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Water-soluble organic carbon over the Pearl River Delta region during fall–winter: spatial variations and source apportionment

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Abstract

Water-soluble organic carbon (WSOC) is a major component of carbonaceous aerosols. However, the detailed information of WSOC origins is still unclear. In the current study, fine particles ($PM_{2.5}$) were collected at one sub-urban and two rural sites in the Pearl River Delta (PRD) region, south China during fall–winter 2008 to measure WSOC and organic tracers of biomass burning (BB) and secondary organic aerosols (SOA) from isoprene, monoterpenes, β-caryophyllene, aromatics and 2-ring polycyclic aromatic hydrocarbons (PAHs). WSOC concentrations ranged from 7.63 to 11.5 $\mu g\,C\,m^{-3}$ and accounted for 38.8–57.9 % of organic carbon (OC). Both WSOC and water-insoluble organic carbon (WIOC) exhibited higher levels at the sub-urban site than the rural sites. Subtracting BB-derived WSOC ($WSOC_{BB}$) from measured WSOC, secondary OC (SOC) and primary OC (POC) were estimated that POC exhibited dominance over SOC and contributed 68–79 % to OC. Significant correlation between WSOC and EC was observed, suggesting that BB could have important contributions to ambient WSOC in the PRD region during fall–winter. Organic tracers were applied to do source apportionment of WSOC, which further confirmed that BB was the dominant contributor, accounting for 42–47 % of measured WSOC. SOC estimated by SOA tracers totally contributed 22–40 % of WSOC, among which anthropogenic SOC (sum of aromatics and 2-ring PAHs, 18–25 %) exhibited dominance over biogenic SOC (sum of isoprene, monoterpenes and β-caryophyllene, 4–15 %). The unexplained WSOC (18–31 %) showed a positive correlation with POC, indicating that this portion might be associated with POC aging.

1 Introduction

Organic aerosols (OA), originated from both direct emission (primary organic aerosol or POA) and secondary formation (secondary organic aerosol or SOA) (De Gouw and Jimenez, 2009), are the major components of fine particulate matter ($PM_{2.5}$). As a large fraction of organic carbon (OC), water-soluble organic carbon (WSOC) is associated with oxygenated and polar compounds. Due to its potential to modify the hygroscopic and optical properties of atmospheric particles (Jung et al., 2011; Zhang et al., 2011), WSOC has caused increasing concerns about its adverse effects on regional air quality and global climate change. To develop effective control strategies for ambient $PM_{2.5}$, it is important to understand the origins of WSOC. So far, however, there has limited knowledge of the sources of WSOC, although the rough estimate can split it into SOA and biomass burning (BB) (Ding et al., 2008a; Snyder et al., 2009; Stone et al., 2008; Weber et al., 2007).

SOA is produced by condensation of oxidation products of volatile organic compounds (VOCs) (Claeys et al., 2004) as well as aerosol aging (Jimenez et al., 2009). Since SOA is primarily composed of oxygenated compounds that are highly water-soluble (Kanakidou et al., 2005), WSOC is often regarded as an indicator of SOA and an increase in WSOC to OC ratio (WSOC/OC) is considered as the enhancement of SOA formation (Weber et al., 2007). However, the origins of SOA itself are still unclear. For SOA precursor emissions, biogenic VOCs (terpenes) were dominated over anthropogenic VOCs (e.g. aromatics) on the global scale (Guenther et al., 1995; Piccot et al., 1992); while anthropogenic SOA could play dominant role, especially in the regions with high human activities (Ding et al., 2008b, 2012; Spracklen et al., 2011; Volkamer et al., 2006). Moreover, POA aging that significantly improved model prediction of SOA (Robinson et al., 2007) could also enhance anthropogenic contributions to estimated SOA. Recently, SOA aging mechanism (Donahue et al., 2012) was discovered which could further short the gap between model prediction and field observation. At the moment, it is still a challenge to quantitatively identify SOA compositions and sources, which limits the further understanding of WSOC origins.

BB aerosol that contributed more than 90 % of global primary OC (POC) emissions (Bond et al., 2004) also contained a large fraction of highly water-soluble compounds (Lee et al., 2008; Viana et al., 2008). An increase in WSOC/OC ratio is also expected when BB events happen. Therefore, the enhancement of WSOC in the ambient can result from the influence of either SOA or BB. Moreover, intense BB could not only deeply influence SOA formation (Ding et al., 2013) but also lead to significant overestimate of bulk SOC by EC-tracer method (Ding et al., 2012) which is widely used for SOC estimation (Turpin and Huntzicker, 1995). To separate SOA and BB contributions to WSOC and avoid BB influence on SOC estimation, specific organic tracers for SOA and BB are essentially needed.

The Pearl River Delta (PRD) is one of the most industrialized and densely populated regions in China. The rapid growth in economy has led to fast increase in anthropogenic emissions of air pollutants (Chan and Yao, 2008). Situated in the subtropical area, biogenic emissions in this region are also expected to be significant during the whole year (Zheng et al., 2010). Previous studies all suggested that air quality during fall–winter was the worst in a year in the PRD region, based on the monitoring of $PM_{2.5}$, O_3, visibility and other criteria pollutants (Ding et al., 2011; Wang et al., 2012; Zhang et al., 2012). Additionally, open burning of agriculture residuals often happens in the sub-urban and rural areas in the PRD during fall–winter (He et al., 2011). Considering the high VOC emissions, the high atmospheric oxidative capacity and the high BB loading, both SOA and BB aerosol should have significant contributions to WSOC in the PRD during this period. In the current study, 24 h $PM_{2.5}$ samples were collected consecutively at three sites in the PRD during fall–winter. WSOC and organic tracers of BB and SOA from isoprene, monoterpenes, β-caryophyllene, aromatics and 2-ring PAHs were measured with the purposes (1) to acquire the spatial distribution of WSOC over the PRD; (2) to estimate bulk SOC in the significant BB-influence season; and (3) to apportion WSOC in detail based on the specific organic tracers.

2 Experimental section

2.1 Field sampling

$PM_{2.5}$ samples were collected using high volume samplers (Tisch Environmental, Inc.) at a flow rate of 1.1 $m^3\,min^{-1}$ at two rural sites: Wangqingsha (WQS) and Dinghushan (DHS) and one sub-urban site: Guangzhou institute of geochemistry (GIG). As Fig. 1 showed, WQS site is located in the central of PRD and surrounded by city clusters (e.g. Hong Kong, Guangzhou, Shenzhen, Foshan and Dongguan) 60 km away and adjacent to the Pearl River estuary. The sampler was put on the rooftop, about 30 m above ground, of a seven-floor building in a high school (22° 42′ N, 113° 32′ E). Since the surrounding terrain is flat with large farmland nearby and rare traffic, this site serves as an ideal location to monitor the regional background levels of air pollutants in the PRD (Ding et al., 2012). Dinghushan Biosphere Reserve (23° 09′–23° 11′ N, 112° 31′–112° 34′ E) located in the northwest of PRD (Fig. 1), is covered by sub-tropical evergreen broadleaf forest and pine forest with monsoon climate (Yi et al., 2007). The sampler was put on the top of a hill (∼ 100 m above ground, 23° 10′ N, 112° 33′ E) at the eastern edge of the reserve. At the foot of the hill are local resident and industry areas and farmland (Fig. 1). Biogenic VOCs (BVOCs) emitted from local vegetations could be mixed and reacted here with anthropogenic pollutants transported from the adjacent region. Observation at DHS site can provide information about the influence of anthropogenic emissions on forest area. GIG is situated 5 km away from downtown Guangzhou and served as a sub-urban site. There are two highways in the south and west, respectively and farmlands in the northeast (Fig. 1). The sampler was put on the rooftop, about 20 m above ground, of a four-floor building in the institute (23° 09′ N, 113° 22′ E).

Field campaigns were carried out during fall–winter (November to December) considering the severe air pollution and BB influence (Ding et al., 2011; He et al., 2011). At WQS site, sampling was undertaken from 10 November to 9 December 2008. After that, the sampler was moved to GIG site and collected samples from 10 to 25 December 2008. At DHS site, samples were collected from 19 November to 25 December 2008. 24 h sampling (19 p.m.–19 p.m.) was taken during all campaigns. Pre-fired 8 inch × 10 inch quartz filters were covered with aluminum foil and stored in a bag containing silica gel at 4 °C before and –20 °C after collection. A total of 82 field samples (30 at WQS, 37 at DHS and 15 at GIG) were collected with 2 field blanks for each site.

2.2 Chemical analysis

A punch (1.5 cm × 1.0 cm) of each filter was taken for the measurements of OC and EC using the thermo-optical transmittance (TOT) method (NIOSH, 1999) by OC/EC Analyzer (Sunset Laboratory Inc.). An additional punch of 2.54 cm diameter was taken from each filter and extracted in 20 mL of 18-Mohm milliQ water and sonicated for 60 min in an ice-water bath (Ding et al., 2008a). After filtered, the extract was analyzed for WSOC using a TOC analyzer (Shimadzu TOC-V_{CPH}). Ambient OC, EC and WSOC were corrected using field blanks.

To identify the source contributions of SOA and BB to WSOC, these filters were extracted by mixed solvents and analyzed for SOA and BB tracers by GC-MSD after methylation and silylation. The detailed information of organic tracer analysis is described elsewhere (Ding et al., 2011, 2012). There are eleven tracers involved for SOC estimation, including three isoprene SOA tracers (2-methylthreitol, 2-methylerythritol, 2-methylglyceric acid), five monoterpene SOA tracers (*cis*-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid), one β-caryophyllene SOA tracer (β-caryophyllinic acid), one toluene SOA tracer (2,3-dihydroxy-4-oxopentanoic acid) and one 2-ring PAHs SOA tracer (phthalic acid). BB tracer, levoglucosan was also measured for BB-derived WSOC ($WSOC_{BB}$) estimation. *cis*-Pinonic acid, pinic acid, phthalic acid and levoglucosan were quantified by authentic standards. Due to lack of standards, isoprene SOA tracers were quantified using erythritol (Ding et al., 2008a); monoterpene SOA tracers (3-methyl-1,2,3-butanetricarboxylic acid, 3-hydroxyglutaric acid and

3-hydroxy-4,4-dimethylglutaric acid) were quantified using pinic acid; β-caryophyllinic acid and 2,3-dihydroxy-4-oxopentanoic acid were quantified using octadecanoic acid and azelaic acid, respectively, due to their approximate retention times (Ding et al., 2012). Table 1 listed all the tracers and their concentrations at the three sites.

3 Result and discussion

3.1 Spatial variations

As summarized in Table 2, WSOC levels were higher at sub-urban site ($11.5 \pm 4.29\,\mu g\,C\,m^{-3}$ at GIG) as compared to the rural sites ($8.62 \pm 3.99\,\mu g\,C\,m^{-3}$ at WQS and $7.63 \pm 2.37\,\mu g\,C\,m^{-3}$ at, DHS). During fall–winter, the concentrations of WSOC in Chinese megacities were reported as $9.6 \pm 3.8\,\mu g\,C\,m^{-3}$ in Guangzhou, $6.7 \pm 3.0\,\mu g\,C\,m^{-3}$ in Shanghai, 7.5 ± 4.9 C $\mu g\,m^{-3}$ in Beijing (Feng et al., 2006) and $20.53–35.58\,\mu g\,C\,m^{-3}$ in Nanjing (Wang et al., 2002). WSOC observed at four sites in the PRD was in the range of 2.13 to $4.00\,\mu g\,C\,m^{-3}$ during winter (Huang et al., 2012a). Our measurements were comparable with these data in Chinese cities but much higher than those (∼ 1–$2\,\mu g\,C\,m^{-3}$) in Europe (Viana et al., 2007) and United States (Ding et al., 2008a; Weber et al., 2007) during the same season. Although WSOC levels at DHS were the lowest among the three sites, the shares of WSOC in OC (WSOC/OC) there, were the highest (57.9 %); and WSOC exhibited significant correlation with OC (Fig. 2a). All these indicated the dominant role of water soluble compounds in OC at the forest site. WQS (38.8 %) and GIG (42.2 %) had the similar OC contributions from WSOC. WSOC/OC observed in this study were comparable with those (20–51 %) over the PRD region (Ho et al., 2006; Huang et al., 2012a), higher than those (∼ 20 %) in Tokyo (Miyazaki et al., 2006) but lower than those (44–72 %) in the southeastern United States (Ding et al., 2008a).

It is worth noting that WSOC was significantly correlated with EC (Fig. 2b). EC is major from diesel exhaust and BB (Ke et al., 2007) and can be regarded as a primary

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tracer; while WSOC mainly comes from SOA and BB (Ding et al., 2008a). If samples were deeply influenced by BB, it is expected that WSOC and EC are correlated well with each other. In fact, fall–winter is the harvest season of crop in the PRD region. Our previous study observed the great enhancement of BB in the PRD during fall–winter (Ding et al., 2012). Since SOA could not contain EC, the positive correlation between WSOC and EC suggested that BB had significant contributions to WSOC in the PRD region during fall–winter.

Water-insoluble organic carbon (WIOC) is mostly from primary emissions (Park and Cho, 2011), such as vehicle exhaust (Miyazaki et al., 2006) and can be calculated as:

$$\mathrm{WIOC} = \mathrm{OC} - \mathrm{WSOC} \quad (1)$$

Among the three sites, the average level of WIOC was the highest at GIG ($16.9 \pm 7.96\,\mu\mathrm{g\,C\,m^{-3}}$), largely due to the more influence of primary emissions near urban Guangzhou. Located in the downwind of the PRD region, WQS site also showed high WIOC concentration ($13.9 \pm 5.39\,\mu\mathrm{g\,C\,m^{-3}}$), probably resulting from the transport of primary pollutants from the adjacent city clusters. The WIOC levels at DHS site ($5.74 \pm 2.56\,\mu\mathrm{g\,C\,m^{-3}}$) were much lower than those at above two sites by a factor of 2–3, indicating the less influence from primary emissions at the forest site. WIOC was dominated in OC at WQS and GIG with the fractions of WIOC in OC (WIOC/OC) 61.2 % and 57.8 %, respectively. Moreover, WIOC exhibited higher correlation coefficient with OC than WSOC at all sites (Fig. 2 a and c). This is more obvious at GIG site that only WIOC was correlated with OC. Since WIOC comes from primary emissions, the higher WIOC/OC and the higher correlation coefficient of WIOC vs. OC as compared to WSOC implied that OC over the PRD was dominantly from primary sources during fall–winter.

Since both WIOC and EC are emitted from primary sources, WIOC exhibited good correlation with EC (Fig. 3d). Miyazaki et al. (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). 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 changing from place to place and about 2–3 times higher than those in urban Tokyo, suggesting additional sources of WIOC other than motor vehicle over the PRD region.

3.2 Source apportionment of carbonaceous aerosols

Since WSOC is mainly derived from BB and SOC (Weber et al., 2007), SOC can be is estimated as (Ding et al., 2008a):

$$\mathrm{SOC_{total}} = \mathrm{WSOC} - \mathrm{WSOC_{BB}} \tag{2}$$

where $\mathrm{SOC_{total}}$ is the total amount of SOC, including the known precursor-produced SOC (Kleindienst et al., 2007) and other processes produced SOC, such as the aging of POA (Robinson et al., 2007) and SOA (Donahue et al., 2012) as well as aqueous-phase heterogeneous reactions (Ervens et al., 2011). WSOC is the measured value. $\mathrm{WSOC_{BB}}$ is BB derived WSOC, which can be estimated using ambient tracer concentration (C_tracer) and the factor, $(f_\mathrm{tracer/WSOC})_\mathrm{BB}$, of tracer in WSOC from BB sources (Eq. 3).

$$\mathrm{WSOC_{BB}} = C_\mathrm{tracer}/(f_\mathrm{tracer/WSOC})_\mathrm{BB} \tag{3}$$

As a typical BB tracer, levoglucosan is always applied to access the impact of BB (Puxbaum et al., 2007; Simoneit et al., 1999). The factors of levoglucosan in WSOC from BB sources were reported as 0.0994 µg µgC^{-1} (1210 ng m^{-3} levoglucosan in 12.17 µg C m^{-3} WSOC) in a prescribe fire plume (Ding et al., 2008b) and 0.0806 µg µgC^{-1} (129 ng m^{-3} levoglucosan in 1.6 µg C m^{-3} WSOC) in the events of open burning of rice straw residues (Viana et al., 2008). The spatial distribution of BB over the PRD region showed that straw burning was the major type of BB in the central PRD; while both forest fire and straw burning had significant contributions around

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DHS (He et al., 2011). Since our campaign was undertaken in the straw burning season, $(f_{\mathrm{tracer/WSOC}})_{\mathrm{BB}}$ of 0.0806 µg µgC^{-1} was applied to estimated ambient WSOC$_{\mathrm{BB}}$ at WQS and GIG. And the 1 : 1 combination (0.090 µg µgC^{-1}) of forest fire and straw burning was applied to estimated ambient WSOC$_{\mathrm{BB}}$ at DHS.

When WSOC$_{\mathrm{BB}}$ is estimated, SOC$_{\mathrm{total}}$ and POC can be calculated by Eqs. (2) and (4), respectively.

$$\mathrm{POC} = \mathrm{OC} - \mathrm{SOC}_{\mathrm{total}} = \mathrm{WIOC} + \mathrm{WSOC}_{\mathrm{BB}} \tag{4}$$

The estimated POC levels were 17.8 ± 7.18 µg C m^{-3}, 9.13 ± 3.08 µg C m^{-3} and 22.5 ± 7.73 µg C m^{-3} at WQS, DHS and GIG, respectively. Such a spatial pattern is similar as those of primary species, EC and WIOC (Table 2). The dominance of POC was observed during the whole campaign (Fig. 3) that the fractions of POC in OC (POC/OC) were 78 ± 11 %, 68 ± 15 % and 79 ± 9 % at WQS, DHS and GIG, respectively. This demonstrated that POC was the dominant contributor to OC during fall–winter over the PRD region. As compared to POC, the estimated SOC$_{\mathrm{total}}$ was much lower and the concentrations were 4.78 ± 2.34 µg C m^{-3} at WQS, 4.18 ± 2.35 µg C m^{-3} at DHS and 5.97 ± 3.41 µg C m^{-3} at GIG. Previous studies always considered the increase of OC/EC ratio as the enhancement of SOC (Na et al., 2004; Turpin and Huntzicker, 1995; Zeng and Wang, 2011). This may be true during summer with intense photochemical reactions and rare BB influence. However, under BB impact with high OC/EC ratio (Fine et al., 2002; Zhang et al., 2007), elevated OC/EC ratio could not indicate the enhancement of SOC. This was confirmed that there was no significant correlation observed between OC/EC ratio and SOC/OC at all sites ($p > 0.05$).

To get insight into the origins of WSOC, SOA tracers were applied to estimate the precursor-produced SOC (SOC$_{\mathrm{precursor}}$). Such a SOA-tracer method was first proposed by Kleindienst et al. (Kleindienst et al., 2007) with the assumption that in the ambient the mass fractions of tracers in SOC ($f_{\mathrm{tracer/SOC}}$) remained the same as those from chamber simulations. When determining the concentrations of these tracers in the ambient, SOC from different precursors can be estimated as:

$$\mathrm{SOC} = C_{\mathrm{tracer}}/f_{\mathrm{tracer/SOC}} \tag{5}$$

where C_{tracer} is the sum of all tracers' concentrations for a certain precursor. Table 2 listed the tracers observed at the three sites and the $f_{\mathrm{tracer/SOC}}$ for different precursors. These data were further used to estimate SOC from isoprene ($\mathrm{SOC_I}$), monoterpenes ($\mathrm{SOC_M}$), β-caryophyllene ($\mathrm{SOC_C}$), aromatics ($\mathrm{SOC_A}$) and 2-ring PAHs ($\mathrm{SOC_P}$), respectively. It should be noted that there were nine tracers involved in the source profile of monoterpene SOC (Kleindienst et al., 2007). However, only five of the nine monoterpene SOA tracers were detected in the current study. To lower the uncertainty induced from different tracer compositions, the $f_{\mathrm{tracer/SOC}}$ with five monoterpene SOA tracers (Table 2) was calculated based on another chamber simulations (Offenberg et al., 2007) of the same research group. The $f_{\mathrm{tracer/SOC}}$ with five monoterpene SOA tracers ($0.059\,\mu\mathrm{g}\,\mu\mathrm{g\,C}^{-1}$) was one fourth of that with nine tracers ($0.231\,\mu\mathrm{g}\,\mu\mathrm{g\,C}^{-1}$) (Kleindienst et al., 2007).

Figure 4 showed the source apportionment of WSOC over the PRD region during fall–winter. BB was the predominant contributor, accounting for 42–47 % of measured WSOC. And the estimated $\mathrm{WSOC_{BB}}$ concentrations were $3.85 \pm 2.62\,\mu\mathrm{gC\,m}^{-3}$, $3.39 \pm 1.67\,\mu\mathrm{gC\,m}^{-3}$ and $5.55 \pm 2.62\,\mu\mathrm{g\,C\,m}^{-3}$ at WQS, DHS and GIG, respectively. In Chinese city clusters, the sub-urban and rural areas are mostly surrounded and occupied by farmland, respectively. Open burning of agriculture residues is very often during harvest season and leads to deteriorating air quality (Huang et al., 2012b; Qu et al., 2012; Wang et al., 2009). Thus, BB is an important primary source to carbonaceous aerosols over the PRD region during fall–winter.

$\mathrm{SOC_{precursor}}$ contributed 22–40 % of WSOC with the highest at DHS and the lowest at GIG. The shares of $\mathrm{SOC_A}$ and $\mathrm{SOC_P}$ in WSOC were 12–18 % and 6–8 %, respectively (Fig. 4). Since both aromatics and PAHs are mainly from anthropogenic emissions, the sum of $\mathrm{SOC_A}$ and $\mathrm{SOC_P}$ could be regarded as the SOC from anthropogenic precursors which contributed 18–25 % of measured WSOC. It is interesting to note that the SOC from anthropogenic precursors exhibited little spatial difference that the concentrations were 2.28 ± 1.58 µg C m^{-3}, 2.06 ± 0.97 µgC m^{-3} and 2.13± 1.14 µg C m^{-3} at WQS, DHS and GIG, respectively. This implied that anthropogenic SOA had regional influence over the whole PRD. As compared to anthropogenic SOC, biogenic SOC (sum of SOC$_I$, SOC$_M$ and SOC$_C$) had minor contributions, only accounting for 7 % and 4 % of WSOC at WQS and GIG, respectively. Significant enhancement of SOC$_M$ (11 %) was observed at DHS. This is expected since DHS site is located in the forest area where pine forest, one of the major forest types, could emit large amounts of monoterpenes all the year (Geron et al., 2000). Biogenic SOC contributed 15 % of measured WSOC at DHS. The dominance of anthropogenic SOC over the PRD region was also observed at WQS from summer to winter (Ding et al., 2012).

WSOC$_{BB}$ and SOC$_{precursor}$ together explained 69–82 % of measured WSOC. The unexplained fraction ranged from 18 % to 31 % among the three sites. DHS site with low POC exhibited not only the lowest unexplained fraction but also the lowest unexplained WSOC concentration; while GIG site with high POC showed the highest values in the both. Moreover, the unexplained WSOC displayed a significant correlation with POC (Fig. 5). All these suggested that the unexplained WSOC might be associated with POA aging. POA emitted from fossil fuel combustion and BB can form large amounts of SOA during aging processes (Hennigan et al., 2011; Weitkamp et al., 2007). As model predicted, POA aging could contribute one third of global OA (Jathar et al., 2011). Constrained by aerosol mass spectrometer data, the estimated SOA (23 Tg a^{-1}) from POA aging contributed 16 % of global SOA (140 Tg a^{-1}) (Spracklen et al., 2011). Although it would contain SOC formed by processes uncaptured by the current SOA-tracer method and POA emitted from sources other than BB, the unexplained WSOC might be regarded as the upper limit of SOC from POA aging.

4 Conclusions

In this study, spatial variations of WSOC in $PM_{2.5}$ were determined over the PRD region during fall–winter and the detailed information about WSOC origins were first reported based on the specific organic tracers of BB and SOA. WSOC exhibited higher levels at the sub-urban site than the rural sites and accounted for 38.8–57.9 % of OC. A new method was developed to estimate SOC and POC by subtracting BB-derived WSOC from measured WSOC, which indicated the dominance of POC with the OC contribution exceeding 70 %. The correlation between WSOC and EC implied that BB could have significant contributions to ambient WSOC in the PRD region during fall–winter, which was further confirmed by the source apportionment results that BB accounted for 42–47 % of measured WSOC. The WSOC contributions from anthropogenic SOC were estimated to be 18–25 %; while biogenic SOC had minor contributions to WSOC (4–15 %). The unexplained WSOC (18–31 %) showed a positive correlation with POC, indicating that this portion could be largely due to SOC from POA aging.

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References

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J.-H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, D14203, doi:10.1029/2003JD003697, 2004.

Chan, C. K. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42, 1–42, 2008.

Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencser, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, Atmos. Environ., 38, 4093–4098, 2004.

De Gouw, J. and Jimenez, J. L.: Organic aerosols in the earth' atmosphere, Environ. Sci. Technol., 43, 7614–7618, 2009.

Ding, X., Zheng, M., Yu, L., Zhang, X., Weber, R. J., Yan, B., Russell, A. G., Edgerton, E. S., and 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., 42, 5171–5176, 2008a.

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, 2008b.

Ding, X., Wang, X., and Zheng, M.: The influence of temperature and aerosol acidity on biogenic secondary organic aerosol tracers: observations at a rural site in the central Pearl River Delta region, South China, Atmos. Environ., 45, 1303–1311, 2011.

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

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.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinnig, M.-C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, P. Natl. Acad. Sci. USA, 109, 13503–13508, 2012.

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, doi:10.5194/acp-11-11069-2011, 2011.

Feng, J., Hu, M., Chan, C. K., Lau, P. S., Fang, M., He, L., and Tang, X.: A comparative study of the organic matter in $PM_{2.5}$ from three Chinese megacities in three different climatic zones, Atmos. Environ., 40, 3983–3994, 2006.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States, Environ. Sci. Technol., 36, 1442–1451, 2002.

Geron, C., Rasmussen, R., Arnts, R. R., and Guenther, A.: A review and synthesis of monoterpene speciation from forests in the United States, Atmos. Environ., 34, 1761–1781, 2000.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions J. Geophys. Res., 100, 8873–8892, 1995.

He, M., Zheng, J., Yin, S., and 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.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W.-M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., J. L. Collett Jr., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, Atmos. Chem. Phys., 11, 7669–7686, doi:10.5194/acp-11-7669-2011, 2011.

Ho, K. F., Lee, S. C., Cao, J. J., Li, Y. S., Chow, J. C., Watson, J. G., and Fung, K.: Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong, Atmos. Chem. Phys., 6, 4569–4576, doi:10.5194/acp-6-4569-2006, 2006.

Huang, H., Ho, K. F., Lee, S. C., Tsang, P. K., Ho, S. S. H., Zou, C. W., Zou, S. C., Cao, J. J., and Xu, H. M.: Characteristics of carbonaceous aerosol in $PM_{2.5}$: Pearl Delta River Region, China, Atmos. Res., 104, 227–236, 2012a.

Huang, X., Li, M., Li, J., and Song, Y.: A high-resolution emission inventory of crop burning in fields in China based on MODIS Thermal Anomalies/Fire products, Atmos. Environ., 50, 9–15, 2012b.

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, doi:10.5194/acp-11-7727-2011, 2011.

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., Dunlea, E. 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.

Jung, J., Kim, Y. J., Aggarwal, S. G., and Kawamura, K.: Hygroscopic property of water-soluble organic-enriched aerosols in Ulaanbaatar, Mongolia during the cold winter of 2007, Atmos. Environ., 45, 2722–2729, 2011.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.

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.

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.

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., and 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, doi:10.5194/acp-12-8711-2012, 2012.

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.

Na, K., Sawant, A. A., Song, C., and Cocker III, D. R.: Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California, Atmos. Environ., 38, 1345–1355, 2004.

NIOSH: Method 5040 Issue 3 (Interim): Elemental carbon (diesel exhaust), in: NIOSH Manual of Analytical Methods, National Institute of Occupational Safety and Health, Cincinnati, OH, 1999.

Offenberg, J. H., Lewis, C. W., Lewandowski, M., Jaoui, M., Kleindienst, T. E., and Edney, E. O.: Contributions of toluene and α-pinene to SOA formed in an irradiated toluene/α-pinene/NO_x/ air mixture: Comparison of results using ^{14}C content and SOA organic tracer methods, Environ. Sci. Technol., 41, 3972–3976, 2007.

Park, S. S. and Cho, S. Y.: Tracking sources and behaviors of water-soluble organic carbon in fine particulate matter measured at an urban site in Korea, Atmos. Environ., 45, 60–72, 2011.

Piccot, S., Watson, J., and Jones, J.: A global inventory of volatile organic compound emissions from anthropogenic sources, J. Geophys. Res., 97, 9897–9912, 1992.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, J. Geophys. Res., 112, D23S05, doi:10.1029/2006JD008114, 2007.

Qu, C., Li, B., Wu, H., and Giesy, J. P.: Controlling air pollution from straw burning in China calls for efficient recycling, Environ. Sci. Technol., 46, 7934–7936, 2012.

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.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmos. Environ., 33, 173–182, 1999.

Snyder, D. C., Rutter, A. P., Collins, R., Worley, C., and Schauer, J. J.: Insights into the origin of water soluble organic carbon in atmospheric fine particulate matter, Aerosol Sci. Technol., 43, 1099–1107, 2009.

Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., Zhang, Q., Canagaratna, M. R., Allan, J., Coe, H., McFiggans, G., Rap, A., and Forster, P.: Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, Atmos. Chem. Phys., 11, 12109–12136, doi:10.5194/acp-11-12109-2011, 2011.

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, doi:10.5194/acp-8-1249-2008, 2008.

Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS, Atmos. Environ., 29, 3527–3544, 1995.

Viana, M., Maenhaut, W., ten Brink, H. M., Chi, X., Weijers, E., Querol, X., Alastuey, A., Mikuška, P., and Večeřa, Z.: Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities, Atmos. Environ., 41, 5972–5983, 2007.

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.

Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected, Geophys. Res. Lett., 33, L17811, doi:10.1029/2006GL026899, 2006.

Wang, G., Niu, S., Liu, C., and Wang, L.: Identification of dicarboxylic acids and aldehydes of PM_{10} and $PM_{2.5}$ aerosols in Nanjing, China, Atmos. Environ., 36, 1941–1950, 2002.

Wang, G., Kawamura, K., Xie, M., Hu, S., Cao, J., An, Z., Waston, J. G., and Chow, J. C.: Organic molecular compositions and size distributions of Chinese summer and autumn aerosols from Nanjing: characteristic haze event caused by wheat straw burning, Environ. Sci. Technol., 43, 6493–6499, 2009.

Wang, X., Ding, X., Fu, X., He, Q., Wang, S., Bernard, F., Zhao, X., and 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., 24, 72–77, 2012.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J. A., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, J. Geophys. Res., 112, D13302, doi:10.1029/2007JD008408, 2007.

Weitkamp, E. A., Sage, A. M., Pierce, J. R., Donahue, N. M., and Robinson, A. L.: Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber, Environ. Sci. Technol., 41, 6969–6975, 2007.

Yi, Z., Wang, X., Sheng, G., Zhang, D., Zhou, G., and Fu, J.: Soil uptake of carbonyl sulfide in subtropical forests with different successional stages in south China, J. Geophys. Res., 112, D08302, doi:10.1029/2006JD008048, 2007.

Zeng, T. and Wang, Y.: Nationwide summer peaks of OC/EC ratios in the contiguous United States, Atmos. Environ., 45, 578–586, 2011.

Zhang, X., Lin, Y.-H., Surratt, J. D., Zotter, P., Prévôt, A. S. H., and Weber, R. J.: Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: a contrast in secondary organic aerosol, Geophys. Res. Lett., 38, L21810, doi:10.1029/2011GL049385, 2011.

Zhang, Y.-X., Shao, M., Zhang, Y.-H., Zeng, L.-M., He, L.-Y., Zhu, B., Wei, Y.-J., and Zhu, X.-L.: Source profiles of particulate organic matters emitted from cereal straw burnings, J. Environ. Sci., 19, 167–175, 2007.

Zhang, Y., Wang, X., Blake, D. R., Li, L., Zhang, Z., Wang, S., Guo, H., Lee, F. S. C., Gao, B., Chan, L., Wu, D., and Rowland, F. S.: Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China, J. Geophys. Res., 117, D15306, doi:10.1029/2011JD017356, 2012.

Zheng, J., Zheng, Z., Yu, Y., and Zhong, L.: Temporal, spatial characteristics and uncertainty of biogenic VOC emissions in the Pearl River Delta region, China, Atmos. Environ., 44, 1960–1969, 2010.

Table 1. Organic tracers over the PRD region and the conversion factors for $WSOC_{BB}$ and SOC estimate.

	Organic tracers	Tracer concentrations ($ng\,m^{-3}$)			$(f_{tracer/WSOC})_{BB}$ or $f_{tracer/SOC}$ ($\mu g\,\mu g\,C^{-1}$)	Reference
		WQS	DHS	GIG		
$WSOC_{BB}$	Levoglucosan	310 (80.5–1156)	305 (25.8–777)	447 (105–792)	straw burning 0.0806 forest fire 0.0994 0.0900	Viana et al. (2008) Ding et al. (2008a) 1 : 1 Combination
Isoprene SOC	2-Methylglyceric acid	4.75 (1.40–16.7)	3.74 (0.42–12.5)	4.55 (1.11–8.17)	0.155	Kleindienst et al. (2007)
	2-Methyltetrols	16.0 (2.34–58.3)	13.4 (0.98–72.7)	11.8 (3.92–26.5)		
Monoterpene SOC	cis-Pinonic acid	6.73 (0.64–39.3)	35.1 (1.78–101)	6.32 (0.93–17.7)	0.059	Offenberg et al. (2007)
	Pinic acid	0.99 (0.24–2.52)	2.93 (nd-6.44)	0.87 (0.10–2.81)		
	3-Methyl-1,2,3-butanetricarboxylic acid	3.56 (0.07–13.9)	9.47 (0.53–21.9)	1.13 (0.09–4.99)		
	3-Hydroxyglutaric acid	3.57 (0.38–14.7)	3.77 (0.22–8.64)	2.80 (0.68–5.43)		
	3-Hydroxy-4,4-dimethylglutaric acid	1.59 (nd-7.15)	2.42 (0.05–6.10)	0.94 (nd-3.78)		
β-Caryophyllene SOC	β-Caryophyllenic acid	3.25 (0.53–13.4)	3.55 (0.11–6.33)	3.56 (1.04–11.63)	0.023	Kleindienst et al. (2007)
Aromatics SOC	2,3-Dihydroxy-4-oxopentanoic acid	13.1 (1.70–48.9)	11.0 (0.94–22.7)	11.1 (3.15–31.2)	0.00797	Kleindienst et al. (2007)
2-Ring PAHs SOC	Phthalic acid	24.4 (9.58–38.8)	25.6 (8.74–57.7)	28.0 (13.1–51.2)	0.0388	Kleindienst et al. (2012)

Table 2. Carbonaceous species at different sites during fall–winter over the PRD (µgC m^{-3}).

	WQS (Rural) (10 Nov ~ 9 Dec)					DHS (Rural) (19 Nov ~ 25 Dec)					GIG (Sub-urban) (10 Dec ~ 25 Dec)				
	Average	Median	Min	Max	SD	Average	Median	Min	Max	SD	Average	Median	Min	Max	SD
OC	22.5	22.6	10.1	43.7	8.00	13.4	13.3	6.83	21.3	3.86	28.4	26.7	13.0	44.9	9.14
EC	4.29	4.23	2.47	7.05	1.16	1.92	2.01	0.77	3.03	0.53	7.31	6.54	3.14	21.4	4.38
OC/EC	5.29	5.03	3.74	9.57	1.41	7.08	6.97	5.17	10.5	1.28	4.42	4.22	2.04	7.83	1.56
WSOC	8.62	7.83	3.69	21.6	3.99	7.63	7.38	3.40	13.1	2.37	11.5	10.9	6.38	20.5	4.29
WIOC	13.9	13.5	2.45	27.5	5.39	5.74	5.46	0.54	10.5	2.56	16.9	13.7	6.59	31.1	7.96
WSOC/OC (%)	38.8	34.5	20.4	75.7	11.6	57.9	55.6	37.7	92.	13.5	42.2	44.4	18.8	62.6	13.1
WIOC/EC	3.24	3.18	0.99	6.34	1.03	2.97	3.12	0.71	5.47	1.12	2.59	2.29	1.09	4.35	1.13
$\mathrm{SOC_I}$	0.13	0.11	0.02	0.47	0.10	0.11	0.08	0.01	0.51	0.11	0.11	0.10	0.04	0.23	0.05
$\mathrm{SOC_M}$	0.28	0.23	0.08	0.72	0.18	0.91	0.82	0.12	2.34	0.44	0.20	0.17	0.08	0.49	0.12
$\mathrm{SOC_C}$	0.14	0.12	0.02	0.58	0.12	0.15	0.15	0.00	.28	0.07	0.15	0.12	0.05	0.51	0.12
$\mathrm{SOC_A}$	1.65	1.21	0.22	6.19	1.43	1.39	1.31	0.12	2.87	0.77	1.40	1.23	0.40	3.95	0.97
$\mathrm{SOC_P}$	0.63	0.63	0.25	1.00	0.20	0.66	0.66	0.23	1.49	0.25	0.72	0.74	0.34	1.32	0.23
$\mathrm{SOC_{Precursor}}$	2.83	2.44	0.80	8.90	1.88	3.22	3.23	0.75	5.67	1.17	2.59	2.26	1.16	6.17	1.36
$\mathrm{SOC_{total}}$	4.78	4.69	0.62	10.6	2.34	4.18	4.40	0.00	9.35	2.35	5.97	5.87	1.08	14.0	3.41
POC	17.8	16.9	4.60	36.5	7.18	9.13	9.12	2.82	14.9	3.08	22.5	22.6	9.69	35.5	7.73
$\mathrm{WSOC_{BB}}$	3.85	3.34	1.00	14.3	2.62	3.39	3.06	0.29	8.63	1.67	5.55	4.63	1.30	9.83	2.62
Other	2.39	2.36	0.00	6.73	2.07	1.39	0.73	0.00	6.06	1.63	3.72	3.10	0.00	12.4	3.30

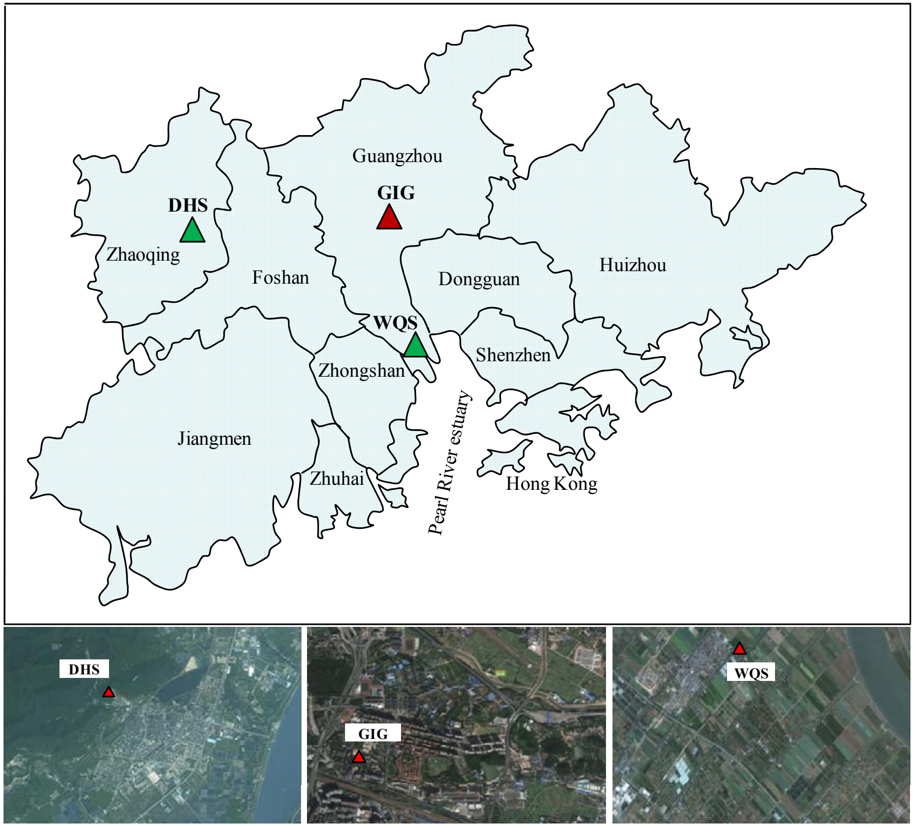

Fig. 1. Sampling sites in the PRD.

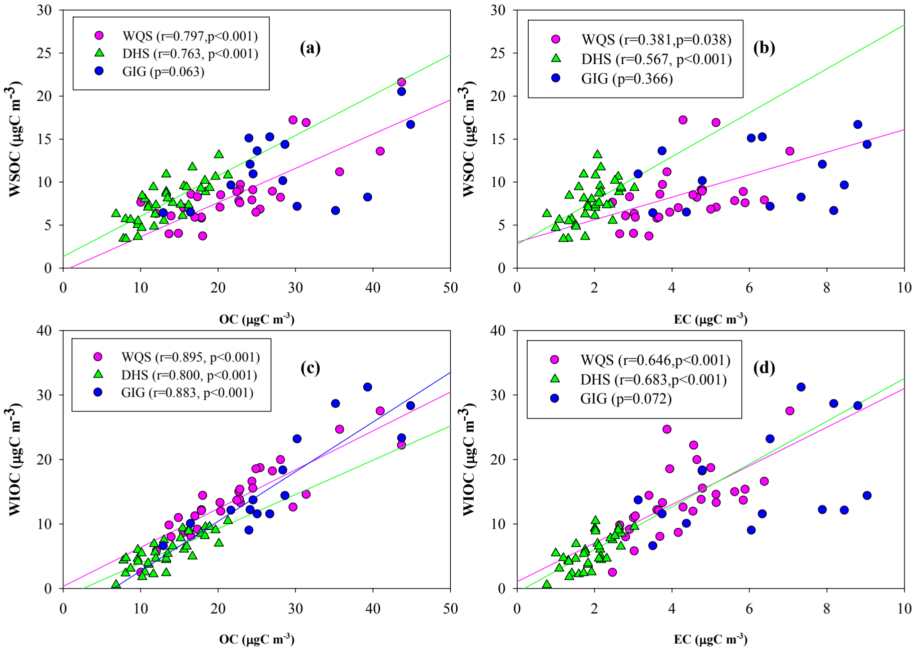

Fig. 2. Correlation analyses among carbonaceous species. **(a)** WSOC vs. OC, **(b)** WSOC vs. EC, **(c)** WIOC vs. OC, **(d)** WIOC vs. EC.

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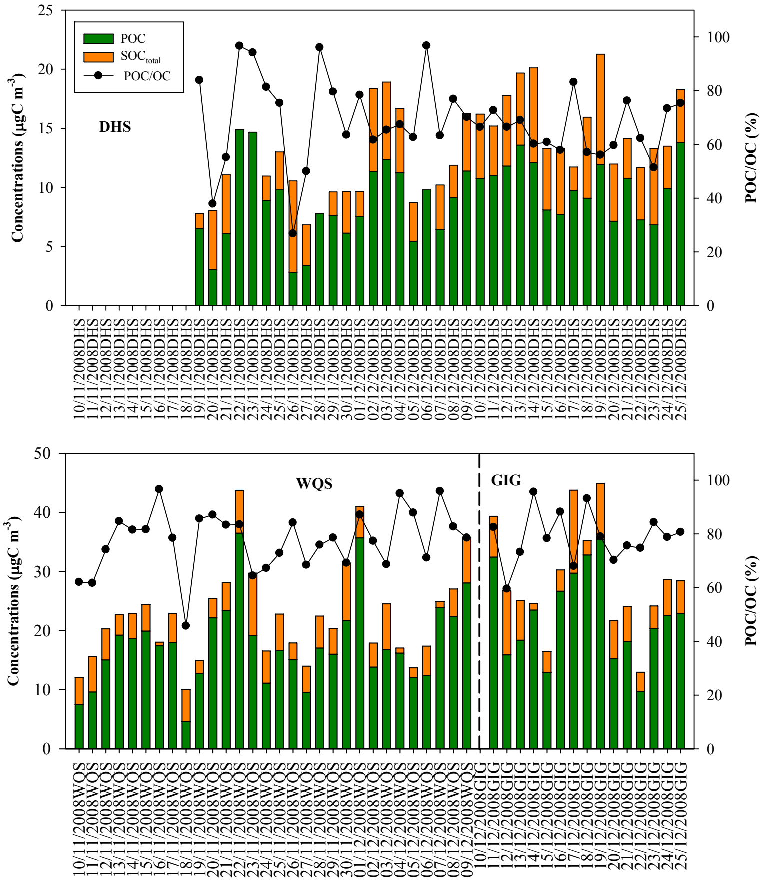

Fig. 3. Day-to-day variations of estimated SOC and POC at three sites.

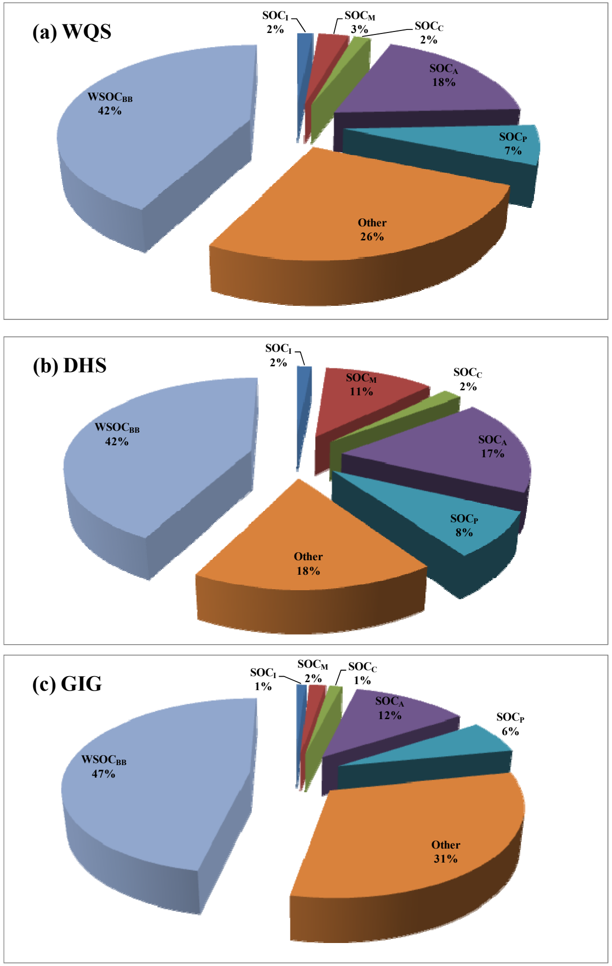

Fig. 4. Source apportionment of WSOC at three sites.

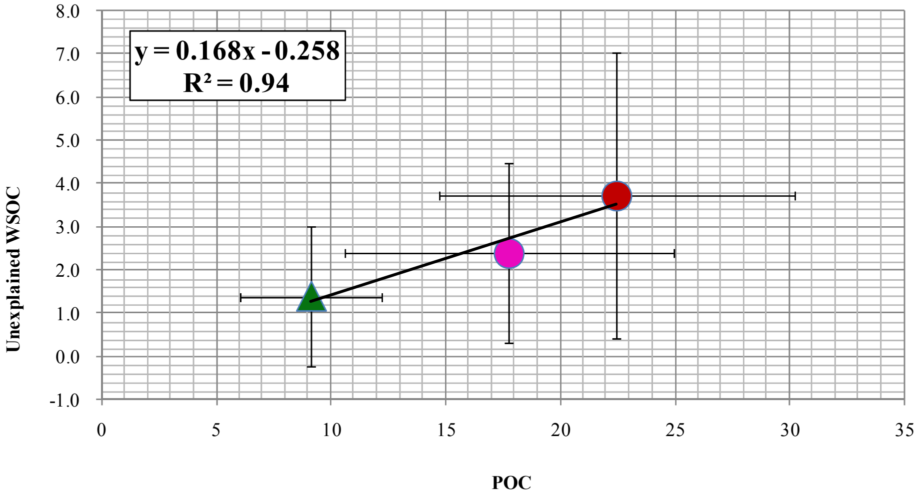

Fig. 5. Correlation between unexplained WSOC and POC. Green triangle, pink circle and red circle represent DHS, WQS and GIG, respectively.