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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mixing state of individual submicron carbon-containing particles and their seasonal variation in urban Guangzhou, China" *by* G. Zhang et al.

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Zhang et al have represented the results obtained from the investigation of mixing state of sub-micron carbon containing particles during spring and fall period of 2010 using an instrument called single particle aerosol mass spectrometer. Based on the cluster analysis of single particle mass spectra they further classified observed particles biomass burning, organic carbon, fresh elemental carbon, etc. The paper appears to be well written and data represented could be of potentially important due to its origin from a geographical area of highly growing concern. I believe that with some major modifications suggested here and as pointed out by Referee #1 manuscript may

achieve the adequate standards of ACP for publication.

General comment: I echo the concern raised by Referee #1 that data points are too limited to draw the conclusions which authors have presented. They have gone to draw too many, mostly speculative, conclusions from the time limited dataset. I would suggest they focus on the more conclusive findings of the study. I believe that the figures represented in supplement appear to be more important and self-explanatory than the figures in main text. One can notice that from while reading that authors have referred to supplementary figures too many times. I would suggest merging or re-plotting some of the figures to bring supplementary figures in main text. I also think lots of the references from the previous studies from the same region are missing (like PRIDE PRD campaigns).

Response: We would like to thank the reviewer for his/her useful comments and recommendations for the improvement of the manuscript. We agreed with the comments, and have clarified that the results presented here represents a case study of seasonal variation of carbon-containing particles in Guangzhou during spring and fall seasons. The title has now been changed to 'Mixing state of individual submicron carbon-containing particles during spring and fall season in urban Guangzhou, China: a case study' according to the comments by Referee 1. The conclusion section was also revised to focus on the conclusive findings, please refer to Lines 424-443 in the revised manuscript. Fig. S1 from Supplementary Material has been moved to the manuscript in the revised version. Many figures were also re-plotted for the clarity as suggested. PRIDE-PRD campaigns indeed provided much insight into the physical and chemical properties of carbonaceous aerosol in the PRD region, and thus it has been added to the introduction section, please refer to Lines 61-68. General and specific comments have been addressed below.

Specific comments:

1 Introduction:

I would request authors to rewrite the introduction as it does not explicitly in line with the major conclusion of this study. One major concern is authors have mentioned about Monsoon in the introduction saying it affects their number fraction as a function of aerodynamic diameter. This statement is not clear and should be supported by a reference. But except attributing the low concentration of aerosols they have not discussed anything; in spite of the fact that data is too short to study the effect of seasonal variation.

Response: We agreed with the comment. The introduction has now been revised according to the suggestion. According to Referee 1, some of the description on the importance in the climate system of carbonaceous aerosols was removed, and we focused upon the introduction on the current understanding of sources and processes of carbonaceous aerosols accordingly. We have reviewed the previous studies on the mixing state of carbonaceous aerosols mainly using single particle mass spectrometer in Shanghai, China, and also other regions, such as California, USA. Please refer to Lines 72-105 in the revised manuscript. Results from PRIDE-PRD campaign on the physical and chemical properties of carbonaceous aerosol in the PRD region have also been added to the introduction section, please refer to Lines 61-68. The sentence about Monsoon affects number fraction of carbon-containing particles as a function of aerodynamic diameter was deleted. We also have clarified that this paper presents a case study rather than seasonal variations. The title has now been changed to "Mixing state of individual submicron carbon-containing particles during spring and fall season in urban Guangzhou, China: a case study".

2 Experimental set-up and data analysis

Authors have not detailed the issues related with the calibration and other factors of the instrument used in this study. I am not really able to follow what authors mean by 700000 individual particles were investigated. Does that mean the measurements were not continuous? This needs to be properly explained. That is not clear from any of the figures presented in the manuscript.

Response: This work is mainly concerned with the mixing state of carbon-containing particles in the PRD region by application of a SPAMS. This instrument has already been applied in our previous study (Bi et al., 2011), and the issue in detail related to the calibration and other factors of the instrument have been provided in the original and cited publication by Li et al. (2011). Therefore, these issues were only briefly described in the experimental section, please refer to Lines 137-143. Over the period of study, SPAMS measurements were nearly continuous, for $\sim$21 and $\sim$15 days during spring and fall period, respectively. 700,000 individual particles were collected with the positive and negative mass spectra, please refer to Lines 121-124 Typically, SPAMS detected 2000 particles per hour, and the number might vary between several hundred (during clean condition) and several thousand (in polluted episodes). We believe that this amount of data for each period is sufficient to perform a statistical analysis, and thus to present representative results in this study. We have also added the sentence "This amount of data should be sufficient to perform a statistical analysis, and thus to provide representative results in this study" to clarify the representativeness of data, please refer to Lines 145-147 in the revised manuscript. We have also reviewed some similar studies by other groups and found that the number of analyzed particles, 600,000-700,000 for $\sim$25 days (Qin and Prather, 2006; Sullivan and Prather, 2007), were comparable or less than the number of particles collected in our work. The SMPS+C data used in this study do not have complete overlap with the SPAMS instrument. How does that affect the overall conclusions need to be explained. The scale factor obtained from a comparison between SMPS + C data and single particle mass spectrometer (SPMS) data was generally assumed to be certain and might be applied for SPMS data for scaling without overlapping of the SMPS + C (Rehbein et al., 2012), since the detection efficiency of SPAMS was dominantly affected by dva. In this study, the measurement data from the SMPS + C was only used to provide an indicative scale result of different carbon-containing particle types, and only applied when they were overlapping with the SPAMS data, such as Fig. 7, please refer to Lines 386-390 in the revised manuscript. We did not apply the SMPS + C data to the other period

which did not overlap with SPAMS data. We also note that the results from SMPS + C were not the focus of this study and did not affect the main conclusion of the work.

3. Results and discussions

Page 32713 Line 21: How do authors, based on single particle analysis, confirmed that most of the carbon containing particles are internally mixed?

Response: From Fig. 1, we observed that more than 60% and 80% of carbon-containing particles also contained nitrate (-46[NO2]- and -62[NO3]-) and sulfate (-97[HSO4]-), respectively. Thus we confirmed that most of the carbon-containing particles are internally mixed, please refer to Lines 195-197.

Page 32715 Line 13: Absence of coexistence. . . I rather believe it weak existence as it appears it is not completely absence.

Response: We have changed "absence of coexistence" to "weak existence", please refer to Lines 243-244 in the revised manuscript.

Same page Line 25: It is probably not dry but relatively less humid.

Response: We have changed "dry" to "less humid", please refer to Line 255 in the revised manuscript.

Page 32716 Line 7: Somehow I get the feeling from this sentence that biomass is not having any EC, is it true?

Response: Particle types were assigned according to the specific mass spectral characteristic of particles after being clustered. The single particle mass spectra of Biomass class typically contained a very intense potassium signal (m/z 39) with relatively low intensity positive carbonaceous ion peaks as described in previous studies (Pratt et al., 2011; Qin and Prather, 2006). Other signatures in Biomass class may be weak due to the extremely high sensitivity of laser to the potassium in the particles (Gross et al., 2000). Based on the in-situ measurements by Pratt et al. (2011), the average mass

fractions for fresh biomass smoke plume particles were estimated to be 89% organics, 5% black carbon, 3% nitrate, 0.6% sulfate, 0.3% ammonium, and 2% chloride. Consequently, the Biomass type may contain some EC. We have clarified it in the revised manuscript, please refer to Lines 213-214.

Page 32717 Line 3: It is very strong claim that it should facilitate the formation of SOA on EC core without any substantial evidence from the data presented.

Response: We have added the reference "Tan et al. (2009)" to provide more detail of the discussion on the SOA formation, please refer to Lines 290-293 in the revised manuscript. Tan et al. (2009) suggested that stagnant meteorological condition during the fall should facilitate the formation of SOA on the EC core. However, we did not have enough evidence for the favorable formation of SOA on the EC cores, and the reason was likely to be the size distribution of EC-Sulfate particles between spring and fall seasons, as discussed in section 3.2.1.

Page 32718 Line 9: If biomass burning is more how regional transport is differentiated? Also if it is more, then how S and N increased in larger particle is not clear to me.

Response: It is hard and also there is a lack of evidence to differentiate the regional transport Biomass particles from local sources. As discussed in section 3.2, biomass burning contribution was higher during fall period echoes those from previous studies conducted in PRD region. Measurements during the PRIDE-PRD 2004 campaign concluded that inputs from the biomass burning are prevalent during the dry northeast monsoon period (Gnauk et al., 2008; Hagler et al., 2006). Zhang et al. (2010) also suggested that biomass burning activities in neighboring and/or rural regions could present a significant impact on an ambient urban aerosol level in the PRD region during the PRIDE-PRD 2006 campaign. The authors also believed that there were limited local biomass burning activities in the urban area. Therefore, we suggested that Biomass particles might be primarily contributed from the regional transport during the fall period, based on the fire dot analysis and air mass trajectories. Firstly, air mass tra-

jectories showed that the dominant air masses were from oceanic areas during spring period. The relative abundance of precipitation resulted in minimizing the influence of biomass burning from long range transport, although during spring period there were also many fire dots in the neighboring regions. Therefore, this fraction of Biomass particles was likely due to the local or nearby sources, which was significantly lower than those during fall period, please refer to Lines 271-285 in the revised manuscript. Secondly, as discussed in section 3.2, fire dot maps (Fig. S3) showed that fire dots in the Northeast of Guangzhou were intense due to the biomass burning after harvest period during fall season, and the air parcels also transported through these areas to the urban Guangzhou. We believed that particles due to regional or long range transport experienced sufficient ageing processes, typically via an addition of secondary species like sulfate and nitrate (Johnson et al., 2005; Roldin et al., 2011), which lead to the growth of particles (Moffet and Prather, 2009). Therefore, the content of S and N should increase in larger particle. Moffet and Prather (2009) reported that aged soot particles were with larger shell/core ratios compared to fresh ones, an indicative of larger fraction of secondary species in larger particles.

4 Conclusions

Based on the suggestions given above the conclusions are requested to be revised.

Response: We have changed the conclusion based on the comments. We have changed "Air masses from the northeastern agricultural areas imported a large amount of ammonia into the urban Guangzhou, therefore it contributed to the low acidity of aerosols during the fall period" to "Air masses from the northeastern agricultural areas imported a large amount of ammonia into the urban Guangzhou, leading more frequent appearance and strong intensity of ammonium signal in individual particles durig the fall season, which might have influence on the particle acidity". The implication was also changed to "These results, by direct single particle observation, provide a reference of mixing state for calculating light extinction, or even modeling the climate forcing of aerosol in the PRD region, with an improvement of validity. They might also help to

identify the source and to reveal the atmospheric processes of carbon-containing particles in the PRD region", please refer to Lines 431-443 in the revised manuscript.

Technical corrections:

There are some typos and references need to be checked. The captions of the figures are too small to read and should be increased.

Response: We have checked the typos and references, and have revised them accordingly. Several figures (Figs. 3-8) have been re-plotted with larger captions, please refer to these figures in the revised manuscript.

Page 32709 Line10: It could be "research" instead of researchers.

Response: We agreed with the comment. The introduction section has been rewritten and this sentence has been removed.

Reference

Bi, X. H., Zhang, G. H., Li, L., Wang, X. M., Li, M., Sheng, G. Y., Fu, J. M., and Zhou, Z.: Mixing state of biomass burning particles by single particle aerosol mass spectrometer in the urban area of PRD, China, Atmos. Environ., 45, 3447-3453, doi: 10.1016/j.atmosenv.2011.03.034, 2011. Gnauk, T., Müller, K., van Pinxteren, D., He, L. Y., Niu, Y. W., Hu, M., and Herrmann, H.: Size-segregated particulate chemical composition in Xinken, Pearl River Delta, China: OC/EC and organic compounds, Atmos. Environ., 42, 6296-6309, 2008. Gross, D. S., Galli, M. E., Silva, P. J., and Prather, K. A.: Relative sensitivity factors for alkali metal and ammonium cations in single particle aerosol time-of-flight mass spectra, Anal. Chem., 72, 416-422, 2000. Hagler, G. S., Bergin, M. H., Salmon, L. G., Yu, J. Z., Wan, E. C. H., Zheng, M., Zeng, L. M., Kiang, C. S., Zhang, Y. H., Lau, A. K. H., and Schauer, J. J.: Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China, Atmos. Environ., 40, 3802-3815, doi: 10.1016/j.atmosenv.2006.02.032, 2006. Johnson, K. S., Zuberi, B., Molina, L. T., Molina, M. J., Iedema, M. J., Cowin, J. P.,

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C13580/2013/acpd-12-C13580-2013-supplement.zip

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