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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Water-soluble organic carbon over the Pearl River Delta region during fall–winter: spatial variations and source apportionment" *by* X. Ding et al.

X. Ding et al.

xiangd@gig.ac.cn

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Reply to Referee #2

General comments: This manuscript presents a thorough analysis of spatial variation and sources of WSOC in southern China including suburban and rural areas when biomass burning activities are intensive. The authors give a clear picture of sources of carbonaceous aerosol. From the analysis, it shows that during the study period (fall-winter), POC is about 70-80% of OC and WSOC is about 40-60% of OC. Biomass burning, SOC, and unexplained POA aging component contribute about 40-50%, 20-

40% and 18-30% to WSOC, respectively. The results are based on applying levoglucosan as a tracer for estimating biomass burning contribution and individual tracers of SOC to estimate each source contribution to SOC. However, there are still a few things that need to clarify. If the authors can provide more information in the text, it will be helpful and supportive.

1) For example, SOC is also important in summer. Why do the authors pick fall-winter period and exclude summer period?

Reply: Yes, SOC is important in summer. We did collect samples at WQS site during summer in 2008 and found that SOC was about three times higher than WSOCBB (averagely 2.81 vs. 1.00 μgC/m3) during summer. Unfortunately, there was no sample collected at other two sites. This is the main reason why only fall-winter data were discussed in the current manuscript.

2) How are we so sure that biomass burning is most active in fall-winter? Are there other evidences to show that biomass burning is active in this region during fall-winter such as satellite data for the fire counts?

Reply: We appreciate the suggestion. Satellite data do provide evidences to show active biomass burning during fall-winter in the PRD. As MODIS Fire Map (http://firms.modaps.eosdis.nasa.gov/firemap/) showed, fall –winter (such as November) had much more fire counts than other seasons (such as June) (Figure 1 a and b). Another study (He et al. 2011) focusing on biomass burning emissions over the PRD demonstrated that there had significant increases in both fire counts and the emissions of gases and particles during November to December (see Figure 1 c and d below). In fact, previous study in Shenzhen, one of the megacities in the PRD, revealed that the contribution of BB to WSOC increased from 58% in summer to 76% in winter (Huang et al., 2006). Moreover, significant correlation was observed between WSOC and the biomass burning tracer, levoglucosan ($p<0.001$, Figure 2), providing an additional evidence that biomass burning was an important source to WSOC. In the revised

manuscript, we added the satellite maps of fire counts and made some discussions as "BB emissions over the PRD were significant increases during November to December (He et al. 2011). As MODIS Fire Map (http://firms.modaps.eosdis.nasa.gov/firemap/) showed, fall–winter (such as November) had much more fire counts than other seasons (such as June) in the PRD. Previous study in the PRD revealed that the contribution of BB to WSOC reached 76% in winter (Huang et al., 2006). Our previous study also observed the great enhancement of BB in the PRD during fall-winter (Ding et al., 2012). Moreover, a significant correlation was observed between WSOC and BB tracer, levoglucosan, providing an additional evidence that BB had significant contributions to WSOC in the PRD region during fall-winter."

He, M.; Zheng, J.; Yin, S.; Zhang, Y. Trends, temporal and spatial characteristics, and uncertainties in biomass burning emissions in the Pearl River Delta, China Atmos. Environ., 45, 4051-4059, 2011

Huang, X.-F., Yu, J. Z., He, L.-Y., and Yuan, Z.: Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms, Journal of Geophysical Research: Atmospheres, 111, D22212, doi: 10.1029/2006JD007408, 2006.

3) When they perform WSOC source apportionment, the unexplained simply goes to POA aging which requires more supporting and convincing data/evidence and analysis. Does the rural site show more POA aging component than suburban site?

Reply: The nature of POA aging is the partitioning and photochemical processing of intermediate VOC (IVOC) and semi-VOC (SVOC) fractions of POA (Miracolo et al., 2010; Robinson et al., 2007). As model predicted, POA aging (including IVOC and SVOC) could contribute 60% of global SOA budget (49.8 Tg yr-1 in 82.9 Tg yr-1) (Jathar et al., 2011). Considering the predominant role of POC (exceeding 70% of OC) in the PRD during our campaigns, POA aging should be an important input of SOA that could not be captured by the current SOA-tracer method. The significant correlation between

unexplained WSOC and POC also indicated that this portion might be associated with POC aging. At present, there is no specific component measured by GC-MSD to track POA aging, which limits the further checking of the influence of POA aging on unexplained WSOC. On the other hand, there might have other sources contributing to unexplained WSOC, such as SOA formed from aqueous-phase heterogeneous reactions and from other unknown precursors. However, only based on our observation, it is difficult to distinguish POA aging from other processes. Thus, further study is needed to get insight into these "untraditional" SOA in the highly polluted PRD. In the revised manuscript, we mentioned this as "It should be noted that there might have other sources contributing to unexplained WSOC, such as SOA formed from unknown precursors and from aqueous-phase heterogeneous reactions (Ervens et al., 2011). Thus, further study is needed to get insight into this unexplained portion in the highly polluted PRD."

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, Atmos. Chem. Phys., 11, 11069-11102, 2011.

Jathar, S. H., Farina, S. C., Robinson, A. L., and Adams, P. J.: The influence of semivolatile and reactive primary emissions on the abundance and properties of global organic aerosol, Atmos. Chem. Phys., 11, 7727-7746, 2011.

Miracolo, M. A., Presto, A. A., Lambe, A. T., Hennigan, C. J., Donahue, N. M., Kroll, J. H., Worsnop, D. R., and Robinson, A. L.: Photo-oxidation of low-volatility organics found in motor vehicle emissions: Production and chemical evolution of organic aerosol mass, Environ. Sci. & Technol., 44, 1638-1643, 2010.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 2007.

4) Do the POC and SOC split agree well with the EC/OC method?

Reply: We used POC/OC to show the POC and SOC split. As Figure 3 showed, the POC shares in OC that estimated by WSOC method and EC method respectively had no correlation with each other at each site. Our previous study demonstrated that EC-method would overestimate SOC during fall-winter, largely due to the influence of biomass burning. Thus, it is not surprised that the results from these two methods have no agreement.

Overall, this manuscript is well written and data are of high quality. It helps the understanding of sources and characteristics of WSOC in Pearl River Delta, China. I suggest for publication after minor revision.

Specific Comments: 1) Phthalic acid is used as tracer for 2-ring PAH SOA tracer. Is there a good reference? Are there other sources for phthalic acid?

Reply: Based on chamber simulations, Kleindienst et al. (2012) pointed out that phthalic acid was a unique tracer for 2-ring PAH SOA and reported the mass fractions of phthalic acid in SOA from the photo-oxidation of naphthalene and its methyl analogs. In the original manuscript, we calculated the mass fraction of phthalic acid in SOC (0.0388) to estimate ambient SOC from 2-ring PAH. Recently, another paper from the same research group directly provided the mass fraction of phthalic acid in SOC (0.0402) in the presence of NOx and estimate SOC over the United States (Lewandowski et al., 2013). In the revised manuscript, we recalculated the 2-ring PAH SOC using the published convert factor (0.0402). Such a recalculation only lowered the levels of 2-ring PAH SOC by 3.4% but had no influence on our previous conclusions.

Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Docherty, K. S. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides Atmos. Chem. Phys., 12, 8711-8726, 2012.

Lewandowski, M.; Piletic, I. R.; Kleindienst, T. E.; Offenberg, J. H.; Beaver, M. R.; Jaoui, M.; Docherty, K. S.; Edney, E. O. Secondary organic aerosol characterisation at field sites across the United States during the spring–summer period Int. J. Environ. Anal. Chem., 1-20, 2013.

2) Based on correlation between WSOC and EC, the authors suggest that it is primarily due to biomass burning. What about contribution from motor vehicle emissions, which is one of the major sources in China? Is vehicular emission an important source to EC?

Reply: Soot is the major component of EC. We measured isotope (14C) of soot in some samples from DHS and WQS. As Figure 4 showed, modern soot contributed near 50% at DHS and 40% at WQS. Thus, biomass burning which is the sole source of modern soot should be very important during fall-winter in the PRD. As the isotope (14C) showed, fossil soot had the contribution more than 50% at DHS and 60% at WQS. Although we could not quantify the contribution of motor vehicle to fossil soot, we believe that motor vehicle emission should be an important source of EC.

3) Page 10, Line 2: (ftracer/WSOC)=0.0806, what is the reference for this ratio? Is there any way to estimate uncertainty associated with this ratio, and the uncertainty with biomass burning estimate?

Reply: Viana et al., (2008) reported 129 ng/m3 levoglucosan and 1.6 μgC/m3 WSOC in the events of open burning of rice straw residues. We used these data to calculate the factor (0.0806 μg/μgC) to estimate straw burning WSOC. We mentioned this in Page 9 Line 22 of the ACPD manuscript. To evluate the uncertainty of the ratio, the feasible way is to collect all available data of levoglucosan and WSOC in different biomass burning source samples and then calculate the ratio and its deviation. Unfortunately, at present there is no WSOC value available in previous biomass burning source profiles. Only two filed observations in the events of open burning of rice straw residues (Viana et al., 2008) and prescribed forest fires (Yan et al., 2008; Ding et al., 2008) provided

both levoglucosan and WSOC data.

Ding, X.; Zheng, M.; Yu, L.; Zhang, X.; Weber, R. J.; Yan, B.; Russell, A. G.; Edgerton, E. S.; Wang, X. Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic carbon in the southeastern United States Environ. Sci. Technol. 2008, 42, 5171-5176.

Viana, M.; López, J. M.; Querol, X.; Alastuey, A.; García-Gacio, D.; Blanco-Heras, G.; López-Mahía, P.; Piñeiro-Iglesias, M.; Sanz, M. J.; Sanz, F.; Chi, X.; Maenhaut, W. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain Atmos. Environ. 2008, 42, 1941-1957.

Yan, B.; Zheng, M.; Hu, Y. T.; Lee, S.; Kim, H. K.; Russell, A. G. Organic composition of carbonaceous aerosols in an aged prescribed fire plume Atmos. Chem. Phys. 2008, 8, 6381-6394.

4) Page 11, Line 12: ftracer/SOC: are five or nine tracers used? And why?

Reply: In the current study, the ftracer/SOC for monoterpenes included five tracers. Kleindienst et al.(2007) provided the ftracer/SOC for monoterpenes with nine tracers. However, only five of the nine monoterpene SOA tracers were detected in this study. Our previous study found that monoterpene SOC might be underestimated using the five tracers and the ftracer/SOC of nine tracers (Wang et al 2013). To lower the uncertainty induced from different tracer compositions, the ftracer/SOC with five monoterpene SOA tracers was calculated based on another chamber simulations (Offenberg et al., 2007) of the same research group.

Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Lewis, C. W.; Bhave, P. V.; Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location Atmos. Environ., 41, 8288-8300, 2007.

Offenberg, J. H.; Lewis, C. W.; Lewandowski, M.; Jaoui, M.; Kleindienst, T. E.; Edney,

E. O. Contributions of toluene and α-pinene to SOA formed in an irradiated toluene/α-pinene/NOx/ air mixture: Comparison of results using 14C content and SOA organic tracer methods Environ. Sci. Technol., 41, 3972-3976, 2007.

Wang, S.; Wu, D.; Wang, X.-M.; Fung, J. C.-H.; Yu, J. Z. Relative contributions of secondary organic aerosol formation from toluene, xylenes, isoprene, and monoterpenes in Hong Kong and Guangzhou in the Pearl River Delta, China: an emission-based box modeling study J. Geophys. Res., 118, 507-519, 2013.

5) Page 12, Lines 17-18: Is there any more supporting evidence for aging POA contribution to unexplained part? Could there be other possibilities?

Reply: Based on the observed high POC over the PRD as well as the significant correlation between unexplained WSOC and POC, we proposed that POA aging might be important contributor to unexplained WSOC. Unfortunately, there is no specific component measured by GC-MSD to track POA aging. We could not accurately estimate the influence of POA aging on unexplained WSOC. There might have other sources contributing to unexplained WSOC, such as SOA formed from aqueous-phase heterogeneous reactions and from other unknown precursors. However, at present, it is difficult to distinguish POA aging from other processes, such as SOA from unknown precursors and aqueous processes. Thus, further study is needed to get insight into these “untraditional” SOA in the highly polluted PRD. In the revised manuscript, we mentioned this as “It should be noted that there might have other sources contributing to unexplained WSOC, such as SOA formed from unknown precursors and from aqueous-phase heterogeneous reactions (Ervens et al., 2011). Thus, further study is needed to get insight into this unexplained portion in the highly polluted PRD.”

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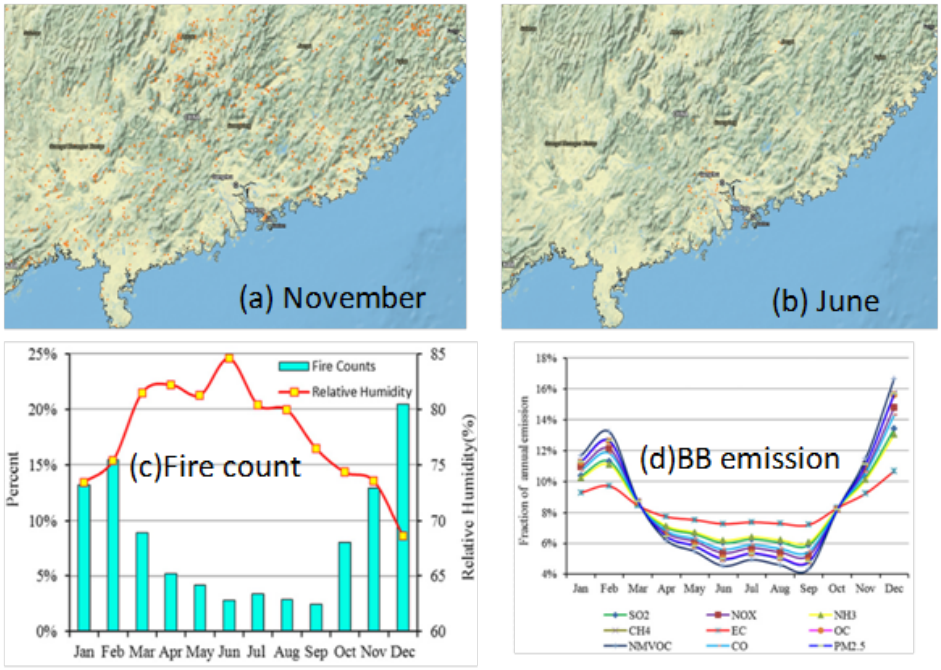

Fig. 1. BB influence over the PRD

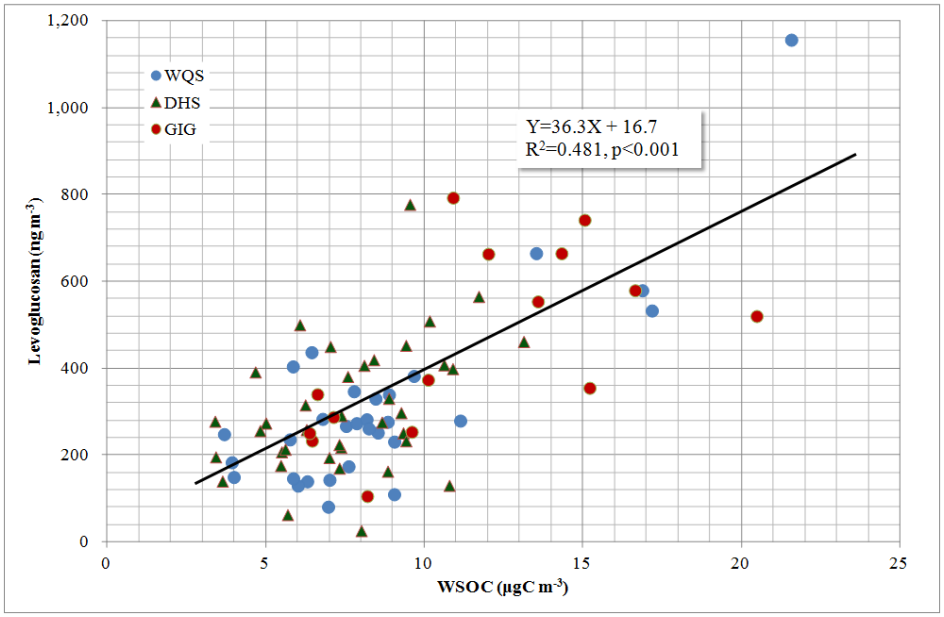

Fig. 2. Correlation between WSOC and levoglucosan

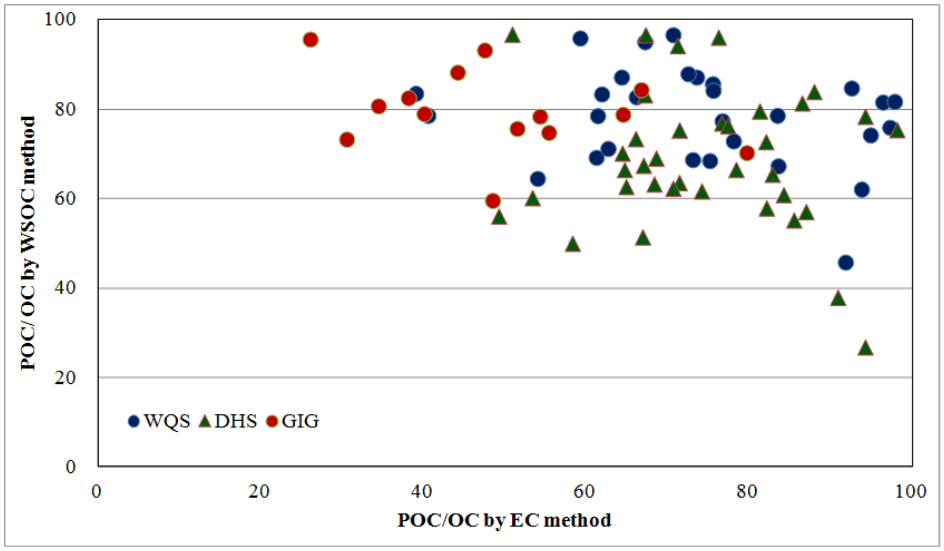

Fig. 3. Disagreement of POC/OC by two methods

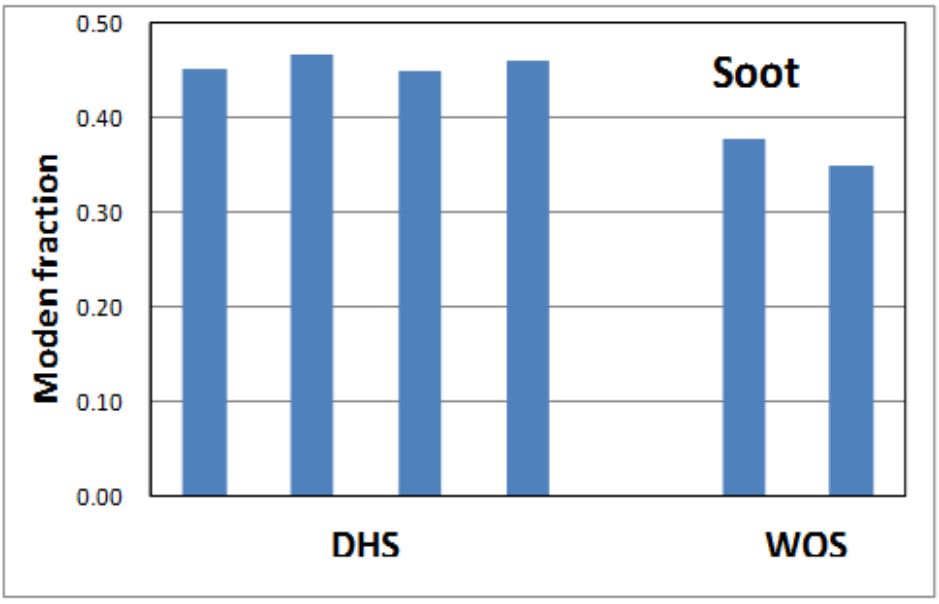

Fig. 4. Modern fraction of soot by 14C