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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of submicron aerosols at a rural site in Pearl River Delta of China using an Aerodyne High-Resolution Aerosol Mass Spectrometer" *by* X.-F. Huang et al.

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In this paper, the authors report the HR-AMS measurement results in a rural site downwind of a highly polluted area of the Pearl River Delta region in China. Results show that in addition to a substantial fraction of organics (∼34%), sulfate still has a substantial fraction (∼34%) in the non-refractory PM1 materials measured by AMS. Among the organics, PMF analysis reveals that organic aerosols during the sampling period contain mainly LV-OOA, SV-OOA, and BBOA. Elemental analysis was performed and compared with values from the literature, as well as lab experimental results from the same group. Meteorological conditions were also examined to understand the con-

centration variation during the campaign. The results are interesting and fit well in the scope of ACP, in that they show several features, including high sulfate content, aged organics, BBOA influence etc., of the aerosols in this rural site. These features, however, scattered throughout the manuscript. It is recommended for publication after some modification concerning several points as below.

Major comments: 1. Introduction. As mentioned above, the major points that the authors want to deliver are not easy to grasp. One of the reasons is that the introduction does not provide enough general information in the very beginning. Some information is provided in paragraph 1, but it would be better to expand this paragraph with the actual focus of the results in the current study. Paragraph 2 is remotely related to the science that is discussed here thus can be shrunk into a few sentences. Reply: Following this review comment, we have rephrased the introduction part to highlight the purpose and focus of this paper as below. "The Pearl River Delta (PRD) region lies in the southeastern coastal part of China and is noted for its flourishing manufacturing and export industries. The urbanization in PRD is now characterized by several big cities like Guangzhou, Shenzhen, and Hong Kong and many medium-small cities linked by dense highways. The rapid economic development and urbanization in PRD in the recent decades comes with the consequence of severe deterioration of its atmospheric environment from urban to regional scale. For example, the annual mean PM2.5 concentrations were reported to range from 29 (for regional background site) to 71 (for urban site) μg m-3 in PRD with organic matter and sulfate as the most abundant constituents (Hagler et al., 2006). The air pollution problems in PRD have been a major concern of the national government of China and have raised global scientific interest (Streets et al., 2006; Zhang et al., 2008). As aerosol particles are a complicated mixture of various species, deep understanding of variation of aerosol chemical and physical properties is essential for the purposes of source identification and pollution control. Most previous aerosol studies in PRD were based on filter sampling followed by laboratory analysis, which provided datasets at a coarse time resolution like a day. The coarse time resolution of the aerosol datasets cannot match the actual faster variation of aerosol

properties in the real atmosphere, which strongly favors highly time-resolved on-line measurement techniques. In order to characterize in depth the variation of chemical and physical properties of fine particles in the atmosphere of PRD, an intensive monitoring campaign supported by the project "Synthesized Prevention Techniques for Air Pollution Complex and Integrated Demonstration in Key City-Cluster Region" launched by the Ministry of Science and Technology, China, was organized by Peking University in PRD during October–November, 2008. As part of this campaign, we deployed an Aerodyne high-resolution aerosol mass spectrometer for measurement of submicron aerosol particles downwind of the most polluted central PRD area, in order to better characterize the particulate pollution features in the well mixed and more aged regional air. It was the first application of a high-resolution aerosol mass spectrometer in PRD. Utilizing the advantages of the high-resolution aerosol mass spectrometer, highly-time resolved species variations, elemental analysis and source apportionment of organic aerosol in the atmosphere of PRD were systematically studied in this paper."

2. P25846, L26. Alfarra et al. (2007) used a CE of 0.7 for BBOA based on comparison of NR-PM1 + EC vs. TEOM mass. The last part of the sampling period of the current study was strongly influenced by BBOA, as stated by the authors. The authors need to justify the usage of CE 0.5 throughout the whole campaign. Reply: In Alfarra et al., (2007), they used CE=0.5 for the March campaign but CE=0.7 for the December campaign. Their justification for CE=0.7 during the December campaign was based on a comparison of the total AMS and elemental carbon mass to the total PM1 mass measured by a TEOM during measurements of wood burning emissions in a LABORATORY experiment (which is expected to be totally dominated by organic aerosols). However, in our case, what we measured was still ambient aerosols (which still have many other species like sulfate and nitrate). To check the use of CE=0.5 for the whole campaign in our study, we made the NR-PM1+BC vs. SMPS volume plots separately for the BB and non-BB periods. The results give very similar slopes (slope=1.40, R2=0.84 for the non-BB period; slope=1.44, R2=0.90 for the BB period), so we think a CE=0.5 is suitable for the whole campaign in this study.

3. P25851, L20. The authors attribute the relatively high N/C ratio during the biomass-burning period to the secondary reactions of NH3 and NOx (better clarify that the reactions under concern are with organics) and burning of N-containing soil materials. These are reasonable, but what would be more plausible is the explanation from Laskin et al. (ES&T, 2009, 43, 3764), which shows that the N-heterocyclic alkaloid compounds (ubiquitously present in biomass fuels) might contribute substantially to the N-containing compounds of BBOA. Reply: We have clarified in the sentence that it is "secondary reactions of NH3 and NOx with organics". In a recent publication of our group (He et al., 2010), we used HR-ToF-AMS to measure the burning emissions of six typical biomass materials in the laboratory, including wood of fir, pine, willow, wattle, sugarcane leaves, and rice straw. However, all these emissions gave N/C ratios of less than 0.02, as stated in the manuscript. On the other hand, Laskin et al. (2009) have found high abundance of N-heterocyclic alkaloids in biomass burning aerosols in test burns of ponderosa pine in the US. So, following this comment, we have added this point as another possible explanation for the high N/C ratios observed in this study by adding the following sentences to the manuscript. "Another possibility is that, biomass burning in PRD may also include other high N-containing biomass materials that were not tested by He et al. (2010), since Laskin et al. (2009) have found high abundance of N-heterocyclic alkaloids in biomass burning aerosols in test burns of ponderosa pine in the US."

4. P25851, L25. "the evolution of bulk organic . . .of PRD might be somewhat different from that. . .". Heald et al. (2010) talked about the possible reasons for the deviation of the slope from -1 in the Van Krevelen diagram. To support the characteristics of aerosols in this rural site during the campaign, it would be better to discuss more specifically about what is the possible reason(s) for this deviation observed. Reply: The relevant discussion has been expanded as below: "The slope is shallower than those ($\sim$1.0) observed in Riverside, the Central Amazon Basin, and Mexico City (Heald et al., 2010). As suggested by Heald et al. (2010), the shallower slope of OA in the Van Krevelen diagram can reflect different aging mechanisms (such as greater tendency

of alcohol addition) and/or relative mixes of fresh and aged air masses in the PRD environment."

5. P25864, Fig 2. The numbers of mass percentages in (f) are totally different from those in the text. It should be stated in the caption if these numbers are calculated in a different way from those in the text (33.8%, 33.75, 14.0% etc.). The color code for BC (black) in (f) is ambiguous because in (c) it refers to PM1. Reply: We are sorry that the original Fig. 2f has some errors. Now, Fig. 2f is updated. The color code for PM1 is changed to grey to make it different from the color of BC.

6. The diurnal patterns of BC, N/C, and PMF-resolved BBOA, which should all be strongly related to the biomass burning activity as suggested by the authors, are quite different if not completely distinct. Any reason behind this? Reply: As stated in the manuscript, the N/C and other ratios are influenced by relative organic constitutions rather than absolute organic concentrations, so it is reasonable that the N/C diurnal pattern is different from those of BC and BBOA concentrations. As mentioned in the manuscript, some correlation between BC and BBOA (R2=0.49) and between BC and acetonitrile (R2=0.46) can indicate that biomass burning was an important source of BC, but may not be a dominant source of BC. As a downwind site of polluted central PRD, the BC at Kaiping may still be significantly influenced by the fossil fuel emissions in the upwind area by regional transport. For the BC and BBOA diurnal patterns, their major features are similar, that is the lower concentrations in the afternoon due to higher mixing layers. Compared to BC, BBOA had a morning peak and an evening peak due to local emissions because we know that biomass burning emits much more OM than BC. Therefore, we think it is reasonable to have different diurnal patterns of BC, N/C, and PMF-resolved BBOA.

7. Overall, the manuscript has several good points on: 1) relatively high mass concentration and high sulfate fraction in NR-PM1 compared to other regions in the world; 2) aged aerosols supported by several types of analyses including O/C, LV-OOA fraction, and correlation of OOA with sulfate and nitrate etc.; 3) evidence of BBOA influence at

the end of the campaign. To connect the dots, it would be better to summarize these in a coherent conclusion, rather than merely repeating the abstract as it is now. Reply: Following this suggestion, the conclusion part has been rephrased as below. "Based on the HR-ToF-AMS measurement at a rural site downwind of the highly-polluted central PRD area during October–November, 2008, the PM1 mass concentrations in 10 min-resolution varied largely between 2.4 and 150 μg m$-$3, with a mean value of 33.1 μg m$-$3. Organics and sulfate were the most abundant species, each accounting for $\sim$1/3 of the total mass, respectively. The high concentration levels of PM1 mass and sulfate are a feature of fine aerosol particles in PRD in comparison with other similar measurements in developed countries. Secondary orgnic aerosol was found to dominate the OA at this rural site with the following characteristics: 1. the O/C ratio had a clear diurnal pattern that is consistent with that of photochemical activity; 2. PMF analysis indicated that LV-OOA and SV-OOA totally accounted for about three quarters of the total OA; 3. the sum of LV-OOA and SV-OOA showed high correlation with the sum of sulfate and nitrate, strongly confirming their secondary nature. It is interestingly found that BBOA comprised a large OA fraction of about a quarter in this campaign, with its concentration highly elevated after November 12 due to the open field burning of crop residues after harvest in PRD. High N/C ratios were found to be closely associated with biomass burning. Analysis of meteorological influence supported that regional transport from the central PRD area was the major origin of the PM1 components observed at this rural site."

Minor comments: 1. P25850, L20-23. Looks odd. "an absence of morning peak" of BC because of rush-hour traffic? Reply: The sentences have been rephrased as below to clarify the meaning: "It is interesting to note that in the BC diurnal pattern there was an absence of a morning peak. The morning BC peak due to rush-hour traffic and low boundary layer was observed in many previous urban studies (Lin et al., 2009; Han et al., 2009; Aiken et al., 2009). The missing morning BC peak in this campaign, however, is well consistent with the fact that Kaiping is free of significant local traffic emissions."

2. P25851, L26. This statement needs more caution and some updated references, since 1.4 has been used for a while and there are a whole lot more of other suggested numbers (Table 1 in Chan T.W. et al., ACP, 2010, 10, 2393). Reply: The original sentences may be inaccurate for what we intended to say. Now, it is revised as below: "The OM/OC ratio highly correlates with the O/C ratio (R2=0.98), having a mean value of 1.77$\pm$0.08. The OM/OC ratio has been extensively used to convert organic carbon mass to organic matter mass in filter-based aerosol chemistry studies, and 1.8 should be a reasonable approximate OM/OC ratio for the Kaiping rural site based on the HR-ToF-AMS elemental analysis."

3. Typos. P25843, L22, a redundant comma; P25848, L13, L25, the symbol of "$\sim$" should be between letters and numbers? Reply: Correction made.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 25841, 2010.