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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.

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This manuscript analyzes 24-hr filter measurements of OC, EC, WSOC and selected organic tracer compounds at three sites in the Pearl River Delta (PRD) region during the fall-winter season in 2008. The authors attempted to attribute the sources of WSOC based on concentrations of tracers for different sources, i.e., biomass burning and different types of secondary organic aerosols.

Unfortunately, there are many issues with the analysis method adopted by the authors, making the conclusions drawn from the data highly questionable. I recommend a rejection of the manuscript and urge the authors reanalyze their data. Specifically, my comments are elaborated as follows.

Major comments: 1) Their methods of splitting WSOC and deriving POC and SOC have fundamental flaws. In Equation 4 (POC = OC - SOCtotal = WIOC + WSOCBB) and the related text, the authors mixed up the two terms SOCtotal and WSOCSOA (WSOC that is not from BB, which is another source of error that will be discussed later). The fact that SOA formation is a major source of WSOC does not mean that all SOA are water-soluble. Comparisons between field observations of WSOC and oxygenated organic aerosol (OOA) measured by AMS suggest that WSOC is only _40-80% of SOC, depending on sampling locations and dominant aerosol source/SOA formation pathways [Kondo et al., 2007; Zhang et al., 2013]. In addition, chamber studies have revealed that SOA formed from various anthropogenic and biogenic precursors have different hygroscopicity [e.g., Varutbangkul et al., 2006]. SOA formed through aqueous phase reactions are thought to be highly water-soluble [Ervens et al., 2011 and references therein]. Likewise, SOA may have a considerable contribution to WIOC in PRD, which might explain the higher WIOC/EC ratio in PRD than Tokyo (Page 13781, Line 1-5). Thus, it is fundamentally wrong to apportion WSOC into SOCprecursor, WSOCBB and unexplained WSOC. SOCprecursor calculated by the authors that contain non water-soluble compounds will also lead to an underestimation of the unexplained WSOC fraction. In order to make this method valid, the authors need to calculate WSOCSOA using a different set of parameters.

Reply: We admit SOCtotal and WSOCSOA are different in definition that the former represents all SOC and the latter is indicative of water-soluble carbon of SOA. However, the levels of SOCtotal and WSOCSOA could be approximate. Previous study in Mexico City found that WSOC could be fully explained by the sum of WSOCBB and unexplained OC (Stone et al., 2008, Figure 1a). And the latter was calculated by OC subtracting primary OC (POC) which was well apportioned by chemical mass balance (CMB) model. The unexplained OC in Mexico City could be approximate to total SOC

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(SOCtotal = OC - POC) (Zheng et al., 2002; Ke et al., 2008; Ding et al., 2008). On the other hand, the unexplained OC in Mexico City that indeed reflected the difference between measured WSOC and WSOCBB (WSOC - WSOCBB) could be regarded as water-soluble carbon of SOA (WSOCSOA). Thus, the level of SOCtotal could be approximate to that of WSOCSOA, although SOCtotal and WSOCSOA are different in definition. In the air of Tokyo, Kondo et al., (2007) found oxygenated organic carbon (OOC) measured by AMS was significantly correlated with WSOC (Figure 1b) and 94% of OOC were water soluble in summer, providing an additional evidence that SOCtotal could be approximate to that of WSOCSOA. Very recently, Feng et al., (2013) estimated SOC in Shanghai using the same method (SOC = WSOC – WSOCBB), which provided a reasonable results of SOC amount and seasonal trend. In the revised manuscript, we add some discussions about SOCtotal and WSOCSOA as: "Since WSOC is mainly derived from BB and SOA (Weber et al., 2007), WSOC from SOA (WSOCSOA) can be estimated as (Ding et al., 2008a): SOCtotal $\approx$ WSOCSOA = WSOC – WSOCBB (2) Previous study in Mexico City found that WSOC could be fully explained by the sum of WSOCBB and unexplained OC (Stone et al., 2008). Since the latter was calculated by OC subtracting POC which was well apportioned by chemical mass balance (CMB) model, the level of unexplained OC could be approximate to that of total SOC (SOCtotal) (Zheng et al., 2002; Ke et al., 2008; Ding et al., 2008b). On the other hand, the unexplained OC in Mexico City indeed reflected the difference between measured WSOC and WSOCBB and could be regarded as WSOCSOA. Thus, the level of SOCtotal could be approximate to that of WSOCSOA. In the air of Tokyo, 94% of oxygenated organic carbon (OOC) were water soluble in summer (Kondo et al., 2007), providing an additional evidence that SOCtotal could be approximate to that of WSOCSOA."

To check the water soluble fraction of SOA, we analyzed two filters that obtained from chamber simulations of SOA formation from typical biogenic (α-phellandrene) and anthropogenic (toluene) precursors. The characterization of our 30 m3 indoor chamber was described in detail elsewhere (Wang et al., 2013). As Figure 2 showed, SOC was almost water soluble that WSOC/SOC reached 95% for α-phellandrene and 88% for toluene. It should be noted that our chamber simulations only last five hours. Previous study demonstrated that oxidation state and hygroscopicity would increase during the evolution of OA (Jimenez et al., 2009). Thus, if considering long time evolution of these precursor-produced SOA, SOCprecursor could be all water soluble. In the revised manuscript, we added some discussions as "To check whether SOCprecursor was totally water soluble, we analyzed SOC and WSOC of two samples obtained from chamber simulations of SOA formation from typical biogenic (α-phellandrene) and anthropogenic (toluene) precursors. The results revealed that the fraction of WSOC in SOC (WSOC/SOC) reached 95% for α-phellandrene and 88% for toluene after five hours reaction. If considering the increases in oxidation state and hygroscopicity during the evolution of OA (Jimenez et al., 2009), WSOC/SOC would be even higher. These demonstrated that SOC produced from both biogenic and anthropogenic precursors were highly water soluble."

The reviewer also mentioned that water-soluble fractions of SOA could be estimated by the comparison of WSOC and OOA in the ambient. However, although OOA is always regarded as SOA, POA such as biomass burning OA (BBOA) and cooking OA (COA) (He et al., 2010; Williams et al., 2010; Ge et al., 2012) also contain oxygenated species and have contributions to measured OOA. Thus, SOA concentration might be overestimated if attributing all measured OOA to SOA. Moreover, since BBOA and COA have less water soluble components than SOA, water-soluble fractions of SOA would be underestimated if simply comparing WSOC and OOA.

For WIOC/EC ratio, we believe the high value in the PRD is largely due to BB influence. BB samples exhibited higher WIOC/EC, reaching 2.46 in the prescribed fire plume (Lee et al., 2008) and 2.88 in the events of open burning of rice straw residues (Viana et al., 2008). The WIOC/EC ratios were 3.24±1.03, 2.97±1.12 and 2.59±1.13 at WQS, DHS and GIG, respectively. Obviously, WIOC/EC ratios in our study were about 2-3 times higher than those in urban Tokyo (1.0±0.1, major from motor vehicle) (Miyazaki et al., 2006) but close to BB. As we replied to referee #2, all the facts (BB emissions, satellite

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data, and significant correlations of WSOC with EC and levoclucosan) demonstrated that BB had significant enhancement in the PRD region during fall-winter. Thus, the high WIOC/EC over the PRD region during fall-winter was largely due to BB other than motor vehicle. We added some discussions in the revised manuscript as "Miyazaki et al. (2006) found the ratios of WIOC to EC (WIOC/EC) were very stable (1.0±0.1) during the whole year in urban Tokyo and pointed out that motor vehicle was an important source of WIOC based on the significant correlations of WIOC with EC and carbon monoxide (CO). On the contrary, BB exhibited higher WIOC/EC, reaching 2.46 in the prescribed fire plume (Lee et al., 2008) and 2.88 in the events of open burning of rice straw residues (Viana et al., 2008). The WIOC/EC ratios were 3.24±1.03, 2.97±1.12 and 2.59±1.13 at WQS, DHS and GIG, respectively. Obviously, WIOC/EC ratios in this study were about 2-3 times higher than those in urban Tokyo but close to BB. Thus, the high WIOC/EC over the PRD region during fall-winter was largely due to BB other than motor vehicle."

All above results and discussions provid solid evidences that the level of SOCtotal is approximate to that of WSOCSOA and SOC produced from both biogenic and anthropogenic precursors are highly water soluble. Thus, we believe that the methods of splitting WSOC and deriving POC and SOC are valid.

Ding, X., Zheng, M., Edgerton, E. S., Jansen, J. J., and Wang, X.: Contemporary or fossil origin: Split of estimated secondary organic carbon in the southeastern United States, Environ. Sci. Technol., 42, 9122–9128, 2008.

Ge, X., Setyan, A., Sun, Y., and Zhang, Q.: Primary and secondary organic aerosols in Fresno, California during wintertime: Results from high resolution aerosol mass spectrometry, J. Geophys. Res., 117, D19301, doi: 10.1029/2012jd018026, 2012.

He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos. Chem.

Phys., 10, 11535-11543, 2010.

Ke, L., Ding, X., Tanner, R. L., Schauer, J. J., and Zheng, M.: Source contributions to carbonaceous aerosols in the Tennessee Valley Region, Atmos. Environ., 41, 8898-8923, 2007.

Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo, J. Geophys. Res., 112, D01203, 10.1029/2006JD007056, 2007.

Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., and Schauer, J. J.: Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006, Atmos. Chem. Phys., 8, 1249-1259, 2008.

Wang, X., Liu, T., Bernard, F., Ding, X., Wen, S., Zhang, Y., Zhang, Z., He, Q., Lü, S., Chen, J., Saunders, S., and Yu, J.: Design and characterization of a smog chamber for studying gas-phase chemical mechanisms and aerosol chemistry, Atmos. Meas. Tech. Discuss., 6, 7735-7769, 2013.

Williams, B. J., Goldstein, A. H., Kreisberg, N. M., Hering, S. V., Worsnop, D. R., Ulbrich, I. M., Docherty, K. S., and Jimenez, J. L.: Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds, Atmos. Chem. Phys., 10, 11577-11603, 2010.

Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E. S.: Source apportionment of PM2.5 in the southeastern United States using solvent-extractable organic compounds as tracers, Environ. Sci. Technol., 36, 2361-2371, 2002.

Lee, S., Kim, H. K., Yan, B., Cobb, C. E., Hennigan, C., Nichols, S., Chamber, M., Edgerton, E. S., Jansen, J. J., Hu, Y., Zheng, M., Weber, R. J., and Russell, A. G.: Diagnosis of aged prescribed burning plumes impacting an urban Area, Environ. Sci. Technol., 42, 1438-1444, 2008.

Miyazaki, Y., Kondo, Y., Takegawa, N., Komazaki, Y., Fukuda, M., Kawamura, K., Mochida, M., Okuzawa, K., and Weber, R. J.: Time-resolved measurements of water-soluble organic carbon in Tokyo, J. Geophys. Res., 111, D23206, doi: 10.1029/2006jd007125, 2006.

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., and Maenhaut, W.: Tracers and impact of open burning of rice straw residues on PM in Eastern Spain, Atmos. Environ., 42, 1941-1957, 2008.

Feng, J., Li, M., Zhang, P., Gong, S., Zhong, M., Wu, M., Zheng, M., Chen, C., Wang, H., and Lou, S.: Investigation of the sources and seasonal variations of secondary organic aerosols in PM2.5 in Shanghai with organic tracers, Atmos. Environ., 79, 614-622, 2013.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525-1529, 2009.

2) To help the reviewers (and the readers) better assess the robustness of the analysis, the authors should discuss explicitly the (substantial) uncertainty associated with the tracer-based method, specifically the uncertainty due to the over-simplification of applying laboratory-derived single parameters to calculate SOA mass from the ambient

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samples. Moreover, it is highly possible that many other SOA precursors that contribute to the WSOC (and OC) concentration sampled at PRD are not considered in their method. How would this affect the outcome and the subsequent analysis?

Reply: We agree that the tracer-based method has significant uncertainty, due to the simplification of applying chamber-derived parameters to calculate SOCprecursor in the ambient samples. First, this method is limited by the number of identified SOA tracers and chamber parameters which may not represent all ambient situations and thus lead to significant uncertainties (Kleindienst et al. 2007). Second, El Haddad et al. (2011) found that the choice of SOA tracers might also introduce great uncertainty in SOC estimation. Third, our previous study discovered that OA evolution during long-range transport could lead to the underestimation of SOCprecursor by SOA-tracer method in remote areas (Ding et al., 2013). Last but important, since there are only five types of SOA precursors involved in the current study, it is highly possible that other SOA precursors that contribute to the WSOC (and OC) in the PRD are not considered. Thus, the current estimated results might underestimate SOCprecursor in the PRD. In the revised manuscript, we added discussions about the uncertainty associated with SOCprecursor estimation as “It should be noted that there might have significant uncertainties in the simplification of applying chamber-derived parameters to calculate SOCprecursor in the ambient samples. This method is limited by the number of identified SOA tracers and chamber parameters which may not represent all ambient situations and thus lead to significant uncertainties (Kleindienst et al. 2007). The choice of SOA tracers might also introduce great uncertainty in SOC estimation (El Haddad et al. 2011). OA evolution during long-range transport could lead to the underestimation of SOCprecursor by SOA-tracer method in remote areas (Ding et al., 2013). Moreover, since there are only five types of SOA precursors involved in the current study, it is highly possible that other SOA precursors that contribute to the WSOC (and OC) in the PRD are not considered. Thus, the current estimated results might underestimate SOCprecursor in the PRD.”

Ding, X., Wang, X., Xie, Z., Zhang, Z., and Sun, L.: Impacts of Siberian biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: Primary and secondary organic tracers, Environ. Sci. & Technol., 47, 3149-3157, 2013.

El Haddad, I., Marchand, N., Temime-Roussel, B., Wortham, H., Piot, C., Besombes, J. L., Baduel, C., Voisin, D., Armengaud, A., and Jaffrezo, J. L.: Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille, Atmos. Chem. Phys., 11, 2059-2079, 2011.

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., and 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.

3) One of the major conclusions of this study is that the “unexplained” WSOC by the SOA tracer method is likely from photochemical aging of POA in the atmosphere, supported by the “strong” correlation between the “unexplained” WSOC and POC (Figure 5). First of all, an r2 value of the fit based on three data point is problematic. Further, as discussed above, the invalid approach to deriving unexplained WSOC and POC makes the relationship between the two not meaningful. Finally, there are many possible mechanisms other than POA aging can be used to explain the discrepancy (if any) in the WSOC closure calculation, for example, missing SOA precursors (IVOC/SVOC) [de Gouw et al., 2011] and aqueous SOA formation. The authors should explore these and other mechanisms and provide more evidence that this unexplained fraction is due to POA aging and not other processes.

Reply: As discussed above, the approaches of splitting WSOC and deriving POC and SOC are valid; and our estimations of WSOCBB and SOCprecursor are reasonable. We admit that unexplained WSOC in the current study might have other sources, such as SOA formed from aqueous-phase heterogeneous reactions (Ervens et al., 2011) and from other unknown precursors. IVOC/SVOC from primary sources, such as fresh oil (de Gouw et al., 2011), diesel and gasoline vehicles (Gentner et al., 2012) have high SOA yields and are important SOA sources. Previous study has illustrated the semi-volatile character of POA (Robinson et al., 2007). And the nature of POA aging is the partitioning and photochemical processing of IVOC/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. We also checked the correlations between POC and unexplained WSOC using all the data, the correlation was still significant ($p<0.01$, Figure 3), indicating that the unexplained WSOC might be associated with POA aging. At the moment, only based on our observation data, 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 "un-traditional" SOA in the highly polluted PRD. In the revised manuscript, we re-wrote the last paragraph to discuss the potential sources of unexplained WSOC as "WSOCBB and SOCprecursor together explained 69-82% of measured WSOC. Therefore, there should have other sources contributing to unexplained WSOC which ranged from 18% to 31% among the three sites. Previous study has illustrated the semi-volatile character of POA (Robinson et al., 2007). The partitioning and photochemical processes of intermediate VOC (IVOC) and semi-VOC (SVOC) emitted from primary sources, such as fresh oil (de Gouw et al., 2011), diesel and gasoline vehicles (Gentner et al., 2012) do produce large amounts of SOA (Miracolo et al., 2010; Robinson et al., 2007). As modeling 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. Figure 7 presented the correlation between unexplained WSOC and POC. The forest site, DHS exhibited the lowest levels of POC and unexplained WSOC; while the sub-urban site, GIG presented the highest concentrations of the both. Correspondingly, unexplained WSOC displayed a significant correlation with POC, indicating that the unexplained portion might be associated with POA aging. 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). Further study is needed to get insight into these "untraditional" SOA in the highly polluted PRD."

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Ahmadov, R., Atlas, E. L., Bahreini, R., Blake, D. R., Brock, C. A., Brioude, J., Fahey, D. W., Fehsenfeld, F. C., Holloway, J. S., Le Henaff, M., Lueb, R. A., McKeen, S. A., Meagher, J. F., Murphy, D. M., Paris, C., Parrish, D. D., Perring, A. E., Pollack, I. B., Ravishankara, A. R., Robinson, A. L., Ryerson, T. B., Schwarz, J. P., Spackman, J. R., Srinivasan, A., and Watts, L. A.: Organic aerosol formation downwind from the deepwater horizon oil spill, Science, 331, 1295-1299, 2011.

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.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, PNAS, 109, 18318-18323, 2012.

Jathar, S. H., Farina, S. C., Robinson, A. L., and Adams, P. J.: The influence of semi-volatile 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.

Tkacik, D. S., Presto, A. A., Donahue, N. M., and Robinson, A. L.: Secondary organic aerosol formation from intermediate-volatility organic compounds: cyclic, linear, and branched alkanes, Environ. Sci. & Technol., 46, 8773-8781, 2012.

4) The authors used the correlation between WSOC and EC as one and the only piece of evidence that WSOC is mainly associated with biomass burning throughout the manuscript. However, a strong correlation between WSOC and EC does not necessarily indicate a biomass-burning source to WSOC since vehicular emissions also contribute to both WSOC and EC concentrations. Influences due to meteorology further confound the picture. It is also unclear why the authors didn't correlate WSOC with levoglucosan, a biomass burning tracer that is commonly used and was also quantified in the study.

Reply: We appreciate the suggestion. In fact, besides the correlation between WSOC and EC, WSOC did exhibit significant correlation with levoglucosan, providing an additional evidence that WSOC was mainly associated with biomass burning (Figure 4). He et al. (2011) studied biomass burning emissions over the PRD and found significant increases in fire emissions during November to December. 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). Considering our estimation that 42–47% of measured WSOC came from biomass burning as well as all the information from other studies,

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we believe biomass burning was the dominant contributor to WSOC in the PRD during fall-winter. In the revised manuscript, we added the figure of correlation between WSOC and levoglucosan 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 (Figure 3), 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 (Figure 4), providing an additional evidence that BB had significant contributions to WSOC in the PRD region during fall-winter."

Minor comments: Page 13780, Line 13-15: The observation of high WIOC at WQS is somewhat contradicting with the site description on Page 13777, Line 9-12. Why is WQS considered a rural site with rare traffic and representing "regional background" when both WIOC and POC concentrations were almost as high as those at the suburban site? The authors need to better reconcile their knowledge about the site and the observations.

Reply: The WQS site is located in the central of PRD and surrounded by megacities (Guangzhou, Donggguan, Foshan, Shenzhen, Zhongshan, etc. Figure 5). Although there has little local emission, air pollutants emitted in above megacities could transport to WQS. As a regional monitoring station in the PRD Regional Air Quality Monitoring Network which was jointly established by the Guangdong Provincial Environmental Protection Monitoring Centre (GDEMC) and the Environmental Protection Department of the Hong Kong Special Administrative Region (HKEPD), many studies have been undertaken at WQS to monitor regional background of air pollution (Guo et al., 2009; Yuan et al., 2012; Ding et al., 2012; Wang et al., 2012; Wang et al., 2013). As Figure 6 showed, almost all air masses at WQS during our campaign came from the north and

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passed through Guangzhou and Dongguan, probably leading to high WIOC and POC concentrations observed there.

Guo, H.; Jiang, F.; Cheng, H. R.; Simpson, I. J.; Wang, X. M.; Ding, A. J.; Wang, T. J.; Saunders, S. M.; Wang, T.; Lam, S. H. M.; Blake, D. R.; Zhang, Y. L.; Xie, M. Concurrent observations of air pollutants at two sites in the Pearl River Delta and the implication of regional transport Atmos. Chem. Phys. 2009, 9, 7343-7360.

Yuan, B.; Chen, W.; Shao, M.; Wang, M.; Lu, S.; Wang, B.; Liu, Y.; Chang, C.-C.; Wang, B. Measurements of ambient hydrocarbons and carbonyls in the Pearl River Delta (PRD), China Atmos. Res. 2012, 116, 93-104.

Ding, X.; Wang, X.; Gao, B.; Fu, X.; He, Q.; Zhao, X.; Yu, J.; Zheng, M. Tracer based estimation of secondary organic carbon in the Pearl River Delta, South China J. Geophys. Res. 2012, 117, D05313, doi: 10.1029/2011JD016596.

Wang, X.; Ding, X.; Fu, X.; He, Q.; Wang, S.; Bernard, F.; Zhao, X.; Wu, D. Aerosol scattering coefficients and major chemical compositions of fine particles observed at a rural site in the central Pearl River Delta, South China J. Environ. Sci. 2012, 24, 72-77.

Wang, X.; Liu, H.; Pang, J.; Carmichael, G.; He, K.; Fan, Q.; Zhong, L.; Wu, Z.; Zhang, J. Reductions in sulfur pollution in the Pearl River Delta region, China: Assessing the effectiveness of emission controls Atmos. Environ. 2013, 76, 113-124.

Page 13781, Line 9: SOCtotal also includes WSOC and WIOC from vehicle emissions.

Reply: The source profiles of vehicle exhaust did show that there had polar species, such as fatty acids (Schauer et al 1999; 2002). However, the source apportionment of WSOC based on PMF model in the PRD (Huang et al., 2006) and Shanghai (Feng et al., 2013) revealed that vehicle emissions had no contribution to WSOC. These results suggested that although vehicle emissions had polar compounds, their contributions to ambient WSOC were very minor or could be ignored. If so, our estimation of SOCtotal should exclude the influence of vehicle emissions, since the two parameters (ambient

WSOC and estimated WSOCBB) for SOCtotal estimation in this study had no contribution from vehicle emissions.

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

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks, Environ. Sci. Technol., 1999, 33, 1578-1587.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles, Environ. Sci. Technol., 2002, 36, 1169-1180.

Page 13783, Line 28: Can the authors provide some explanation of why SOC from anthropogenic sources exhibit little spatial variation whereas POC does?

Reply: POC is directly emitted from emission sources; while SOC is produced by condensation of oxidation products of precursors. Due to high human activities, it is expected that POC exhibits high levels in urban and sub-urban areas. Although the emissions of anthropogenic precursors are also high in urban and sub-urban areas, it will take several to dozens hours to oxidize these precursors and form SOA in the air. During this period, air transport and mixing would compromise the spatial difference of anthropogenic SOC on a regional scale.

Page 13785, Line 5: Splitting WSOC into WSOCBB and SOC based on levoglucosan concentration is not a new analytical method.

Reply: We developed such a method to split WSOC into WSOCBB and SOC in our previous study (Ding et al., 2008). In the current manuscript, we applied this method to estimate WSOCBB and SOC in the PRD. We have mentioned this in the manuscript as

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“Since WSOC is mainly derived from BB and SOA (Weber et al., 2007), WSOC from SOA (WSOCSOA) can be estimated as (Ding et al., 2008a)……”. In the conclusion section, we changed the statement.

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

Page 13785, Line 8: The high fraction of WSOCBB in the total WSOC is not evidence that WSOC is mainly from BB since WSOCBB is calculated using levoglucosan with the assumption that BB contributes to WSOC concentration.

Reply: Besides the correlation between WSOC and EC, WSOC did exhibit significant correlation with levoglucosan, providing an additional evidence that WSOC was mainly associated with biomass burning. Considering our estimation that 42–47% of measured WSOC came from biomass burning as well as the results from other studies, we believe biomass burning was the dominant contributor to WSOC in the PRD during fall-winter. (Please see the details in our reply above)

Technical corrections: Page 13774, line 11-13: This sentence needs rewording.

Reply: This sentence has been reworded as “Secondary OC (SOC) and primary OC (POC) were estimated by subtracting BB-derived WSOC (WSOCBB) from measured WSOC. And the results showed that POC exhibited dominance over SOC, contributing 68-79% of OC.”

Page 13774, line 18: totally→ in total

Reply: Revised

Page 13775, line 7: add “formation” after “SOA”

Reply: Revised

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Page 13775, line 23: short the gap→close the gap

Reply: Revised

Page 13776, line 3: overestimate→overestimation

Reply: Revised

Page 13776, line 21: delete "with the purpose"

Reply: Revised

Page 13778, line 12: filtered→ filtration

Reply: Revised

Page 13779, line 17: shares→share; were→ was

Reply: Revised

Page 13779, line 26: major→mainly

Reply: Revised

Page 13780, line 2: deeply→strongly, greatly or largely

Reply: Revised

Page 13783, Equation 5: change "SOC" to "SOCprecursor"

Reply: Revised

Page 13783, line 6: SOCtoluene is probably more precise than SOCaromatics

Reply: As mentioned by Kleindienst (2007), the toluene SOA tracer, 2,3-dihydroxy-4-oxopentanoic acid, was also formed during photooxidation of other aromatic hydrocarbons, such as xylenes and other methylated benzenes. Thus, it is reasonable to attribute the tracer of toluene to monocyclic aromatics. Accordingly, it is proper to regard SOC that estimated using 2,3-dihydroxy-4-oxopentanoic acid as aromatics-derived SOC (SOCaromatics).

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. 2007, 41, 8288-8300.

Page 13783, line 26: I believe PAHs are included in the aromatics

Reply: In the original manuscript, we want to state that both monocyclic aromatic hydrocarbons and PAHs are mainly from anthropogenic emissions. In the revised manuscript, we used “monocyclic aromatic hydrocarbons” replacing “aromatics”.

Page 13785, line 7: OC contribution ! contribution to OC

Reply: Revised

Reference de Gouw, J. et al., Science, 331, 1295-1299, 2011. Ervens, B. et al., Atmos. Chem. Phys., 11, 11069–11102, 2011. Kondo, Y. et al., J. Geophys. Res., 112, D01203, doi:10.1029/2006JD007056, 2007. Varutbangkul, V. et al., Atmos. Chem. Phys., 6, 2367–2388, 2006. Zhang, X. et al., Environ. Sci. Technol., 47, 3685-2693, 2013. Interactive comment on Atmos. Chem. Phys. Discuss., 13, 13773, 2013. âĂČ

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 13773, 2013.

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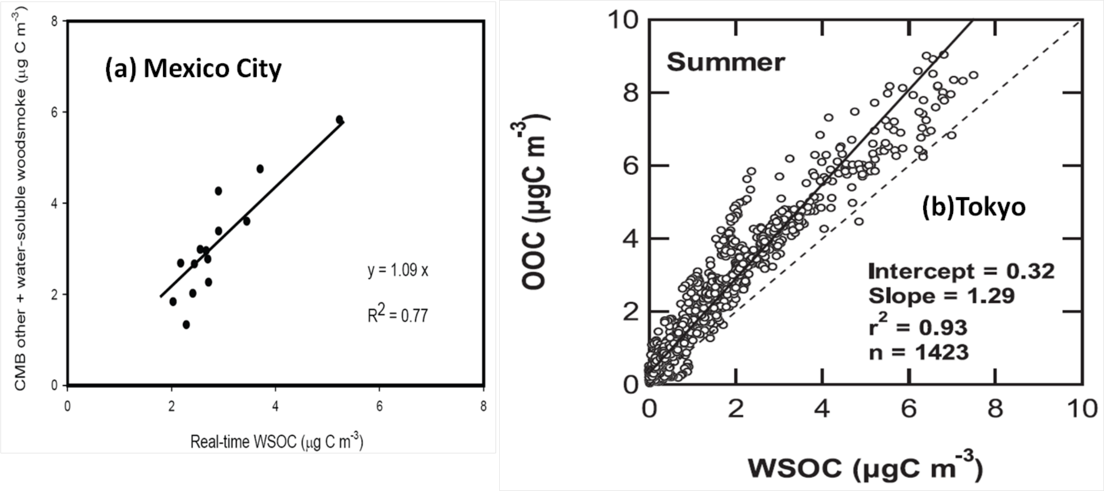

Fig. 1. Correlation of WSOC with CMB other+WSOCBB (a) and OOC (b)

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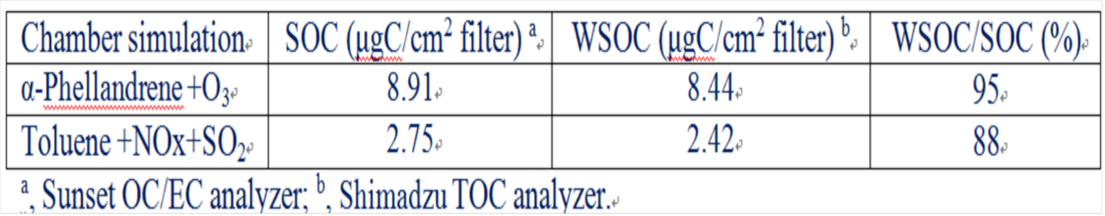

Chamber simulation	SOC (μgC/cm^2 filter) [a]	WSOC (μgC/cm^2 filter) [b]	WSOC/SOC (%)
α-Phellandrene +O_3	8.91	8.44	95
Toluene +NO_x+SO_2	2.75	2.42	88

[a], Sunset OC/EC analyzer; [b], Shimadzu TOC analyzer.

Fig. 2. Chamber results of α-phellandrene and toluene

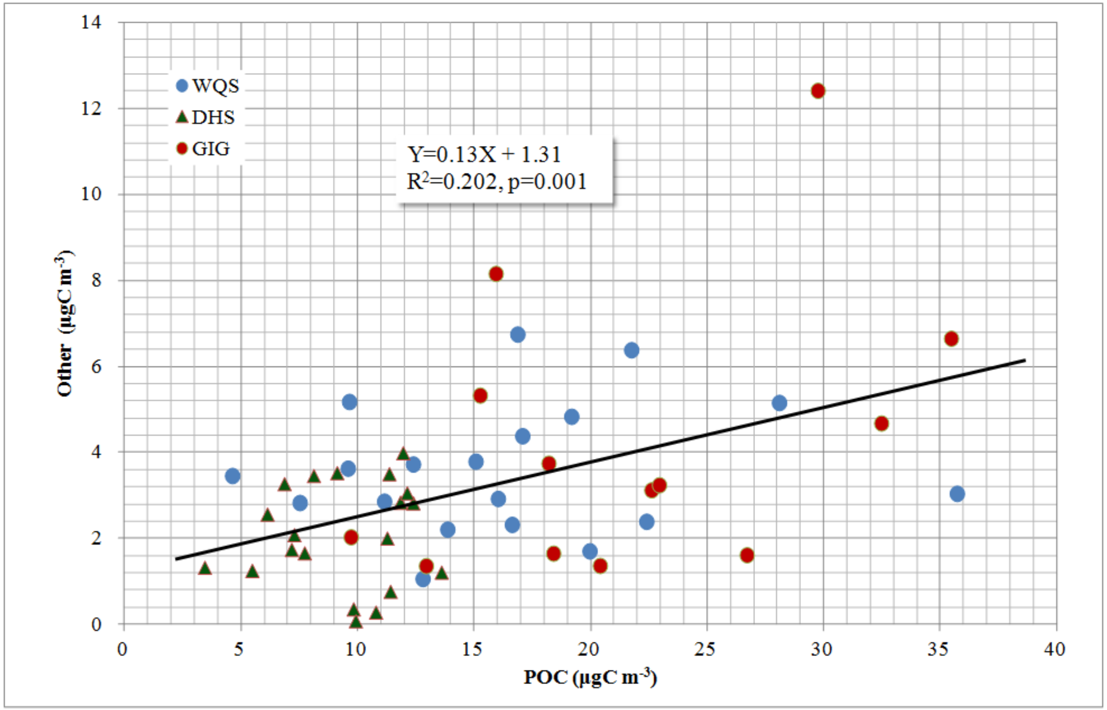

Fig. 3. Correlation between unexplained WSOC and POC

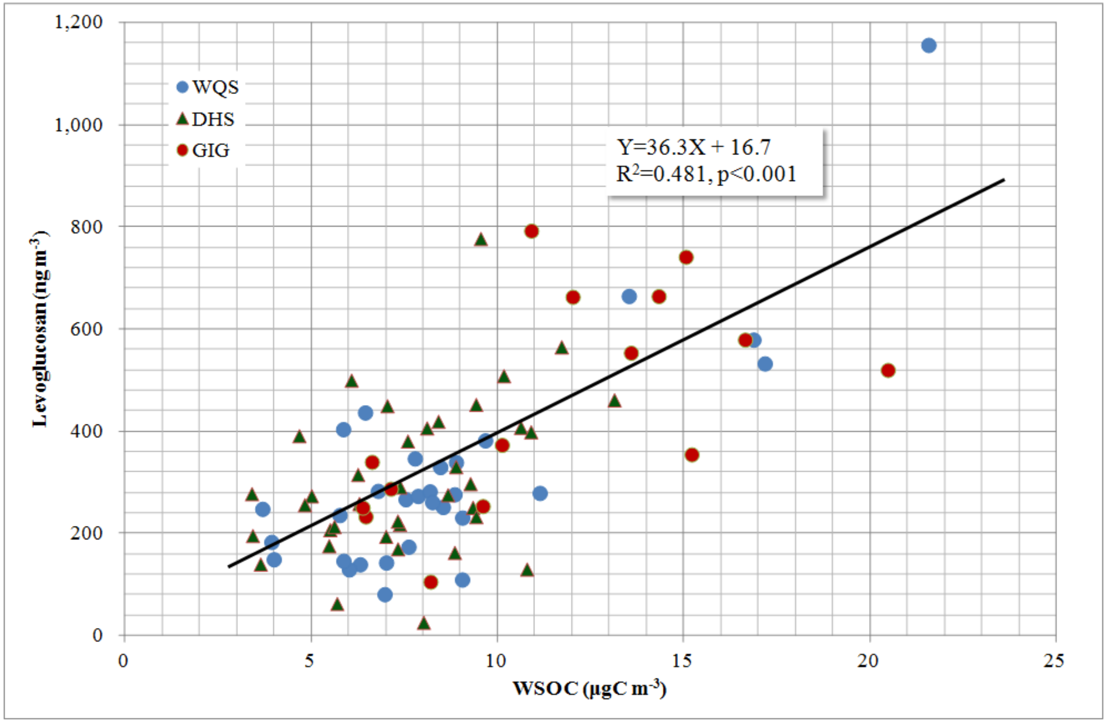

Fig. 4. Correlation between WSOC and levoglucosan

Fig. 5. PRD Regional Air Quality Monitoring Network

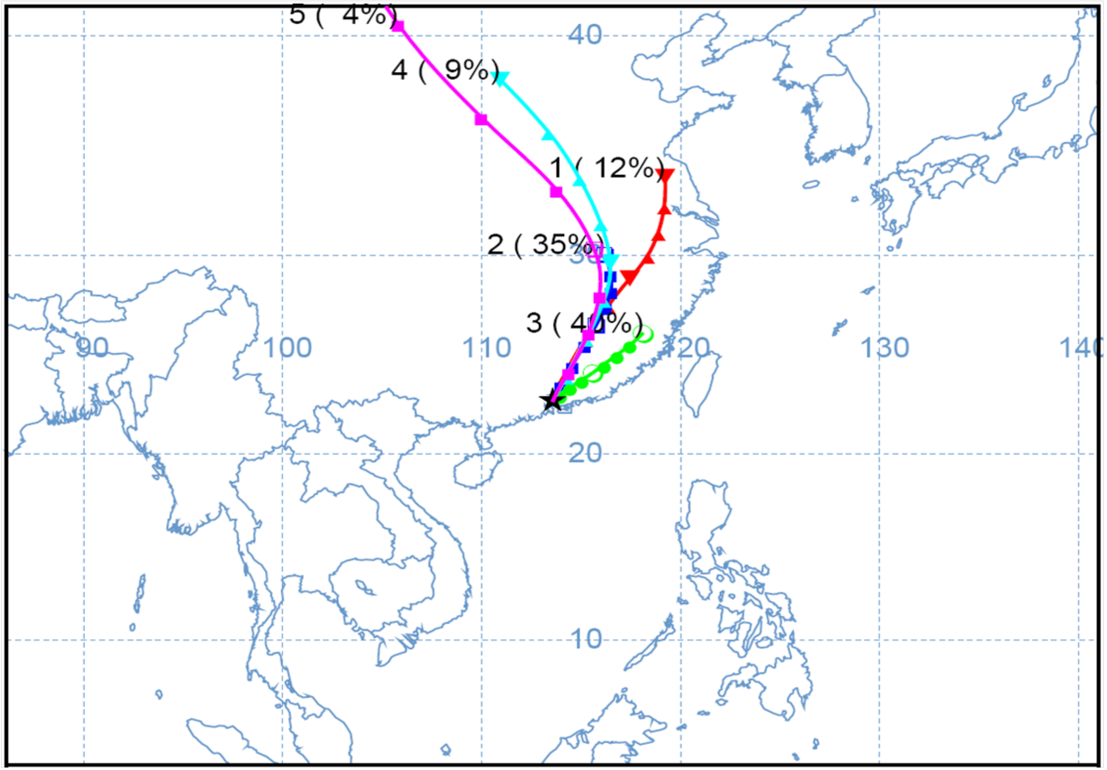

Fig. 6. Air mass clusters at WQS using HYSPLIT