environment, 38, 4447–

676   4456, doi:10.1016/j.atmosenv.2004.05.016, 2004.

677 Chatterjee, A., Adak, A., Singh, A.K., Srivastava, M.K., Ghosh, S.K., Tiwari, S.,

678   Devara, P.C.S., and Raha, S.: Aerosol chemistry over a high altitude station at

679   northeastern Himalayas, India, PLoS ONE, 5, e11122, doi: 10.1371/journal.

680   pone.0011122, 2010.

681 Chen, S.Y., Huang, J.P., Zhao, C., Qian, Y., Leung, L.R. and Yang, B.: Modeling the

682   transport and radiative forcing of Taklimakan dust over the Tibetan Plateau: A

case study in the summer of 2006, Journal of Geophysical Research, 118, 797–812, doi:10.1002/jgrd.50122, 2013a.

Chen, H.Z., Wu, D., Liao, B.T., Mao, X., Zhuang, H.B., Li, L., Liu, A.M., Li, H.Y., and Li, F.: Influence of different acidic gases and relative humidity on the chlorine loss of marine aerosols, Acta Scientiae Circustantiae, 33, 1141-1149, 2013b (in Chinese with English Abstract).

Clegg, S.L., Brimblecombe, P., and Wexler, A.S.: Thermodynamic Model of the System $H^+−NH_4^+−SO_4^{2-}−NO_3^−−H_2O$ at Tropospheric Temperatures, The Journal of Physical Chemistry A, 102, 2137-2154, doi: 10.1021/jp973042r, 1998.

Cohen J.B., and Lecoeur, E.: Decadal-scale relationship between measurements of aerosols, land-use change, and fire over Southeast Asia, Atmospheric Chemistry and Physics Discussion, 15, 26895-26957, doi:10.5194/acpd-15-26895-2015, 2015.

Cohen, J. B.: Quantifying the Occurrence and Magnitude of the Southeast Asian Fire Climatology, Environmental Research Letter, 9, 114018, doi:10.1088/1748-9326/9/11/114018, 2014.

Cohen, J. B., and Wang, C.: An Estimate of Global Black Carbon Emissions Using a Top-Down Kalman Filter Approach, Journal of Geophysical Research , 119, 1-17, doi:10.1002/2013JD019912, 2013.

Cohen, J. B., and Prinn, R.G.: Development of a fast, urban chemistry metamodel for inclusion in global models, Atmospheric Chemistry and Physics, 11, 7629-7656, doi:10.5194/acp-11-7629-2011, 2011.

705 Cohen, J. B., Prinn, R.G., and Wang, C.: The Impact of detailed urban-scale

706   processing on the composition, distribution, and radiative forcing of

707   anthropogenic aerosols, Geophysical Research Letters, 38, L10808,

708   doi:10.1029/2011GL047417, 2011.

709 Chung S.H., and Seinfeld, J.H.: Climate response of direct radiative forcing of

710   anthropogenic black carbon, Journal of Geophysical Research, 110, D11102, doi:

711   10.1029/2004JD005441, 2005.

712 Dasgupta, P.K., Campbell, S.W., Al-Horr, R.S., Ullah, S.M.R., Li, J.Z., Amalfitano, C.,

713   and Poor, N.D.: Conversion of sea salt aerosol to $NaNO_3$ and the production of

714   HCl: Analysis of temporal behavior of aerosol chloride/nitrate and gaseous

715   HCl/HNO_3concentrations with AIM, Atmospheric Environment, 41, 4242-4257,

716   doi:10.1016/j.atmosenv.2006.09.054, 2007.

717 Delene, D.J. and Ogren, J.A.: Variability of aerosol optical properties at four North

718   American surface monitoring sites, Journal of the Atmospheric Sciences, 59,

719   1135-1150, doi: http://dx.doi.org/10.1175/ 1520-0469(2002)059 <1135:VOAOPA>

720   2.0.CO;2, 2002.

721 Draxler, R.R., and Hess, G.D.: An overview of the HYSPLIT_4 modeling system of

722   trajectories, dispersion, and deposition, Australian Meteorological Magazine, 47,

723   295-308, 1998.

724 Dubovik, O., Smirnov, A., Holben, B.N., King, M.D., Kaufman, Y.J., Eck, T.F., and

725   Slutsker, I.: Accuracy assessments of aerosol optical properties retrieved from

726   Aerosol Robotic Network (AERONET) Sun and sky radiance measurements,

Journal of Geophysical Research, 105, 9791-9806, doi: 10.1029/2000JD900040, 2000.

Ervens, B., Turpin, B.J., and Weber, R.J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmospheric Chemistry and Physics, 11, 11069-11102, doi:10.5194/acp-11-11069-2011, 2011.

Giglio, L., Csiszar, I., and Justice, C.O.: Global distribution and seasonality of active fires as observed with the Terra and Aqua Moderate Resolution Imaging Spectroradiometer (MODIS) sensors, Journal of Geophysical Research, 111, G02016, doi: 10.1029 / 2005JG000142, 2006.

Giglio, L., Kendall, J.D., and Mack, R.: A multi-year active fire data set for the tropics derived from the TRMM VIRS, International Journal of Remote Sensing, 24, 4505- 4525, doi: 10.1080/0143116031000070283, 2003.

Han, Y., Han, Z., Cao, J.J., Chow, J.C., Watson, J.G., An, Z.S., Liu, S.X., and Zhang, R.J.: Distribution and origin of carbonaceous aerosol over a rural high-mountain lake area, Northern China and its transport significance, Atmospheric Environment, 42, 2405-2414, doi:10.1016/j.atmosenv.2007.12.020, 2008.

Harrison, R.M., and Pio, C.A.: Size differentiated composition of inorganic atmospheric aerosols of both marine and polluted continental origin, Atmospheric Environment, 17, 1733-1738, doi:10.1016/0004-6981(83)90180-4, 1983.

Heald, C.L. and Spracklen, D.V.: Atmospheric budget of primary biological aerosol particles from fungal spores, Geophysical Research Letters, 36, L09806, doi:

749   10.1029/2009GL037493, 2009.

750 Huang, J.P., Wang, T.H., Wang, W.C., Li, Z.Q. and Yan, H.R.: Climate effects of dust

751   aerosols over East Asian arid and semiarid regions, Journal of Geophysical

752   Research, 119, 11398–11416, doi: 10.1002/2014JD021796, 2014.

753 Huang, X.F., Yu, J.Z., He, L.Y., and Hu. M.,: Size distribution characteristics of

754   elemental carbon emitted from Chinese vehicles: results of a tunnel study and

755   atmospheric implications, Environmental Science & Technology, 44, 5355–5360,

756   doi: 10. 1021 /es0607281, 2006.

757 Huang, Z.E., Harrision, R.M., Allen, A.G., James, J.D., Tilling, R.M. and Yin, J.X.:

758   Field intercomparison of filter pack and impactor sampling for aerosol nitrate,

759   ammonium, and sulphate at coastal and inland sites, Atmospheric Research, 71,

760   215-232, doi:10.1016/j.atmosres.2004.05.002, 2004.

761 Hsu, S.C., Liu, S.C., Kao, S.J., Jeng, W.L., Huang, Y.T., Tseng, C.M., Tsai, F.J., Tu,

762   J.Y., and Yang, Y.: Water-soluble species in the marine aerosol from the northern

763   South China Sea: High chloride depletion related to air pollution, Journal of

764   Geophysical Research, 112, D19304, doi:10.1029/2007JD008844,2007.

765 Kim, S.W., Berthier, S., Raut, J.C., Chazette, P., Dulac, F., and Yoon, S.C.: Validation

766   of aerosol and cloud layer structures from the space-borne lidar CALIOP using a

767   ground-based lidar in Seoul, Korea, Atmospheric Chemistry and Physics, 8,

768   3705-3720, doi:10.5194/acp-8-3705-2008, 2008.

769 Jacobson, M.Z.:   Global direct radiative forcing due to multicomponent

770   anthropogenic and natural aerosols, Journal of Geophysical Research, 106,

771   1551-156, doi: 10.1029/2000JD900514, 2001.

772   Lan, Z.J., Chen, D.L., Li, X., Huang, X.F., He, L.Y., Deng, Y.G., Feng, N., and Hu, M.:

773   Modal characteristics of carbonaceous aerosol size distribution in an urban

774   atmosphere of South China, Atmospheric Research, 100, 51-60,

775   doi:10.1016/j.atmosres.2010.12.022, 2011.

776   Levy, R., Remer, L., Kleidman, R., et al.: Global evaluation of the Collection 5

777   MODIS darktarget aerosol products over land, Atmospheric Chemistry and

778   Physics, 10, 10399-10420, doi:10.5194/acp-10-10399-2010, 2010.

779   Levy, R., Remer, L., and Dubovik, O.: Global aerosol optical properties and

780   application to Moderate Resolution Imaging Spectroradiometer aerosol retrieval

781   over land, Journal of Geophysical Research, 112, 1-15, doi:

782   10.1029/2006JD007815, 2007.

783   Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., and Turpin, B.J.: Aqueous chemistry

784   and its role in secondary organic aerosol (SOA) formation, Atmospheric

785   Chemistry and Physics, 10, 10521-10539, doi: 10.5194/acp-10-10521-2010, 2010.

786   Liu, Y., Huang, J., Shi, G., Takamura, T., Khatri, P., Bi, J., Shi, J., Wang, T. Wang, X.,

787   and Zhang B.: Aerosol optical properties and radiative effect determined from

788   sky-radiometer over Loess Plateau of Northwest China, Atmospheric Chemistry

789   and Physics, 11, 11455–11463, doi: 10.5194/acp-11-11455-2011, 2011.

790   Liu, S., Hu, M., Slanina, S., He, L.Y., Niu, Y.W., Bruegemann, E., Gnauk, T. and

791   Herrmann, H.: Size distribution and source analysis of ionic compositions of

792   aerosols in polluted periods at Xinken in Pearl River Delta (PRD) of China,

Atmospheric Environment, 42, 6284-6295, doi: http://dx.doi.org/10.1016/j. atmosenv.2007.12.035, 2008.

Lu, Q., Zheng, J.Y., Ye, S.Q., Shen, X.L., Yuan, Z.B. and Yin, S.S.: Emission trends and source characteristics of SO_2, NOx, PM_{10} and VOCs in the Pearl River Delta region from 2000 to 2009, Atmospheric Environment, 76, 11-20, doi: http://dx.doi.org/10.1016/j.atmosenv.2012.10.062, 2013.

Meng, Z., and Seinfeld, J.H.: On the source of the submicrometer droplet mode of urban and regional aerosols, Aerosol Science and Technology, 20, 253- 265, doi: 10.1080 /02786829408959681, 1994.

Myhre, G., et al.: Radiative forcing of the direct aerosol effect from AeroCom Phase II simulations, Atmospheric Chemistry and Physics, 13, 1853-1877, doi:10.5194/acp-13-1853-2013, 2013.

Morisette, J.T., Giglio, L., Csiszar, I. and Justice, C.O.: Validation of the MODIS active fire product over Southern Africa with ASTER data, International Journal of Remote Sensing, 26, 4239-4264, doi: 10.1080/01431160500113526, 2005a.

Morisette, J.T., Giglio, L., Csiszar, I., Setzer, A., Schroeder, W., Morton, D. and Justice, C.O.: Validation of MODIS active fire dectection productes derived from two algorithms, Earth Interaction, 9, 1-23, doi: http://dx.doi.org/10.1175/EI141.1, 2005b.

Petrenko, M., Kahn, R., Chin, M., Soja, A., Kucsera, T., and Harshvardhan,: The use of satellite-measured aerosol optical depth to constrain biomass burning emissions source strength in the global model GOCART, Journal of Geophysical Research,

117, D18212, doi: 10.1029/2012JD017870, 2012.

Pierson, W.R., and Brachaczek, W.W.: Coarse and fine particle atmospheric nitrate and HNO₃(g) in Claremont, California, during the 1985 nitrogen species methods comparison study, Atmospheric Environment, 22, 1665–1668, doi:10.1016/0004-6981(88)90394-0, 1998.

Pillai, P.S., and Moorthy, K.K.: Aerosol mass-size distributions at a tropical suburban environment: response to mesoscale and synoptic processes, Atmospheric Environment, 35, 4099- 4112, doi:10.1016/S1352-2310(01)00211-4, 2001.

Pio, C., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., and Schock, M.: Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west–east transect across Europe, Journal of Geophysical Research-Atmospheres, 112, D23S02, 10.1029/2006JD008038, 2007.

Ramanathan, V., and Garmichael, G.: Global and regional climate changes due to black carbon, Nature Geoscience, 1, 221-227, doi:10.1038/ngeo156, 2008.

Remer, L.A., Mattoo, S., Levy, R.C., Munchak, L.A.: MODIS 3km aerosol product: algorithm and global perspective, Atmospheric Measurement Techniques, 6, 1829–1844, doi:10.5194/amt-6-1829-2013, 2013.

Remer, L., Kaufman, Y., Tanre, D., Mattoo, S., Chu, D.A., Martins, J.V., Li, R.R., Ichoku, C., Levy, R.C., Kleidman, R.G., Eck, T.F, Vermote, E. and Holben, B.N.: The MODIS Aerosol Algorithms, Products, and Validation, Jouranl of

837   Atmospheric Science, 62, 947-973, doi: 10.1175/JAS3385.1, 2005.

838   Rosenfeld, D., Sherwood, S., Wood, R., and Donner, L.: Climate effects of aerosol-

839   cloud interactions, Science, 343, 379-380, doi: 10.1126/science.1247490, 2014.

840   Schuster, G.L., Dubovik, O., and Holben, B.N.: Angstrom exponent and bimodal

841   aerosol size distributions, Journal of Geophysical Research, 111, D07207, doi: 10.

842   1029 /2005JD006328, 2006.

843   Seinfeld, J., and Pandis, S.: Atmospheric Chemistry and Physics: From Air Pollution

844   to Climate Change, John Wiley & Sons, New York, 2006.

845   Situ, S.P, Guenther, A., Wang, X.M., Jiang, X.X., Turnipseed, A., Wu, Z.Y., Bai, J.H.,

846   and Wang, X.X.: Impacts of seasonal and regional variability in biogenic VOC

847   emissions on surface ozone in the Pearl River delta region, China, Atmospheric

848   Chemistry and Physics, 13, 11803- 11817, doi:10.5194/acp-13-11803-2013, 2013.

849   Stelson, A.W. and Seinfeld, J.H.: Relative humidity and temperature dependence of

850   the ammonium nitrate dissociation constant, Atmospheric Environment, 16, 983-

851   992, doi:10.1016/0004-6981(82)90184-6, 1982.

852   Stohl, A., Hittenberer, M., and Wotawa, G.: Validation of the Lagrangian particle

853   dispersion model Flexpart against large-scale tracer experiment data, Atmospheric

854   Environment, 32, 4245-4264, doi:10.1016/S1352-2310(98)00184-8, 1998.

855   Tao, J., Ho, K.F., Chen, L.G., Zhu, L.H., Han, J.L., and Xu, Z.C.: Effect of chemical

856   composition of $PM_{2.5}$ on visibility in Guangzhou, China, 2007 Spring, Particulogy,

857   7, 68-75, doi: 10.1016/j.partic.2008.11.002, 2009.

858   Tsigaridis, K., et al.: The AeroCom evaluation and intercomparison of organic aerosol

in global models, Atmospheric Chemistry and Physics, 14, 10845-10895, doi:10.5194/acp-14-10845-2014, 2014.

Volkamer, R., Ziemann, P.J., and Molina, M.J.: Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seedeffect on SOA yields due to organic photochemistry in the aerosol aqueous phase, Atmospheric Chemistry and Physics, 9, 1907-1928, doi: 10.5194/acp-9-1907-2009, 2009.

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

Wang, Z., et al.: Source and variation of carbonaceous aerosols at Mount Tai, North China: results from a semi-continuous instrument, Atmospheric Environment, 45, 1655-1667, doi: 10.1016/j.atmosenv.2011.01.006, 2011.

Wang, Y., Zhuang, G.S., Tang, A.H., Yuan, H., Sun, Y.L., Chen, S. and Zheng, A.H.: The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing, Atmospheric Enviornment, 39, 3771-3784, doi:10.1016/j.atmosenv.2005.03.013, 2005.

Yang, X. and Wenig, M.: Study of columnar aerosol size distribution in Hong Kong, Atmospheric Chemistry and Physics, 9, 6175-6189, doi:10.5194/acp-9-6175-2009, 2009.

Yao, X.H., Ling, T.Y., Fang, M. and Chan, C.K.: Comparison of thermodynamic predictions for in situ pH in $PM_{2.5}$, Atmospheric Environment, 40, 2835-2844, doi:10.1016/j.atmosenv.2006.01.006, 2006.

Yao, X.H., Lau, A.P.S., Fang, M., Chan, C.K., and Hu, M.: Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 2—dicarboxylic acids, Atmospheric Environment, 37, 3001-3007, doi:10.1016/S1352-2310(03)00256-5, 2003a.

Yao, X.H., Fang, M. and Chan, C.K. The size dependence of chloride depletion in fine and coarse sea-salt particles, Atmospheric Environment, 37, 742-751, doi:10.1016/S1352-2310(02)00955-X, 2003b.

Yu, C., Chen, L.F., Li, S.S., Tao, J.H. and Su, L.: Estimating Biomass Burned Areas from Multispectral Dataset Detected by Multiple-Satellite, Spectroscopy and Spectral Analysis, 35, 739-745, doi:10.3964/j.issn.1000-0593(2015)03-0739 -07, 2015.

Zhang, Z.S., Engling, G., Zhang, L.M., Kawamura, K., Yang, Y.H., Tao, J., Zhang, R.J., Chan, C.Y. and Li, Y.D.: Significant influence of fungi on coarse carbonaceous and potassium aerosols in a tropical rainforest, Environmental Research Letters, 10, 034015, doi:10.1088/1748-9326/10/3/034015, 2015.

Zhang, Z.S., Engling, G., Chan, C.Y., Yang, Y.H., Lin, M., Shi, S., He, J., Li, Y.D., and Wang, X.M.: Determination of isoprene-derived secondary organic aerosol tracers (2-methyltetrols) by HPAEC-PAD: Results from size-resolved aerosols in a tropical rainforest, Atmospheric Environment, 70, 468- 476, doi:10.1016/j.atmosenv. 2013.01.020, 2013a.

Zhang, Q., Tie, X.X., Lin, W.L., Cao, J.J., Quan, J.N., Ran, L., and Xu, W.Y.: Variability of SO_2 in an intensive fog in North China Plain: Evidence of high

solubility SO$_2$, Particuology, 11, 41-47, doi:10.1016/j.partic.2012.09.005, 2013b.

Zhao, Y.L., and Gao, Y.: Mass size distributions of water-soluble inorganic and organic ions in size-segregated aerosols over metropolitan Newark in the US east coast, Atmospheric Environment, 42, 4063-4078, doi:10.1016/j.atmosenv.2008.01.032, 2008a.

Zhao, Y.L., and Gao, Y.: Acidic species and chloride depletion in coarse aerosol particles in the US east coast, Science of The Total Environment, 407, 541- 547, doi:10.1016/j.scitotenv.2008.09.002, 2008b.

Zheng, J.Y., He, M., Shen, X.L., Yin, S.S., and Yuan, Z.B.: High resolution of black carbon and organic carbon emissions in the Pearl River Delta region, China, Science of The Total Environment, 438, 189-200, doi: http://dx.doi.org/10.1016/j.scitotenv.2012.08.068, 2012.

Zheng, J.Y., Zhang, L.J., Che, W.W., Zheng, Z.Y. and Yin, S.S.: A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment, Atmospheric Environment, 43, 5112- 5122, doi: http://dx.doi.org/10.1016/j.atmosenv.2009.04.060, 2009.

Zhou, S.Z., Davy, P.K., Wang, X.M., Cohen, J.B., Liang, J.Q., Huang, M.J., Fan, Q., Chen, W.H. Chang, M., Ancelet, T. and Trompetter, W.J.: High time-resolved elemental components infine and coarse particles in the Pearl River Delta region of Southern China: Dynamic variations and effects of meteorology, Science of the Total Environment, doi: 10.1016/j.scitotenv.2016.05.194, 2016 (in press).

Zhou, Y., Xue, L.K., Wang, T., Gao, X.M., Wang, Z., Wang, X.F., Zhang, J.M., Zhang,

925   Q.Z., and Wang, W.X.: Characterization of aerosol acidity at a high mountain site

926   in central eastern China, Atmospheric Environment, 51, 11-20,

927   doi:10.1016/j.atmosenv.2012.01.061, 2012.

928   Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S.: Size distributions of particulate

929   sulfate, nitrate and ammonium at a suburban site in Hong Kong, Atmospheric

930   Environment,33, 843- 853, doi:10.1016/S1352-2310(98)00305-7, 1999.

Figures

Figure 1. Location of sampling sites in Southern China: GZ (Guangzhou), ZH
(Zhuhai), and JFM (Jianfeng Mountain) and their surrounding environments

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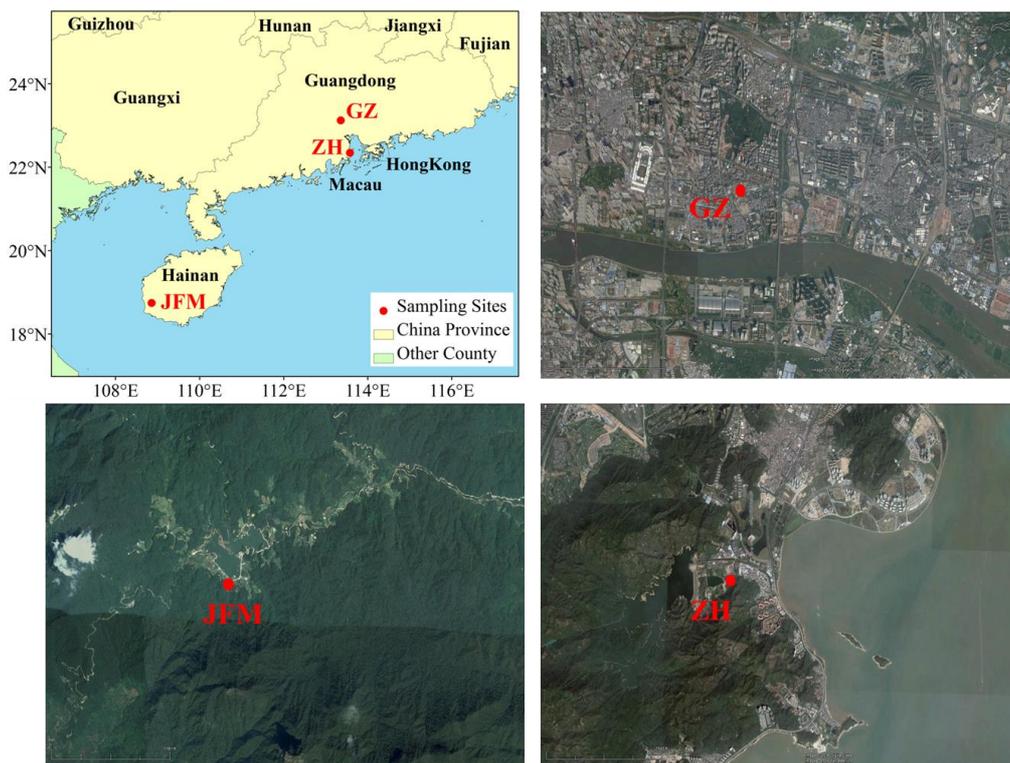
Figure 2. Time series of PM_{18} chemical compositions at the three sites during the

2010 wet season.
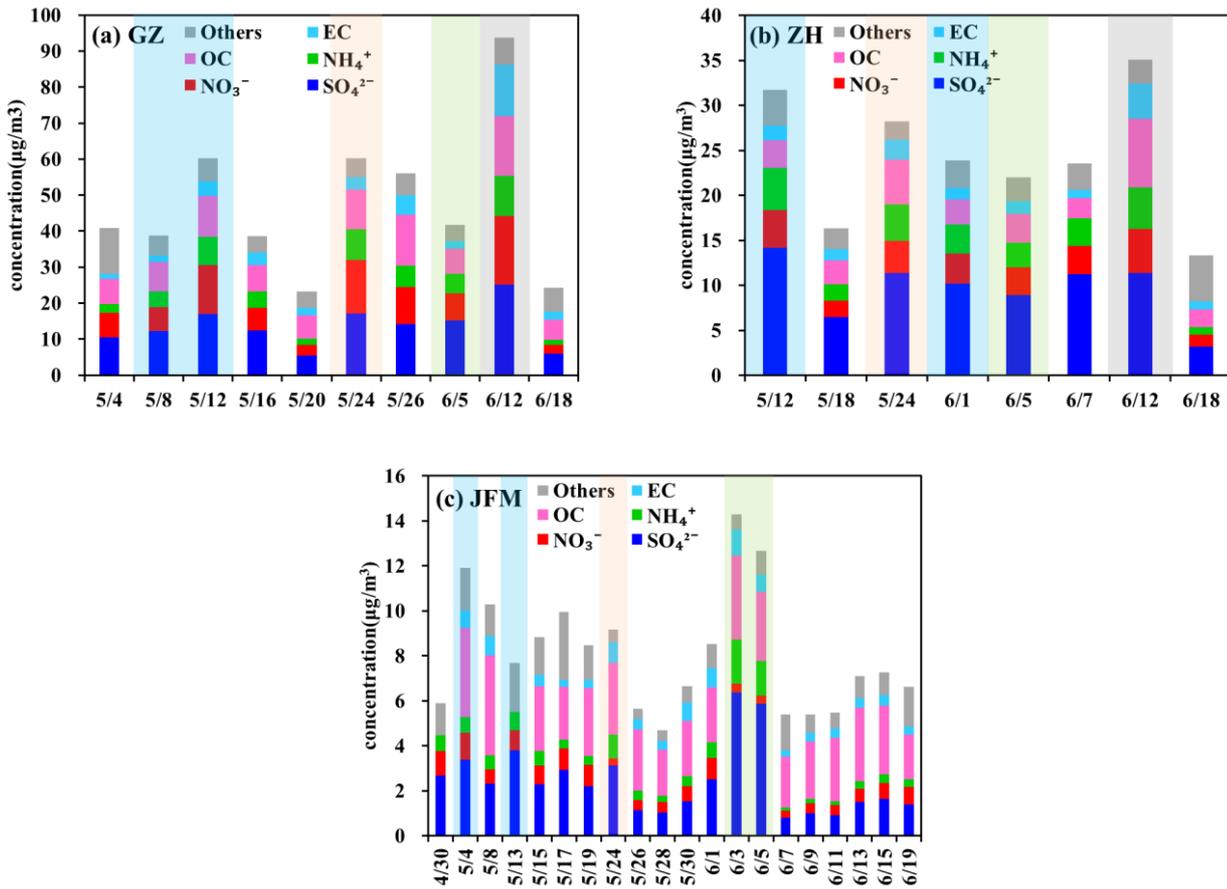
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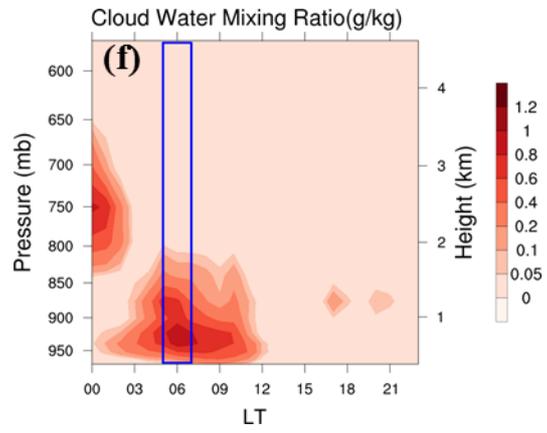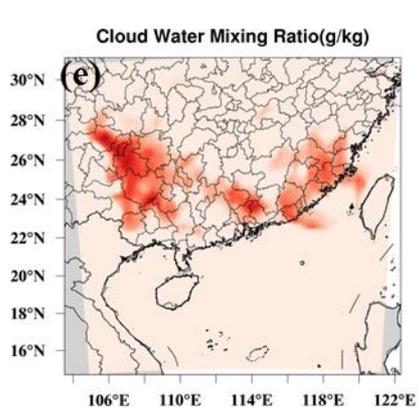**Figure 3.** The mass size distribution of major compositions (SO_4^{2-}, NO_3^-, NH_4^+, OC
977 and EC) at the three sites during study period (SO$_4^{2-}$ is plotted against the right
978 Y-Axes)

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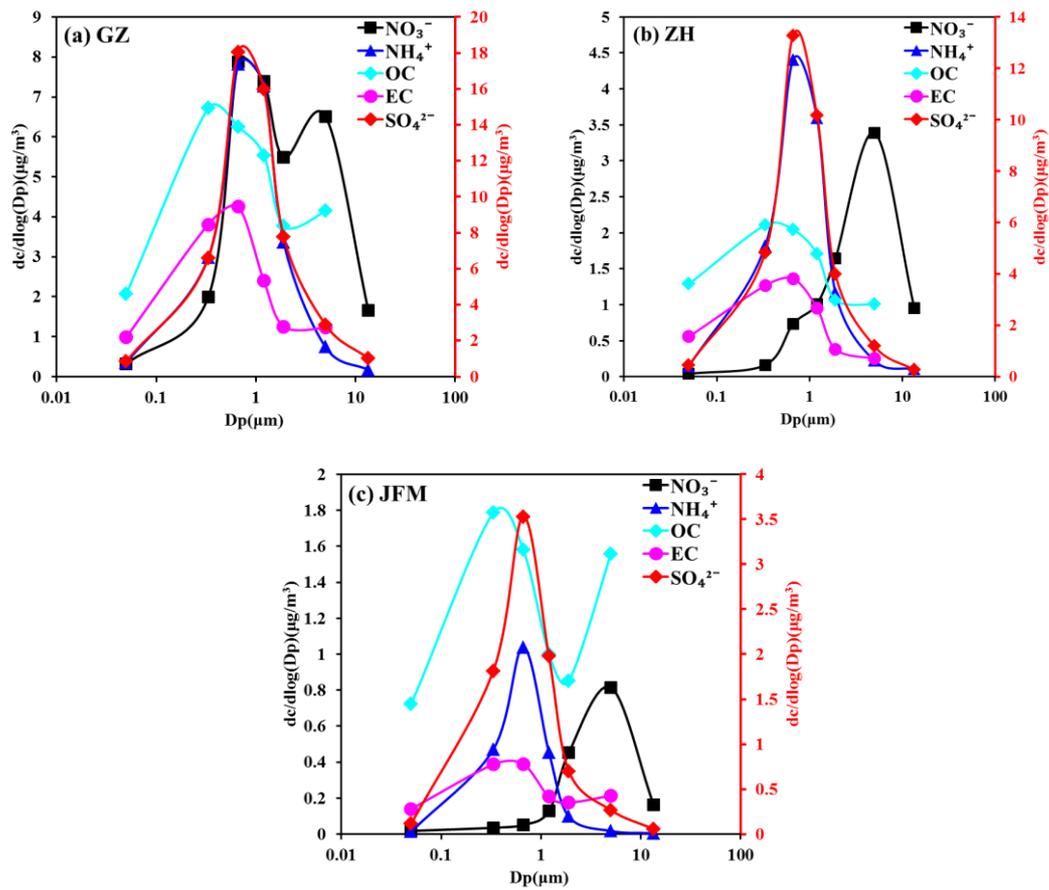
Figure 4. Case study on 8th May. in GZ ((a)The cloud fraction over Southern China; (b)Distribution of simulated average 2 m relative humidity at 05:00-07:00 LT; (c) The time series of observational visibility, wind speed, relative humidity and the depression of dew point (time resolution was 30mins); (d) The time series of monitoredmean SO_2 during 2009-2010 and SO_2 on 8th May ;(e) Distribution of simulated average cloud; (f) The time-height distribution of simulated cloud water mixing ratio on 8th May; (g-h) The time-height of simulated Aitken and accumulation mode SO_4^{2-})
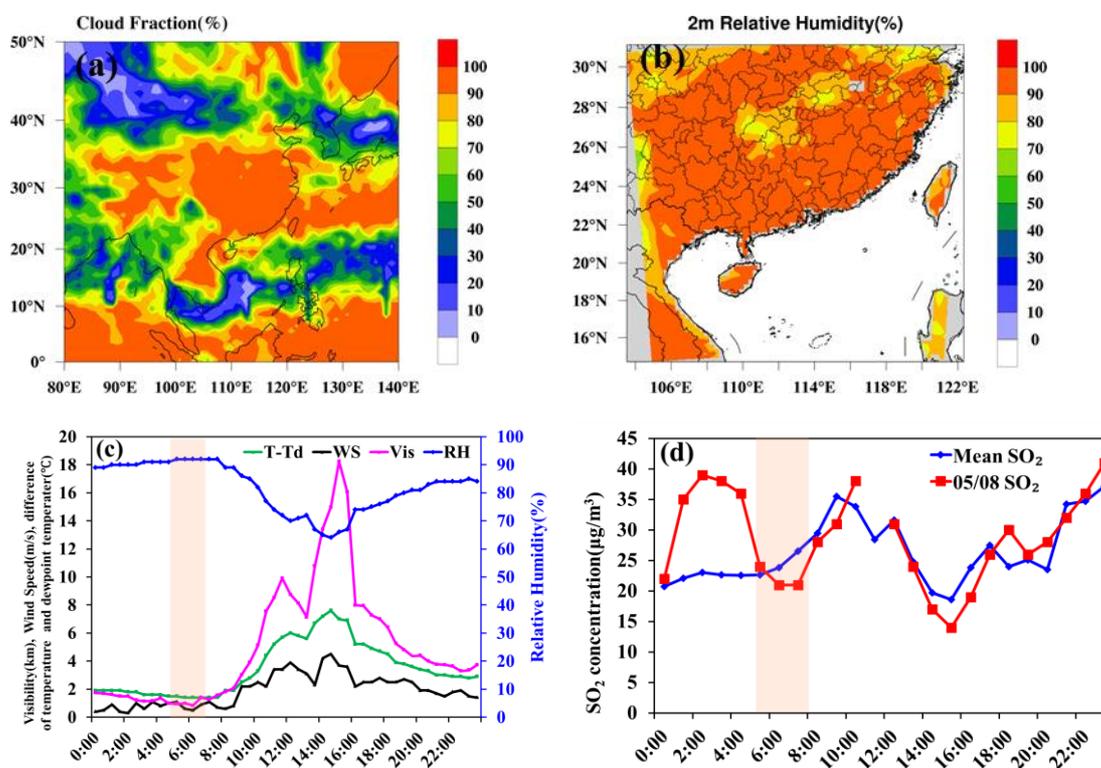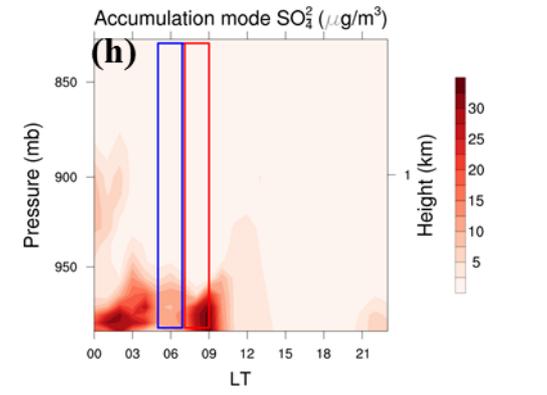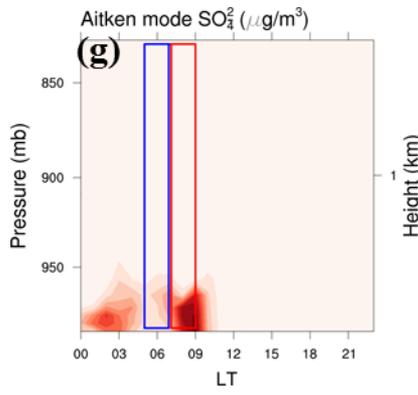
Cloud Water Mixing Ratio(g/kg)

Cloud Water Mixing Ratio(g/kg)

Aitken mode SO$_4^2$ (μg/m^3)

Accumulation mode SO$_4^2$ (μg/m^3)

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Figure 5. The mass size distribution of (a-c) Na$^+$ and Cl$^-$ and (d) percentage of chloride depletion at the three sites
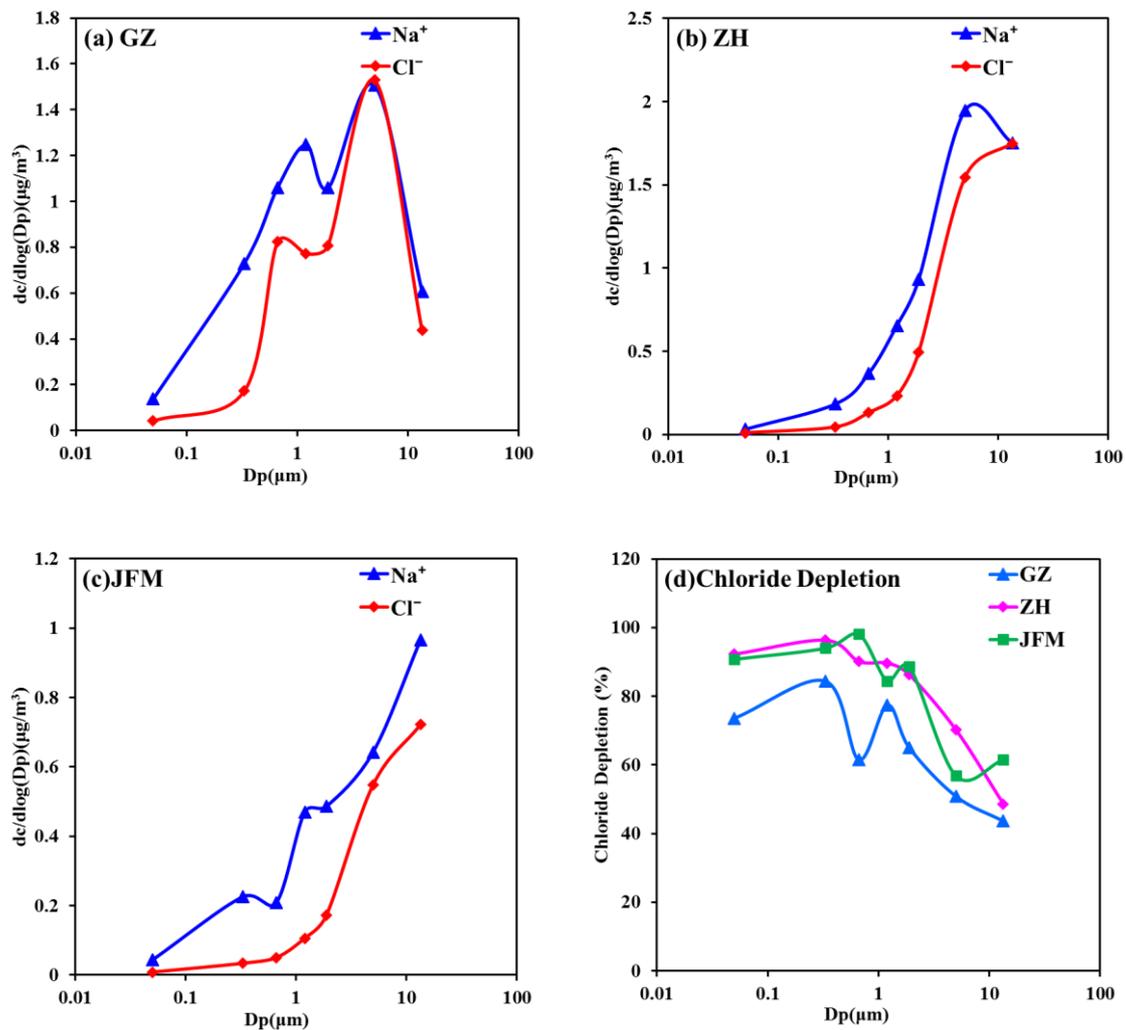
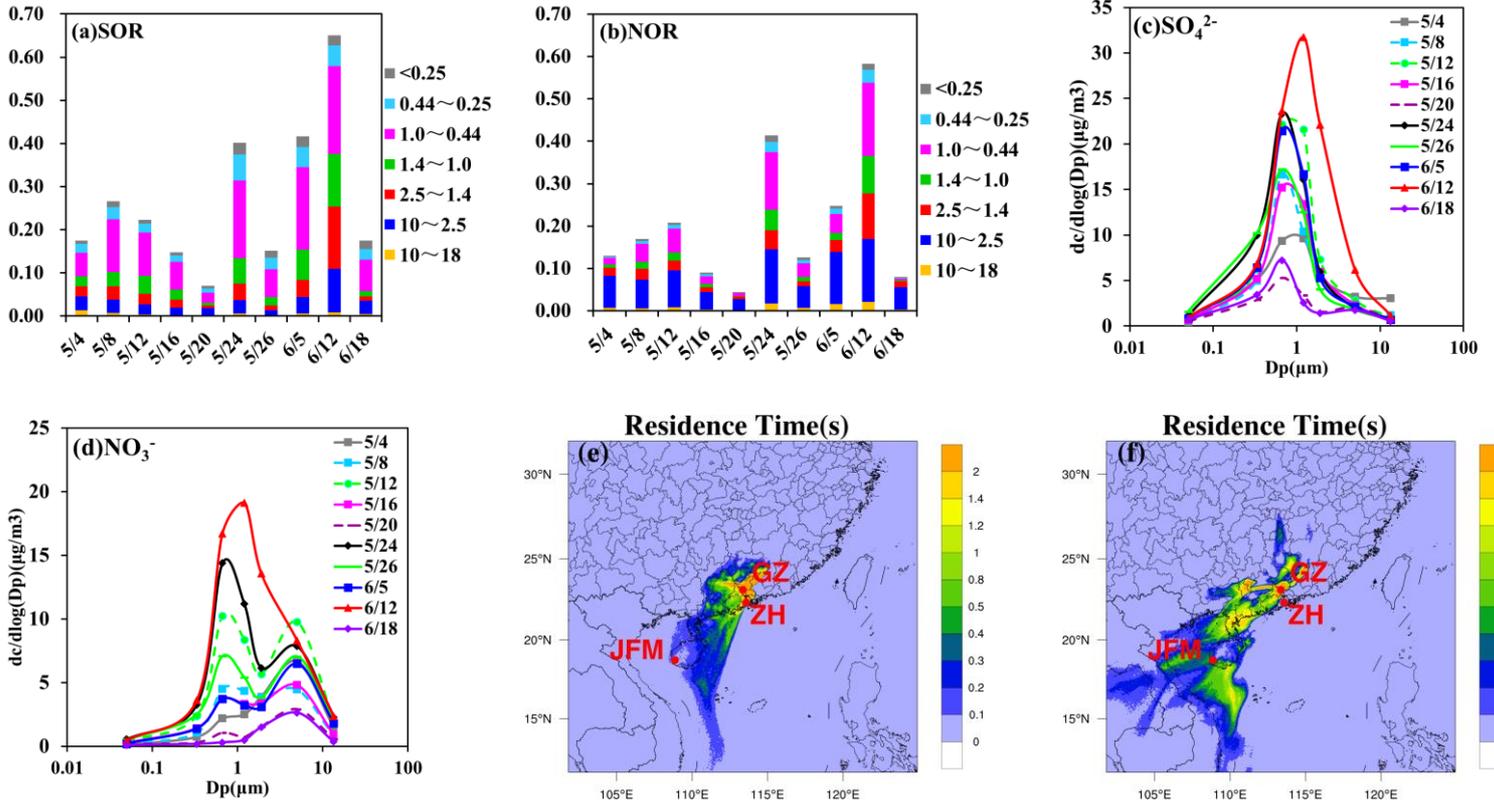**Figure 6.** Case study on 12th Jun. in GZ ((a-b) The time series of SOR and NOR; (c-d)

995 The mass size distribution of SO_4^{2-} and NO_3^-; (e-f) FLEXPART-WRF total column

996 residence times over the last 72h arriving in GZ on 12th Jun. at 100m and 1000m)

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Figure 7. Case study on 1st, 3rd and 5th Jun. in JFM ((a-b) FLEXPART-WRF total

999   column residence times on over the last 72h arriving in JFM on 1st Jun. at 100m and

1000   1000m; (c-d) and (e-f) same at (a-b) but on 3rd and 5^{th}Jun. respectively; (g-h) The

1001   mass size distribution of SO_4^{2-} and NO_3^-)
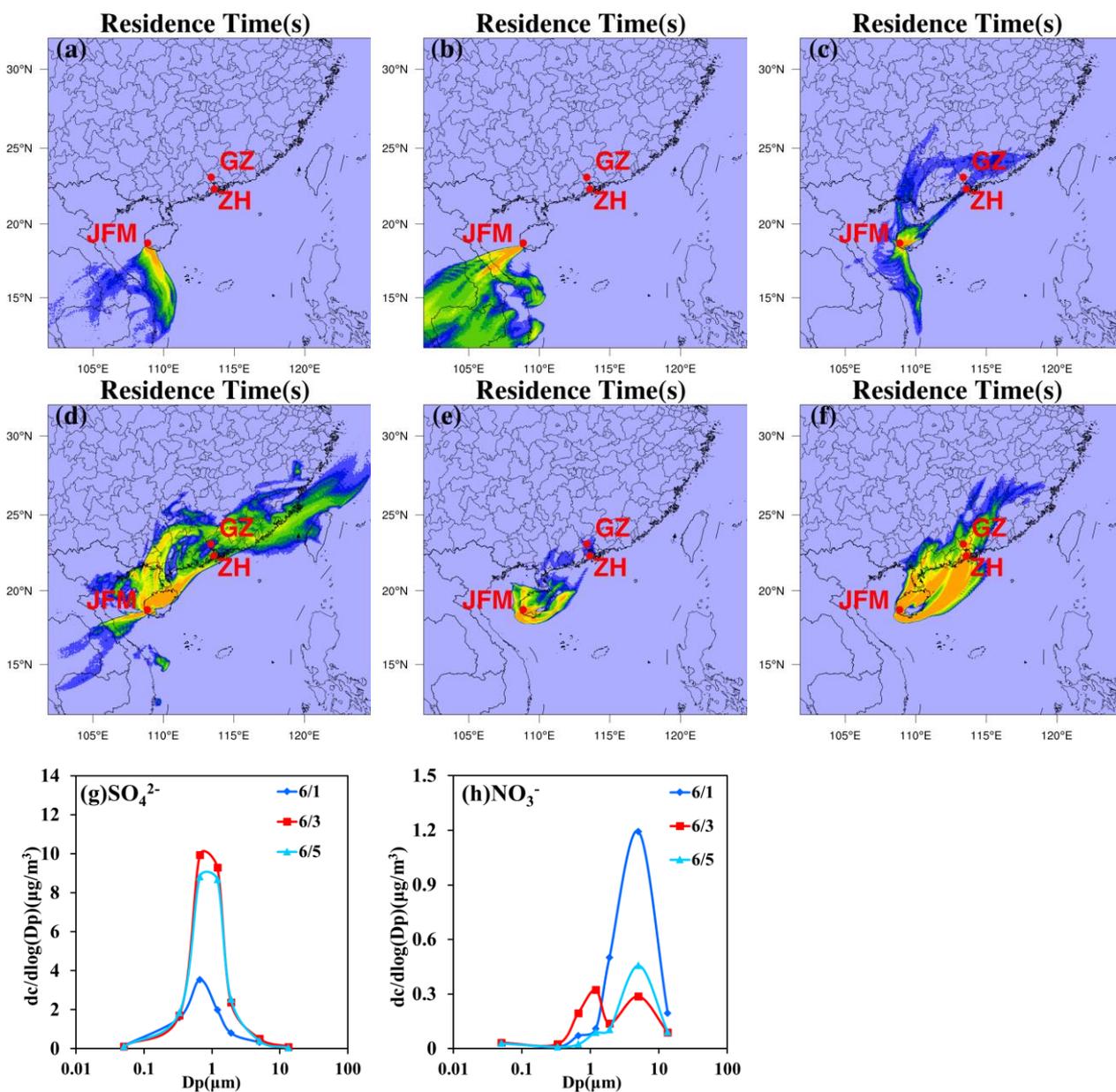

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1005   **Figure 8.** Spatially averaged/aggregated statistics of (a) MODIS Fire numbers (Count)

1006   and (b) Fire Radiative Power (FRP) over Southeast Asia for May and June 2010. The

1007   statistics represent the respective Count [total number of burning 1kmx1km pixels]

1008   and average FRP [W/m^2 per 1kmx1km pixel] over the whole of Southeast Asia and

1009   the specific regions where the AOD (as an indicator for smoke) has its highest levels

1010   of variability: EOF1 and EOF2.
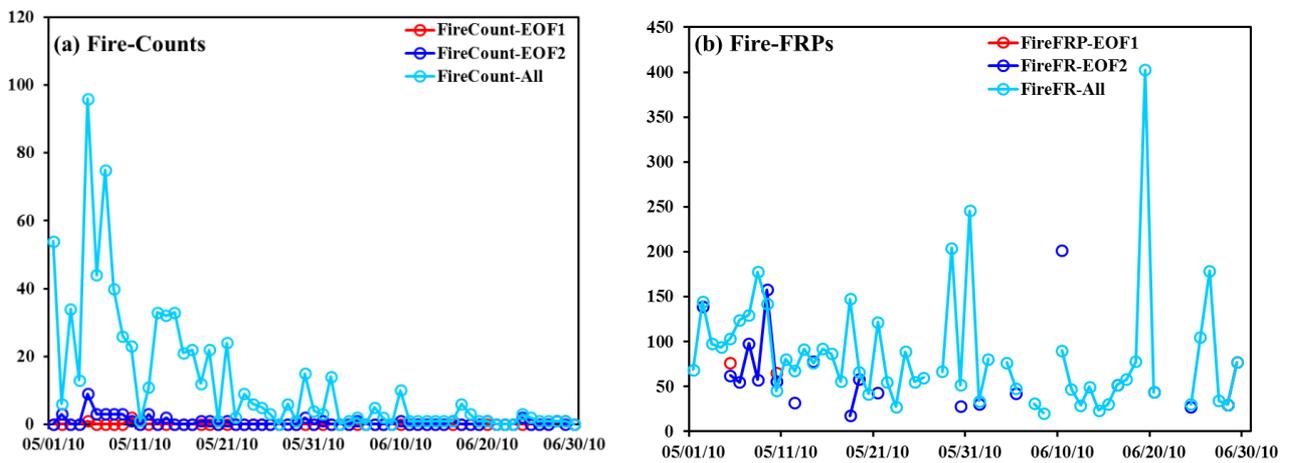

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1019 **Figure 9.** Average spatial distribution of the (a) mean and (b) standard deviation of

1020 daily MODIS AOD from May 1st through June 30th 2010
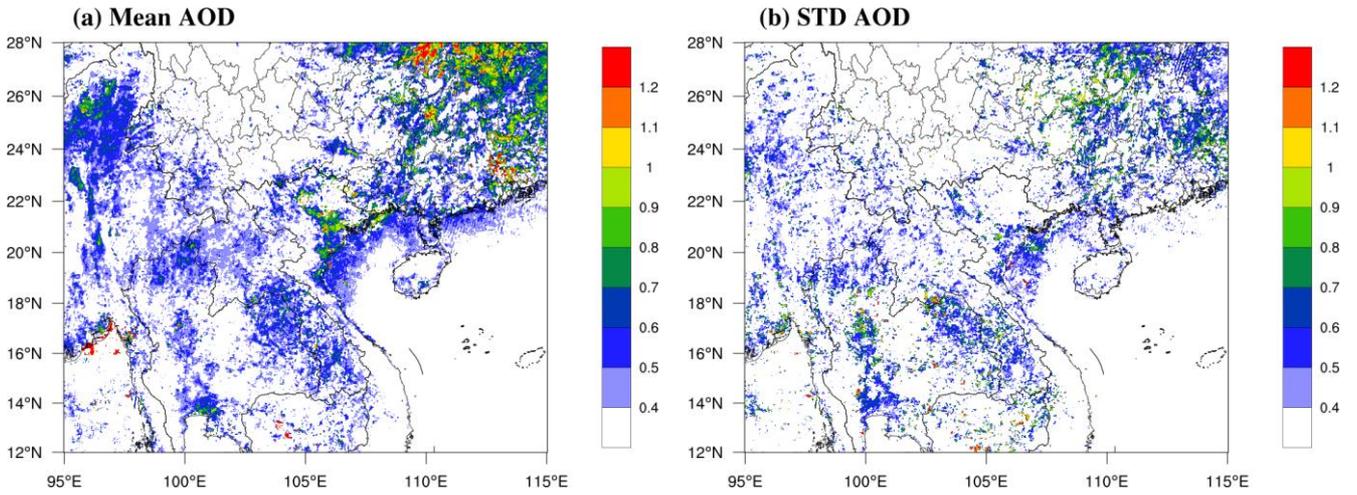
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Figure 10. The time-varying statistics of the AOD averaged over the first two EOFs

1035   of the AOD (reflecting the regions most impacted by AOD variance or smoke from

1036   fires) and the average K$^+$ concentration and average ratio of OC/EC in the three sites.

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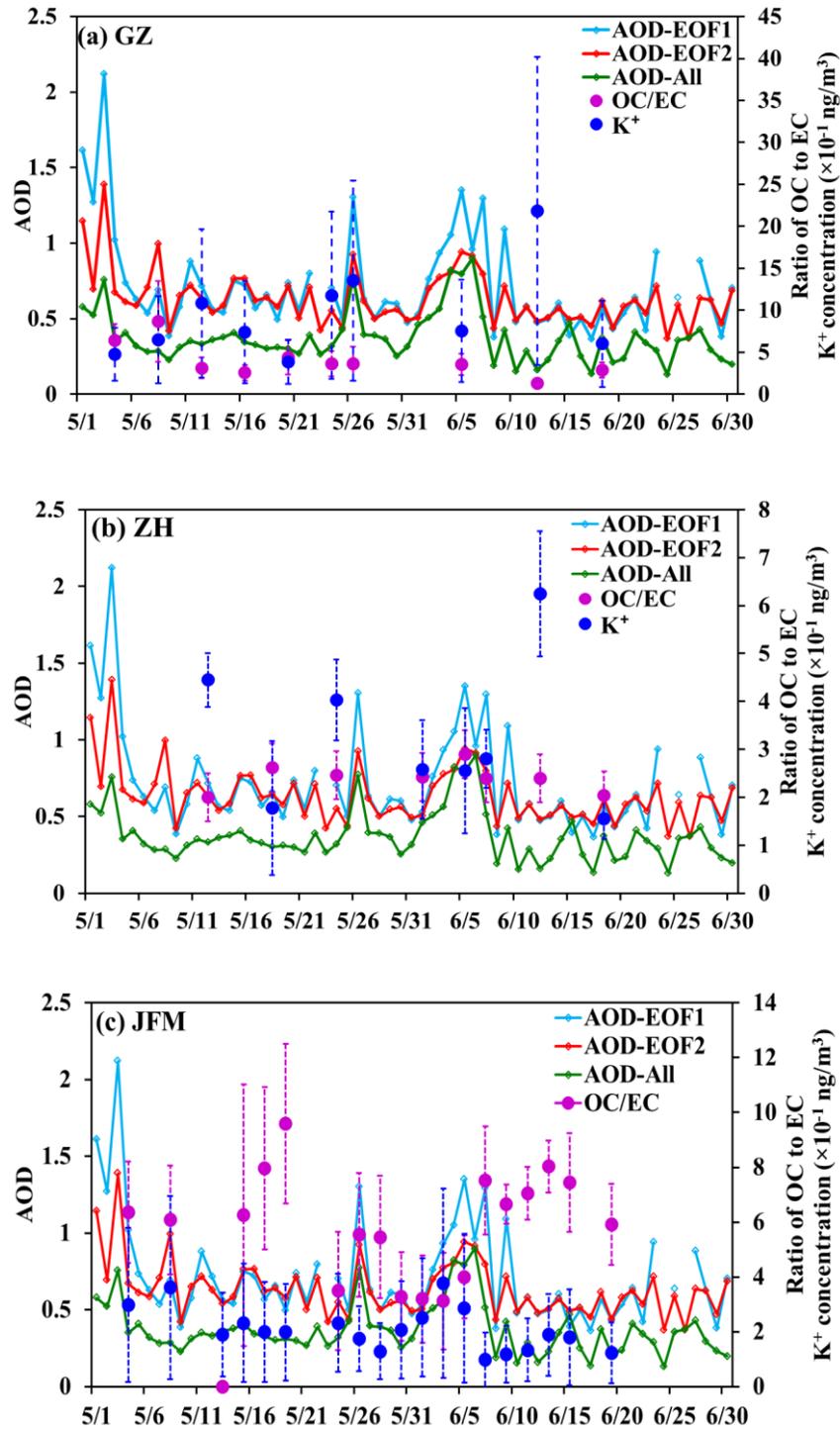
Tables

Table 1. Average concentration and standard deviation [μg m^{-3}] of chemical

components in the given size-resolved particles (and their percentage of PM$_{10}$) at the

three sites during the 2010 wet season.

Site	Size	Sum of measured species	SO$_4^{2-}$	NO$_3^-$	NH$_4^+$	OC	EC
GZ	PM$_{1.0}$	24.4±10.9	8.0±3.1 (60.2)	3.0±2.4 (34.5)	3.4±1.7 (64.2)	5.5±2.0 (57.9)	2.9±2.6 (72.5)
	PM$_{2.5}$	34.9±17.3	11.7±5.2 (88.0)	5.0±4.0 (57.5)	4.9±2.9 (92.5)	7.2±2.7 (75.8)	3.4±3.2 (85.0)
	PM$_{10}$	46.7±20.6	13.3±5.8	8.7±5.2	5.3±3.1	9.5±3.7	4±3.8
ZH	PM$_{1.0}$	12.9±4.5	6.3±2.1 (66.3)	0.3±0.3(10.3)	2.2±0.8 (71.0)	2.4±1.1 (66.7)	1.3±0.8 (76.5)
	PM$_{2.5}$	18.1±6.8	8.8±3.2 (92.6)	0.9±0.8 (31.0)	3.0±1.2 (96.8)	3.0±1.5 (83.3)	1.5±0.9 (88.2)
	PM$_{10}$	23.7±7.3	9.5±3.4	2.9±1.1	3.1±1.3	3.6±1.9	1.7±1.0
JFM	PM$_{1.0}$	4.4±1.6	1.8±1.0 (75.0)	0.1±0.1 (16.7)	0.5±0.3 (83.3)	1.5±0.7 (57.7)	0.3±0.2 (60.0)
	PM$_{2.5}$	5.8±2.3	2.2±1.5 (91.7)	0.2±0.1 (33.3)	0.6±0.5 (99.0)	1.8±0.8 (69.2)	0.4±0.2 (80.0)
	PM$_{10}$	8.0±2.6	2.4±1.5	0.6±0.3	0.6±0.5	2.6±1.1	0.5±0.3

1042   **Table 2.** Statistical parameters of samples with air masses from ocean

Site	Date	Droplet mode sulfate ($\mu g\ m^{-3}$)	Percentage of sulfate in droplet mode (%)	T (°C)	RH (%)	P (hPa)	WS (m s^{-1})	Low Cloud cover (%)
GZ	2010/5/8	7.4	61	27.5	82.0	997.1	1.9	70
	2010/5/12	11.1	65	25.0	77.5	1002.9	1.5	60
ZH	2010/5/12	9.5	67	24.9	83.0	1006.1	3.4	70
	2010/6/1	6.8	67	24.8	80.0	1002.0	5.1	70
JFM	2010/5/4	2.2	64	22.0	83.0	916.9	1.0	70
	2010/5/13	2.5	67	23.7	75.8	918.3	1.8	70

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