Carbonaceous aerosols in megacity Xi'an, China: Implications of thermal/optical protocols comparison

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HIGHLIGHTS
- OC/EC split ratio is a key to evaluate the cooling versus warming effects of aerosols.
- Over twofold difference in EC concentrations and OC/EC ratios by different protocols.
- Good correlations between char and HULIS-C suggest common sources, likely the widespread biomass burning in the region.
- Char/soot ratios contrast OC/EC ratios in seasonal variation.
- Char and soot should be considered in chemical transport and climate models.

ABSTRACT
Carbonaceous aerosol is an important component that influences the environment, climate, and human health. Organic and elemental carbon (OC and EC) are the two main constituents of carbonaceous aerosols that have opposite, i.e., cooling versus warming, effects on the Earth’s radiation balance. Knowledge on the variability of OC/EC splits measured by different thermal/optical protocols is useful for understanding the uncertainty in the climate models. This study shows good correlations within OC or EC (r² > 0.83, P < 0.001) across the IMPROVE, IMPROVE_A, and EUSAAR_2 protocols for both ambient aerosol samples and biomass burning samples. However, EC concentrations differ by more than two folds, and OC/EC ratios differ up to a factor of 2.7. The discrepancies were attributed to the selection between the reflectance and transmittance corrections and the different peak inert-atmosphere temperature. The IMPROVE and IMPROVE_A protocols also quantified different char and soot concentrations, two subtypes of EC with distinct chemical and optical properties. Char, but not soot, was found to correlate with the humic-like substances (HULIS) content in the samples, suggesting that both char and...
1. Introduction

Carbonaceous aerosol constitutes 20–50% of PM2.5 mass (particulate matter with an aerodynamic diameter <2.5 μm) in most urban areas (Cao et al., 2007; Huang et al., 2014) and is influencing Earth’s climate directly by absorbing and scattering radiation and indirectly by acting as cloud condensation and ice nuclei for cloud and precipitation formation (Jacobson, 2001; Ramanathan and Carmichael, 2008). Carbonaceous aerosol also adversely affects visibility (Watson, 2002) and human health (Janssen et al., 2012; Mauderly and Chow, 2008). However, uncertainties exist due to the complexity of carbonaceous aerosol. Atmospheric carbonaceous aerosol is commonly classified into organic carbon (OC) and elemental carbon (EC). EC, also known as black carbon (BC), is the most important light-absorbing aerosol component in the atmosphere, with an estimated climate forcing of +0.88 (range +0.17 to +1.48) W m−2 (Bond et al., 2013), ranked as the second largest contributor to anthropogenic radiative forcing after carbon dioxide (CO2). On the contrary, OC can cool the atmosphere by increasing Earth’s reflectivity (Chameides and Bergin, 2002). OC and inorganic composition of aerosol can also influence the absorption of EC through lensing effect (Wang et al., 2014). The net climate forcing of carbonaceous aerosol is strongly determined by the OC/EC ratio (Novakov et al., 2005; Saleh et al., 2014; Sato et al., 2010; Chow et al., 2005). However, uncertainties exist due to the complexity of carbonaceous aerosol. Atmospheric carbonaceous aerosol is commonly classified into organic carbon (OC) and elemental carbon (EC). EC, also known as black carbon (BC), is the most important light-absorbing aerosol component in the atmosphere, with an estimated climate forcing of +0.88 (range +0.17 to +1.48) W m−2 (Bond et al., 2013), ranked as the second largest contributor to anthropogenic radiative forcing after carbon dioxide (CO2). On the contrary, OC can cool the atmosphere by increasing Earth’s reflectivity (Chameides and Bergin, 2002).

OC and EC are operationally defined and there is no universally accepted standard method for quantification. The most widely used is the thermal/optical (TO) method (Watson et al., 2005), which has been practiced for over three decades (Gray et al., 1984). Different protocols have been applied (Birch and Cary, 1996; Cavalli et al., 2010; Chow et al., 1993), and comparisons between the different protocols have been made (Chow et al., 2001; Hitzenberger et al., 2006; Hitzenberger and Tohno, 2001; Reisinger et al., 2008). Watson et al. (2005) summarized that while being able to measure total carbon (TC), sum of OC and EC, consistently in aerosol samples, different TO protocols reported large discrepancy (up to a factor of 7) in EC concentrations.

The IMPROVE (Interagency Monitoring of Protected Visual Environments) and IMPROVE_A protocols (Chow et al., 2007) have been implemented in the U.S. Environmental Protection Agency (EPA) non-urban IMPROVE Network and urban Chemical Speciation Network (CSN) since 1987/88 and 2006/07 respectively. Over 200,000 p.m. samples worldwide have been analyzed. The transition of IMPROVE protocol by DRI/OGC analyzer to IMPROVE_A protocol by DRI model 2001 analyzer (Atmoslyt Inc, Calabasas, CA, USA) occurred around 2005. The two protocols differ in temperature by 20–40 °C at each temperature plateau (Table 1) due to the difference between filter and thermocouple temperatures in DRI/OGC analyzer (Chow et al., 2005).

Over the past decade both IMPROVE and IMPROVE_A protocols have been implemented in China using the DRI Model 2001 analyzer e.g. (Cao et al., 2003, 2013; Han et al., 2010), but without distinguishing the difference of the two protocols. Chow et al. (2004) show that IMPROVE reflectance pyrolysis adjustment (i.e., thermal/optical reflectance [TOR]) yielded similar EC results regardless of the temperature protocol used for samples in the U.S. A. However, quantitative comparisons between the two protocols have not been examined in China, especially in urban areas with abundant biomass burning contributions (Huang et al., 2014; Zhang et al., 2014).

The EUSAAR_2 (European Supersites for Atmospheric Aerosol Research) protocol (Cavalli et al., 2010) has been widely used in Europe. This protocol is a modification of the National Institute of Occupational Safety and Health (NIOSH)-like thermal/optical transmission (TOT) protocol with fixed heating duration (Table 1). How it performs for Chinese aerosol samples, with their concentrations being often one order magnitude higher than European samples, needs a further investigation and comparison with IMPROVE and IMPROVE_A protocols.

Han et al. (2007) divided EC into two subtypes: char and soot, corresponding to EC evolved at low temperatures (i.e., 550 or 580 °C in oxidizing atmosphere) representing combustion residues by pyrolysis in smoldering fires, and EC evolved in high temperatures (i.e., >700 or 740 °C in oxidizing atmosphere) representing refractory condensation formed from volatiles in high-temperature flaming fires, respectively (Han et al., 2010; Janssen et al., 2012). Char and soot have different physico-chemical characteristics (Goldberg, 1985; Hammes et al., 2007; Han et al., 2010; Masiello, 2004), with soot being more light absorbing than char (Han et al., 2010). Another light-absorbing component is brown carbon (BrC), an OC component that could originate from smoldering biomass burning or secondary organic aerosol (Andreae and Gelencser, 2006). The chemical nature of BrC is not well elucidated, and it is believed to contain polycyclic aromatic hydrocarbons (PAHs), branched, oxygenated, and/or nitro-PAHs, as well as polycarboxylic acid or humic-like substances (HULIS) (Graber and Rudich, 2006; Duan et al., 2013; Yu et al., 2016).
Hoffer et al. 2006). Several studies have reported substantial HULIS production from biomass burning, particularly the smoldering phase (Asa-Awuku et al., 2008; Hoffer et al., 2006; Lin et al., 2010a; Mayol-Bracero et al., 2002).

As part of an effort to reconcile measurements made by different carbon analyzing protocols in China, this study aimed to evaluate OC and EC measurements as well as char/soot separation in Chinese urban aerosol samples by IMPROVE, IMPROVE_A and EUSAAR_2 protocols using the DRI Model 2001 analyzer. Ambient PM$_{2.5}$ samples from Xi’an, China and source samples from biomass burning were studied. Seasonal variations in TC, OC, EC, char, and soot are discussed in light of potential PM$_{2.5}$ sources and climatic impacts. In addition, the correlations of HULIS with char and soot measured by IMPROVE and IMPROVE_A were investigated to better understand the source of HULIS.

2. Experimental

2.1. Ambient samples

Xi’an city (33°29′–34 44′ N, 107°40′–109 49′ E) located in the Guanzhong Basin is one of the largest tourist cities and on the list of the ten most polluted cities in China (CNEMC, 2013). Biomass burning during winter contributes to >50% of the TC (Zhang et al., 2014). PM$_{2.5}$ samples were collected from the rooftop of a building ~20 m above ground in the campus of Xi’an Jiaotong University using a mini-volume sampler (Airmetrics, Springfield, OR, USA) operating at a flow rate of 5 L min$^{-1}$. Sampling was conducted over a 24-h period (10:00 a.m. to 10:00 a.m. the next day) every 6 days from March 10, 2012 to March 11, 2013. All samples were collected on pre-fired (850 °C for 3 h) and pre-weighed 47 mm Whatman quartz-fiber filters and then stored in a freezer (~20 °C) until analysis.

2.2. Biomass combustion samples

Agricultural waste including wheat straw, rice straw, and corn stalk were collected from the main producing areas in China. Combustion experiments were conducted in a combustion chamber at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS). The combustion chamber (Tian et al., 2015) has a combustion chamber (Tian et al., 2015) with no further calculations.

2.3. Carbon analysis

Mass concentrations were gravimetrically measured using an electronic microbalance with ±1 µg sensitivity (Sartorius, Gottingen, Germany), after which a 0.526 cm$^2$ punch of the filter was taken for carbon analyses. Each of these TO protocols contains two stages: the first is in an inert atmosphere where OC fractions (i.e., OC1-4, see Table 1) are evolved, with the assumption that low-volatility EC fractions are not liberated in an inert helium (He) atmosphere; and the second is in an oxidation atmosphere (98%He/2%O$_2$) that evolves the EC fractions (i.e., EC1-4, see Table 1). An oxidizer (manganese dioxide [MnO$_2$] at 800–900 °C) converts the liberated carbon compounds to CO$_2$, which is then reduced to methane (CH$_4$) by a methanizer and quantified by a flame ionization detector (FID). Heating in an inert environment can generate some pyrolyzed organic carbon (POC), and a laser (633 nm) is used to monitor the reflectance and transmittance of a filter during thermal analysis. POC is defined as the carbon measured after the introduction of a He/O$_2$ atmosphere, but before a split point where reflectance (POC$_R$) or transmittance (POC$_T$) returned to its initial value, while OC and EC are defined as carbon measured before and after the optical split point, respectively. This adjustment assumes that POC attenuates the laser in a similar way as the native EC, although this may not always be true (Chen et al., 2004). TOR and TOT are referred to the reflectance and transmittance pyrolysis adjustment, respectively.

Alternatively, POC may be estimated from the incremental light attenuation throughout the inert heating stage ($\tau_{\text{ATN},\text{POC}}$), thus

$$\tau_{\text{ATN},\text{POC}} = -\ln(\frac{T_{\text{min}}}{T_0})$$

where $T_0$ and $T_{\text{min}}$ are initial and minimum transmittance, measured at the beginning and end of the inert heating stage, respectively (Chow et al., 2004). Most of $\tau_{\text{ATN},\text{POC}}$ should be attributed to the formation of POC, though the uncertainty in POC measurement by TOR or TOT and the variable mass absorption efficiency of POC prevents a strong correlation between $\tau_{\text{ATN},\text{POC}}$ and POC (Chow et al., 2004).

Char was first quantified using the IMPROVE protocol as the low-temperature EC (EC1) minus POC, while the remaining high-temperature EC (EC2 + EC3) was attributed to soot (Han et al., 2007). The differentiation between char and soot has been applied to aerosol, dust, soil, and sediment samples (Han et al., 2009a; Jeong et al., 2013; Kim et al., 2011; Lim et al., 2012; Minoura et al., 2012) and validated with standard reference materials (SRMs) (Zhan et al., 2013).

The carbon concentrations of ambient PM$_{2.5}$ samples were reported in µg m$^{-2}$, while for the vegetation combustion samples the carbon concentrations were directly reported in µg cm$^{-2}$ (of the filter), with no further calculations.

2.4. HULIS-C measurement

HULIS-C extraction follows Lin et al. (2010b) for both the ambient and source samples. A aliquot of filter (1.5–3 cm$^2$) was extracted with ultrapure water in an ultrasonic bath for 40 min and then filtered with a 0.45 µm Teflon syringe filter (Millipore, Billerica, MA) to remove the filter debris and suspended insoluble particles. The hydrochloric acid (HCl, 37%) was added to the extracts to reach pH = 2, then the acidified extracts were loaded on solid phase extraction (SPE) cartridges (Oasis HLB, 30 µm, 60 mg/cartridge, Waters, USA). HULIS, which are expected to be retained by the column, were eluted by 1.5 mL of methanol containing 2% aqueous ammonia (w/w). The resulting eluate was immediately evaporated to dryness under a gentle nitrogen (N$_2$) stream and redissolved in a known amount of ultrapure water. An aliquot of 5 µL extract was then spiked onto a pre-fired (850 °C for 3 h) quartz-fiber filter for quantification of HULIS-C by the DRI Model 2001 Carbon Analyzer. The HULIS-C concentrations reported here were corrected for method blank (~0.01 µg C µL$^{-1}$).

3. Comparison among IMPROVE, IMPROVE_A, and EUSAAR_2 analyses of ambient samples

As shown in Fig. S1, TC measurements were similar among the three protocols with correlation coefficients ($r^2$) >0.99 and near-unity slopes (0.97–1.03) for the 63 samples. This confirms homogeneous sample deposits and complete combustion, as observed in previous studies (Chow et al., 2001; Han et al., 2013).
3.1. Temperature effects on the OC/EC split

Table 2 shows good correlations of OC ($r^2 = 0.95–0.99$) and EC ($r^2 = 0.81–0.96$) among the three protocols, suggesting that regression coefficients may be used to estimate OC and EC from one to another protocol. However, EC concentrations varied by over two folds, whereas differences among the three protocols were smaller for OC (<33%) due to the relatively large fraction of OC in TC (see Table 2).

3.2. Influence of reflectance and transmittance adjustment on OC and EC determination

TOT EC was lower than TOR EC for each respective protocol, which could be attributed to the within-filter POC delaying the OC/EC split by transmittance much more than that by reflectance (Chow et al., 2004; 2001; Han et al., 2013). Ratios of EUSAAR_2 TOT to IMPROVE_A TOT were 1.14 for OC and 0.53 for EC (Table 2). As the within-filter POC increases with PIAT, TOT EC is expected to increase with increasing PIAT (Subramanian et al., 2006). This study found the highest TOT EC (5.6 ± 3.3 μg m$^{-3}$) by IMPROVE and the lowest TOT EC (4.3 ± 2.6 μg m$^{-3}$) by EUSAAR_2, consistent with observation by Chow et al. (2001). However, for geological samples pretreated with acids to remove minerals and carbonate carbon, an
opposite trend was reported (Han et al., 2013), which may be associated with two competing effects caused by an increase in PIAT – one tends to increase the amount of POC, while the other causes more POE to evolve before EC (Cheng et al., 2012). The differences in TOT EC reached 25% among the three protocols.

Table 2 shows that EUSAAR_2 TOT EC is on average ~44% of its TOR EC. Discrepancies between TOR and TOT EC are smaller when measured by the IMPROVE and IMPROVE_A protocols (60% and 58%, respectively), with lower PIATs and an event driven heating duration (the temperature will not advance to next thermal fraction until the FID signal reaches baseline). On average, OC/EC ratios by TOT are 2.04 and 5.75 times the ratios by TOR for IMPROVE and EUSAAR_2, respectively. With the same reflectance or transmittance correction, the variation of PIAT produce different EC concentrations by 1–25%, while the alternation between reflectance and transmittance corrections with the same protocol can produce differences in EC concentrations of 40–56% (Table 1). The use of TOR or TOT adjustment appears to be the dominant factor influencing OC/EC split between the different protocols (e.g., IMPROVE/IMPROVE_A uses TOR and EUSAAR_2 uses TOT by default).

From the thermal analysis, good correlations ($r^2 = 0.60–0.96$) between TC and POER or POEC from the three tested protocols (Fig. S4) suggest that pyrolyzable organic compounds account for a certain fraction of carbonaceous aerosol in Xi’an. Large TC intercepts (~2.9–17 µg m$^{-3}$) in the POC-TC regressions (Fig. S4), i.e., higher than the corresponding sum of average OC1 and OC2, suggest that little POE is associated with OC1 and OC2 (i.e., <300 °C in the inert atmosphere). This is supported by the smallest changes in reflectance and transmittance during the OC1-2 steps.

4. Char and soot measured by different IMPROVE protocols

4.1. Protocol dependence of char and soot quantifications

Table 3 shows that IMPROVE and IMPROVE_A yield different char and soot concentrations. On average, char by IMPROVE_A TOR is ~87% of that by IMPROVE TOR, while soot by IMPROVE_A is only 60% of that by IMPROVE. As soot is the sum of EC2 and EC3, less soot would certainly be measured by IMPROVE_A with higher EC1 temperature and thus less carbon left.

There are strong correlations ($r^2 = 0.93–0.96$) between the char concentrations measured by the two protocols, though the correlation between soot concentrations was weak ($r^2 = 0.28$). The separation of char and soot is complicated for aerosol samples because the existence of oxidants and ions such as Fe$_3$O$_4$, MnO$_2$, and chloride ion could catalyze and accelerate the oxidation of carbon fractions. Soot oxidation is known to be promoted at low temperatures (i.e., <700 °C, the IMPROVE EC2 temperature) with such catalysts (Han et al., 2009b; Novakov and Corrigan, 1995). This partly explains a poor correlation between the soot measurements by IMPROVE and IMPROVE_A. The correlations between soot and other carbon fractions (i.e., TC, OC, EC, and char) were also low. This is also consistent with the different sources of soot (i.e., from flaming fires via gas–to-particle conversion) from other fractions. Like EC, the IMPROVE char concentrations could be inflated by the uncertainties in OC/EC split. The IMPROVE TOR char are therefore higher than their corresponding IMPROVE_A TOR char.

4.2. Comparison of char and soot with HULIS-C

Fig. 1 shows moderate correlations of HULIS carbon with char and EC. With respect to the strength of correlation with HULIS, the order of TOR char > EC > TOT char > TOT EC is found regardless of whether the IMPROVE or IMPROVE_A protocol is used. Char originates mainly from smoldering phases of biomass burning (Han et al., 2010), which is similar to those of HULIS (Graber and Rudich, 2006; Salma et al., 2010). Our finding is consistent with previous studies, which also showed good correlations of char with biomass burning markers such as potassium and levoglucosan (Lim et al., 2012; Minoura et al., 2012). Soot concentrations show no relationships with HULIS-C for both protocols ($r^2 = 0.03$, see Fig. 1 A3 and B3). This supports the differences in sources and formation pathways between HULIS and soot. Soot comes mainly from fossil fuel combustion, especially motor vehicle emissions in urban areas despite that flaming fire of biomass burning also contribute, while HULIS come mainly from smoldering fires as well as secondary organic aerosol formation. The poor correlations between soot and HULIS_C weaken the relations between EC and HULIS-C (Fig. 1).

5. Inter-protocol comparison of biomass combustion samples

OC dominated in TC (83–93%), see Table 4) from biomass combustion emissions, and strong correlations ($r^2 > 0.98$) of OC and TC concentrations were observed among the three different protocols. However, the EC relationships were weaker and variable, with correlation coefficients $r^2 = 0.56–0.84$ (Fig. 2A and B). Biomass combustion samples produced a relatively high proportion of volatile organics, chloride and potassium ions, and mineral dusts (Yokelson et al., 1997), which would catalyze the oxidation of EC on the filter (Han et al., 2009b; Novakov and Corrigan, 1995), leading to the premature evolution of EC. The relatively lower slopes of IMPROVE_A and EUSAAR_2 to IMPROVE EC (Fig. 2A and B) than those for ambient PM$_{2.5}$ samples (Table 2) may be associated with the faster oxidation of EC under higher temperatures with the presence of more oxidants. Ratios of IMPROVE TOR EC to EUSAAR_2 TOT EC produce a slope of 0.88 (Fig. 2A), which is slightly lower than that of the ambient samples (1.01 in Table 2).

Table 3

| Protocols | Orthogonal fit $y$ | Ordinary fit through zero $y$ | $t$-test
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<tbody>
<tr>
<td>x</td>
<td>Equation</td>
<td>$r^2$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>Char</td>
<td>IMPROVE TOR</td>
<td>IMPROVE A TOR</td>
<td>$y = 0.82x + 0.76$</td>
</tr>
<tr>
<td>IMPROVE TOR</td>
<td>IMPROVE A TOT</td>
<td>$y = 0.57x + 0.42$</td>
<td>0.96</td>
</tr>
<tr>
<td>IMPROVE TOR</td>
<td>IMPROVE A TOT</td>
<td>$y = 0.44x + 0.29$</td>
<td>0.93</td>
</tr>
<tr>
<td>IMPROVE TOT</td>
<td>IMPROVE A TOT</td>
<td>$y = 0.79x + 0.59$</td>
<td>0.96</td>
</tr>
<tr>
<td>Soot$^b$</td>
<td>IMPROVE A</td>
<td>$y = 0.68x + 0.10$</td>
<td>0.28</td>
</tr>
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</table>

* $p$ values of $t$-test for the ordinary fit with intercept through zero.

$^b$ Soot is the sum of EC2 and EC3 with no reflectance or transmittance correction.
Average char/soot ratios ranged from 1.4 to 17.3 (average = 5.8) using the IMPROVE TOR protocol, which is within the range of the
reported char/soot ratios for biomass burning samples (Han et al., 2010). However, because the samples used in this study were collected from laboratory-based flaming combustion with high modified combustion efficiencies (MCE > 92%, measured during the sample collection period using real-time CO and CO₂ detectors (Tian et al., 2015)), they were likely to differ from emissions from

![Fig. 2](image-url) Comparison of different carbon fractions measured using the three protocols (IMPROVE, IMPROVE_A, and EUSAAR_2) with the TOR and TOT corrections for 20 biomass combustion samples. (A) IMPROVE TOR EC vs IMPROVE_A and EUSAAR_2 TOR EC, (B) IMPROVE TOT EC vs IMPROVE_A and EUSAAR_2 TOT EC, (C) IMPROVE TOR char vs IMPROVE_A TOR char, (D) IMPROVE TOT char vs IMPROVE_A TOT char, and (E) IMPROVE soot vs IMPROVE_A soot.

<table>
<thead>
<tr>
<th></th>
<th>IMPROVE</th>
<th>IMPROVE_A</th>
<th>EUSAAR_2</th>
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<tbody>
<tr>
<td>TN µg m⁻³</td>
<td>10.04</td>
<td>10.22</td>
<td>9.73</td>
</tr>
<tr>
<td>TOR OC µg m⁻³</td>
<td>7.11</td>
<td>7.26</td>
<td>7.32</td>
</tr>
<tr>
<td>TOR POC µg/m³</td>
<td>1.13</td>
<td>0.95</td>
<td>0.00</td>
</tr>
<tr>
<td>TOR EC µg m⁻³</td>
<td>2.93</td>
<td>2.28</td>
<td>2.41</td>
</tr>
<tr>
<td>TOR OC/EC</td>
<td>1.36</td>
<td>1.67</td>
<td>1.18</td>
</tr>
<tr>
<td>TOT POC µg/m³</td>
<td>2.36</td>
<td>2.11</td>
<td>1.29</td>
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<tr>
<td>TOT OC µg m⁻³</td>
<td>8.58</td>
<td>8.53</td>
<td>8.52</td>
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<tr>
<td>TOT EC µg m⁻³</td>
<td>1.45</td>
<td>1.23</td>
<td>1.21</td>
</tr>
<tr>
<td>TOT OC/EC</td>
<td>2.28</td>
<td>3.07</td>
<td>1.63</td>
</tr>
<tr>
<td>TOR Char µg m⁻³</td>
<td>1.41</td>
<td>1.69</td>
<td>1.63</td>
</tr>
<tr>
<td>TOT Char µg m⁻³</td>
<td>−0.07</td>
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<td>0.47</td>
</tr>
<tr>
<td>Soot µg m⁻³</td>
<td>0.62</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>TOR Char/soot</td>
<td>0.92</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>TOT Char/soot</td>
<td>−0.05</td>
<td>0.38</td>
<td>0.38</td>
</tr>
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Table 5 Summary of the concentrations of the carbon fractions (µg m⁻³) in PM₂.₅ (N = 63) in Xi’an, China, measured using the three different protocols.

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suppressed burning, domestic heating, and cooking, which may have relatively higher char/soot ratios due to their lower MCE.

As the PIAT increases from IMPROVE to IMPROVE_A, it lowers the char and soot concentrations and increases char/soot ratios (Tables 4 and 5). Lower soot concentrations can be attributed to two reasons: (1) the higher EC1 temperature leading to more carbon evolved in OC and EC steps and thus resulting in lower soot yields, and (2) a catalytic effect of soot (Ishiguro et al., 1997) due to the higher temperature in IMPROVE_A EC step that would misclassify soot as POC or char. The IMPROVE and IMPROVE_A soot concentrations are poorly correlated ($r^2 = 0.11$; see Fig. 2). This raises concerns over the char and soot differentiation by different protocols.

### 6. Variations of ambient PM$_{2.5}$ carbon fractions in Xi’an over one year

Table 5 presents the summarized statistics for the carbon fractions of PM$_{2.5}$ in Xi’an measured with the three protocols. The annual average PM$_{2.5}$ mass concentration was 134 ± 80 μg m$^{-3}$ (average ± standard deviation), which is much higher than the Chinese air pollution standard of 35 μg m$^{-3}$, the National Ambient Air Quality Guideline of the European Union (25 μg m$^{-3}$), and the World Health Organization (WHO) Air Quality Guidelines of 10 μg m$^{-3}$. Annual average TC concentration (26.8–277 μg m$^{-3}$) measured by different protocols. Table 5) alone would be close to the Chinese PM$_{2.5}$ standard and exceeds the US EPA PM$_{2.5}$ standard of 12 μg m$^{-3}$. Compared with the 2004 data (Han et al., 2010), however, PM$_{2.5}$ mass and TC concentrations have decreased by ~25% and ~40%, respectively. This is likely, in addition to the meteorological variability, a consequence of pollution control measures made by the local government (Table S1). With the implementation of the new Prevention and Control of Atmospheric Pollution Act of China in 2000 (Cao, 2014), most of chemical factories, coal-fired power plants, and heavy industrials have gradually been moved out from Xi’an. Moreover, with the establishment of the Chinese PM$_{2.5}$ pollution standard in 2011, more strong pollution control measures have been enforced by local governments. It was demonstrated that both a stagnant weather condition and the prevailing East Asian Monsoon (EAM) could impact air quality in the region, although the EAM pattern has not varied much between 2004 and 2013 in northern China (Zhang et al., 2016).

Temporal variations in TC, OC, EC, char and soot concentrations as well as their ratios are shown in Fig. 3. Similar to mass variations, TC, OC, EC, and char all displayed higher winter and lower summer concentrations. This pattern is common in north China (Cao, 2014; Huang et al., 2014) due to the heating season in winter, along with the decrease of boundary layer depth as the temperature cools down. Soot concentrations did not display a clear seasonal variation, with the decrease of boundary layer depth as the temperature cools down. Soot concentrations did not display a clear seasonal variation from biomass burning. Zhang et al. (2014) showed that the concentrations of levoglucosan, a tracer of biomass burning emissions, in Xi’an during winter and fall can be 1-2 orders of magnitude higher than those in summer. The major contribution comes from biomass burning emissions. The vehicular emissions would dominate EC in summer, which is confirmed by the low char/soot ratios (Fig. 3).

The char/soot ratio is useful for source identification. The IMPROVE and IMPROVE_A (using TOR or TOT) produce different char and soot concentrations and their ratios, which would affect source identification. The low-temperature IMPROVE protocol generally produces lower char/soot ratios than those of IMPROVE_A protocol, with the lowest and highest annual char/soot ratio of 2.3 by the IMPROVE TOT and of 7.3 by the IMPROVE_A TOR (see Table 5).

HULIS-C concentrations over the one-year sampling period averaged 4.27 μg m$^{-3}$, accounting for 27.7% of TC, comparable with other studies in China (Lin et al., 2010a). If we assume the OM/OC ratio of 2.0 for HULIS suggested by Poldorri et al. (2008), the proportion of HULIS in PM$_{2.5}$, on average, is ~9.6%. Overall HULIS-C concentrations showed a temporal pattern similar to char and EC concentrations (Fig. 4), with higher winter and lower summer and spring concentrations. This supports the contribution of HULIS from biomass burning. Zhang et al. (2014) showed that the concentrations of levoglucosan, a tracer of biomass burning emissions, in Xi’an during winter and fall can be 1-2 orders of magnitude higher than those in summer. The major contribution comes from domestic biomass burning for heating instead of open fire. However, the HULIS-C/TC and HULIS/mass ratios did not peak in winter. This implies other important sources of HULIS, most likely SOA, in summer (Lin et al., 2010a), which is consistent with the high OC/EC ratios in summer compared with those in spring and fall (Fig. 3).

### 7. Implications

Because OC/EC ratios determine the relative contribution of particle scattering and absorption, they are often used to estimate the radiative forcing of carbonaceous aerosols (Novakov et al., 2005). Comparisons of the routine protocols IMPROVE, IMPROVE_A, and EUAA Repeat show a large difference (a factor of 2.7) in OC/
EC ratios among the protocols. Current models based on aerosol observations and emission inventories may have a potential uncertainty of more than a factor of two when estimating the radiative forcing of carbonaceous aerosols (Sato et al., 2003), which can be partly explained by the differences from OC/EC measurement using the different protocols. Average PM$_{2.5}$ OC/EC ratio in Xi'an during 2012–2013 is ~2.0 using the IMPROVE TOR protocol, in comparison with ~5.7 using the EUSSAR II TOT protocol. Higher IMPROVE TOR EC by IMPROVE protocol would suggest higher warming effects than those of EUSSAR_2 protocol. Direct measurements of aerosol optical properties from primary sources, in conjunction with the OC/EC analysis, can help reduce the uncertainty by recommending the appropriate mass absorption efficiencies of EC in the climate models.

High correlations of OC or EC concentrations determined by the different TO protocols suggest the possibility of reconciling

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**Fig. 3.** Variations of mass concentration and carbon fractions and their ratios in PM$_{2.5}$ of Xi'an city during 2012–2013 using the three protocols (IMPROVE, IMPROVE_A, and EUSSAR_2). (1) A1, B1, and C1, TC and mass concentrations, and their ratios; (2) A2, B2, and C2, TOR OC and EC, and their ratios measured with the three protocols; (3) A3, B3, and C3, TOT OC and EC, and their ratios measured with the three protocols; (4) A4 and B4, TOR char and soot, and their ratios measured with the IMPROVE and IMPROVE_A protocols; and (5) A5 and B5, TOT char and soot, and their ratios measured with the IMPROVE and IMPROVE_A protocols.
Fig. 4. Time series of (A) HULIS-C concentration, (B) HULIS/mass, and (C) HULIS/TC in PM$_{2.5}$ of Xi’an, China during 2012–2013. Note: HULIS concentrations in (B) are estimated using the ratio of OM/OC of 2.0 suggested by Poldori et al. (2008).

References

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.02.023

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