Ambient Characteristics of Elemental Carbon and Black Carbon in the Pearl River Delta and the Application of Elemental Carbon as a Combustion Aerosol Tracer

by

WU Cheng

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This is to certify that I have examined the above PhD thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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Abstract

Black carbon (BC) or elemental carbon (EC) aerosols is a class of refractory and light absorbing fine particulate matter originating from incomplete combustion activities. BC is not only an air pollutant that has an adverse health impact on human beings, but is also a vital climate forcer on both the global and regional scale due to its light absorption ability. Better understanding of BC is needed before effective mitigation measures can be formulated in the Pearl River Delta (PRD) region of China. Existing studies are either ad-hoc studies limited by spatial coverage or have temporal limitation. This thesis work aims to improve the understanding of BC in terms of analytical uncertainties, temporal and spatial distribution, and optical properties. For this study, multiple analytical techniques were employed for characterizing BC and the main findings are summarized below:

(1) Evaluations of the two most widely used carbon analyzer models and analysis protocols are performed by analyzing EC and organic carbon (OC) from PRD samples. The two instruments agree well but discrepancy is found between the two protocols, which is much larger than previous reports on US samples. Temperature ramping parameters and laser correction methods are identified to be the dominant factors leading to the protocol discrepancy. Degree of charring is found to positively correlate with the discrepancy. These results suggest that OC and EC determined by different protocols are not comparable and extra care should be taken for data interpretation from different protocols.
Observation of light absorption coefficients ($\sigma_{\text{abs}}$) and BC concentrations by aethalometers were conducted at five sites in the PRD region in two periods: 16 May-20 June 2008 during the rainy season and 12 December 2008- 8 January 2009 during the dry season. Little difference in BC level was found at a rural site in the PRD between the two sampling periods (2.88 and 2.62 $\mu$g m$^{-3}$). At the PRD urban sites, the daily average concentration of BC ranged from 1.56 to 37.9 $\mu$g m$^{-3}$, higher in the dry season sampling period (12.31 $\mu$g m$^{-3}$) and lower in the rainy season sampling period (6.17 $\mu$g m$^{-3}$). At the urban/suburban PRD sites, BC was observed to have a diurnal pattern of higher concentrations at night and at the urban sites a small peak in the early morning rush hour, implying the significance of vehicular emission.

Due to the refractory nature and its exclusive combustion source origin, EC tracer method has been extensively used for distinguishing primary and secondary OC but seldom assessed. Key to the EC tracer method is to identify an appropriate OC/EC ratio that represents primary combustion emission sources (i.e., $(\text{OC/EC})_{\text{pri}}$) at the observation site. A numerical study is performed to evaluate the accuracy of secondary organic carbon (SOC) estimation by various $(\text{OC/EC})_{\text{pri}}$ calculation schemes, including minimum OC/EC method, percentile (10%) OC/EC method and minimum R squared (MRS) method. Different scenarios are considered, including single primary source, two independent primary sources, and two correlated primary sources scenario. The results show among the three $(\text{OC/EC})_{\text{pri}}$ methods, the MRS method consistently produces the most accurate SOC estimates. Factors affecting the accuracy of SOC estimates are also identified through the numerical experiments.

Application of EC tracer method is conducted on one year hourly OC and EC data (1 February 2012 to 31 January 2013) of a suburban site Nancun (NC) in the city of Guangzhou, China. Results show that an interference of EC co-emitted SOC precursor can cause $(\text{OC/EC})_{\text{pri}}$ overestimation in the afternoon, and diurnal minimum MRS $(\text{OC/EC})_{\text{pri}}$ is adopted to minimized this artifact. In addition, seasonal variations of $(\text{OC/EC})_{\text{pri}}$ are observed (e.g. elevated $(\text{OC/EC})_{\text{pri}}$ in the biomass burning season), therefore $(\text{OC/EC})_{\text{pri}}$ is calculated for individual months to account for such variations. In winter, SOC exhibits higher concentrations, but in summer higher formation activity is observed as evidenced by an elevated SOC/OC ratio. SOC by resolved carbon fractions are also investigated. SOC contributed 38% of low temperature OC and 78% of high temperature OC, implying that most of the high temperature OC (probably more oxygenated) are secondarily formed. Results from 49 individual rain events show that carbonaceous particle mass was reduced 50% on average due to wet removal. The removal rate is uniform for POC, SOC and EC, suggesting that the mixing state of
carbonaceous particles is probably predominated by internal mixing at the sampling site. Higher EC/CO ratio was observed at night time, suggesting the high EC at night is associated with shallow mixing depth as well as higher intensity of primary emissions from diesel trucks, which is consistent with the traffic regulations in the city of Guangzhou.

(5) Optical properties of BC are explored by both numerical study and field measurement. Core-shell Mie simulation is performed to investigate the possible range of the light absorption enhancement factor ($E_{\text{abs}}$). Considering the typical size distribution of BC particles in the PRD, the upper limit of $E_{\text{abs}}$ is estimated at $\sim 2$. The annual average mass absorption efficiency (MAE) at NC is 19.75 m$^2$g$^{-1}$. MAE$_{\text{pri}}$ is proposed to represent the MAE of soot particles without coating. Linear regression and Minimum R Squared (MRS) method are employed for MAE$_{\text{pri}}$ estimation. The annual average estimated MAE$_{\text{pri}}$ by linear regression and MRS is 13.16 and 12.7 m$^2$g$^{-1}$ respectively, implying an annual average enhancement factor of 1.50~1.55. Seasonal variation of MAE exhibit much higher enhancement in summer. Enhancement apportionment shows that in the rainy season the enhancement is mainly associated with SO$_4^{2-}$ and NO$_3^-$, while in the dry season SOC, SO$_4^{2-}$ and NO$_3^-$ are all responsible for the enhancement. BC concentrations from an aethalometer and EC from a RT-ECOC analyzer are compared and the causes of discrepancy are discussed. Retrieval of the light absorption coefficient ($\sigma_{\text{abs}}$) from the RT-ECOC analyzer is demonstrated, and the results are shown to be consistent with the aethalometer.
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鸟隐于天高鱼潜于水深
Chapter 1

1. Research background of black carbon and elemental carbon aerosols

1.1 The importance of black carbon and elemental carbon aerosols

Originating from incomplete combustion, black carbon (BC) is a crucial constituent of atmospheric aerosols. BC is not only an air pollutant that has adverse health impacts on humans (Suglia et al., 2008b), but is also a significant climate forcer due to its ability to absorb light (Jacobson, 2001; Bond et al., 2013). BC can alter the climate in a variety of ways, including by direct forcing (Bond et al., 2011), affecting cloud cover (Koch and Del Genio, 2010) and precipitation (Tao et al., 2012), reducing the albedo of snow and ice (Hansen and Nazarenko, 2004) and causing surface dimming (Wild, 2011). Climate effects of BC could be global or regional (Ramanathan and Carmichael, 2008). However, BC is still not well understood due to the complexity of its emission source, morphology, and temporal and spatial distribution.

Terminology of different BC in atmospheric research includes a broad definition in terms of their origin, morphology, refractoriness and optical properties. To avoid confusion on various terms related to BC, the following explanation is discussed for clarification as recommended by Andreae and Gelencser (2006).

**Black Carbon (BC)**

This term is a definition assuming that all of the light absorption ($\sigma_{abs}$) is due to soot carbon. It should be noted that such an assumption can be invalid when samples are influenced by high concentrations of mineral dust (MD) (e.g. dust storm event) or light absorbing organic carbon (also known as Brown Carbon, BrC) that can absorb light at shorter wavelengths. These interferences from BrC and MD can be minimized by conducting measurements at longer wavelengths (e.g. Infer-Red). $\sigma_{abs}$ can be measured by various optical instruments (aethalometer, photoacoustic spectrometer etc.) and the result is converted to an equivalent soot carbon mass through a conversion factor (mass absorption efficiency, MAE). This definition is more focused on the strong light-absorbing characteristic of soot and the contribution to light absorption.
**Elemental Carbon (EC)**

The term elemental carbon is somewhat misleading since true elemental carbon only exists in three forms: graphite, diamond, and C-60. But in atmospheric chemistry this term is based on an analytical definition referring to a near-elemental soot-carbon like composition that is stable in inert carrier gas and only evolved with the presence of oxygen above a certain temperature during thermal analysis (Huntzicker, 1982; Chow et al., 1993; Birch and Cary, 1996). The term EC is emphasizing refractory nature of temperature and chemical reaction resistance. In contrast, organic carbon (OC) is defined as a carbon fraction that evolved in inert gas during thermal analysis. Identification of EC fraction is method dependent and consequently there is no standard method for EC determination in atmospheric aerosols. As a result, the difference in EC determination by different protocols can be as high as a factor of 5 (Wu et al., 2012; Chow et al., 2001). Considering the definition of EC is emphasizing its refractory properties, the term “refractory carbon” rather than elemental carbon would be more precise and appropriate in describing the nature of this substance.

Conventionally, it is not accurate but is acceptable to use either BC or EC to refer the same strongly light-absorbing refractory substance of particulate matter, although they are measured by different techniques (BC by optical method and EC by thermal optical method).

**Soot/Soot Carbon**

Soot or soot carbon is defined to be a substance formed by incomplete combustion and is frequently present in atmosphere as a fine particle. This definition is based on their origin. Soot particles, usually present as spherules with a diameter of 10-50nm, will cluster together as soon as their formation during combustion to form chain-like aggregates (Wentzel et al., 2003). The morphology of soot particles is transformed by aging processes to grow and be able to uptake water through the particle coating. This definition is emphasizing the origin of these substances.

Unfortunately, carbon-based fuel combustion is still the major approach for energy acquisition on this planet. In an ideal case, fuel combustion would convert all the carbon into CO$_2$. However combustion activity in the real world is non-ideal and contains a certain degree of incomplete combustion, which induces particle emission. The diversity of carbonaceous aerosol emission highly depends on fuel type (e.g. coal, diesel, gasoline, wood, and crop residues), flame temperature, annealing time and oxygen availability. For example, a short annealing time will favor amorphous soot particle formation, while a longer annealing time or higher temperature will lead to soot with fullerenic structures (Grieco et al., 2000). Gas-phase
fuel can mix with oxygen easily, resulting in minimized BC emission compared to liquid and solid fuel. BC emission of liquid fuel depends on its capability of vaporization for combustion. This is the reason why marine vessels, which use heavy oil, will emit substantial BC. Solid fuel combustion like biomass burning requires preheating to breakdown the solid fuel before flaming combustion occurs, which will induce pyrolysis during the process, resulting in more OC emission. As a result, morphology of soot can be highly diverse. Most of the freshly emitted soot particles are bare or thinly coated chain-like aggregates. Typical soot SEM (scanning electron microscope) and TEM (transmission electron microscope) images are shown in Figure 1.1. These aggregated monomers are usually 10~50 nm in diameter. TEM studies suggest that these monomers contain onion-like layers of graphitic platelets (Wentzel et al., 2003). Formation of BC during combustion is dominated by a 3D diffusion-limited cluster aggregation (DLCA) growth mechanism (Dhaubhadel et al., 2006; Jullien et al., 1984). A freeway study has shown that the fractal dimension of soot particles varies from site to site, and positively correlates with the driving/engine load conditions, which are vehicle specific (China et al., 2014). As a result, globally, the emission of BC is very complicated due to the diversity of emission sources across various locations.

Figure 1.1 Morphology of soot. (a) Scanning electron microscope (SEM) and (b) transmission electron microscope (TEM) imagery of typical soot aggregates emitted from high temperature combustion. Figure adopted from (Lack et al., 2014)

Global emission of BC is estimated to be 7500 Gg for the year 2000, with an uncertainty ranging from 2000 to 29000 Gg (Bond et al., 2013). Energy-related burning contributes about 4770 Gg BC emission while the rest 2760 Gg is associated with open biomass burning. Among energy-related emissions, the largest contribution comes from diesel engines (1310 Gg), then
followed by biofuel cooking (1290 Gg) and industrial coal combustion (740 Gg). BC emission exhibits strong spatial diversity around the world. Africa contributes 1690 Gg BC in the year 2000, which is dominated by open burning. BC emission in East Asia is around 1550 Gg and mainly comes from coal burning. Latin America BC emission is 1150 Gg and is strongly associated with open burning. Southeast Asia emitted around 850 Gg BC in the year 2000, mostly from forest fires.

Atmospheric aerosols can scatter and absorb solar radiation, thus significantly impacting global radiative forcing. BC is an important component of atmospheric aerosols, which affect cloud formation, cloud lifetime, cloud cover changes and visibility changes. Traditional points of view consider the fact that aerosols have a cooling effect on the atmosphere, however, aerosols also contain black carbon particles. One unique feature of BC is that it can absorb solar radiation across broad wavelengths. BC is the dominant species contributing to the direct warming effect from particulate matter. The energy transfer process during light absorption by BC makes it a crucial climate forcer which can affect the earth’s energy balance as well as the climate. Since BC can directly absorb solar radiation and heat the lower part of atmosphere, the heating effect of black carbon aerosols may offset the cooling effect of sulfate aerosols and gas minerals (Andreae, 2001). The Intergovernmental Panel on Climate Change (IPCC) started reporting BC radiative forcing from its second report (IPCC, 1996). Since freshly emitted BC undergoes aging in the atmosphere, the optical properties as well as the mixing state of BC will change during atmospheric processing. Conventionally, BC is assumed to be externally mixed in global models. Jacobson (2001) points out that radiative forcing from black carbon should be higher if the mixing state is taken into account, and would make it the third largest contributor after CO₂ and CH₄, and thus BC would have a significant impact on global warming as well as on regional climate change (Ramanathan and Carmichael, 2008). The variable optical properties of BC during its short atmospheric residence time (days to weeks) result in a more complicated radiative forcing estimation than CO₂. IPCC, in its fifth assessment report, estimated that BC has a radiative forcing of +0.64Wm⁻² (directly + indirectly), making BC the third largest contributor to warming following CO₂ and CH₄ (IPCC, 2013) as shown in Figure 1.2.
Besides the direct effect, BC contributes positive radiative forcing when deposited on snow. This effect is also called the snow albedo effect because the surface albedo is decreased when darkened by deposited BC. In the IPCC radiative forcing budget (Figure 1.2), BC radiative forcing from the snow albedo effect amounts to 3-13% of the total BC forcing. Although this effect is limited to areas with snow and ice cover (about 7.5~15% of earth surface), the radiative forcing from some 'hotspots' can be higher than the global average. For example, 1.5 Wm$^{-2}$ radiative forcing in the Tibetan plateau was estimated by Flanner et al. (2007) with an instantaneous forcing as high as 20 Wm$^{-2}$. Model studies (Flanner et al., 2007; Hansen and Nazarenko, 2004) have also found the contribution from BC on Arctic sea ice retreat could be as high as 50%.

In the US, the USEPA began regulating fine and coarse particles in 1997 to further protect public health. Substantial studies have established the linkage between fine particle exposure and a series of adverse effects like premature mortality and increased hospital admission related to cardiovascular and respiratory disease (Bell et al., 2009). Recently, the research community has been focused on distinguishing the health impact from various species.
within PM$_{2.5}$. It should be noted that difficulties still exist to differentiate the health effects of BC from co-emitted species such as OC. But the pool of evidence on health effects associated with BC is still growing. For example, BC is a risk factor for human health in the indoor environment, especially for people that rely on solid fuel for cooking and heating. Recent scientific evidence suggests that BC emitted from indoor solid fuel combustion without proper ventilation is responsible for respiratory morbidity such as through chronic obstructive pulmonary disease (Ramirez-Venegas et al., 2006;Regalado et al., 2006). Impact from biofuel smoke on adverse pregnancies like low birth weight and stillbirth (Pope et al., 2010;Abusalah et al., 2011;Boy et al., 2002) was also reported recently. Existing studies indicate that exposure to fine particle BC in the ambient environment will induce airway inflammation (Delfino et al., 2006;McConnell et al., 2003) and lung function reduction (Suglia et al., 2008a;Gauderman et al., 2007). Besides respiratory effects, cardiovascular impact associated with BC was also observed. Delfino et al. (2010) reported the positive correlation between exposure to BC and blood pressure. Many studies also found an association between heart rate variability (HRV) with elevated BC level (Chuang et al., 2008;Adar et al., 2007;Park et al., 2005b). In an electrocardiograph, the ST-segment represents the period when the ventricles are depolarized. ST-segment depression serves as an indicator for abnormal cardiac conditions like ischemia. The study by Delfino et al. (2011) revealed the positive correlation between ST-segment depression and BC abundance. In China, recent studies also found that fine particles rather than coarse particles, were associated with daily mortality and from cardiorespiratory diseases in Shanghai (Kan et al., 2007). A recent study during the 2008 Beijing Olympic Games found the connection of EC concentration with thrombosis (Rich et al., 2012). Facing the growing public concern of the health impact from PM$_{2.5}$, China announced updated ambient air quality standards in Feb 2012 (MEP, 2012), which regulate PM$_{2.5}$ for the first time. In 2012, the International Agency for Research on Cancer (IARC), which is a branch of the World Health Organization (WHO), classifies diesel engine exhaust (a major contributor of BC in urban areas) as “carcinogenic to humans”. BC is still not directly regulated by emission standards or ambient air quality standards. Some attempts have been made in the US. In 2009, the “Black Carbon Emissions Reduction Act” was proposed to mitigate the effects of black carbon emissions in the United States. Although eventually this bill didn’t pass, a trend of regulating individual species in fine particulate matter is expected in the foreseeable future.
1.2 Review of measurement techniques for black carbon and elemental carbon

Various measurement techniques are discussed here in mainly two categories: EC mass determination and light absorption coefficient ($\sigma_{abs}$) measurement. The first category involves techniques for direct mass determination, while the second category discusses measurement of the amount of light absorbed by BC, which can be used to estimate BC mass by incorporating the multiplier mass absorption efficiency (MAE).

1.2.1 EC mass measurement techniques

**Thermal analysis**

In thermal analysis, OC and EC differentiation is achieved by heating samples to different temperatures based on their disparate thermal stability. One example is the Thermal Magnesium Dioxide (TMO) method proposed by Fung (1990). In TMO, OC is evolved in helium till 525°C and then oxidized to CO$_2$ by MnO$_2$. EC is oxidized in the presence of oxygen under 850°C. CO$_2$ from OC and EC oxidation is reduced to CH$_4$ and then detected by flame ionization detector (FID). Another thermal analysis example is German reference method VDI-2465 part 1. In this method, extractable OC is first removed by solvent extraction. Non-extractable OC is evolved under 500°C while EC is evolved under 700°C, and the emerging CO$_2$ is determined by coulometric titration. VDI-2465 part 1 also serves as the calibration basis of multi-angle absorption photometry (MAAP) (Petzold and Schonlinner, 2004). Thermal analysis coupling time resolved sampling (RP5400, Rupprecht & Patashnick Co, Albany, NY) can provide hourly measurements of OC and EC (Rupprecht et al., 1995). In RP5400, both OC and EC are oxidized in ambient air, which is quite different from other thermal methods that use an inert gas during the OC stage. The major drawback of thermal analysis is that charring of OC is not considered, which produces pyrolyzed carbon causing an overestimation of EC.

**Thermal optical analysis**

Thermal optical analysis (TOA) attempts to correct the charring problem by adding optical measurements of the filter into the system. During a typical TOA, a transmittance (Turpin et al., 1990) or reflectance (Chow et al., 1993) signal of the laser beam passing through the filter is recorded for correction. During the OC analysis stage (inert carrier gas), pyrolyzed carbon (also known as char) is formed due to pyrolysis in Helium, resulting in darkening of the
filter and decreased optical signal. In the EC analysis stage (oxygen introduced to the carrier gas), char and EC are oxidized, resulting in an increase of the laser signal. When the signal returns to the initial level, the amount of carbon in the oxygen stage before this point is considered pyrolyzed carbon (PC). Correction is done by adding PC back into OC. The most widely used protocols are IMPROVE_A (Interagency Monitoring of PROtected Visual Environment) (Chow et al., 2007) and NIOSH (U.S. National Institute for Occupational Safety and Health) (Birch and Cary, 1996), probably due to the availability of corresponding commercial instruments and their adoption in large sampling networks. Unlike IMPROVE, NIOSH protocol only outlines the basic principles without specifying detailed temperature parameters. As a result, many variants of NIOSH implementation exist like in the STN (Speciation Trends Network) and ACE-Asia (Mader et al., 2001). Recently a new protocol (EUSAAR, European Supersites for Atmospheric Aerosol Research) was proposed for OC and EC sample analysis in Europe (Cavalli et al., 2010). The notable feature of EUSAAR is that its maximum temperature (650°C) in OC stage (inert carrier gas) is lower than NIOSH (850°C~900°C) but higher than IMPROVE_A (580°C). Besides bench top analyzers that are designed for offline analysis, field analyzers have also been developed to conduct hourly OC and EC analysis on-site (Turpin et al., 1990).

Although widely used for EC mass determination, TOA still faces many challenges. (1) TOA lacks reference materials for OC and EC, which leading to difficulties in protocol standardization; the current OC and EC determination is protocol dependent and the protocols are not comparable to each other (Chow et al., 2001). (2) The laser correction scheme is based on two assumptions: (a) During the oxygen stage, PC evolves before native EC (2) PC has the same attenuation cross section as EC. Yang and Yu (2002) pointed out that these two assumptions can be violated in ambient samples, but the uncertainty can be minimized by extending the residence time at each temperature stage (Yu et al., 2002). (3) The separation of OC and EC in TOA is ambiguous since an optimal maximum temperature in the helium stage sometimes doesn’t exist due to the complexity of ambient samples. If the temperature is not high enough, it may fail to evolve all the OC fractions on the filter. But if temperature is high enough to evolve all the OC fractions, loss of EC fractions may happen in the helium stage due to the presence of metal oxidants in the sample (Novakov and Corrigan, 1995; Wang et al., 2010), causing a premature OC/EC split. It should be noted that the premature OC/EC split artifact is more pronounced in time resolved OC-EC measurements, because metal oxidants are
accumulated and enriched on quartz filter due to the reuse of quartz filter in sampling/analysis cycles.

Laser induced incandescence technique

Laser induced incandescence (LII) occurs when light absorbing carbon is illuminated by a high intensity laser (e.g. \(1.7 \times 10^5 \text{ Wcm}^{-2}\)) (Schwarz et al., 2010) and heated to vaporization temperature (~4000K) (Schwarz et al., 2006). The heated particle emits black body radiation that can be detected by a PMT (Photomultiplier tube) detector. The mass of the illuminated particle can be derived from the PMT signal. According to the black body radiation theory, the LII wavelength (emitted by the black body) is related to the temperature, and the corresponding radiation wavelength of refractory BC (rBC) at 4000K falls in the visible light range. As a result, to avoid interference from the illuminating laser, infrared laser is adopted for rBC LII detection. Early LII application was widespread in combustion studies owing to its advantage of visualizing the spatial distribution of rBC in the flame (Quay et al., 1994; Shaddix and Smyth, 1996). More applications of LII in atmospheric rBC were seen after work by Stephens (2003). The design eventually became commercialized and the instrument known as SP2 (Single Particle Soot Photometer). One highlight of SP2 is its capability to measure scattered light of the illuminated particle, which is very useful for estimating the optical size through Mie theory and further probing the mixing state of the particle (Gao et al., 2007). Another unique feature of SP2 is its expanded application in measuring liquid samples, including melt streams from ice cores (Kaspari et al., 2011), snow (Schwarz et al., 2012) and precipitation (Ohata et al., 2011). It should be noted that the LII signal measured by the SP2 exhibits a dependence on black carbon type (Laborde et al., 2012). Fullerene soot was found to have a similar response as denuded diesel exhaust on SP2 (within 16%). But the SP2 response to different batches of fullerene soot can be up to 14% different. The SP2 response to a commercial graphite (Aquadag®, Henkel Technologies) is 40% higher than denuded diesel exhaust, implying the potential uncertainty in the SP2 calibration.

1.2.2 Light absorption measurement techniques

Filter transmission method

In the filter transmission method, particles are collected onto a filter substrate (e.g. quartz, Teflon). The filter is placed between a light source and detector before and after particle
collection, then the attenuation coefficient (ATN) can be quantified by the Beer-Lambert law (Eq. 1.1).

\[ ATN = \frac{A \ln \left( \frac{I_0}{I} \right)}{V \Delta t} \]

I₀ and I are the light intensity before and after particle collection, respectively. A is the spot area of particle deposition. V is the volume of air passing through the filter during time interval Δt. However, ATN in the filter transmission method is different from particle \( \sigma_{abs} \) in air (usually ATN is a few times larger than \( \sigma_{abs} \)) due to the following artifacts: (a) multi-scattering in the filter matrix, (b) shadowing effect due to particle loading, and (c) Back scattering due to non-absorbing materials in the particles. Careful correction is needed to retrieve \( \sigma_{abs} \). An early application of this method was the integrating plate (IP) reported by Lin et al. (1973). Clarke (1982) reported a variant of IP (known as integrating sandwich) by adding two highly reflective wafers on both sides of the filter. Since light travels many times between the two reflective wafers, the opportunity of absorption is enhanced. To account for the scattering effect, an integrating sphere (IS) that enable measurement total flux of light rays, was added into the system to improve the measurement (Campbell et al., 1995; Hitzenberger et al., 1996). Automation of filter tape advancement in aethalometer enabled time resolved measurements and greatly expanded the application of the \( \sigma_{abs} \) measurement (Hansen et al., 1982, 1984).

Variants of the aethalometer include the continuous soot monitoring system (COSMOS) that employs a thermal denuder for reducing absorption enhancement due to particle coating, and the spectral optical absorption photometer (SOAP), which conducts measurement at different wavelengths (MÜLler et al., 2009). Petzold and Schonlinner (2004) introduced a new filter based real-time instrument known as the multi-angle absorption photometer (MAAP). By adding extra sensors at multiple angles, MAAP is capable of tracking the scattering correction (Petzold and Schonlinner, 2004). A recent version of the aethalometer can perform measurements at 7 wavelengths (Arnott et al., 2005). It should be noted that extra care should be taken for interpreting multi-wavelength data for distinguishing BC absorption and BrC absorption, because the data correction factors for filter based method are wavelength dependent (Coen et al., 2010). Unless wavelength dependent correction factors can be obtained from a side by side comparison with a reference instrument (e.g. Photoacoustic Spectrometer), BrC \( \sigma_{abs} \) estimation using a multi wavelength filter based instrument is not recommended (Lack et al., 2014).
Photoacoustic technique

Photoacoustic spectroscopy (PAS) is an in situ method for particle and gas $\sigma_{abs}$ measurement that has been making contributions to atmospheric science for more than 30 years (Bruce and Pinnick, 1977; Terhune and Anderson, 1977). In photoacoustic measurements, laser light is directed incident to particles suspended in the air. Light absorption by particles induces a temperature increase of the particle. Heat from the particle transfers to the surrounding air through conduction. Air expands when heated, creating a sound wave that can be detected by a microphone. The signal received by the microphone is proportional to $\sigma_{abs}$, so $\sigma_{abs}$ can be quantitatively determined. In the early days of PAS, the laser source was bulky and intensively power-consuming, thus deployability of photoacoustic techniques for field measurements were limited (Adams et al., 1989). Widespread application of photoacoustic techniques began with the advancement in compact and efficient diode lasers (Patrick Arnott et al., 1999; Petzold and Niessner, 1995). Photoacoustic spectroscopy can provide high time resolution (seconds) response, making it suitable for airborne measurements (Arnott et al., 2006). Recent developments in photoacoustic spectroscopy have focused on multi-wavelength measurements (Ajtai et al., 2010; Haisch et al., 2012; Lewis et al., 2008; Sharma et al., 2013), which can be used for characterizing the wavelength dependency of aerosols associated with BrC (Lack et al., 2012) and mineral dust (Moosmüller et al., 2012). Compared with the filter transmission method, the major advantages of photoacoustic spectroscopy include: 1) in situ measurement that eliminates artifacts present in the filter method, 2) fast response time in seconds, 3) integration with a reciprocal nephelometer in the photoacoustic instrument is very common where the light scattering and absorption coefficients can be determined simultaneously.

Extinction minus scattering technique

Extinction minus scattering (EMS) is a direct $\sigma_{abs}$ measurement method that measures the difference between the extinction coefficient ($\sigma_{ext}$) and scattering coefficient ($\sigma_{scat}$). Early application of EMS was achieved by coupling a multi-pass cell with a reciprocal nephelometer (Gerber, 1979). Recent developments in EMS have focused on the cavity ring-down (CRD) technique for the $\sigma_{ext}$ measurement. Multiple kilometers of effective optical path can be achieved in CRD by using highly reflecting mirrors. As a result, the $\sigma_{ext}$ detection limit can be improved to less than 1 Mm$^{-1}$ (Strawa et al., 2003). Thompson et al. (2008) combined CRD with an integrating sphere nephelometer for $\sigma_{abs}$ determination. An advantage of EMS over
PAS is that EMS can perform measurements at high RH (Wei et al., 2013), while PAS is subject to an interference from water vapor at elevated RH. Hygroscopic growth leading to a light absorption enhancement is still difficult to measure due to the existing instrumental limitations. EMS seems to be a potential technique for solving this problem. Sources of error for EMS include: (a) If the ambient single scattering albedo (SSA) is very high, the error of EMS increases significantly, because $\sigma_{abs}$ is then obtained from the difference of two large quantities and a small deviation in the precursors is relatively large for $\sigma_{abs}$, (b) A truncating effect in the nephelometer can induce errors, and the truncation error correction requires knowing the size distribution of sampled particles, which further limits field deployability.

**Photo-thermal interferometry technique**

The presence of light absorbing particles in the air can alter the effective refractive index (RI) of air, and the $\sigma_{abs}$ of the sampled particles can be estimated by measuring the RI change. Photo-thermal interferometry (PTI) is one of the most commonly used approaches based on this principle (Lin and Campillo, 1985). When light is absorbed by particles, heat is conducted to the surrounding air thus changing the RI. To measure the RI change, two identical laser beams (probe beam and reference beam) split from the same source are used. These two beams pass through identical geometric paths. The “probe” beam travels through the BC containing sample volume that is heated by another high intensity laser. Interference, caused by the sample volume, can be measured by recombining the probe beam and reference beam, where the phase shift between the two beams is proportional to the RI change, allowing quantification of the light absorption (Fluckiger et al., 1985). Interferometry is susceptible to mechanical vibrations, which limits the application for field measurement. Advances have been made by refining the design to provide a more robust measurement (Moosmüller and Arnott, 1996). A recent comparison study shows that PTI can provide similar results to photoacoustic spectroscopy (Cross et al., 2010).

**Remote sensing technique**

Two types of remote sensing techniques are commonly used. One is a ground based measurement (e.g. sun photometer) and the other is satellite measurement. For ground based measurements, the application of the diffuse direct radiation method (Herman et al., 1975) is often used for aerosol light absorption retrieval. Application of absorption retrieval has been demonstrated using sun photometers (Sato et al., 2003). It should be noted that the absorption
optical depth yield from such retrieval is column integrated. Retrieval of light absorption from satellites is even more difficult due to the domination of surface albedo variations during the measurement. The accuracies of satellite remote sensing are still open for debate.

1.3 Review of existing black carbon and elemental carbon studies

1.3.1 Black carbon and elemental carbon studies around the world

Ambient elemental carbon measurements have been conducted by different networks around the world. The Interagency Monitoring of Protected Visual Environments (IMPROVE) began to measure EC in 1989 in rural areas of the US. Urban EC in the US has been measured by the Speciation Trend Network (STN, also known as Chemical Speciation Network, CSN) since 2000. A long term study in the US using IMPROVE data found that EC decreased by over 25% between 1990 and 2004 in remote areas like national parks (Murphy et al., 2011). In California, the BC emission from vehicular sources was reduced to half between 1990 and 2008, which resulted in an observed reduction of ambient EC concentration by 50% (Bahadur et al., 2011). Decrease of BC was also found in Arctic regions with an annual decrease of -2.1 ngm$^{-3}$ per year (1989-2008) based on observations (Hirdman et al., 2010). BC was reduced by 55% at a Canadian arctic site between 1989-2002 (Sharma et al., 2004). In contrast to the decrease of BC in North America and the EU, BC emission in India increased significantly, doubling from 1991 to 2001 (Sahu et al., 2008). A recent inventory study also found a distinct difference in the BC emission trend between developed countries and developing countries (Wang et al., 2014b). BC emissions from the residential and industry sectors (1960-2007) exhibited a declining trend in developed countries, while for developing countries a growing BC emission trend is observed. BC from vehicular emissions in developed countries peaked in late 1970s and then started to decrease, while an increasing trend of BC from vehicular emission was observed in developing counties during the same time and since. However, global BC emission per unit of energy decreased substantially from 1960-2007 owing to the improvement of combustion efficiency from a fuel shift in developing counties.

A study in Mexico city found SSA varied between 0.35~0.87, where the low SSA implies light absorption due to BC (Marley et al., 2009). Low SSA (0.76) was also observed in urban areas in India, with BC concentrations ranging from 6 to 20 µgm$^{-3}$ (Tripathi et al., 2005a). Seasonal variations of BC concentrations in India exhibit a dependence on the monsoon system, where BC peaks in the dry season and reaches a low in the rainy season, emphasizing the
influence of meteorological conditions on BC (Latha and Badarinath, 2005). A study in Houston found that BC will suppress ozone formation by lowering photolysis frequencies in the planetary boundary layer (PBL) (Li et al., 2005).

The vertical distribution of BC as well as the absorption coefficient is essential to understand the climate effect of BC. Aircraft measurements found high BC concentrations (up to 12 µg m\(^{-3}\)) at altitudes of ~2.5 km during the TRACE A experiment over rainforests in Brazil (Pereira et al., 1996). An increase in BC mass fraction with altitude was reported by Novakov et al. (1997) during aircraft measurements in the eastern coast of United States. During the Indian Ocean Experiment (INDOEX) a high abundance of BC was found in the residual continental boundary layer (rCBL, 1.3–3.2km) (Mayol-Bracero et al., 2002). The altitude of BC abundant layers and clouds play an important role for addressing their climate effect (Satheesh, 2002). Presence of a high concentration BC layer was observed by aircraft measurement at a north Indian industrial city (Tripathi et al., 2005b). Tethered balloon soundings in Italy showed BC mass and light absorption decrease sharply from ground to mixing height and become quite constant above the mixing height (Ferrero et al., 2011). High altitude balloon soundings over central India revealed extremely high BC concentration at the 4km height that were 6 times higher than ground level (Babu et al., 2011).

1.3.2 Black carbon and elemental carbon studies in China and the Pearl River Delta region

Since the 1990s, more and more observational studies of black carbon aerosols have been performed in China. Tang et al. (1999) reported a collection of short-term BC observations from a background station in Lin'an in 1991, and in the Lasha area in 1998. In 1994, China's first global background atmospheric observatory was constructed in the Waliguan Mountains of Qinghai at 3810 m above sea level, with valuable research findings related to BC reported by Qin et al.(2001). Wang et al. (2002) measured BC concentrations in the northern suburbs of Beijing in 1992 and from 1996-2001. Chi et al. (2000) reported seasonal abundance of EC in Beijing by using a CHN analyzer and found that high EC in winter may be related to heating. Research in Qiqihar City found a similar seasonal distribution (Sun et al., 1997). Zhu et al.(1996) studied EC particle size distribution in the Pudong Area of Shanghai. Lou et al. (2005) measured BC by the filter based light absorption technique equipped with TSP, PM\(_{10}\) and PM\(_{2.5}\) inlets and found that in Beijing, most BC exist in PM\(_{2.5}\). In 2006, the China Atmosphere Watch Network (CAWNET) was established to measure aerosol speciation and light absorption (Zhang et al., 2008b). From CAWNET the EC loading has been pretty high in both ambient and rural areas
and is more than five times higher than in the US and Europe (Zhang et al., 2012). Unfortunately, filter based PM chemical speciation sampling in CAWNET only lasted for two years. A nationwide long-term PM chemical speciation network is still absent in China.

The Pearl River Delta (PRD) has been one of the fastest growing global economic areas for nearly 30 years, and has become one of the most polluted areas in China. PRD has a total land area of only 8000 square kilometers but a high population density, including mega cities like Guangzhou, Hong Kong, Shenzhen, Dongguan, Zhuhai and Foshan. During the process of urbanization, vegetation reduction, transportation increases, bloom of township enterprises plant, and increasing frequent air pollution incidents have produced concern from both government as well as the public (Wu et al., 2005). High OC and EC concentrations in PM$_{10}$ and PM$_{2.5}$ across the Pearl River Delta region were determined using a DRI carbon analyzer with the IMPROVE protocol, implying an impact of emissions from motor vehicles (Cao et al., 2004). Yu et al. (2004a) studied the abundance of OC and EC in PM$_{10}$ across 10 sites of Hong Kong from 1998-2001 and found that marine vessels at container ports are an important EC source in Hong Kong. Duan et al. (2007) compared the spatial distribution of OC and EC in PM$_{2.5}$ between two mega-cities in the PRD in both summer and winter from 2004–2005. It was found that the EC level in the city of Guangzhou (GZ) is higher than in Hong Kong (HK), OC and EC are correlated in urban GZ but not in urban HK, which is consistent with results from a sampling network led by HKUST in PRD. Zheng et al. (2012) reported a high resolution BC inventory for the year 2009 and estimated an annual BC emission of 39 Mg. Mobile sources (25 Mg) are estimated to be the dominant contributor, followed by industrial combustion (4.8 Mg) and residential combustion (4.5 Mg).

During the PRIDE-PRD extensive measurement campaign, Hu et al. (2012) found high carbonaceous aerosols concentration at night time and in early morning in Guangzhou city using time resolved OC/EC measurement. Andreae et al. (2008) reported high time resolution observations by a photo-acoustic spectrometer in urban Guangzhou during the winter of 2004. Results revealed extreme light absorption could reach as high as 490Mm$^{-1}$, at a corresponding EC concentration of 55μgm$^{-3}$. OC was found to reduce the intercept in the absorption vs EC mass regression when added as the second independent variable, resulting in an apparent mass absorption efficiency (MAE) of 0.76 m$^2$g$^{-1}$ (i.e. slope of the regression), implying the contribution of $\sigma_{abs}$ from internal mixing of OC. A yearlong study at a Hong Kong coastal rural site Hok Tsui (HT) found that the BC level demonstrated a clear seasonal pattern, which is much higher in winter when HT became a receptor site of continental outflow (Cheng et al.,
A tunnel study of EC size distribution in urban Guangzhou found that EC shows a dominant droplet mode which is different from other regions of the world (Huang et al., 2006). Ning et al. (2013) report BC size distribution at urban environment using a tandem SMPS-Aeth system. An integrated approach study (Lee et al., 2013) found BC episodes in Hong Kong significantly associated with regional transport of biomass burning. A study in the mega-city Shenzhen found that cloud-processing could be an important pathway for EC size growth in the droplet mode, making the EC more internally mixed with soluble components (Huang and Yu, 2008). Cheng et al. (2006b) investigated the mixing state of EC at a receptor site Xinken (XK) in the PRD through optical closure study. The mixing state at XK strongly depends on the origin of the air mass where a clear diurnal variation is observed with more internally mixed EC at night and externally mixed during daytime. Recent SP2 studies in the PRD provide time-resolved BC mixing state information. Huang et al. (2011a) reported an increased number fraction of coated BC particles in the daytime, suggesting a strong diurnal pattern of BC mixing state. Light absorption enhancement by a factor of 1.3 at 870 nm is observed in Shenzhen (Lan et al., 2013), confirming the effect of particle aging to alter optical properties in this region.

The uniqueness of BC is its capability of transferring solar energy into heat, which is a potentially important feedback to affect the atmosphere. Reddy and Boucher (2007) reported that the largest contribution of radiative forcing from BC comes from East Asia (0.17 Wm\(^{-2}\)). A modeling study of China found that BC increased rainfall in the south and reduced rainfall in the north (Wu et al., 2008b). During the PRIDE-2004 campaign, an observational based modeling study investigated the impact of BC radiative forcing through a radiative transfer model (Wendisch et al., 2008), and found that the boundary layer height was suppressed due to the heating by BC in the upper PBL, effectively trapping pollutants at the ground level.

1.4 Limitations of existing studies

Large uncertainties still remain for BC in terms of climate change as well as air pollution. Hence, to study BC will benefit both climate change and air pollution research resulting in a win-win situation. However, the linkage between optical properties and the mass of different BC is complicated due to their morphology (mixing state). As a result, great uncertainty remains regarding the amount of light absorbed by BC, which is an important parameter in climate models, and the amount of BC mass which is commonly reported by speciation sampling networks utilizing the thermal optical method.
Carbon in atmospheric aerosols can be divided into three categories based on their thermal stability: organic carbon (OC), elemental carbon (EC) and carbonate carbon (CC). Carbonate carbon is negligible in fine particles for most regions except those under the influence of mineral dust (e.g., Cao et al., 2005). OC and EC are among the major constituents of atmospheric aerosols and their quantification is necessary in understanding the role of aerosols in issues varying from health effects of aerosols and regional visibility degradation to regional and global climate change (Andreae and Gelencser, 2006; Hansen et al., 2005). EC is particularly important to understand how aerosols interact with various components of the climate system due to its strong light absorption capability. A recent study (Wu et al., 2009) found a relatively low (~0.8) Single Scattering Albedo (SSA) across the Pearl River Delta, implying an abundant black carbon concentration in this region.

Despite their importance, there are not definitive standards for OC and EC quantification. Thermal/optical methods are widely used to determine OC and EC in ambient and source aerosols in the atmospheric measurement field. It is also widely recognized that OC and EC are operationally defined by analysis methods, in which analysis temperature programs and the optical charring correction are important factors influencing the reported concentrations of OC and EC. Among the thermal/optical methods, IMPROVE (Chow et al., 1993) and NIOSH (Birch and Cary, 1996) are two mainstream protocols for OCEC analysis around the world. The two protocols differ in temperature programs and in the optical methods for charring correction.

Total carbon (TC) measurements by the two protocols agree well, within ±10% (Chow et al., 2005), but EC concentration was found to differ by a factor of 2–10 when the two protocols were implemented on a DRI analyzer for about 40 ambient samples (Mexico urban, US urban, and nonurban samples) and 19 source samples (Chow et al., 2001). More recent comparisons of the two protocols on other data sets also consistently reported that EC and OC by NIOSH and IMPROVE protocols are not comparable (Chow et al., 2005; Cheng et al., 2011b; Zhi et al., 2011). The NIOSH protocol only outlines the necessary principles for operation, rather than specifies detailed parameters at each temperature step (e.g. residence time). Therefore, a number of NIOSH-derived protocols exist in the literature. As summarized by Watson et al. (2005), the temperature program in NIOSH protocol has been modified by various research groups in their analysis to determine aerosol EC and OC. The modified NIOSH protocols typically differ slightly from the original NIOSH method in the temperature and duration of the thermal ramping steps during the analysis stage that uses He as the carrier gas. A few examples of the modified NIOSH protocols are the STN (Speciation Trends Network in
the US) (Peterson and Richards, 2002), the ACE-Asia (Schauer et al., 2003), HKUST-3 (Yang and Yu, 2002), and HKGL (Sin et al., 2002) protocols.

In practice, the two protocols are often implemented on two different analyzers, that is, the IMPROVE protocol is implemented on a DRI/OGC analyzer while the NIOSH protocol is implemented on a Sunset Laboratory Analyzer (Tigard, OR, USA). Recently a newer DRI analyzer (Model 2001a, Atmoslytic Inc., Calabasas, CA, USA) replaced the old DRI/OGC analyzer for carbon analysis in the IMPROVE network. The default protocol implemented on DRI 2001 analyzers is a modified IMPROVE protocol, termed IMPROVE_A protocol. The temperatures in the IMPROVE_A protocol differ from those in the IMPROVE protocol because new hardware in the DRI 2001 analyzer attains the sample temperature more accurately than does the old hardware. Consequently IMPROVE_A protocol temperatures match more closely the sample temperatures experienced in the analysis using the IMPROVE protocol on the previous models of DRI analyzers. Chow et al. (2007) have shown that comparable OC, EC, and TC are obtained using either the IMPROVE or IMPROVE_A temperature protocols with an optical reflectance correction for sample charring. They also observed that the two temperature protocols yield different, but highly correlated, results for thermally-resolved carbon fractions. In our current work, we have implemented the IMPROVE temperature protocol for comparison with a NIOSH-derived protocol. Both the DRI analyzer and the Sunset analyzer in its recent model provide filter transmittance and reflectance monitoring via a laser throughout the analysis; however, they differ in their instrument design as to the arrangement of the laser relative to the filter.

In the US, the PM$_{2.5}$ Speciation Trends Network has shifted its carbon analysis protocol from NIOSH to IMPROVE_A since 2007 (Chow et al., 2007). In Hong Kong, the NIOSH protocol implemented on Sunset analyzers has been used as the method to determine OC and EC in PM10 for the city’s air quality monitoring network since 1998 (Sin et al., 2002; Yu et al., 2004a). In China, the National Technical Committee on Meteorological Disaster Prevention and Mitigation of Standardization Administration of China has recently been discussing to adopt IMPROVE_A as the standard method to determine OC and EC in ambient aerosols (http://www.sac345.org.cn/upload/userfiles/tfx.pdf). These developments in carbon analysis methods have prompted the necessity of evaluating the following two issues: (1) whether the IMPROVE protocol implemented on a Sunset analyzer would give comparable EC and OC to those determined by implementing the IMPROVE protocol on a DRI analyzer and (2) whether the NIOSH or NIOSH derived protocol implemented on a DRI analyzer would give comparable
EC and OC to those determined by implementing the NIOSH protocol on a Sunset analyzer. Previous protocol comparison studies were conducted either on a single analyzer, e.g., comparison of the NIOSH and IMPROVE protocols on the DRI analyzers (Chow et al., 2004; Chow et al., 2001; Chow et al., 2005; Zhi et al., 2009) or between the DRI analyzer implementing the IMPROVE protocol and the Sunset analyzer implementing the NIOSH protocol (Cheng et al., 2011b; Chow et al., 2005; Zhi et al., 2011). The instrument dependence of EC and OC measurements using the same protocols has yet to be investigated.

BC is not a regulated pollutant in China. Thus BC is not routinely measured in the PRD region. Previous studies are based on ad hoc measurements that fail to characterize the long term trends of BC (Andreae et al., 2008; Huang et al., 2011a). Some studies performed yearlong studies but were limited to a single location (Cheng et al., 2006a). A few studies investigated the spatial abundance of EC but with a limited sample size (Cao et al., 2004). Time resolved measurements are crucial for OC and EC characterization, but existing studies in the PRD were of limited duration (Hu et al., 2012; Verma et al., 2010). Some studies examined the mixing state of BC (Cheng et al., 2006b; Huang et al., 2011a), but the impact on light absorption enhancement is not well understood in the PRD region.

Freshly emitted EC will undergo an aging process in the atmosphere resulting in modification with coatings of additional organic or inorganic material. Evidence of enhanced absorption of solar radiation by EC due to a change of the mixing state to an internal mixture were found from Lorenz-Mie theory calculations (Fuller et al., 1999), global climate models (Bond et al., 2006; Jacobson, 2006; Lesins et al., 2002; Jacobson, 2001), laboratory studies (Schnaiter et al., 2005; Shiraiwa et al., 2010) as well as field measurements (Schwarz et al., 2008; Moffet and Prather, 2009). Some pilot studies in the PRD region have studied the BC mixing state directly using SP2 (Huang et al., 2011a) or indirectly through optical models (Cheng et al., 2006b). The advantage of SP2 to study the mixing state is its capability to perform in-situ single particle measurements (Huang et al., 2011a). However, some challenges still exist: 1) determination of BC coating thickness by SP2 (time delay or Mie scattering method) still has large uncertainties, with coating thickness not even estimated in PRD studies, 2) detection of coating thickness is limited to 70nm, 3) size distribution obtained by SP2 is volume equivalent diameter (VED), which is not comparable to the more widely used aerodynamic diameter/mobility diameter, and 4) non-core-shell type particles have been reported (Moteki et al., 2014; Sedlacek et al., 2012) which challenge the conventional core-shell assumption. Many studies have suggested the enhancement of light absorption at various locations around the
world (Schwarz et al., 2008), but enhancement studies in the PRD are still very limited (Lan et al., 2013).
1.5 Work in this thesis

In this thesis work, multiple analytical approaches are employed to investigate and characterize BC in the PRD region from different perspectives. The main body of this thesis includes following chapters:

Chapter 2: Inter-instrument comparison for ECOC thermal optical analysis is performed, which has been seldom investigated before. Both instruments have a large pool of users, so the results are informative for comparing data from different instruments. Inter-protocol comparison has not been systematically investigated on PRD samples. The inter-protocol comparison results reveal the range of discrepancy on PRD samples between the two most widely used protocols, which is much larger than those reported on US samples. Potential factors that contribute to the discrepancy are identified and discussed. The results emphasize the use of caution when interpreting ECOC data from different protocols.

Chapter 3: Time-resolved BC measurements in different seasons are performed at various locations in the PRD and a remote island in the South China Sea. Both temporal and spatial variations of BC are investigated. Factors that may affect temporal and spatial distribution are analyzed. Diurnal patterns of BC and its contribution to light absorption is also studied.

Chapter 4: The EC tracer method is widely used for distinguishing primary and secondary OC by using EC as a tracer. The key to this method is estimation of a proper primary OC/EC ratio \((\text{OC}/\text{EC})_{\text{pri}}\). But the uncertainties of \((\text{OC}/\text{EC})_{\text{pri}}\) estimation by various approaches along with the EC tracer method are seldom assessed. A pseudo data generation scheme for simulating EC as well as primary and secondary OC is proposed. A systematic evaluation of SOC estimation performance by different \((\text{OC}/\text{EC})_{\text{pri}}\) calculation approaches is performed through a numerical study. Different scenarios are considered to reflect a more realistic situation in the ambient environment. Sensitivity tests are conducted to identify factors that may affect the results.

Chapter 5: One year time-resolved OC and EC measurements are performed in the heart of the PRD. Minimum R squared (MRS) method is employed for SOC estimation. A method to avoid interference of EC by co-emitted SOC precursors in \((\text{OC}/\text{EC})_{\text{pri}}\) estimation is proposed. SOC estimation by carbon fractions using MRS is demonstrated. Correlations between SOC and different compositions are compared. CO/EC ratio analysis is conducted to study the high nighttime EC in Guangzhou.
Chapter 6: Optical properties of BC are studied by both Mie simulation and field measurement. Mie simulation is used to estimate the variability and upper limit of light absorption enhancement in the PRD region. $E_{abs}$ and MAE are estimated from one year of field measurements, and their variation in different seasons is analyzed. BC measured by an aethalometer and EC by a RT-ECOC analyzer are compared. Possible factors that may contribute to the discrepancy are discussed. Retrieval of light absorption coefficients from the RT-ECOC optical measurement is demonstrated.

Chapter 7: Conclusions and future works.
Chapter 2
2. Determination of Elemental and Organic Carbon: Inter-Instrument and Inter-Protocol Comparisons

Chapter summary
Organic carbon (OC) and elemental carbon (EC) are operationally defined due to the lack of definitive standards. Consequently, their quantification is protocol-dependent. IMPROVE and NIOSH are the two widely used thermal/optical protocols for OCEC analysis, differing in temperature programs and in the optical method for charring correction. The IMPROVE protocol is often implemented on a DRI analyzer while the NIOSH protocol is often implemented on a Sunset Laboratory Analyzer. Evaluation of the implementation of the IMPROVE protocol on the Sunset Laboratory analyzer or implementation of the NIOSH or NIOSH-derived protocols on the DRI analyzer has rarely been reported. We analyzed OC and EC in about 100 ambient samples collected in the Pearl River Delta in China by implementing the IMPROVE protocol and a NIOSH-derived (ACE-Asia) protocol on both a DRI Model 2001 analyzer and a Sunset Laboratory analyzer. The total carbon (TC) and EC filter loading as determined by the ACE-Asia protocol on the Sunset analyzer varied from 2.6-67.0 and 0.2-7.4 µg cm⁻², respectively. Inter-instrument comparison indicates that the implementation of the IMPROVE protocol on the Sunset analyzer reports TC, EC, and OC measurements in good agreement with those made on the DRI analyzer. EC and OC analyzed using the ACE-Asia protocol are also in good agreements for measurements implemented on the Sunset and the DRI analyzers. Inter-protocol comparison indicates consistency in TC determination but discrepancies in OC and EC, with the IMPROVE protocol reporting much higher EC than the ACE-Asia protocol. An analysis of different comparison scenarios reveals that the cause of the EC difference could be quantitatively attributed to temperature protocol (thermal effect) and optical pyrolysis correction method (reflectance vs. transmittance). The variation in EC concentrations was more pronounced in samples that produced more charred OC during thermal analysis.
2.1 Introduction

Organic carbon (OC) and elemental carbon (EC) are operationally defined due to the lack of definitive standards. Consequently, their quantification is protocol-dependent. IMPROVE and NIOSH are the two widely used thermal/optical protocols for OCEC analysis, differing in temperature programs and in the optical method for charring correction. The IMPROVE protocol is often implemented on a DRI analyzer while the NIOSH protocol is often implemented on a Sunset Laboratory Analyzer. Evaluation of the implementation of the IMPROVE protocol on the Sunset Laboratory analyzer or implementation of the NIOSH or NIOSH-derived protocols on the DRI analyzer has rarely been reported. In this study, we are aiming investigation of following issues: (1) whether the IMPROVE protocol implemented on a Sunset analyzer would give comparable EC and OC to those determined by implementing the IMPROVE protocol on a DRI analyzer and (2) whether the NIOSH or NIOSH derived protocol implemented on a DRI analyzer would give comparable EC and OC to those determined by implementing the NIOSH protocol on a Sunset analyzer. Previous protocol comparison studies were conducted either on a single analyzer, e.g., comparison of the NIOSH and IMPROVE protocols on the DRI analyzers (Chow et al., 2004; Chow et al., 2001; Chow et al., 2005; Zhi et al., 2009) or between the DRI analyzer implementing the IMPROVE protocol and the Sunset analyzer implementing the NIOSH protocol (Cheng et al., 2011b; Chow et al., 2005; Zhi et al., 2011). The instrument dependence of EC and OC measurements using the same protocols has yet to be investigated.

Another objective of this study is to investigate, through inter-protocol comparisons, how variations in OC and EC reported by the two mainstream protocols are related to differences in temperature programs and in optical charring correction.

2.2 Experimental Section

2.2.1 Sample description

The samples used in this study were PM$_{2.5}$ samples collected in multiple locations in the Pearl River Delta (PRD), China, a region of 54744 km$^2$ that include several mega cities such as Hong Kong, Guangzhou, and Shenzhen. Each sample was collected on prebaked quartz fiber filter for 24 h from midnight to midnight. A total of 61 samples were collected in Nansha, a suburban district of Guangzhou, following a schedule of one sample for every six days over...
a period of one year from July 2007 to August 2008. These samples were collected using one of two mid-volume PM$_{2.5}$ samplers (RAAS, Andersen Instruments, Smyrna, GA and SASS, Met One Instruments, Grants Pass, OR). The two mid-volume samples were deployed during different sampling periods. Another 40 samples were collected at four locations in Hong Kong in November and December 2010, also following a 6-day cycle schedule. These 40 samples were sampled by a hi-vol sampler (Tisch Environmental, Cleves, OH) at a flow rate of 1.13 m$^3$min$^{-1}$. The four sampling locations include a roadside site, two urban sites and a suburban site. After sample collection, the 47 mm quartz filters (Pallflex, Tissuquartz, 2500-QAT-UP) used in the mid-volume samplers were stored in a Petri dish lined with pre-baked aluminum foil to reduce contamination and under -20°C to minimize the loss of volatile species. The 20×25 cm filters (Pallflex, Tissuquartz, 2500-QAT-UP) from the hi-vol samplers were folded and wrapped in pre-baked aluminum foil before storing in the freezer.

2.2.2 Carbon Analysis

One DRI carbon analyzer (Model 2001) (Chow et al., 1993) and one Sunset carbon analyzer (Birch and Cary, 1996) were used to determine EC and OC in this work. The schematic diagrams of the arrangements of the quartz oven and the laser beam in the two analyzers shown in Figure 2.1 indicate the relative position between the laser and the filter. Both the Sunset and DRI analyzers are capable of simultaneously monitoring laser transmittance and reflectance signal for charring correction. The major difference in their optical configurations is that the laser source in the DRI analyzer is installed coaxially with transmittance and reflectance detectors while in the Sunset design there is a ~45° angle between the laser source and the two detectors. Another difference is the pathway by which laser travels from source to detector. In the Sunset analyzer, laser goes through the wall of quartz oven before reaching the filter sample and then the reflectance and transmittance detectors. In the DRI analyzer, laser travels in optical fiber outside the oven and is guided by light pipe when traveling inside the quartz oven.
Figure 2.1 Schematic diagrams of arrangements of quartz tube, sample boat, and monitoring laser for the Sunset analyzer (left) and the DRI Model 2001 analyzer (right).
For carbon analysis on the Sunset analyzer, a filter punch of 1.0 cm\(^2\) in size was removed from each filter sample for analysis. On the DRI analyzer, a filter punch of 0.5 cm\(^2\) was used. The two protocols adopted for analysis are ACE-Asia (a NIOSH-derived protocol) and IMPROVE protocols. The ACE-Asia protocol was used for ECOC analysis during the ACE-Asia campaign (Schauer et al., 2003). It is the same as quartz.par method that is preloaded in the Sunset ECOC analyzer. Analysis of the 61 Nansha samples was conducted using both the ACE-Asia and the IMPROVE protocols and on both the Sunset and DRI analyzers. A total of 244 analysis results were obtained in four combinations of temperature programs and optical charring correction for the 61 Nansha samples on each analyzer. The four combinations are IMPROVE_TOR, IMPROVE_TOT, ACE-Asia_TOT, ACE-Asia_TOR, where IMPROVE and ACE-Asia refer to the temperature programs while TOR and TOT refer to charring correction using reflectance and transmittance, respectively. The 40 Hong Kong samples were analyzed on the Sunset analyzer using both the IMPROVE and the ACE-Asia protocols but their analysis on the DRI analyzer were only carried out using the IMPROVE_TOR protocol.

The detailed temperature programs of the ACE-Asia and IMPROVE protocols are shown in Table 2.1. The major differences between the two protocols are: (1) The maximum temperature in He stage reaches 870°C in the ACE-Asia protocol versus 550°C in the IMPROVE protocol. Different amounts of charred OC are formed as a result; (2) The ACE-Asia_TOT protocol utilizes transmittance signal while the IMPROVE_TOR protocol adopts reflectance signal for pyrolysiss carbon correction. Charred OC and EC have different penetration depths on filter (Chow et al., 2004). Filter transmittance and reflectance apparently would exhibit different sensitivities to charred OC and EC on the filter; (3) In the ACE-Asia protocol, the residence time (RT) is fixed for each temperature step, the duration of which is typically shorter than that needed to return FID signal to baseline. In the IMPROVE protocol, RT of each temperature step is variable and its duration is driven by FID signal slope to ensure the full isolation of carbon fraction in that temperature step. In the implementation of the IMPROVE protocol, the Sunset analyzer determines the FID baseline at the beginning of the analysis. When the FID reading during a temperature step returns to the initial FID baseline, this temperature step ends and the analysis moves to the next temperature step. As a result, the analysis time of the IMPROVE protocol is more than double that of the ACE-Asia protocol. Figure 2.2 shows two typical thermograms of a sample obtained with the ACE-Asia and the IMPROVE protocols on the Sunset analyzer. The thermograms on the DRI analyzer are very similar and shown in Figure 2.2b.
Before analysis of each batch of samples, the instruments were calibrated in the range of 4-90 μgC with sucrose solutions (Sigma-Aldrich) for the DRI analyzer and with the NIST standard reference material SRM1649a for the Sunset analyzer. The sucrose standard concentration was calibrated with SRM1649a. Analysis results (TC, OC and EC) are calculated using programs supplied by the instrument manufacturers. Precisions on both carbon analyzers determined by replicate analysis of aerosol-laden filters were better than 5% for TC, OC, and EC by the IMPROVE_TOR method and better than 5% for TC and OC and better than 8% for EC by the ACE-Asia_TOT method (Figure 2.3). Field Blank samples were obtained at the end of every month. In the inter-instrument comparison study, data are corrected for field blank before comparison.

Table 2.1 Temperature programs of the IMPROVE and ACE-Asia protocols.

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Carbon Fraction</th>
<th>ACE-Asia</th>
<th>IMPROVE ²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C) ¹</td>
<td>RT (s) ¹</td>
<td>T (°C)</td>
</tr>
<tr>
<td>He</td>
<td>OC1</td>
<td>310</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>OC2</td>
<td>475</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>OC3</td>
<td>615</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>OC4</td>
<td>870</td>
<td>90</td>
</tr>
<tr>
<td>He</td>
<td>EC1</td>
<td>550</td>
<td>45</td>
</tr>
<tr>
<td>2% O₂ in He</td>
<td>EC2</td>
<td>625</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>EC3</td>
<td>700</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>EC4</td>
<td>775</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>EC5</td>
<td>800</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>EC6</td>
<td>870</td>
<td>45</td>
</tr>
</tbody>
</table>

¹ T: temperature (°C) and RT: Residence time (seconds).
² The IMPROVE temperature program was used for measurements reported in this work. Another related temperature protocol, termed IMPROVE_A, is typically adopted on DRI Model 2001 carbon analyzers. The IMPROVE_A temperature protocol defines temperature plateaus of 140 °C for OC1, 280 °C for OC2, 480 °C for OC3, and 580 °C for OC4 in a helium (He) carrier gas and 580 °C for EC1, 740 °C for EC2, and 840 °C for EC3 in a 98% He/2% oxygen (O₂) carrier gas (Chow et al., 2007). These temperatures used with the new hardware in DRI Model 2001 better match the sample temperatures experienced in the analysis using IMPROVE protocol on the previous models of DRI analyzers.
Figure 2.2 Example thermograms of an ambient sample using the IMPROVE and ACE-Asia Protocols. (Temperature: Oven temperature during analysis; Laser T: laser transmittance signal; Laser R: laser reflectance signal; T Split: OC/EC split by laser transmittance signal; R Split: OC/EC split by laser reflectance signal; FID: flame ionization detector signal) (a) Sunset Analyzer (b) DRI analyzer
2.3 Results and discussion

Linear regression analyses of the various carbon data in this study were performed using Deming regression, instead of least-square regression method. The ordinary least-square regression method assumes that x values are error free, which induces incorrect slope estimation (Chu, 2005). In comparison, Deming regression (Deming, 1943) accounts for both errors in y and x axis. Hence it was adopted in this paper for all the correlation analysis.

2.3.1 Inter-instrument and inter-protocol comparison of TC measurements

The TC loading in the 61 Nansha samples covers a wide range (4-70 μg cm$^{-2}$). Nansha, located in a suburban district of Guangzhou, is a receptor site year around, impacted by pollution transported from upwind urban areas and having little locally generated emissions. Under the influence of predominant winds, Nansha is downwind urban Guangzhou in fall and winter and downwind Hong Kong in spring. PM$_{2.5}$ in Nansha collected over the period of a year could represent a diverse range of aerosols in this region. The TC measurements of the 61

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Figure 2.3 Precision of TC, OC and EC determination by the ACE-Asia TOT and the IMPROVE TOR protocol for measurements made on the Sunset and DRI analyzers.
Nansha samples reported by the two instruments agree well for both the ACE-Asia and IMPROVE protocols, which is an expected result and consistent with previous comparison studies (Chow et al., 2005). As shown in Figure 2.4a, high correlation coefficients ($R^2 > 0.99$) and near-unity slopes were found for both protocols (0.99 for both the IMPROVE protocol and ACE-Asia protocol). TC deviations between the two protocols as a function of filter loading are shown in Figure 2.4b. Most samples fall in the range of ±20%, confirming good agreement in TC measurements between the two analyzers. Increasing TC deviations, but still within ±25%, were observed in the lower filter loading samples as these levels are closer to minimal detection limit. The results suggest that both instruments are robust on reporting equivalent TC with both the ACE-Asia and IMPROVE protocols.

Inter-protocol TC comparison shows good agreement as well, as shown in Figure 2.5a. Unity slopes (1.02 on the DRI and 0.97 on the Sunset analyzers) and high correlation ($R^2 > 0.99$) obtained from this comparison are similar to those reported in a previous study (Chow et al., 2001). Deviations in TC (±10%) are small on both DRI and Sunset (Figure 2.5b), indicating that TC equivalence by the ACE-Asia and the IMPROVE protocols is independent of instrument.

![Figure 2.4 Inter-instrument comparison (DRI Model 2001 vs. Sunset) of total carbon (TC). The format for regression line is $y = ax + b$. P is the P value for paired t-test. (a) TC concentrations by the DRI Model 2001 analyzer vs. by the Sunset analyzer (Open squares are TC data obtained with the IMPROVE protocol; open circles are TC data obtained with the ACE-Asia protocol.) (b) Deviations in TC determined on the two analyzers.](image-url)
Figure 2.5 Inter-protocol Total Carbon (TC) comparison (ACE-Asia vs. IMPROVE). The format for regression line is $y = ax + b$. $P$ is the $P$ value for paired t-test. (a) TC concentrations by the two protocols on the Sunset analyzer (open circles) and on the DRI Model 2001 analyzer (open squares). (b) Deviations in TC by the two protocols.

2.3.2 IMPROVE_TOR protocol: Inter-Instrument comparison of EC and OC measurements

The combined data sets of the 61 Nansha samples and the 40 Hong Kong samples were used in inter-instrument comparison of the IMPROVE protocol. High correlations of IMPROVE_TOR OC and EC ($R^2=0.99$) were observed between measurements made by the two different analyzers (Figure 2.6). The regression slopes of IMPROVE_TOR measurements by the two analyzers (Sunset vs. DRI) were $0.92\pm 0.01$ for OC and $1.05\pm 0.02$ for EC. Both values are close to unity, indicating good agreement between the two instruments. Concentration deviations for most samples are within $\pm 25\%$ for OC (Figure 2.6b) and $\pm 20\%$ for EC (Figure 2.6d). These results demonstrated that implementing the IMPROVE_TOR protocol on the Sunset analyzer produced OC and EC measurements equivalent to those made using the IMPROVE_TOR protocol on the DRI analyzer.
Figure 2.6 Comparison of IMPROVE_TOR OC and EC measurements by the Sunset and the DRI Model 2001 analyzers.

The samples for comparison include 61 mid-volume samples collected in Nansha and 40 high-volume samples collected at four sites in Hong Kong. The format for regression line is $y=ax+b$. $P$ is the P value for paired t-test.

(a) Deming regression plot of inter-instrument comparison of IMPROVE_TOR OC concentrations, (b) Deviations in IMPROVE_TOR OC measurements by the two analyzers. (c) Deming regression plot of inter-instrument comparison of IMPROVE_TOR EC concentrations. (d) Deviations in IMPROVE_TOR EC concentrations by the two analyzers.

$$\begin{align*}
a &= 0.98 \pm 0.02 \\
b &= -0.84 \pm 0.43 \\
R^2 &= 0.994 \\
N &= 101 \\
p &< 0.0001
\end{align*}$$

$$\begin{align*}
a &= 1.12 \pm 0.02 \\
b &= 0.00 \pm 0.39 \\
R^2 &= 0.990 \\
N &= 101 \\
p &< 0.0001
\end{align*}$$
2.3.3 ACE-Asia_TOT protocol: Inter-Instrument comparison of EC and OC measurements

Slopes close to unity (1.04 for OC and 0.97 for EC) were obtained between measurements made on the two analyzers (Figure 2.7a and Figure 2.7c), indicating equivalent determination of OC and EC with the ACE-Asia protocol on the two instruments. High correlations were also found, with $R^2=0.99$ for OC and $R^2=0.93$ for EC. OC deviations were mostly within ±10% but larger deviations in EC (±20%) were observed (Figure 2.7b and Figure 2.7d). Four EC data pairs (marked in the circle in Figure 2.7c) were judged to be outliers and excluded in the regression analysis. A close examination of raw data revealed that the laser signal had a minimum value of less than 20 during analysis of these samples on the DRI analyzer, approaching the lower end of the laser transmittance signal range (0-2500) reported by the analyzer. The DRI analyzer assigns an uncertainty value of 10 with its transmittance measurement. As a result, a greater uncertainty was expected in relying on transmittance for OC and EC demarcation for the low laser samples. The low laser problem only occurred when implementing the ACE-Asia_TOT protocol on the DRI analyzer. This is likely due to more charring formed in the analysis using the ACE-Asia_TOT protocol as a result of the higher maximum temperature in the analysis stage in the He carrier gas.
Figure 2.7 Comparison of ACE-Asia_TOT OC and EC measurements by the Sunset and the DRI Model 2001 analyzers.

The format for regression line is $y = ax + b$. $P$ is the $P$ value for paired t-test. (a) Deming regression plot of inter-instrument comparison of ACE-Asia_TOT OC concentrations, (b) Deviations in ACE-Asia_TOT OC measurements by the two analyzers. (c) Deming regression plot of inter-instrument comparison of ACE-Asia_TOT EC concentrations (open circles represent normal samples while open squares represent low laser samples). The low laser samples were excluded in the regression analysis. (d) Deviations in ACE-Asia_TOT EC concentrations by the two analyzers.
2.3.4 Comparison of EC and OC by IMPROVE_TOR and ACE-Asia_TOT Protocols

Due to the different temperature evolution and laser correction method, OC and EC reported by IMPROVE_TOR and NIOSH_TOT are not comparable (Chow et al., 2001). Our inter-protocol comparison also confirmed this conclusion as shown in Figure 2.8. OC reported by the IMPROVE_TOR is on average 0.56 times the OC by ACE-Asia_TOT on the Sunset analyzer and 0.62 times on the DRI analyzer. EC reported by IMPROVE_TOR is higher than ACE-Asia_TOT as shown in Figure 2.8b, with a slope of 5.42 on Sunset and 4.31 on DRI analyzer. This EC ratio between the IMPROVE_TOR and NISOH_TOT is not only analyzer-dependent, but also dependent on sample location and sample composition because of the spatiotemporally varying nature of ambient aerosol. The slope obtained in this study is within the range reported by previous studies, including 2~6 by (Chow et al., 2001), ~3.4 by (Chow et al., 2004), and 1.6 by (Zhi et al., 2009).

![Inter-protocol comparisons of OC and EC measurements](image)

Figure 2.8 Inter-protocol comparisons of OC and EC measurements. The format for regression line is \( y = ax + b \).

(a) Comparison of ACE-Asia_TOT OC and IMPROVE_TOR OC on the Sunset analyzer (open circles) and on the DRT 2001 analyzer (open squares) (b) Comparison of ACE-Asia_TOT EC and IMPROVE_TOR EC on the Sunset analyzer (open circles) and on the DRI Model 2001 analyzer (open squares).
2.3.5 Discussion on EC comparison

Potential causes for difference in EC concentrations determined by the ACE-Asia_TOT and IMPROVE_TOR protocols include the thermal factor (different temperature steps) and laser correction factor (transmittance vs. reflectance). The main differences in the thermal factor between the two protocols are related to the maximum temperature in He stage (T_{max,He}) and RT of each temperature plateau. T_{max,He} affects not only the allocation of the carbon fraction that is liberated in the He stage in ACE-Asia protocol or in the He/O_2 stage in IMPROVE but also the amount of char formed in the He stage in both protocols. RT affects char formation as a longer RT in the first few temperature steps could reduce pyrolysis (Yu et al., 2002). Zhi et al (2009) found that the effect of T_{max,He} is more important than RT on the measured EC.

Chow et al. (2001) found that OC4 in the NIOSH protocol was approximately equivalent to the difference between EC by the two protocols. This conclusion is confirmed by our comparison for samples collected in the PRD, China (Figure 2.9). A comparison was made between ACE-Asia OC4+AEC (apparent EC, sum of all EC fractions that evolve after the carrier gas was switched to the O_2/He mixture) and IMPROVE AEC. Clear equivalence relations can be found from the close-to-unity slope values and high R^2 values (0.99) on both instruments (Figure 2.9a). Small differences (±15%) between these two quantities shown in Figure 2.9b also confirmed that this agreement is instrument independent. However, we need to note that the relative proportions of pyrolyzed OC and native EC (the EC that is originally present in the sample before the thermal analysis) in the two equivalent quantities are dependent on the analysis temperature programs. They are different between two analyses of the same sample obtained with different temperature programs. As shown in Figure 2.9a, the major different between NIOSH and IMPROVE due to temperature effect is associated with OC4 in the NIOSH protocol. As a result, the IMPROVE EC is always higher than NIOSH EC. These conclusion is consisted with the results of Chow et al. (2004) and valid for other locations. The degree of divergence between two protocols also depends on the charring fractions in samples. If the samples contain higher amount of charring fraction, the difference between the two protocols is larger.
Figure 2.9 Equivalence of ACE-Asia OC4+AEC and IMPROVE AEC. The format for regression line is $y = ax + b$.

(a) Deming regression plots of ACE-Asia OC4+AEC vs. IMPROVE AEC on the Sunset analyzer (open squares) and on the DRI Model 2001 analyzer (open circles) (b) Deviations between ACE-Asia OC4+AEC vs. IMPROVE AEC.

Different laser correction methods are envisioned to result in different OC/EC split as laser reflectance and transmittance respond to different parts of pyrolyzed OC and EC on the filter. Chow et al. (2004) revealed that char penetrated deeper in quartz fiber filters than EC and that liberation of char and EC by oxidation is from surface to deeper part of filter. As transmittance signal accounts for EC and char throughout the whole filter while reflectance signal only accounts for EC and char on the filter surface, the reflectance signal would return to the initial value earlier than the transmittance signal, which leads to earlier OC/EC split by the reflectance method as shown in Figure 2.2. Chen et al. (2004) did a model study using K-M theory and concluded that the diversity of char and EC absorption efficiencies further contribute to variation in EC reported by different laser correction methods.

For the exploration of the effects of temperature steps and the laser correction and the instrument setup, four scenarios of different combinations of these factors are compared for each analyzer. They include: (1) ACE-Asia_TOT, (2) ACE-Asia_TOR, (3) IMPROVE_TOT, and (4) IMPROVE_TOR. Correlations of EC measurements between different pairs of analysis scenarios are summarized in Table 2.2.
For the investigation of the thermal effect, pairs of analysis scenarios with the same laser correction method but different temperature programs are compared in Figure 2.10a for data obtained on the Sunset analyzer. With TOR charring correction, EC by the IMPROVE temperature program was ~1.77 times the EC by the ACE-Asia temperature. This result is different from that reported by Chow (2004), which found equivalency of TOR EC by IMPROVE and NIOSH protocols. Further study is needed to investigate whether reflectance correction is independent of temperature protocol in thermal/optical analysis. With TOT charring correction, EC by the IMPROVE temperature program was ~1.64 time the EC by the ACE-Asia temperature program. It can be interpreted that the difference between the IMPROVE and ACE-Asia temperature programs caused a factor of ~1.7 (average of 1.77 and 1.64) difference on EC concentration, regardless whether TOT or TOR was used for charring correction. Data obtained on the DRI analyzer also found similar thermal factors between the two temperature programs (1.65 for reflectance-based measurements and 1.62 for transmittance-based measurements) (Table 2).
The effect of laser correction for charring on EC results is examined in Figure 2.10b for measurements made on the Sunset analyzer. The plot clearly shows that the reflectance-based EC measurements are higher than the transmittance-based EC measurements by a factor of 3.07 (IMPROVE temperature program) and 3.41 (ACE-Asia temperature program). Similar laser correction effects were also found on the DRI analyzer, i.e., 2.60 for measurements using the IMPROVE temperature program and 3.36 for measurements using the ACE-Asia temperature program. Chow et al. (2004) also examined the laser correction factor using EC data by the IMPROVE and NISOH temperature programs obtained on a DRI analyzer. They found that the reflectance-based EC measurements was 1.4 times the transmittance-based EC using the IMPROVE temperature program and the factor was 3.3-5.0 using the NIOSH temperature protocol. In our samples, the variability in EC determined by reflectance (EC\textsubscript{TOR}) vs. transmittance (EC\textsubscript{TOT}) was more pronounced for samples that produced more charred OC during analysis. The difference between EC\textsubscript{TOR} and EC\textsubscript{TOT} was roughly proportional to the amount of charred OC (Figure 2.11). This observation confirms the suggestion by Chen et al. (2004) that the EC bias caused by charring correction methods was larger for samples having higher ratios of charred OC/EC. A recent study in Europe (Maenhaut et al., 2011) also found

\[ a = 1.77 \pm 0.11 \]
\[ b = -1.83 \pm 0.70 \]
\[ R^2 = 0.894 \]
\[ N = 61 \]

\[ a = 1.64 \pm 0.10 \]
\[ b = -0.28 \pm 0.29 \]
\[ R^2 = 0.901 \]
\[ N = 61 \]
that the ratio of EC by IMPROVE_TOR to EC by NIOSH_TOT increased in samples significantly influenced by wood burning, which are expected to have more char formation during analysis.

Figure 2.11 Difference of EC as determined using filter reflectance vs. transmittance as a function of the amount of charred OC.
(a) EC determined using ACE-Asia temperature program. (b) EC determined using IMPROVE temperature program.

We further found that the variation between EC by IMPROVE_TOR and ACE-Asia_TOT can be quantitatively described to be the combined impact of charring optical correction and temperature program. On the Sunset analyzer, the multiplication of the thermal effect factor (1.71) and the laser correction factor (3.24) yields a value of 5.54, very close to the regression slope value of 5.42 between EC data obtained with the IMPROVE_TOR and ACE-Asia_TOT protocol (Table S1, online supplemental information). Similarly, on the DRI analyzer, the product of the two factors is 4.89, also close to the regression slope value of 4.31 between EC data obtained with the IMPROVE_TOR and ACE-Asia_TOT protocol.
2.4 Conclusions and implications

For historical reasons, the IMPROVE_TOR protocol is often implemented on DRI carbon analyzers while the NIOSH_TOT protocol is often implemented on Sunset analyzers. In this work, we have demonstrated that EC and OC determined by implementing the IMPROVE_TOR protocol on a Sunset carbon analyzer are equivalent to those obtained with a DRI 2001 carbon analyzer implementing the IMPROVE_TOR protocol. We also shown that the ACE-Asia-TOT protocol, a NIOSH-derived protocol, implemented on a DRI analyzer reports equivalent EC and OC concentrations to those obtained with a Sunset analyzer. In another words, despite difference in their instrument design in monitoring filter transmittance and reflectance, the two types of analyzers are capable of reporting equivalent EC and OC when using the same analysis protocol.

Inter-protocol comparison of OC and EC indicate that measurements by the IMPROVE_TOR and the ACE-Asia_TOT protocols are not comparable. The same conclusion was reached in previous comparison studies by other researchers. On the Sunset analyzer, EC concentrations reported by the IMPROVE_TOR method were on average 5.4 times those by the ACE-Asia_TOT protocol for the about 100 ambient samples collected in the PRD, China. The cause of the EC difference can be quantitatively attributed to differences in temperature programs and in optical charring correction methods, with the latter playing a more important role. The difference in EC by the two protocols was further found to be more prominent in samples that produced more charring during the analysis. This implies that the variation in EC concentrations as determined by the two commonly adopted protocols is sample-dependent and that there is not a universal factor to convert EC determined by one protocol to that by the other protocol.

The selection of analysis protocol for OCEC analysis depends on following factors:

1) Research purpose. If the research purpose is focus on source apportionment, IMPROVE protocol is recommended. The major reason is that the carbon fractions (e.g. OC1~OC4, EC1~EC3) are better resolved in IMPROVE due to the longer retention time of each temperature steps. These carbon fractions are very useful in receptor models like CMB and PMF. Using carbon fractions as input in CMB or PMF can provide more information for source apportionment than using OC and EC alone. For other research purpose, e.g. collaboration between different research groups, it’s important to make sure that the same protocol is used. Because the translation of OC and EC between different protocols is not available. If different
protocols are employed, the results are not comparable. The transition of OCEC protocol in STN network from NIOSH to IMPROVE is good example of keeping data consistency between different sampling networks (Chow et al., 2004).

2) Loading of the samples. The laser transmittance signal in DRI analyzer is weaker than Sunset analyzer due to the quartz light pipe used. The quartz light pipe in DRI analyzer is useful to suppress the mirage effect of laser signal, but also result in weaker laser signal. For urban samples that have high EC concentrations, the laser signal may not be sufficient for OC/EC split. The problem is even worse when Hi-vol samples are used. As a result, the Sunset analyzer is recommended for urban samples.
Chapter 3
3. Black carbon observation in various locations of Pear River Delta region, China

Chapter summary
Black carbon (BC) is an important atmospheric constituent as an air pollutant and as a climate forcer. To our knowledge, field measurements of BC have not been reported over the South China Sea. Observation of light absorption coefficients ($\sigma_{\text{abs}}$) and BC concentrations by Aethalometer were conducted at five sites in the Pearl River Delta (PRD) region, South China in two periods: 16 May-20 June 2008 in rainy season and 12 December 2008- 8 January 2009 in dry season. Little difference in BC level was found at a rural site in PRD between the two sampling periods (2.88 and 2.62 $\mu$g m\(^{-3}\)). At the PRD urban sites, the daily average concentration of BC ranged from 1.56 to 37.9 $\mu$g m\(^{-3}\), higher in the dry season sampling period (12.31 $\mu$g m\(^{-3}\)) and lower in the rainy season sampling period (6.17 $\mu$g m\(^{-3}\)). The observed average $\sigma_{\text{abs}}$ values in rainy vs. dry season sampling period are 119 vs. 62 Mm\(^{-1}\) at the PRD urban sites, 29 vs. 26 Mm\(^{-1}\) at the PRD background site, and 8.4 vs. 7.2 Mm\(^{-1}\) at the marine site. At urban/suburban PRD sites, BC was observed to have a diurnal pattern of higher concentrations at night and at the urban sites a small peak in the early morning rush hour.
3.1 Introduction

Aerosol, as an important climate forcer, has attracted increasing attention in the atmospheric research community (Lohmann and Lesins, 2002; Menon et al., 2002; Penner et al., 2004). Atmospheric aerosols scatter and absorb solar radiation, thus significantly impacting the climate (Babu and Moorthy, 2001; Reddy and Venkataraman, 2000; Tao et al., 2012). Black carbon (BC) is an important component of atmospheric aerosols, affecting visibility, cloud formation, cloud cover and lifetime. IPCC started reporting radiative forcing due to BC aerosol since its second report (IPCC, 1996). The heating effect of BC aerosols may offset the cooling effect of sulfate and mineral aerosols (Andreae, 2001). If the mixing state of BC is taken into account, the radiative forcing of BC is estimated to be sufficiently strong to make BC the third most significant global warming contributor after CO$_2$ and CH$_4$ (Jacobson, 2001). A more recent study suggests BC is now possibly the second largest “global average warming agent” even ahead of methane (Cohen and Wang, 2013). BC aerosols could also have direct and indirect impacts on regional climate change (Ramanathan and Carmichael, 2008; Wang, 2013).

Asian BC aerosol attracted attention of scientists worldwide due to its widespread and increasing atmospheric abundance. In 1999, European and American scientists found that southern Asia is often shrouded in a brown cloud of aerosols 3 km thick, referred to as the Asian Brown Cloud by many researchers (Ramanathan et al., 2002; Engling and Gelencser, 2010). In China, this phenomenon is often simply referred to as “haze” (Wu, 2005; Wu et al., 2007; Wu et al., 2005). Later, the similar phenomenon was found over every continent, more commonly known as the atmospheric brown cloud. The widespread presence of BC suggests that the role of BC as a warming forcing needs to be studied in order for the assessment of aerosol’s role in global and regional climate change (Ramanathan and Carmichael, 2008) and for the attribution of contributions by individual countries. It has become clear that high-resolution spatial and temporal observations of radiation parameters of aerosol are essential data for assessment of the impact of Chinese aerosols on global and regional climate change.

In this work, we report BC and aerosol light absorption measurements by Aethalometers in May-June 2008 in the rainy season and in December 2008-January 2009 in the dry season and their variations in these two sampling periods in a remote location over the South China Sea (SCS) and at six continental locations in South China. The marine location is Yongxing Island (YX) of the Xisha Islands in SCS. The continental locations include Nancun (NC), Panyu (PY), Xinken (XK) and Mt. Maofeng (Maofengshan (MFS) in Chinese), Dongguan (DG) in...
the PRD region in Guangdong Province and Yangshuo (YS) in Guangxi Zhuang Autonomous Region. PRD, the second largest delta in China, has been one of the fastest growing economic areas for nearly 30 years and among the most polluted areas in China. PRD has a total land area of 8000 km$^2$ and a high population density. It is home to multiple mega cities including Guangzhou, Hong Kong, Shenzhen, Dongguan, Zhuhai, and Foshan. The urbanization in PRD has led to vegetation reduction, increased demand in transportation, and blooming of township enterprises, which in turn have resulted in increasingly frequent air pollution episodes (Wu et al., 2005).

Southern Mainland China is in a subtropical monsoon climate and the northern part of SCS is in a tropical monsoon climate. This region is influenced by two different monsoons, that is, SCS monsoon and Northeast monsoon. April to May is the transition period of the Northeast monsoon to the SCS monsoon. June to September is the SCS monsoon-dominated period. October is the transition period of the SCS monsoon to the Northeast monsoon. November to March is the Northeast monsoon-dominated period. October to April in the following year is the dry season in southern China as a result of the controlling influence of the northeast monsoon. May to September is the rainy season due to the dominant influence of the SCS monsoon.
3.2 Field Observations

3.2.1 Sampling locations

The Institute of Tropical and Marine Meteorology (ITMM) started to establish a monitoring network for atmospheric compositions over the PRD in 2003, and since that time a total of nine monitoring stations have been established. The observations presented in this paper include data from five long-term stations (NC, PY, XK, MFS, and DG) in PRD and two short-term stations outside PRD in South China. The station locations are shown in Figure 3.1. Among the stations, NC, PY, XK and MFS are located in different districts in the city Guangzhou, the biggest mega-city in southern China. MFS is located on the top of Mt. Maofeng (535 m ASL) and 20 km northeast to downtown Guangzhou. MFS, due to its high altitude and its rural location, represents the background condition of the PRD region. NC is a suburban site in the center of PRD, situated on the top of the highest peak (141 m ASL) in Guangzhou’s Panyu district. At 141 m ASL, this station is less impacted by ground-level local emissions, thus approximately representing the average atmospheric mixing characteristics in the PRD region. PY is an urban surface site and 7 km southwest to the NC station, representing urban conditions in Guangzhou. Due to a busy road only 140 m away from the station, significant influence of vehicular emissions is expected for the PY site. XK is a rural surface site, 60 km south to downtown Guangzhou. The prevailing northerly winds in dry season make XK a receptor site of pollution in Guangzhou. DG is in a suburban neighborhood in the city Dongguan, one of the largest manufacturing centers in China.

The two short-term observation stations are YS in Guangxi and YX Island in the middle of the South China Sea. YS is a small tourist city, surrounded by mining and metallurgical industries in the area. YX Island has an elevation of 5.6 m, an area of 1.82 km² and a population of ~500. The distance between YX Island and the center of PRD is approximately 730 km. YX Island, owing to its geographical location, represents the average situation of northern part of the South China Sea. It is noted that YX island is on the route of marine vessels travelling from middle-east, Africa and Europe to East Asia (Kaluza et al., 2010).

Observations reported in this work were carried out in two periods, May 16- June 20, 2008 in the rainy season and December 12, 2008 - January 8, 2009 in the dry season. Due to a lack of instruments, the same instrument was first deployed to YS from May 16 to May 21 then
moved to YX for the remaining rainy season observation. The instrument remained at YX for the dry season observation, thus no observation was made at YS in the dry season.

Figure 3.1 Average black carbon concentrations during rainy and dry season sampling periods across different sampling sites in column plots on the map (column plots in different maps are on the same scale and the unit of the associated numbers is µg m⁻³).

The table in the figure summarizes characteristics of the sampling sites in this study. (a) Location of the study region in China (b) Location of the two short-term sites: oceanic site at Yongxing island (YX) and the urban site Yangshuo (YS). (c) Location of the long-term sites in the Pearl River Delta, including Maofengshan (MFS), Nancun (NC), Panyu (PY), Dongguan (DG), and Xinken (XK).

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yongxing island (YX), SCS</td>
<td>Oceanic rural</td>
<td>16.83°N</td>
<td>112.33°E</td>
<td>5.6</td>
</tr>
<tr>
<td>Maofengshan (MFS), PRD</td>
<td>Rural</td>
<td>23.33°N</td>
<td>113.48°E</td>
<td>535</td>
</tr>
<tr>
<td>Nancun (NC), PRD</td>
<td>Suburban</td>
<td>23.00°N</td>
<td>113.35°E</td>
<td>141</td>
</tr>
<tr>
<td>Panyu (PY), PRD</td>
<td>Urban</td>
<td>22.93°N</td>
<td>113.32°E</td>
<td>12</td>
</tr>
<tr>
<td>Dongguan (DG), PRD</td>
<td>Suburban</td>
<td>22.97°N</td>
<td>113.73°E</td>
<td>43</td>
</tr>
<tr>
<td>Xinken, (XK), PRD</td>
<td>Rural</td>
<td>22.71°N</td>
<td>113.55°E</td>
<td>6.7</td>
</tr>
<tr>
<td>Yangshuo (YS), GX</td>
<td>Urban</td>
<td>24.77°N</td>
<td>110.50°E</td>
<td>75</td>
</tr>
</tbody>
</table>

3.2.2 Sampling instruments

In this study, six Aethalometers (AE-31-HS, AE-31-ER and AE-16-ER, Magee Scientific Company, Berkeley, CA, USA) were deployed to determine aerosol absorption
coefficients and BC concentrations. The AE-31 models measure light attenuation at seven wavelengths, i.e., 370, 470, 520, 590, 660, 880, and 950 nm. The AE-16 model has only one measurement channel at 880 nm. These instruments were operated to provide continuous observations with a time resolution of 5 min. Light attenuation measured by Aethalometers is dominated by BC, as other constituents in the atmospheric particles absorb negligible amount of solar radiation at visible and infrared range (Moosmuller et al., 2009). BC concentration is then derived from the attenuation measurement by adopting specific values for attenuation cross-section. The latter was obtained from comparison of attenuation and EC mass, which was determined to be 16.6 using a thermal analysis method developed in Lawrence Berkeley Laboratory (LBL) (also known as evolved gas analysis method) (Gundel et al., 1984) and used in the Aethalometers in reporting BC. It should be noted that Aethalometer BC is not equivalent to EC determined using the more widely adopted NIOSH or IMPROVE thermal/optical protocol. The multiplier 16.6 (specific attenuation cross-section, SACS) is an empirical conversion factor that converts attenuation to mass concentration. SACS has a different physical meaning from mass absorption efficiency (MAE), which converts absorption to mass concentration. Attenuation reported by Aethalometers suffers from sampling artifacts due to aerosol loading, filter matrix, and scattering effect (Coen et al., 2010). Therefore correction is needed to obtain absorption coefficient ($\sigma_{abs}$) from attenuation. SACS already contains information of artifacts correction and MAE. For this reason, the value of SACS is usually larger (~ 2 times higher at 550nm) than MAE and SACS cannot be directly compared with MAE reported in literature.

The Aethalometers were installed inside containers, with their inlets located 2 m above the container roof. A conductive silicone tubing (TSI, Shoreview, MN, USA) was used in the inlet system to minimize particle losses due to static charge. The Aethalometer deployed in YS and YX Island during the rainy season were equipped with a 2.5 $\mu$m cyclone while a 10 $\mu$m cyclone was used for the instruments at the other stations. The sampling flow rate was either 3 or 5 L min$^{-1}$ (Wu et al., 2009). Routine flow calibration and blank tests were performed before sampling. A threshold value of attenuation for the periodical advancing of the filter tape was set at 100.

Measurements of $\sigma_{abs}$ and BC by the Aethalometers deployed in this study are applied for a correction factor derived from an inter-instrument comparison exercise. In 2004, we made two sets of side-by-side observations, one set using an Aethalometer (880 nm) and a Photoacoustic Spectrometer (PAS, 532 nm) from Max Planck Institute in a downtown location in
Guangzhou, and the second set using an Aethalometer and a Multi-Angle Absorption Photometry (Carusso/MAAP, 637 nm) in a rural location near Guangzhou at the same time. The photo-acoustic method is more accurate in determining light absorption than the filter-based method, which may be subject to sampling artifacts linked to aerosol loading, filter matrix, and scattering effect (Coen et al., 2010). The light absorption measurement between Aethalometer and PAS is well correlated and an empirical formula as shown below is obtained (Wu et al., 2009):

$$\sigma_{\text{PAS,532nm}} = 0.51 \sigma_{\text{AE,880nm}} + 0.82$$  \hspace{1cm} 3.1

Where $\sigma_{\text{PAS,532nm}}$ is the light absorption coefficient at 532 nm measured by PAS and $\sigma_{\text{AE,880nm}}$ is the light absorption coefficient at 880 nm measured by the Aethalometer. Similarly, an empirical formula was obtained to relate BC mass measurements by MAAP and the Aethalometer (Wu et al., 2009):

$$BC_{\text{MAAP}} = 0.897 \times BC_{\text{AE}} - 0.062$$  \hspace{1cm} 3.2

$\sigma_{\text{abs}}$ reported in this work has been corrected with Eq. 3.1 while BC mass has been corrected using Eq. 3.2.

Aethalometers report both $\sigma_{\text{abs}}$ and BC. It is important to keep in mind that $\sigma_{\text{abs}}$ is what Aethalometers directly measure while BC by Aethalometer is derived from $\sigma_{\text{abs}}$ measurement assuming that Mass Absorption Efficiency (MAE) of BC aerosol is a constant during the sampling period. However, in reality MAE varies in time and space, depending on the mixing state of BC (Bond and Bergstrom, 2006). As a result, BC concentration data have additional uncertainties due to the uncertainty introduced by the constant multiplier (MAE). Data in this paper are mainly presented in the form of BC mass concentrations. The detailed results of light absorption measurements are provided as supplemental materials.

3.3 Results

3.3.1 BC time series

Hourly variations of BC and meteorological parameters during the measurement campaigns are shown in Figure 3.2a for the rainy season sampling period and Figure 3.2b for the dry season sampling period. Concentration distributions in the form of histograms are also
shown next to the respective time series plots in Figure 3.2. The histograms show that YX has the sharpest frequency distribution among all sites in both the rainy and dry season sampling periods as a result of small temporal variation in BC concentrations. The weak temporal variation characteristic confirmed the nature of YX as a super-regional background site. For most of time, BC in YX was at a low level of $\sim 0.5 \, \mu g \, m^{-3}$ in the rainy season sampling period and $\sim 0.6 \, \mu g \, m^{-3}$ in the dry season sampling period. A few concentration spikes were observed in YX during the sampling campaign. The cause of these episodic events was investigated by examining $\sigma_{abs}$ at different wavelength. Absorption Angstrom Exponent (AAE) can be considered as an indicator of mixing state. AAE of pure BC is close to 1 (Moosmuller et al., 2011) and the value increases as BC mixes with either light absorbing organic carbon (i. e., brown carbon (BrC)) (Kirchstetter et al., 2004) or non-light absorbing materials such as sulfate (Lack and Cappa, 2010). The observed average AAE in YX was 0.97 in rainy season sampling period and 1.06 in dry season sampling period (Figure 3.3). This level of AAE is lower than those found over the East China Sea (1.3) (Chung et al., 2012). The temporal variations of AAE and $\sigma_{abs}$ (Figure 3.4) show that the AAE varied from 0.5 to 2 during the sampling period, but the AAE variation was much smaller during two episodic events (14-17 December 2008 and 1-3 January 2009, highlighted in yellow in Figure 3.4). This phenomenon suggests that the elevated $\sigma_{abs}$ during the episodes were likely influenced by more “fresh soot” (such as a passing ship) in comparison to those on the regular days.

The measurements indicated that BC variations in MFS were independent of the other PRD sites in the rainy season sampling period, as shown in Figure 3.2 and also evidenced by the low inter-site correlations in Table 3.1. This result suggests that transport of BC from ground level to an altitude as high as that of MFS (435 m) was not effective. In the dry season sampling period, BC in MFS was weakly correlated with the urban sites PY and NC. The weak BC influence from the source region of PRD on MFS supports the characterization of MFS as a site representing the PRD background conditions. The BC data histogram at MFS in rainy season sampling period is different from those at the other sites, most likely related to the intermittent data at MFS (Figure 3.2a).
Table 3.1 Inter-site correlation (Pearson’s $r$) of hourly light absorption data in the Pearl River Delta Region

<table>
<thead>
<tr>
<th>Pair</th>
<th>Rainy Season</th>
<th>Dry Season</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC vs. PY</td>
<td>0.83</td>
<td>0.49</td>
</tr>
<tr>
<td>NC vs. MFS</td>
<td>-0.17</td>
<td>0.30</td>
</tr>
<tr>
<td>NC vs. DG</td>
<td>0.66</td>
<td>0.72</td>
</tr>
<tr>
<td>NC vs. XK</td>
<td></td>
<td>0.70</td>
</tr>
<tr>
<td>MFS vs. PY</td>
<td>-0.21</td>
<td>0.48</td>
</tr>
<tr>
<td>MFS vs. XK</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>MFS vs. DG</td>
<td>-0.11</td>
<td>0.17</td>
</tr>
<tr>
<td>PY vs. XK</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>PY vs. DG</td>
<td>0.65</td>
<td>0.48</td>
</tr>
<tr>
<td>XK vs. DG</td>
<td></td>
<td>0.77</td>
</tr>
</tbody>
</table>
Figure 3.2 Time series of BC hourly concentrations, temperature, atmospheric pressure, wind speed, and precipitation
(a) rainy season sampling period (b) dry season sampling period. The bar plots overlaying on the BC plots at YX and PY show the mixing height from balloon measurements. The histograms shown to the right of BC time series plots are the frequency distributions of BC concentrations. In the temperature time series plots, the red curve is measurements for Baiyun airport, 17 km west to MFS, and is considered to represent meteorological conditions in the northern part of PRD; the green curve is for NC and the purple curve is for XK. In the station pressure plots, the grey areas represent XK and the light blue for NC. In the wind speed plots, red is for the Baiyun airport, purple for XK. In the precipitation plots, grey bars are for XK and light blue for urban Guangzhou.
Figure 3.3 Distribution of Absorption Angstrom Exponent (AAE) values at YX. (a) Rainy season and (b) Dry season.
Figure 3.4 Time series variations (5 min data) of: (a) Absorption Angstrom Exponent (AAE) at YX during rainy season; (b) $\sigma_{\text{abs}}$ at seven wavelengths at YX during rainy season; (c) AAE at YX during dry season; (d) $\sigma_{\text{abs}}$ at seven wavelengths at YX during dry season. The highlighted areas mark two episodic events observed during dry season.
NC, located at an altitude of 141 m, could represent the average mixing conditions of air pollutants in the urban region of Guangzhou. This is supported by the high correlations of BC at NC with BC at PY, XK and even DG (Table 3.1). In the rainy season sampling period, the BC variation trend at NC is very similar to those at PY and DG, and the latter two areas are among the major BC source regions in PRD. In the dry season sampling period, BC variation trend at NC was similar to that at DG and a higher inter-site correlation was observed between the two sites ($r$: 0.72 in the dry season vs. 0.66 in the rainy season sampling period).

By comparison, the less removal of BC in the dry season sampling period makes the diurnal variations of BC at PY more closely track the diurnal pattern of transportation emissions. As a result, a broader concentration distribution histogram was observed at PY in the dry season sampling period than at other sites, consistent with the site characteristic of PY being in close proximity to sources. Variation in mixing height plays an important role in affecting BC concentrations for the urban sites. The most severe episodes at PY recorded during the two sampling periods were all associated with low mixing heights. During 30 May to 1 June, BC concentration was extremely high (peak concentration close to 40 μg m$^{-3}$) and the mixing height, obtained through balloon sounding in Guangzhou, was only 500 m (approximately half of those on regular days) (Figure 3.2a). Similar episodic events recorded during 26-29 December during the dry season sampling period were observed to coincide with low mixing height, which was only 200 ~300 m (Figure 3.2b).

At XK, a much smaller percentage of valid data was obtained in the rainy season sampling period due to instrument problems. Consequently, only measurements in the dry season sampling period are discussed for XK. In the dry season sampling period, the prevailing northeasterly wind in the PRD region places XK downwind of both DG and NC. BC in XK was well correlated with DG and NC during the dry season sampling period, consistent with the source-receptor relationship among the sites. It is also noted that higher BC level was observed at the rural site XK than that at the suburban surface site DG. This may suggest that there were additional strong BC sources impacting XK.
3.3.2 Spatial variation in BC

The spatial variation in seasonal average BC concentrations is shown in Figure 3.1, with the highest BC occurring at the surface sites in the PRD, followed by the sites at elevated altitudes (i.e., NC and MFS), and the lowest BC at the oceanic site YX Island. The limited measurements of BC in YS, Guangxi in the rainy season sampling period indicated the average BC (6.93 μg m⁻³) at this site is comparable to those observed at the PRD urban locations. The BC level in YS is unexpectedly high, considering it is mainly a tourist town. The sampling site at YS was near a major road (~130 m). Local transportation emissions could be a significant source of measured BC. Emissions from nearby mining and metallurgical industries may have an impact on BC level as well. It is not possible to further speculate the relative contributions of local and regional sources due to the short measurement period and lack of other measurements at YS. The daily average concentration of BC varied from 0.21 to 2.14 μg m⁻³ at the oceanic site YX Island, 0.71 to 5.43 μg m⁻³ at the PRD regional background site MFS, 2.33 to 15.97 μg m⁻³ at the elevated site NC, and 1.56 to 37.9 μg m⁻³ among the ground sites in South China. In the dry season sampling period, the average BC reached as high as 12.31 μg m⁻³ at the three PRD ground sites (PY, XK, and DG) and 7.68 μg m⁻³ at the elevated NC site, much higher than the average level (2.88 μg m⁻³) observed at MFS, the mountaintop site. The same vertical spatial gradient was observed in the rainy season sampling period.

Table 3.2 compares BC mass concentrations as measured by Aethalometers in this study with those reported in the literature for other locations. The overall campaign average of BC at the four PRD urban/rural receptor sites is 9.48 μg m⁻³. As shown in Table 3.2, BC in the PRD is not the highest among urban areas in China, but the level is much higher than urban areas elsewhere in the world, such as Paris (1.66 μg m⁻³) (Healy et al., 2012), New York (1.38 μg m⁻³) (Venkatachari et al., 2006), and Mexico City (3.4 μg m⁻³) (Salcedo et al., 2006).

The campaign average of BC at MFS is similar to the level reported for rural locations in China, such as Hong Kong (2.4 μg m⁻³) (Cheng et al., 2006a) and Beijing (2.12 μg m⁻³ by (Yan et al., 2008) and 2.37 μg m⁻³ by (Zhou et al., 2009).

The BC level at YX Island is comparable to those reported for coastal areas in Europe, such as Baltic Sea (0.6 μg m⁻³) (Bycenkiene et al., 2011) and Mediterranean (~0.7 μg m⁻³) (Saha and Despiau, 2009), but higher than those observed over southwest Indian Ocean (0.43 μg m⁻³) (Bhugwant et al., 2000) and the Pacific Ocean (0.006 μgm-3, Bodhaine, 1995). The higher BC
at YX may partially be attributed to emissions from passing-by marine vessels (Kaluza et al., 2010).

Table 3.2 Comparison of BC concentrations (μg m\(^{-3}\)) obtained by Aethalometers at different locations in the world.

<table>
<thead>
<tr>
<th>Location</th>
<th>Site Characteristics</th>
<th>Sampling Period</th>
<th>Inlet</th>
<th>BC mass</th>
<th>Correction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yongxing Island (YX), China</td>
<td>Oceanic rural, (South China Sea) Rural</td>
<td>May-Jun 2008 Dec 2008-Jan2009</td>
<td>PM(_{10})</td>
<td>0.54</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Maofengshan (MFS), Guangzhou, China</td>
<td>Rural, (Pearl River Delta)</td>
<td>May-Jun 2008 Dec 2008-Jan2009</td>
<td>PM(_{10})</td>
<td>2.62</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Nancun (NC)</td>
<td>Suburban, (Pearl River Delta)</td>
<td>Dec 2008-Jan2009 May-Jun 2008</td>
<td>PM(_{10})</td>
<td>2.88</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Panyu (PY), Guangzhou, China</td>
<td>Urban, (Pearl River Delta)</td>
<td>Dec 2008-Jan2009 May-Jun 2008</td>
<td>PM(_{10})</td>
<td>8.42</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Dongguan(DG), China</td>
<td>Suburban, (Pearl River Delta)</td>
<td>Dec 2008-Jan2009 May-Jun 2008</td>
<td>PM(_{10})</td>
<td>10.11</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Xinken (XK), Guangzhou, China</td>
<td>Rural, (Pearl River Delta)</td>
<td>Dec 2008-Jan2009</td>
<td>PM(_{10})</td>
<td>12.61</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Yangshuo (YS), China Hong Kong, China</td>
<td>Urban (Guangxi) Coastal Rural (Pearl River Delta)</td>
<td>May-Jun 2008 Jun 2004- May 2005</td>
<td>PM(<em>{1.3}), PM(</em>{2.5})</td>
<td>6.93</td>
<td>Yes</td>
<td>Cheng et al. (2006a)</td>
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<tr>
<td>Makou Loa, USA</td>
<td>Oceanic rural (Pacific Ocean)</td>
<td>1990-1993 /</td>
<td>0.006</td>
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<tr>
<td>Toulon, France</td>
<td>Urban Coastal (Mediterranean)</td>
<td>2005 Winter</td>
<td>PM(_{1.3})</td>
<td>0.95</td>
<td>No</td>
<td>Saha and Despias (2009)</td>
</tr>
<tr>
<td>La Réunion Island, French</td>
<td>Urban Coastal (Indian Ocean)</td>
<td>Nov 1996 Apr, Sep 1998 /</td>
<td>0.43</td>
<td>No</td>
<td>Bhagwant et al. (2000)</td>
<td></td>
</tr>
<tr>
<td>Preila, Lithuania</td>
<td>Coastal Rural (Baltic Sea)</td>
<td>2008-2009</td>
<td>PM(_{1.3})</td>
<td>0.6</td>
<td>No</td>
<td>Bycenkiene et al. (2011)</td>
</tr>
<tr>
<td>Shangdianzi, China</td>
<td>Rural (Beijing, North China Plain)</td>
<td>Apr2003-Jan2005 TSP</td>
<td>2.12</td>
<td>Yes</td>
<td>Yan et al. (2008)</td>
<td></td>
</tr>
<tr>
<td>Changping, China</td>
<td>Rural (Beijing, North China Plain)</td>
<td>Jun-Jul 2005</td>
<td>PM(_{1.3})</td>
<td>2.37</td>
<td>No</td>
<td>Zhou et al. (2009)</td>
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<tr>
<td>Taicang, China</td>
<td>Suburban (Shanghai Yangtze delta)</td>
<td>May-Jun 2005</td>
<td>PM(_{1.3})</td>
<td>5.47</td>
<td>No</td>
<td>Cao et al. (2009)</td>
</tr>
<tr>
<td>Xi’an, China</td>
<td>Suburban (Guanzhong Plain)</td>
<td>Sep 2003- Aug 2005</td>
<td>PM(_{1.3})</td>
<td>14.7</td>
<td>No</td>
<td>Cao et al. (2009)</td>
</tr>
<tr>
<td>Fresno, USA</td>
<td>Urban</td>
<td>Jan-Dec 2000</td>
<td>PM(_{1.3})</td>
<td>1.17</td>
<td>No</td>
<td>Watson and Chow (2002)</td>
</tr>
<tr>
<td>New York, USA</td>
<td>Urban</td>
<td>Jan-Feb 2004 /</td>
<td>1.38</td>
<td>No</td>
<td>Venkatachali et al. (2006)</td>
<td></td>
</tr>
<tr>
<td>Paris, France</td>
<td>Urban</td>
<td>Jan-Feb 2010</td>
<td>PM(_{1.3})</td>
<td>1.66</td>
<td>Yes</td>
<td>Healy et al. (2012)</td>
</tr>
<tr>
<td>Mexico City, Mexico</td>
<td>Urban</td>
<td>Apr 2003</td>
<td>PM(_{1.3})</td>
<td>3.4</td>
<td>No</td>
<td>Salcedo et al. (2006)</td>
</tr>
<tr>
<td>Tomsk, Russia</td>
<td>Urban</td>
<td>Summer 1997-2008</td>
<td>PM(_{1})</td>
<td>1.9</td>
<td>No</td>
<td>Kozlov et al. (2011)</td>
</tr>
</tbody>
</table>

*Correction refers to amendment of Aethalometer measurements due to sampling artifacts related to aerosol loading, filter matrix and scattering effect (Coen et al., 2010).*
3.3.3 Seasonal variation in BC

For the understanding of seasonal variation of BC, variations in mixing height, monthly average wind flow patterns, and air mass origins are examined. Mixing height data by balloon sounding are available at YX and Guangzhou. The distributions of mixing height data in the two measurement periods are plotted in Figure 3.5. Seen from Figure 3.5, the mean values of the mixing height at GZ were similar (~1070 m in the rainy season sampling period and ~1050 m in the dry season sampling period), while the most probable mixing heights in the two seasons differed by ~340 m (1420 vs. 1080 m, respectively). The mean values of the mixing height at YX were 650 m in the rainy season and ~800 m in the dry season sampling period. It appears that the seasonal variation in mixing height was unlikely the driving factor for the observed BC difference in the two sampling periods (Figure 3.1).

Figure 3.5 Frequency distribution of measured mixing height data by balloon sounding.
Figure 3.6 shows the monthly average wind stream patterns for June and December 2008. The wind stream patterns for other months in 2008 are also examined and shown in Figure 3.7. April to May is the transition period of the Northeast monsoon to the SCS monsoon, with wind shifting from northeast to southwest over SCS. Under the dominant influence of the SCS monsoon, June to September show highly similar wind patterns, with southwest prevailing wind over SCS. November to March, mainly under the influence of the Northeast Monsoon, share similar air flow patterns, with Northeast prevailing wind over SCS. Thus, the two sampling periods in our study represent the typical wind patterns of their corresponding seasons.

During the rainy season PRD was significantly affected by two different air flows. For most of the time, PRD was affected by the southerly air flow that originated from the vast ocean. On a few days PRD was affected by the northeasterly air flow, which was related to specific weather systems such as typhoons and troughs. For example, during 15-22 May 2008, the tropical typhoon Halong (Figure 3.8) was approaching the Philippines, and this large-scale weather system shifted the prevailing wind in PRD to northeasterly. During the dry season, PRD was influenced by the strong northeast monsoon, which brought polluted air masses from the more economically-developed regions in the eastern Asia. The reversed wind fields in the rainy and dry seasons result in different dispersion conditions in the PRD region.
Figure 3.6 South China Sea monthly average wind stream maps. (a) June 2008, South China Sea monsoon and (b) December 2008, Northeast monsoon
Figure 3.7 Individual monthly average wind streams of East Asia in 2008
Air mass origins were surveyed through plotting air mass back trajectories at the sampling locations for all sampling days using data by the HYSPLIT-4 model (Draxler and Rolph, 2012). YX (16.33°N, 112.83°E), MFS (23.33°N, 113.48°E) and NC (23.00°N, 113.36°E) are selected as the reference points for the back trajectories calculation to represent the northern part of SCS and the PRD region. Height of 150 m is chosen to track the path of air masses which would eventually arrive at the NC and YX in the previous 72 h while for MFS the height was set as 535 m to represent the real situation. Figure 3.9 shows the back trajectories of air masses arriving at YX, MFS, and NC in both rainy and dry season sampling periods. Back trajectories at different heights are also tested. The overall patterns are very similar at different altitudes within the mixing height. The ensemble of back trajectories is also consistent with the monthly average wind stream.
Figure 3.9 The back trajectories (72h) of the air masses arriving at Yongxing Island and the Pearl River Delta at 8:00 am local time on each day. (a) Yongxing (YX) island (150 m ASL) from May 16 2008 to June 20 2008; (b) Yongxing (YX) Island (150 m ASL) from December 12 2008 to January 8 2009; (c) Maofengshan (MFS) (535 m ASL) from May 16 2008 to June 20 2008; (d) Maofengshan (MFS) (535 m ASL) from December 12 2008 to January 8 2009; (e) Nancun (NC) (150 m ASL) from May 16 2008 to June 20 2008; (f) Nancun (NC) (150 m ASL) from December 12 2008 to January 8 2009.

As seen from the BC measurements, the monsoon system has a significant impact on the seasonal contrast in BC loading in the PRD urban region. Strong seasonal variations were seen at the ground sites (PY and DG) and the elevated site (NC) in PRD where measurements were available in both the rainy and dry seasons. The BC concentrations were significantly higher in the dry season sampling period, with an average of 12.31 μg m⁻³ in the dry season.
sampling periods and 6.17 μg m$^{-3}$ in the rainy season sampling period. In the rainy season sampling period, stronger dispersion condition (wind speed: 2.91 vs. 2.15 m s$^{-1}$ in the rainy season vs. dry season sampling period) along with abundant rainfall, resulted in stronger removal of BC from the atmosphere in the source region. The total precipitation was ~450 mm in the rainy sampling period, accounting for ~30% of the annual precipitation. The BC concentration decreased during rain events (Figure 3.2a), indicating that wet deposition was one cause for lower BC in the rainy season sampling period. Take the rain event on 6-7 June 2008 (78 mm rainfall from 3:00 to 6:00 next day) as an example. The average BC concentration in the 24-h before rain was 5.87 μg m$^{-3}$ at NC and 9.47 μg m$^{-3}$ at PY. During the 27-h rain event, the BC concentration dropped to 2.73 μg m$^{-3}$ at NC and 5.28 μg m$^{-3}$ at PY.

In comparison, the variations of BC between the two sampling periods at MFS were small, i.e., 2.62 μg m$^{-3}$ in the rainy season sampling period vs. 2.88 μg m$^{-3}$ in the dry season sampling period. In the dry season MFS is upwind of the PRD region, making it an indicator for super-regional transport (i.e., transport from outside the PRD region). Considering that air masses during cold front are cleaner as they come from high altitude, the BC average excluding cold front days would be more appropriate to represent the influence from eastern China in dry season. This concentration (3.19 μg m$^{-3}$) is 20% higher than the rainy season sampling period (2.62 μg m$^{-3}$). This may imply that super-regional transport is not the major cause for elevated BC observed at the PRD urban areas in the dry season. The higher abundance of BC in the air may be associated with weaker dispersion conditions in dry season (Wu et al., 2008a), including wind speed reduction (~35% lower than the rainy season sampling period in this study).

The seasonal variation of BC at YX Island was small, with an average BC of 0.54 μg m$^{-3}$ in the rainy season sampling period and 0.67 μg m$^{-3}$ in the dry season sampling period. In the rainy season, the north-central area of the South China Sea was mainly controlled by the South China Sea monsoon, which originated from the vast ocean. Occasionally in the rainy season, YX Island is under control of the northerly air flow related to the weather system activity, such as the period of 15-22 May (Figure 3.9). In the dry season YX is downwind of East China Sea, Taiwan Strait and part of the coastal areas of eastern China. The difference in air mass origins may explain the slightly higher BC level in the dry season than the rainy season sampling period.
3.3.4 BC Diurnal variation

Diurnal variations of BC are shown in Figure 3.10 for the rainy and dry season sampling periods. Two cold front events occurred during the sampling period, evidenced by elevated station pressure, rapid drop in temperature, and stronger wind (Figure 3.2b). During the two cold front periods (period A: 22 – 24 December 2008; period B: 29 December 2008 – 3 January 2009), the diurnal pattern was very different from the overall diurnal pattern in dry season sampling period, so the cold front diurnal pattern is plotted separately in Figure 3.10.

A discernible diurnal pattern in BC was observed at the continental urban/suburban sites in that BC concentrations were higher at night and there was a small peak in the early morning. The lowest BC usually occurred in early afternoon in both the rainy and dry season sampling periods. This observation is consistent with observations reported in the previous studies conducted in PRD region (Andreae et al., 2008; Garland et al., 2008; Verma et al., 2010). Higher BC in night is a combined result of lower mixing height after sunset and increased emissions from diesel trucks in the evening, which are associated with the traffic regulation in this region (Garland et al., 2008). In the dry season sampling period, the evening peak at DG and XK was more pronounced and broader than the morning peak, with the evening peak extending to overlap the morning peak.
Figure 3.10 Diurnal variations of BC concentrations at six monitoring sites in the rainy sampling period, dry season sampling period, and during cold front periods. The error bars represent one standard deviation. The sites are (a) Yongxing Island (YX), (b) Maofengshan (MFS), (c) Nancun (NC), (d) Panyu (PY), (e) Dongguan (DG), (f) Xinken (XK) in dry season sampling period and Yangshuo (YS) in rainy season sampling period.

Passing cold fronts usually bring strong wind and air from high attitudes to the PRD region, resulting in significant reductions in BC concentrations, which were observed across all the PRD sites as shown in Figure 3.2b. During the cold front periods, the evening BC peak was larger than the morning peak at all PRD sites, which may be attributable to two causes. First, the activity intensity of heavy duty vehicles in nighttime was as high as daytime in Guangzhou urban areas till midnight (Verma et al., 2010). Second, the nighttime wind speed was weaker than daytime and the mixing height was lower in nighttime. These two factors acted together, making the nighttime peak more pronounced than the morning peak. As the strong wind during the cold front events would effectively carry away pollutants, providing an opportunity to reveal the fresh local emission pattern in one day. This pattern of peaking in the evening is consistent with the heavy duty vehicles activity pattern in urban Guangzhou (6:00–24:00), as reported by
Verma et al. (2010), implying the significance of BC emissions from the transportation sector. The identical diurnal pattern in DG and XK was consistent with their high inter-site correlation in the dry season sampling period \( r = 0.77 \).

At MFS, the PRD background site, the diurnal pattern in the dry season sampling period was very similar to those at the urban/suburban sites in PRD, but the diurnal pattern in the rainy season sampling period was hardly discernible.

A diurnal variation pattern in BC was discernible at YX, likely a result of operation pattern in the local diesel generator for power. The period with elevated BC coincided with the office hours (LT 7:00-12:00 and 14:00-18:00). During the non-office hours, BC was almost flat. The two peaks of BC were higher in the dry season sampling period.

### 3.3.5 BC Light absorption

Light absorption coefficients \( (\sigma_{\text{abs}}) \) data are summarized for the dry and rainy season sampling periods separately in Table 3.3 and compared in Figure 3.11. Daily average \( \sigma_{\text{abs}} \) across all sites varied from 4 to 352 \( \text{Mm}^{-1} \) during the sampling campaign. The continent average of \( \sigma_{\text{abs}} \) was tenfold that at the oceanic site YX Island. \( \sigma_{\text{abs}} \) observations in this study are compared with those reported in previous studies in Table 3.3. \( \sigma_{\text{abs}} \) in Guangzhou during the dry season sampling period of 2009 was significantly higher than those measured in 2004 for both urban (188 \( \text{Mm}^{-1} \) in 2009 vs. 91 \( \text{Mm}^{-1} \) in 2004) and rural (119 \( \text{Mm}^{-1} \) in 2009 vs. 70 \( \text{Mm}^{-1} \) in 2004) sites (Andreae et al., 2008; Cheng et al., 2008). The observed \( \sigma_{\text{abs}} \) at MFS, a background site in PRD, was 26 \( \text{Mm}^{-1} \) in the rainy season sampling period and 29 \( \text{Mm}^{-1} \) in the dry season sampling period, lower than previous observations in the northern rural area of city Guangzhou (42.5 \( \text{Mm}^{-1} \)) (Garland et al., 2008), comparable to those found in Yangtze Delta (23 \( \text{Mm}^{-1} \)) (Xu et al., 2002) and in North China Plain (17.5 \( \text{Mm}^{-1} \)) (Yan et al., 2008), but higher than those in South East Asia (15 \( \text{Mm}^{-1} \)) (Li et al., 2012). The \( \sigma_{\text{abs}} \) observed at the PRD urban area is much higher than those in urban areas around the world, e.g., Mexico City (Marley et al., 2009), Tokyo (Nakayama et al., 2010) and a few US cities (Chow et al., 2009; Thompson et al., 2012).
Figure 3.11 Average light absorption coefficients ($\sigma_{abs}$) in Mm$^{-1}$ during rainy and dry seasons across different sampling sites in column plots on the map (column plots in different maps are on the same scale).

The enclosed table summarizes the characteristics of sampling sites in this study. (a) Location of the study region in China, (b) Location of two short-term sites: the oceanic site at Yongxing island (YX) and the urban site Yangshuo (YS). (c) Location of the long-term sites in PRD, including Maofengshan (MFS), Nancun (NC), Panyu, (PY), Dongguan (DG), Xinken(XK).
Table 3.3 Comparison of light absorption measurements (Mm⁻¹) at different locations in the world

<table>
<thead>
<tr>
<th>Location</th>
<th>Site characteristics</th>
<th>Sampling Duration</th>
<th>Inlet</th>
<th>Method</th>
<th>(\sigma_{abs, std} @ \text{wavelength} )</th>
<th>Correction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yongxing Island (YY2)</td>
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<td>PM1.5</td>
<td>AE</td>
<td>7.21±0.23@532nm²</td>
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<td>This work</td>
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<td>Dec 2008-Jan 2009</td>
<td>PM1.5</td>
<td>AE</td>
<td>8.37±0.88@532nm²</td>
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<td>Guangzhou, China</td>
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<td>May-Jun 2008</td>
<td>PM1.5</td>
<td>AE</td>
<td>26.45±1.88@532nm²</td>
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<td>53.47±3.24@532nm²</td>
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<td>PM1.5</td>
<td>AE</td>
<td>73.10±4.64@532nm²</td>
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<td>Wu et al. (2009)</td>
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<td>Nancun (NC), Guangzhou, China</td>
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<td>2004-2007 (Dry season)</td>
<td>PM1.5</td>
<td>AE</td>
<td>47.10±3.44@532nm²</td>
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<td>PM1.5</td>
<td>PAS</td>
<td>91±60@532nm /</td>
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<td>Xinken, Guangzhou, Rural</td>
<td>4 Oct -5 Nov 2004</td>
<td>PM1.5</td>
<td>MAA</td>
<td>70±42@550nm /</td>
<td></td>
<td></td>
<td>Cheng et al. (2008)</td>
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<tr>
<td>Backgarden, Rural</td>
<td>June 2006</td>
<td>PM1.5</td>
<td>PAS</td>
<td>42.5±5.6 @532nm /</td>
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<td>Hong Kong, China</td>
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<td>May-Jun 1998</td>
<td>TSP</td>
<td>PSAP</td>
<td>7.65 @565nm /</td>
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<td>Mauna Loa, USA</td>
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<td>1990-1993</td>
<td>/</td>
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<td>0.058±0.050nm /</td>
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<td>Barrow, USA</td>
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<td>1988-1993</td>
<td>/</td>
<td>AE</td>
<td>0.41±0.550nm /</td>
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<td>Apr 2003-Jan 2005</td>
<td>TSP</td>
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<td>47±8@617nm² /</td>
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<td>China Plain)</td>
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<td>P</td>
<td>43@27±637nm² /</td>
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<td>(Yangtze)</td>
<td>Nov 1999</td>
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<td>2 Nov 2009-2010</td>
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<td>MAA</td>
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<td>Aug 2007</td>
<td>/</td>
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<td>Pasadena, CA, USA</td>
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<td>PM1.5</td>
<td>AM</td>
<td>4±532nm /</td>
<td></td>
<td>Thompson et al. (2012)</td>
</tr>
</tbody>
</table>

1AE: Aethalometer; PAS: Photo Acoustic Spectrometer; MAAP: Multi Angle Absorption Photometer; PSAP: Particle Soot Absorption Photometer; AM: Albedo Meter
2\(\sigma_{abs}\) reported at 532 nm is calculated from 880 nm measurement following an empirical formula reported by Wu et al. (2009).
3\(\sigma_{abs}\) reported at 550 nm by Cheng et al. (2008) was calculated from MAAP measurement at 630 nm following power law, assuming AAE of soot to be 1.
4During the GAW2005 workshop, it was reported that the operation wavelength of MAAP was 637 nm rather than 670 nm as stated by the manufacturer (Müller et al., 2011).
5\(\sigma_{abs}\) at 532 nm was calculated from PSAP measurement at 565 m following the power law (assuming AAE of soot to be 1).
6The MAAP result was converted to 550 nm using the power law. The absorption Angstrom coefficients were obtained from 7λ Aethalometer (Marley et al., 2009).
7Correction refers to amendment of measurements due to sampling artifacts related to aerosol loading, filter matrix and scattering effect for the filter based instrument (e.g. AE, PSAP) (Coen et al., 2010).
3.4 Summary

We report in this work the observations of BC concentrations and absorption coefficients ($\sigma_{abs}$) by Aethalometers in Yongxing Island of South China Sea (a superregional background site) and five continental locations in southern China mainland during two sampling periods in the rainy season and dry season of 2008. BC loading at the South China Sea background site showed little difference between the two sampling periods, with an average of 0.54 $\mu$g m$^{-3}$ in the rainy season sampling period and 0.67 $\mu$g m$^{-3}$ in the dry season sampling period. Light absorption at YX is comparable but slightly higher than other coastal areas around the world. The BC level at the PRD background site (Maofengshan at 535 m ASL) also had a small difference, with 2.88 $\mu$g m$^{-3}$ in the dry season and 2.62 $\mu$g m$^{-3}$ in the rainy season sampling period. The level at this regional background site is very similar to those found in North China Plain. The average concentration of BC in the PRD urban area is 12.31 $\mu$g m$^{-3}$ in the dry season sampling period and a significantly lower level (6.17 $\mu$g m$^{-3}$) was found in the rainy season sampling period. The BC level in the PRD region is much higher than other urban areas around the world. Inter-site correlation analysis of BC measurements reveals that temporal variations of BC were correlated between certain sites. The strength of the correlations showed seasonal dependency, implying that the monsoon systems play an important role in transport and spatial distribution of BC. A diurnal pattern of higher BC concentrations was observed at night at most of the PRD sites and at some sites a small peak in the early morning was observed. Our analysis suggests that the diurnal variation pattern is mainly a result of vehicular emissions.
Chapter 4
4. Determination of Primary combustion source OC/EC ratio using ambient OC and EC measurements: Secondary OC-EC correlation minimization method

Chapter summary
Elemental carbon (EC), due to its exclusive origin in primary combustion sources, has been widely used as a tracer to track the portion of co-emitted primary organic carbon (OC) and, by extension, to estimate secondary OC (SOC) from ambient observations of EC and OC. Key to this EC tracer method is to determine an appropriate OC/EC ratio that represents primary combustion emission sources (i.e., (OC/EC)_pri) at the observation site. The conventional approaches include regressing OC against EC of a fixed percentile of the lowest (OC/EC) ratio data (usually 5-20%) or relying on a subset of sampling days dominated by local emissions and under conditions of low photochemical activities. The serious drawback of these approaches is rooted in its empirical nature, i.e., a lack of clear quantitative criteria in the selection of data subsets for the (OC/EC)_pri determination. We examine here a method that derives (OC/EC)_pri through calculating a hypothetical set of (OC/EC)_pri and SOC followed by seeking the minimum of the coefficient of correlation (R^2) between SOC and EC. The hypothetical (OC/EC)_pri that generates the minimum R^2(SOC,EC) would then represent the actual (OC/EC)_pri ratio if variations of EC and SOC were independent. We term this approach as the Minimum R Squared Method (MRS) and it has a clear quantitative criterion for (OC/EC)_pri calculation. The general concept embodied in the MRS method was initially proposed by Millet et al. (2005), but this method has not been evaluated of its accuracy or utility since its debut. This work describes numerical experiments set out to evaluate the accuracy of SOC estimation by the MRS method and compare with two commonly used methods, minimum OC/EC (OC/EC_{min}) and OC/EC percentile (OC/EC_{10%}). EC and OC with known proportion of SOC, all assumed to be log-normally distributed, are numerically produced through Mersenne twister pseudorandom number generator. Three scenarios are considered, including a single primary source, two independent primary sources, and two correlated primary sources. Among the three methods, the MRS method consistently produces SOC estimates of the best accuracy. Unbiased SOC estimation by OC/EC_{min} and OC/EC_{10%} only valid when the left tail of OC/EC distribution happened situated at the position of (OC/EC)_pri distribution peak. However, such an assumption
is fortuitous rather than norm. In contrast, MRS can provide unbiased SOC estimation since it is insensitive to the relative position of OC/EC and (OC/EC)_{pri} distributions. Sensitivity test on measurement uncertainty demonstrate the superior accuracy of MRS to the other two approaches on SOC estimation.

4.1 Introduction

Organic Carbon (OC) and Elemental Carbon (EC) are among the major components of fine particular matter (PM$_{2.5}$) (Malm et al., 2004). EC is a product of carbon fuel-based combustion processes and is exclusively associated with primary emissions whereas OC can be from both direct emissions and be formed through secondary pathways. Differentiation between primary organic carbon (POC) and secondary organic carbon (SOC) is indispensable for probing atmospheric aging processes of organic aerosols and formulating effective emission control policies. However, direct SOC measurement is not yet feasible, as there lacks knowledge of its chemical composition at the molecular level. Due to its exclusive source origin in primary combustion sources, EC was first proposed by Turpin and Huntzicker (1991) to serve as the tracer to track POC from primary combustion sources and, by extension, to estimate SOC as SOC is simply the difference between OC and POC. This EC tracer method only requires OC and EC measurement. Its simplicity has led to wide adoption in studies reporting ambient OC and EC measurements (e.g., Castro et al., 1999; Cao et al., 2004; Yu et al., 2004b).

The key issue to the EC tracer method is to determine an appropriate OC/EC ratio that represents primary combustion emission sources (i.e., (OC/EC)_{pri}) at the observation site. A number of approaches have been used to derive (OC/EC)_{pri}. One approach is to regress OC vs. EC in a fixed percentile subset of data with the lowest OC/EC ratio (usually 5-20%) (Lim and Turpin, 2002; Lin et al., 2009). The second approach is to rely on data collected on a subset of sampling days dominated by local emissions and under conditions of low photochemical activities (Turpin and Huntzicker, 1995). These approaches have the drawback in that there is not a clear quantitative criterion in the selection of data subsets for the (OC/EC)_{pri} determination. Millet et al. (2005) was the first to propose an algorithm that explores the inherent anti-correlation between pollutants from primary emissions (e.g., EC) and products of secondary formation processes (e.g., SOC) to derive the primary ratios for species with multiple source types (e.g., (OC/EC)_{pri}). More specifically, for the determination of (OC/EC)_{pri}, the assumed (OC/EC)_{pri} value is varied continuously. At each hypothetical (OC/EC)_{pri}, SOC is calculated for the data set and a correlation coefficient value ($R^2$) of EC vs. SOC (i.e., $R^2(\text{EC}, \text{SOC})$) is
generated. The series of $R^2$ (EC, SOC) values are then plotted against the assumed $(OC/EC)_{pri}$ values. If variations of EC and SOC are independent, the assumed $(OC/EC)_{pri}$ corresponding to minimum $R^2$(EC,SOC) would then represent the actual $(OC/EC)_{pri}$ ratio. Such an approach obviates the need for an arbitrary selection criterion, as the algorithm seeks the minimum point, which is unique to the data set. Hereafter for the convenience of discussion, we call this method minimum $R$ squared (MRS) method.

With ambient OC and EC samples, accuracy of SOC by different $(OC/EC)_{pri}$ estimation methods is difficult to evaluate due to the lack of direct SOC measurement. The objective of this study is to investigate, through numerical simulations, the bias of SOC estimates by three different implementations of the EC tracer method. Hypothetical EC, $(OC/EC)_{pri}$, POC, and SOC values are generated by a computer program, then the SOC estimates are compared with the “true” SOC as defined by the synthetic datasets. As such, quantitative uncertainty assessment can be achieved.

### 4.2 EC tracer methods

If OC and EC concentrations are available and primary OC from non-combustion sources is negligible, SOC can be estimated using EC as the tracer for combustion source POC(Turpin and Huntzicker, 1995):

\[
OC_{pri} = (OC/EC)_{pri} \times EC + OC_{non}
\]

\[
SOC = OC_{total} - (OC/EC)_{pri} \times EC
\]

where $(OC/EC)_{pri}$ is the OC/EC ratio in freshly emitted combustion aerosols, and $OC_{total}$ and EC are available from ambient measurements. The key step of the EC tracer method is therefore to identify an appropriate $(OC/EC)_{pri}$ ratio that represents primary emissions impacting the sampling site.

Various approaches in deriving $(OC/EC)_{pri}$ reported in the literature are either based on emission inventory(Gray et al., 1986) or ambient observation data. In the ambient measurements-based approach, three methods are commonly used in previous studies: (1) Using a subset data that are collected when OC and EC are dominated by local emissions and under conditions of low photochemical activities (Turpin and Huntzicker, 1995). (2) Taking the minimum OC/EC ratio during the study period to approximate $(OC/EC)_{pri}$ (Castro et al., 1999). (3) Selecting a reasonable percentile subset of the lowest OC/EC data to represent primary emission dominated samples. The selection of percentile subset is arbitrary due to a lack of quantitative criteria, and 5-20% have been reported (Lin et al., 2009; Lim and Turpin,
In comparison, the MRS Method as described in the previous section (Millet et al., 2005) has largely been overlooked, with only one study reporting its use (Hu et al., 2012) since its debut. This was likely a result of a lack of information on its method performance in combination with that its basis relying on the correlation of SOC with EC is less straightforward.

A conceptual illustration of the MRS method is shown in Figure 4.1, using a set of 7217 hourly ambient measurements at a suburban location in the Pearl River Delta region (PRD), China made in a period of one year. A brief account of the field ECOC analyzer and its field operation is provided in the supplemental information (SI) document. Detailed description of the measurement results and data interpretation at this site are discussed in Chapter 5.

![Figure 4.1 Illustration of the minimum R squared method (MRS) to determine OC/ECpri using one year’s hourly OC and EC measurements at a suburban site in the Pearl River Delta, China. The red curve shows the correlation coefficient ($R^2$) between SOC and EC as a function of assumed OC/ECpri. The black curve is the frequency distribution of OC/EC ratio for the entire OC and EC data set. The shaded area in tan represents the accumulative frequency curve of OC/EC ratio.](image-url)
4.3 Evaluation of Minimum R Squared Method: numerical studies

The objective of this study is to evaluate the uncertainty in estimating SOC by the various EC tracer implementation methods through conducting numerical experiments in that EC and OC (with known break-down of POC and SOC) are numerically synthesized. Different algorithms are then applied to the “synthesized” OC and EC data sets to derive (OC/EC)_{pri} then SOC.

4.3.1 Data generation

We first examine ambient OC and EC for the purpose of identifying distribution features that can serve as the reference basis for parameterization in the numerical experiments. Hourly EC and OC measurement data for a year at three sites in PRD, one suburban site in Guangzhou, a general urban site and a roadside site in Hong Kong, with more than 7000 data at each site, are plotted in Figure 4.2-4.6 with both entire data set and seasonal subset. The distributions of OC, EC and OC/EC are fitted by both normal and log-normal distribution curves and then examined by Kolmogorov–Smirnov (K-S) test. The K-S statistic D indicate that log-normal fits better than normal distribution. Therefore, log-normal distribution is adopted to constrain OC, EC and OC/EC during data generation in our numerical experiments.

The probability density function (PDF) of log-normal distribution of measurement x is:

\[ f(x; \mu, \sigma) = \frac{1}{x\sigma\sqrt{2\pi}} \times e^{-\frac{(\ln(x) - \mu)^2}{2\sigma^2}} \]  

The two parameters, \( \mu \) and \( \sigma \), are related to the average and standard deviation of x through the following equations:

\[ \mu = \ln(\text{avg}) - 0.5 \times \ln(1 + \frac{\text{std}^2}{\text{avg}^2}) \]  

\[ \sigma = \sqrt{\ln(1 + \frac{\text{std}^2}{\text{avg}^2})} \]

Realistic average and standard deviation values of EC, POC and OC (e.g. referring Figure 4.2-4.6 and Table 4.1) are adopted during pseudo random number generation to generate \( \mu \) and \( \sigma \), then the synthetic EC and OC data sets.
Figure 4.2 Frequency distributions of OC, EC and OC/EC ratio in ambient samples recorded at three locations in the Pearl River Delta region, China. 
(a)-(c) Nancun, a suburban site in Guangzhou, (d)-(f) Mong Kok, an urban roadside site in Hong Kong, (g)-(i) Tsuen Wan, a general urban site in Hong Kong. Grey areas represent frequency distribution, green dashed lines represent cumulative frequency distribution, red lines are normal fitting, and blue lines are log-normal fitting. D represent the Kolmogorov–Smirnov statistic, C represent critical value. If D<C, the samples follow corresponding distribution.
Figure 4.3 Seasonal frequency distributions of OC observed at the suburban site Nancun in the Pearl River Delta region.
(a)-(d) represent spring, summer, fall, and winter, respectively. Grey areas represent frequency distributions, green dashed lines represent accumulation frequency distributions, red lines represent normal fitting, blue lines represent log-normal fitting. D represent the Kolmogorov–Smirnov statistic, C represent critical value. If D<C, the samples follow corresponding distribution.
Figure 4.4 Seasonal frequency distributions of EC observed at the suburban site Nancun in the Pearl River Delta region. (a)-(d) represent spring, summer, fall, and winter, respectively. Grey areas represent frequency distributions, green dashed lines represent accumulation frequency distributions, red lines represent normal fitting, blue lines represent log-normal fitting. D represent the Kolmogorov–Smirnov statistic, C represent critical value. If D<C, the samples follow corresponding distribution.
Figure 4.5 Seasonal frequency distributions of OC/EC ratio observed at the suburban site Nancun in the Pearl River Delta region. (a)-(d) represent spring, summer, fall, and winter, respectively. Grey areas represent frequency distributions, green dashed lines represent accumulation frequency distributions, red lines represent normal fitting, blue lines represent log-normal fitting. D represent the Kolmogorov–Smirnov statistic, C represent critical value. If D<C, the samples follow corresponding distribution.
Figure 4.6 Frequency distribution of OC/EC ratio observed at Mong Kok, a roadside site in Hong Kong.

The rush hour (7:00-9:00) OC/EC ratio can represent (OC/EC)$_{pri}$. Grey areas represent frequency distributions, green dashed lines represent accumulation frequency distributions, red lines represent normal fitting, blue lines represent log-normal fitting. D represent the Kolmogorov–Smirnov statistic, C represent critical value. If D<C, the samples follow corresponding distribution.
<table>
<thead>
<tr>
<th>Location</th>
<th>Site Type</th>
<th>Sampling Period</th>
<th>Time resolution</th>
<th>RSD&lt;sub&gt;EC&lt;/sub&gt; (%)</th>
<th>RSD&lt;sub&gt;SOC&lt;/sub&gt; (%)</th>
<th>SOC estimation method</th>
<th>( f_{Soc} ) mass fraction (%)</th>
<th>Reference</th>
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<td>Hong Kong, PRD</td>
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<td>25% 6% 79%</td>
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<td>Hong Kong, PRD</td>
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<td>EC tracer PMF</td>
<td>65% 46% 89%</td>
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<td>Guangzhou, PRD</td>
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<td>1 hr</td>
<td>154% 115%</td>
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<td>EC tracer</td>
<td>47% 80%</td>
<td>(Hu et al., 2012)</td>
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<tr>
<td>Guangzhou, PRD</td>
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<td>Feb 2012 – Jan 2013</td>
<td>1 hr</td>
<td>86% 86%</td>
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<td>41% 0% 86%</td>
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<tr>
<td>Beijing</td>
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<td>Winter 2005 Spring 2006 Summer 2006 Fall 2006</td>
<td>1 hr</td>
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<td></td>
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<td>19% 27% 45% 23%</td>
<td>(Lin et al., 2009)</td>
</tr>
<tr>
<td>Pittsburgh</td>
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<td>Jul. 2001 – Aug. 2002</td>
<td>2-4 hr</td>
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<td></td>
<td>EC tracer</td>
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<td>(Polidori et al., 2006)</td>
</tr>
<tr>
<td>Mt. Tai, China</td>
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<td>Mar. – Apr. 2007 Jun. – Jul. 2007</td>
<td>1 hr</td>
<td>89% 69%</td>
<td></td>
<td>EC tracer</td>
<td>60% 73%</td>
<td>(Wang et al., 2012)</td>
</tr>
<tr>
<td>Jeju Island, Korea</td>
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<td>May – Jun. 2009 Aug – Sep 2009</td>
<td>1 hr</td>
<td>53% 117% 102%</td>
<td></td>
<td>EC tracer</td>
<td>31% 18%</td>
<td>(Batmunkh et al., 2011)</td>
</tr>
</tbody>
</table>
The Mersenne twister (MT) (Matsumoto and Nishimura, 1998), a pseudorandom number generator, is used in data generation. MT is provided as a function in Igor Pro (WaveMetrics, Inc. Lake Oswego, OR, USA). The system clock is utilized as the initial condition for generation of pseudorandom numbers. The data generated by MT has a very long period of $2^{19937} - 1$, permitting large data size and ensuring that pseudorandom numbers are statistically irrelevant between each data generation. The later feature allows producing the independent relationship between EC and non-combustion related SOC data. MT also allows assigning log-normal distribution during pseudorandom number generation to constrain the data. In a previous study, Chu (2005) used a variant of sine functions to simulate POC and EC, which limits the data size up to 120. In addition, the frequency distributions of POC and EC exhibit multiple peaks, a characteristic that is not realistic for ambient measurements.

The procedure of data generation for the single emission source scenario is illustrated in Figure 4.7 and implemented by scripts written in Igor Pro. EC is first generated with the following parameters specified: sample size ($n$), average and relative standard deviation (RSD%) of the whole data set. The EC data set statistically follows log-normal distribution, while the sequence of each data point is randomly assigned. POC is then calculated by multiplying EC and $(OC/EC)_{pri}$. For simplicity, $(OC/EC)_{pri}$ is set to be a single value. SOC data is independently generated in a similar way to that for EC. The sum of POC and SOC then yields the synthesized OC. OC and EC data generated in this way are used to evaluate the accuracy of SOC estimates by different implementations of the EC tracer method. Data generation for scenarios of two primary emission sources is similar to single source and the steps are illustrated in Figure 4.8.
Figure 4.7 Schematic diagram of pseudorandom number generation for single emission source scenario that assume (OC/EC)_{pri} is a single value.

The data series (EC and SOC), which are generated by Mersenne twister (MT) pseudorandom number generator, statistically follow log-normal distribution, but the sequence of each data point is randomly assigned.

Figure 4.8 Schematic diagram of pseudorandom number generation for two primary emission sources. The data series (EC1, EC2 and SOC), which are generated by Mersenne twister (MT) pseudorandom number generator, statistically follow log-normal distribution, but the sequence of each data point is randomly assigned.
4.3.2 Scenario Study

Three scenarios are considered. Scenario 1 (S1) considers one single primary emission source. Scenario 2 (S2) considers two correlated primary emission sources, i.e., two sets of EC, POC, and each source with a single but different (OC/EC)_pri value. An example of S2 is combined vehicular emissions from diesel-fuelled and gasoline-fuelled vehicles. These two sources of vehicular emissions have different (OC/EC)_pri but often share similar temporal variation pattern, making them well correlated. Scenario 3 (S3) considers two independent primary emission sources and simulates an ambient environment influenced by two independent primary emission sources, e.g. local vehicular emissions (lower (OC/EC)_pri) and regional biomass burning (higher (OC/EC)_pri).

In the following numerical experiments, three (OC/EC)_pri estimation methods are examined and compared, including MRS, OC/EC_{10%} and OC/EC_{min}. As the single point OC/EC_{min} in ambient samples may be subjected to large random uncertainties, data with the lowest 1% OC/EC are adopted instead to derive OC/EC_{min}.

4.3.2.1 Single primary source scenario

Both OC/EC_{10%} and OC/EC_{min} methods rely on a subset of ambient OC and EC data to approximate (OC/EC)_pri. Figure 4.9 provides a conceptual illustration of the relationships between (OC/EC)_pri and the ambient OC/EC data, both are described to exhibit a log-normal distribution. As primary emissions move away from sources and aging processes start in the atmosphere, SOC is added to the particle OC fraction, elevating OC/EC above (OC/EC)_pri. This in effect broadens the OC/EC distribution curve and shifts the distribution to the right along the OC/EC axis, and the degree of broadening and shift depends on degree of aging process. The conventional EC tracer method using OC/EC_{10%} and OC/EC_{min} assumes that the left tail of ambient OC/EC distribution is very close to (OC/EC)_pri. This assumption, however, is fortuitous, rather than the norm. Two parameters, the distance between the means of the (OC/EC)_pri and ambient OC/EC distributions and the relative breadth of the two distributions, largely determines the closeness of the approximation of OC/EC_{10%} and OC/EC_{min} to (OC/EC)_pri. The distance between the two distributions depends on the fraction of SOC in OC (i.e., f_{SOC}) while the width of the ambient OC/EC distribution is closely associated with RSD of SOC (RSD_{SOC}) and the width of the (OC/EC)_pri distribution is reflected in RSD_{POC} and RSD_{EC}. As shown in Figure 4.9a, only an appropriate combination of distance of the two distribution means and variances could lead to a close approximation of the (OC/EC)_pri by OC/EC_{10%} or OC/EC_{min}.
(i.e., the left tail of OC/EC distribution). If the ambient aerosol has a significant f_{SOC} shifting the ambient OC/EC distribution such that its left tail is beyond (OC/EC)_{pri} (Figure 4.9b), then the left tail would overestimate (OC/EC)_{pri}. Underestimation of (OC/EC)_{pri} could also happen in theory as shown in Figure 4.9c if the ambient minimum OC/EC (left tail) is less than the mean of the (OC/EC)_{pri} distribution (i.e., under conditions of very small f_{SOC}).

![Diagram](image)

**Figure 4.9** Conceptual diagram illustrating three scenarios of the relationship between (OC/EC)_{pri} and ambient OC/EC measurements. Both are assumed to be log-normally distributed. (a) Ambient minimum (left tail) equals to the peak of (OC/EC)_{pri}. (b) Ambient minimum OC/EC (left tail) is larger than the mean of (OC/EC)_{pri}. (c) Ambient minimum OC/EC (left tail) is less than the peak of (OC/EC)_{pri}.

The above analysis reveals f_{SOC}, RSD_{SOC}, RSD_{POC}, and RSD_{EC} are key parameters in influencing the accuracy for SOC estimation. As a result, they are chosen in the subsequent sensitivity tests in probing the SOC estimate bias under conditions of different carbonaceous aerosol compositions.

SOC estimation bias in S1 as a function of RSD_{SOC} and RSD_{EC} are shown in Figure 4.10a and Figure 4.10b. The SOC estimate by MRS is not affected by the magnitude of RSD_{EC} and RSD_{SOC}, and in excellent agreement with the true values (Figure 4.10). In comparison, SOC by OC/EC_{10%} and OC/EC_{min} is consistently biased lower and the degree of negative bias becomes larger with decreasing RSD_{SOC} or RSD_{EC}. The OC/EC_{10%} method always produces larger negative bias than the OC/EC_{min} method. At RSD_{SOC} and RSD_{EC} at 50%, SOC estimate has a -14% bias by (OC/EC)_{min} and a -45% bias by (OC/EC)_{10%}. These results confirm the hypothesis illustrated in the conceptual diagram (Figure 4.9) that the validity of using the left tail of OC/EC distribution depends on the distance of its distribution mean from (OC/EC)_{pri} and the distribution breadths. Both OC/EC_{10%} and the OC/EC_{min} methods would underestimate SOC and the degree of underestimation by the OC/EC_{10%} method is worse.
4.3.2.2 Scenarios assuming two primary sources

In real atmosphere, multiple combustion sources are the norm. We next evaluate the performance of the MRS Method in scenarios of two primary sources and arbitrarily dictate that the (OC/EC)\textsubscript{pri} of source 1 is lower than source 2. Common configurations in S2 and S3 include: \( \text{EC}_{\text{total}} = 2\pm0.4 \, \mu\text{g m}^{-3} \); proportion of source 1 EC to total EC (\( f_{\text{EC1}} \)) varies from 0 to 100\%; ratio of the two (OC/EC)\textsubscript{pri} values (\( \gamma_{\text{pri}} \)) vary in the range of 2~8.

In Scenario 2 (i.e., two correlated primary sources), the following three factors are examined, including \( f_{\text{EC1}}, \gamma_{\text{pri}} \) and \( f_{\text{SOC}} \), to probe their effects on SOC estimation. By varying \( f_{\text{EC1}} \), the effect of different mixing ratios of two sources can be examined, as \( f_{\text{EC1}} \) is expected to vary within the same ambient data set as a result of spatiotemporal dynamics of air masses. MRS reports unbiased SOC, irrespective of different \( f_{\text{EC1}} \) and \( f_{\text{SOC}} \) or \( \gamma_{\text{pri}} \) (Figure 4.11). In comparison, SOC by OC/EC\textsubscript{10\%} and OC/EC\textsubscript{min} are underestimated. The degree of underestimation depends on \( f_{\text{SOC}} \), e.g., -12\% at \( f_{\text{SOC}} = 25\% \) versus -20\% at \( f_{\text{SOC}} = 40\% \) in the OC/EC\textsubscript{min} method while the magnitude of underestimate has a very weak dependence on \( f_{\text{SOC}} \) in the OC/EC\textsubscript{10\%} method, staying around -40\% as \( f_{\text{SOC}} \) is doubled from 20\% to 40\%. The degree of SOC bias by OC/EC\textsubscript{10\%} and OC/EC\textsubscript{min} are independent of \( f_{\text{EC1}} \) and \( \gamma_{\text{pri}} \). Because as examined in S1, SOC bias is associated with RSD\textsubscript{EC}, RSD\textsubscript{SOC} and \( f_{\text{SOC}} \). Since two primary sources are well correlated, RSD\textsubscript{EC} is equivalent between the two sources. As a result, the
overall RSD_{EC} is constant when f_{EC1} and γ_{pri} varied. So the SOC bias is independent of f_{EC1} and γ_{pri}.

In summary, in scenarios of two well-correlated primary combustion sources, MRS always produces unbiased SOC estimates while OC/EC_{min} and OC/EC_{10%} consistently underestimate SOC, with OC/EC_{10%} producing larger negative bias.

![Figure 4.11](image)

**Figure 4.11 SOC bias in Scenario 2 (two correlated primary emission sources of different (OC/EC)_{pri}) as estimated by four different EC tracer methods denoted in red, blue and yellow.**

(a) SOC bias as a function of f_{EC1}. Results shown here are calculated using f_{SOC} = 40% as an example. (b) Range of SOC bias shown in boxplots for four f_{SOC} conditions (20%, 25%, 30% and 40%). (c) Range of SOC bias shown in boxplots for four γ_{pri} conditions (2, 4, 6 and 8). The symbols in the boxplots are white circles for average, the line inside the box for median, the box boundaries representing the 75th and the 25th percentile, and the whiskers representing the 95th and 5th percentile.

As for Scenario 3 in which two independent primary sources co-exist, SOC estimates by MRS could be biased and the degree and direction of bias depends on f_{EC1}. Figure 4.12a shows the variation of SOC bias by different EC tracer methods with f_{EC1} when f_{SOC} is fixed at 40%. The variation of SOC bias by MRS with f_{EC1} follows a pseudo-sine curve, exhibiting negative bias when f_{EC1} < 50% (i.e., EC is dominated by source 2, the higher (OC/EC)_{pri} source) and positive bias when f_{EC1} > 50% and the range of bias are confined to -20% to -40% under the condition of f_{SOC} = 40%. In comparison, the OC/EC_{min} and OC/EC_{10%} methods again consistently underestimate SOC by more than -50%, with the bias worsened in the OC/EC_{10%} method.

The bias variation range becomes narrower with increasing f_{SOC} in the MRS method, as shown by the boxplots for four f_{SOC} conditions (20%, 40%, 60%, and 80%) in Figure 4.12b. The MRS-derived SOC bias range is reduced from -20 to +40% at f_{SOC} = 40% to -10 to +20% at f_{SOC} = 60%, further to -6 to +10% at f_{SOC} = 80%. In the other two methods, the SOC bias does
not improve with increasing $f_{\text{SOC}}$. Dependence of SOC estimation bias on $\gamma_{\text{pri}}$ is examined in Figure 4.12c showing the higher $\gamma_{\text{pri}}$ induce higher amplitude of the SOC bias. If OC is dominated by SOC (e.g., $f_{\text{SOC}} = 80\%$), SOC bias by MRS is within 10%.

![Figure 4.12](image)

A variant of MRS implementation (denoted as MRS') is examined, with the important difference that EC$_1$ and EC$_2$, attributed to source 1 and source 2, respectively, are used as inputs instead of total EC. With the knowledge of EC breakdown between the two primary sources, $(OC/EC)_{\text{pri1}}$ can be determined by MRS from EC$_1$ and OC$_{\text{total}}$. Similarly $(OC/EC)_{\text{pri2}}$ can be calculated by MRS from EC$_2$ and OC$_{\text{total}}$. SOC is then calculated with the following equation:

$$SOC = OC_{\text{total}} - (OC/EC)_{\text{pri1}} \times EC_1 - (OC/EC)_{\text{pri2}} \times EC_2$$

MRS' produces unbiased SOC, irrespective the different carbonaceous compositions (Figure 4.12). However, we note that there is a great challenge in meeting the data need in using MRS’ as EC$_1$ and EC$_2$ are not available.

In scenario 3, the simulation results imply that three factors are associated with the SOC bias by MRS, including: $f_{\text{EC1}}$, $\gamma_{\text{pri}}$ and $f_{\text{SOC}}$. The first factor controls whether SOC bias by MRS is positive or negative. The latter two affect the degree of SOC bias. For high $f_{\text{SOC}}$ conditions, the bias could be acceptable. If EC$_1$ and EC$_2$ can be differentiated for calculating individual $(OC/EC)_{\text{pri}}$ of each source, unbiased SOC estimation is achievable regardless of what values $f_{\text{EC1}}$, $\gamma_{\text{pri}}$ and $f_{\text{SOC}}$ take.
4.3.3 Impact of measurement uncertainty

In the preceding numerical analysis, the simulated EC and OC are not assigned any measurement uncertainty; however, every EC and OC measurement is associated with a certain degree of measurement uncertainty. We next examine the influence of OC and EC measurement uncertainty on SOC estimation accuracy by different EC tracer methods. The uncertainties are assumed to follow a uniform distribution and generated separately by MT. It is also assumed that the uncertainty ($\varepsilon_{EC}$ or $\varepsilon_{OC}$) is proportional to the concentration of EC and OC through the multiplier $\gamma_{unc}$ (i.e., relative measurement uncertainty).

\begin{align*}
-\gamma_{unc} EC & \leq \varepsilon_{EC} \leq \gamma_{unc} EC \\
-\gamma_{unc} OC & \leq \varepsilon_{OC} \leq \gamma_{unc} OC
\end{align*}

4.7
4.8

The measurement uncertainties of POC and SOC are then back-calculated following uncertainty propagation formula and assuming the same relative measurement uncertainty for POC and SOC (Harris, 2010)

\[ \gamma'_{unc} = \gamma_{unc} \sqrt{\frac{OC^2}{POC^2 + SOC^2}} \]

4.9

\begin{align*}
-\gamma'_{unc} POC & \leq \varepsilon_{POC} \leq \gamma'_{unc} POC \\
-\gamma'_{unc} SOC & \leq \varepsilon_{SOC} \leq \gamma'_{unc} SOC
\end{align*}

4.10
4.11

The simulated EC, POC and SOC with measurement uncertainties (abbreviated to $EC_{simulated}$, $POC_{simulated}$ and $SOC_{simulated}$ respectively) are determined as:

\begin{align*}
EC_{simulated} &= EC_{true} + \varepsilon_{EC} \\
POC_{simulated} &= POC_{true} + \varepsilon_{POC} \\
SOC_{simulated} &= SOC_{true} + \varepsilon_{SOC}
\end{align*}

4.12
4.13
4.14

Sensitivity tests of SOC estimation as a function of relative measurement uncertainty ($\gamma_{unc}$) and $f_{SOC}$ is performed as shown in Figure 4.13. Fixed input parameters include: N=8000; EC = 2±1 μgm$^{-3}$; (OC/EC)$_{pri}$ = 0.5. Studies by Chu (2005) and Saylor et al. (2006) both suggest ROA (Ratio of average, see SI for details) is the best estimator of the expected primary OC/EC ratio because it mathematically equivalent to the true regression slope when the data contains no intercept. ROA is confirmed as the best representative of (OC/EC)$_{pri}$ for SOC estimation, which shows no bias towards $\gamma_{unc}$ or $f_{SOC}$ change. MRS overestimate SOC and the positive bias increases with $\gamma_{unc}$ while decreases with $f_{SOC}$. SOC by OC/EC$_{min}$ and OC/EC$_{10\%}$ exhibit larger bias than MRS. For example, as shown in Figure 4.13a, when $f_{SOC}$ =20% and $\gamma_{unc}$ = 10%, the bias of SOC by MRS, OC/EC$_{10\%}$ and OC/EC$_{min}$ is 8%, 28% and 36%, respectively. With increasing $f_{SOC}$, the bias of SOC by OC/EC$_{min}$ decreases while the bias of SOC by OC/EC$_{10\%}$
increases when $\gamma_{unc} = 10\%-20\%$. MRS always demonstrates the best performance in SOC determination among three representatives of (OC/EC)$_{pri}$. When $\gamma_{unc}$ could be controlled within 20%, the SOC bias by MRS does not exceed 23% when f$_{SOC}$=20%. If the f$_{SOC}$ ratio falls in the range of 60-80% and $\gamma_{unc}$ is <20%, SOC by OC/EC$_{min}$ revealed similar performance to SOC by MRS, but SOC by OC/EC$_{10\%}$ still shows a large bias (~41%) (Figure 4.13c and Figure 4.13d).

Sensitivity study of SOC estimation as a function of $\gamma_{unc}$ and (OC/EC)$_{pri}$ is performed as shown in Figure 4.14. All three (OC/EC)$_{pri}$ representatives are sensitive to $\gamma_{unc}$ but insensitive to the magnitude of (OC/EC)$_{pri}$. In single primary source scenario (S1), it is proved that the performance of MRS on SOC estimation is mainly affected by $\gamma_{unc}$ and partially related to f$_{SOC}$. Other factors like (OC/EC)$_{pri}$ and EC concentration will not affect the performance of MRS on SOC estimation.

![Figure 4.13 Bias of SOC determination as a function of relative measurement uncertainty ($\gamma_{unc}$) and SOC/OC ratio (f$_{SOC}$) by different approaches of estimating (OC/EC)$_{pri}$, including ratio of averages (ROA), minimum R squared (MRS), OC/EC$_{10\%}$, and OC/EC$_{min}$. Fixed input parameters: N=8000; EC = 2±1 $\mu$g m$^{-3}$; (OC/EC)$_{pri}$ = 0.5. Variable input parameters: (a) f$_{SOC}$ =20%, SOC = 0.25±0.13 $\mu$gC m$^{-3}$, (b) f$_{SOC}$ =40%, SOC = 0.67±0.33 $\mu$gC m$^{-3}$, (c) f$_{SOC}$ =60%, SOC = 1.5±0. 75 $\mu$gC m$^{-3}$, and (d) f$_{SOC}$ =80%, SOC = 4±2 $\mu$gC m$^{-3}$]
Figure 4.14 Variation of bias of SOC determination with measurement uncertainty under four different (OC/EC)\textsubscript{pri} (a) (OC/EC)\textsubscript{pri} = 0.5, (b) (OC/EC)\textsubscript{pri} = 1, (c) (OC/EC)\textsubscript{pri} = 2, and (d) (OC/EC)\textsubscript{pri} = 6, demonstrating dependence on $\gamma\text{unc}$ while no effects by (OC/EC)\textsubscript{pri}.

The different representatives of (OC/EC)\textsubscript{pri} include ratio of averages (ROA), minimum R squared method (MRS), OC/EC\textsubscript{10\%}, OC/EC\textsubscript{min}. Fixed input parameters: N=8000; EC = $2 \pm 1 \mu g m^{-3}$, and f\textsubscript{soc}=60\%. 
### 4.4 Caveats of MRS method and its applications to ambient data

Table 4.2 compares the results of numerical experiments on the performance in terms of SOC estimation bias by different EC tracer methods assuming typical variation characteristics of ambient ECOC data. It is clear that MRS is superior over the two conventional methods (OC/EC_{10\%} and OC/EC_{\text{min}}) in SOC estimation accuracy.

When employing EC tracer method on ambient samples, MRS is preferred since it can provide more accurate SOC estimation. If the sampling site is dominated by single primary source (similar to Scenario 1), MRS can perform much better than the traditional OC/EC percentile and minimum approaches. Two issues should be paid attention to when applying MRS: (1) MRS rely on the irrelevance of EC and SOC. This assumption could be invalid if a fraction of SOC is formed from semivolatile POC (here referred as SOC_{svP})(Robinson et al., 2007). Since POC is well correlated with EC, this SOC_{svP} is be attributed to POC by MRS, causing SOC underestimation. The interference of SOC_{svP} and corresponding solution are discussed in the next chapter. (2) OC_{non-comb} will be attributed to SOC if only EC is used as a tracer. If the abundance of OC_{non-comb} is small comparing to SOC, such approximation is acceptable. If the abundance of OC_{non-comb} is not negligible, identification of its contribution is needed. If a stable tracer for OC_{non-comb} is available, determination of OC_{non-comb} contribution by MRS is possible, since this scenario mathematically equivalent to S3 (e.g., relabel EC2 to tracer of OC_{non-comb} and POC to OC_{non-comb}). When POC and OC_{non-comb} are both identified from OC_{total}, SOC estimation accuracy by MRS can be further improved.

If the sampling site is influenced by two correlated primary source with distinct (OC/EC)_{pri} (Scenario 2, e.g. urban areas that have vehicular emission from both gasoline and diesel), MRS is still much more reliable than the traditional OC/EC percentile and minimum approaches.

If the sampling site is influenced by two independent primary sources with distinct (OC/EC)_{pri} (Scenario 3, e.g. vehicular emission and biomass burning), SOC estimation by MRS is better than the other two conventional methods. But the user should recognize the possible bias may exist that its degree depends on relative abundance between the two sources. If tracers for each primary source are available, unbiased SOC estimation is possible by employing these tracers in MRS.
Beside time resolved measurement, 24 hour filter based off line measurement of OC and EC have accumulated plenty results around the world that are potentially useful for MRS application. To explore the impact of sampling average duration (e.g., hourly vs. daily), we test our one year hourly data by averaging them into longer interval (2-24 hours). The 24 hr-averaged samples yield a (OC/EC)$_{pri}$ of 2.53, 12% higher than the (OC/EC)$_{pri}$ derived from hourly data (2.26). The elevated MRS (OC/EC)$_{pri}$ is associated with narrowed OC/EC distribution when averaging interval increase( Figure 4.15). As many filter-based PM$_{2.5}$ speciation network conduct sampling every six days, we further extract the every-six-day samples for the MRS calculation, which yield the OC/EC$_{pri}$ in the range of 2.37 – 2.75 (5-22% higher than the OC/EC$_{pri}$ from the hourly data).

![Figure 4.15 Effect of data averaging interval on OC/EC distribution and MRS.](image)

The bottom x axis represent averaging interval (e.g. 1 hr is the original data time resolution, 2 hr referring average 1 hr data into 2 hr interval data, 24 hr means average 1 hr data into 24hr interval data). The top x axis represent the data point of corresponding data averaging interval (e.g. 7217 data points for 1hr interval and 334 data points for 24hr data). Y axis represent OC/EC ratio. Distributions of OC/EC ratio at varies averaging interval are shown by box plot. The symbols in the boxplots are white circles for average, the line inside the box for median, the box boundaries representing the 75th and the 25th percentile, and the whiskers representing the 95th and 5th percentile. The red sphere represent calculated (OC/EC)$_{pri}$ by MRS.
Table 4.2 Summary of numerical study results by different scenarios.

<table>
<thead>
<tr>
<th>Tested parameter</th>
<th>SOC bias</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MRS(^b)</td>
<td>MRS(^c)</td>
<td>OC/EC(_{min})</td>
</tr>
<tr>
<td>Scenario 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single source</td>
<td>RSD(_{EC})</td>
<td>±4%</td>
<td>-13% ~ -7%</td>
<td>-43% ~ -36%</td>
</tr>
<tr>
<td></td>
<td>RSD(_{SOC})</td>
<td>±4%</td>
<td>-11% ~ -4%</td>
<td>-42% ~ -22%</td>
</tr>
<tr>
<td></td>
<td>(\gamma)(_{unc})</td>
<td>+10%</td>
<td>-12% ~ 20%</td>
<td>-43% ~ -32%</td>
</tr>
<tr>
<td>Scenario 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two correlated sources</td>
<td>f(_{EC1})</td>
<td>±4%</td>
<td>-20%</td>
<td>-40%</td>
</tr>
<tr>
<td></td>
<td>(\gamma)(_{pri})</td>
<td>±4%</td>
<td>-20%</td>
<td>-40%</td>
</tr>
<tr>
<td></td>
<td>f(_{SOC})</td>
<td>±4%</td>
<td>-20%</td>
<td>-40%</td>
</tr>
<tr>
<td>Scenario 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two independent sources</td>
<td>f(_{EC1})</td>
<td>-20% ~ 40%</td>
<td>±10%</td>
<td>-50%</td>
</tr>
<tr>
<td></td>
<td>(\gamma)(_{pri})</td>
<td>-20% ~ 40%</td>
<td>±10%</td>
<td>-50%</td>
</tr>
<tr>
<td></td>
<td>f(_{SOC})</td>
<td>-20% ~ 40%</td>
<td>±10%</td>
<td>-50%</td>
</tr>
</tbody>
</table>

\(^{a}\) Results shown here are obtained assuming the following representative ambient conditions: RSD\(_{EC}\) 50-100%; f\(_{SOC}\) 40-60%; \(\gamma\)\(_{unc}\) 20%; \(b^+\)" represents SOC overestimation and "-" represents underestimation; ‘MRS’ In S3, EC1 and EC2 are used for SOC calculation.
Chapter 5
5. Characterization of carbonaceous aerosols in the Pearl River Delta region from one year time-resolved measurements

Chapter summary
One year of organic carbon (OC) and elemental carbon (EC) observations was conducted hourly from 1 February 2012 to 31 January 2013 by using a semi-continuous thermal-optical transmittance (TOT) carbon analyzer at the suburban site Nancun (NC) in the city of Guangzhou. Annual average OC, EC and total carbon (TC) concentrations (±1sd) at NC site are 7.20±5.68, 2.64±2.28 and 9.84±7.80 µgCm$^{-3}$ respectively. The Minimum R squared (MRS) method is applied for primary OC/EC ratio estimation. Results show that interference of EC co-emitted secondary organic carbon (SOC) precursors can cause an overestimation of $(OC/EC)_{pri}$ in the afternoon, and the diurnal minimum MRS estimation of $(OC/EC)_{pri}$ is adopted to minimize this artifact. In addition, seasonal variations of $(OC/EC)_{pri}$ are observed (e.g. elevated $(OC/EC)_{pri}$ in the biomass burning season), therefore $(OC/EC)_{pri}$ is calculated for individual months to account for such variations. The annual average estimated SOC is 2.96±2.55 µgCm$^{-3}$, accounting for 41% of OC mass. In winter SOC exhibits a higher concentration, but in summer higher formation activity is observed as evidenced by an elevated SOC/OC ratio. In winter SOC is correlated with NO$_3^-$, while during summertime SOC is correlated with O$_3$ and SO$_4^{2-}$. SOC by resolved carbon fractions is investigated. SOC contributed 38% of low temperature OC (evolved <600 °C) and 78% of high temperature OC (evolved between 600 °C and 840°C), implying that most of the high temperature OC (probably more oxygenated) is secondarily formed. Results from 49 individual rain events show that carbonaceous particle mass is reduced by 50% on average due to wet removal. The removal rate is uniform for POC, SOC and EC, suggesting that internal mixing is likely the dominating mixing state of carbonaceous particles at the sampling site. A higher EC/CO ratio was observed from midnight to morning, suggesting the high EC at night is associated with shallow mixing depth as well as a higher intensity of primary emission from diesel trucks due to the traffic regulations in the city of Guangzhou, while the high EC in the morning rush hour is associated with enhanced traffic activities.
5.1 Introduction

Carbonaceous aerosols, a major component of fine particulate matter (PM$_{2.5}$), have drawn much attention in the community due to their unique impact on human health and climate. In contrast to this significance, the current understanding of carbonaceous aerosols is still limited for resolving climate and health issues, and even classification of carbonaceous aerosols is still controversial (Gelencsér, 2004). Carbonaceous PM can be categorized into elemental carbon (EC) and organic carbon (OC). Such classification is mainly based on thermal optical analysis (TOA) that distinguishes EC and OC based on their chemical and thermal stability. However, differentiation of EC and OC by TOA is simply operationally defined. During the analysis, OC evolved in the first stage without the presence of oxygen and then EC is combusted by introducing oxygen in the second stage. Consequently, EC and OC determination is protocol dependent but TOA is still widely used in 24-hr filter based PM speciation networks (Chow et al., 2001). The volatility properties utilized in TOA are linking back to the origin of EC and OC. EC are chemically inert refractory materials coming from incomplete combustion activities including vehicular emission (Birch and Cary, 1996), biomass burning (Martins et al., 1998) and coal burning (Zheng et al., 2012). In addition, EC has the ability to absorb visible light, making it the third largest climate warming forcer following CO$_2$ and CH$_4$ (IPCC, 2013). Unlike EC, OC could be primarily or secondarily formed, making its chemical composition highly diverse. Primary organic carbon (POC) comes from varies primary sources, including vehicular emission (Huang et al., 2014b), biomass burning (Simoneit, 2002), and cooking and trash burning (Mohr et al., 2009). OC can also be secondarily formed (secondary organic carbon, SOC) through oxidation of volatile organic compounds (VOCs) followed by gas/particle partitioning (Hallquist et al., 2009).

The Pearl River Delta (PRD) region has experienced immense economic growth and urbanization in the last three decades. As one the fastest developing regions in China, the PRD is also suffering frequent episodic air pollution events (Wu et al., 2005). In the 1950s, the annual number of haze days (visibility<10km & RH<90%) in PRD was less than 10, but after the 1980s the number of haze days increased dramatically to 150 days per year due to fine PM pollution (Deng et al., 2008). Effective control strategies for PM requires scientific understanding of the fine mode chemical composition. A large body of studies have been conducted in the PRD to investigate the physical and chemical properties of carbonaceous aerosols, which contribute a large fraction of the fine PM mass (30~40%) in the PRD region (Hagler et al., 2006; Huang et
A high abundance of OC and EC have been reported in the PRD (Cao et al., 2004), but most of these PRD studies are based on 24hr filter sampling that lack diurnal information. Andreae et al. (2008) reported an extensive measurement campaign focused on the optical properties of carbonaceous aerosols conducted in urban Guangzhou (GZ) during the winter of 2004. The study found that beside EC, OC also contributed to light absorption in GZ. Cheng et al. (2006b) investigated the mixing state of elemental carbon through an optical closure study at the receptor site Xinken (XK) in the PRD. That study found the mixing state at XK strongly depended on the origin of the air mass, and a clear diurnal variation was observed, where the EC was more internally mixed at nighttime and externally mixed during daytime. Some ad hoc studies conducted time resolved OCEC measurements for a short time (Verma et al., 2010; Hu et al., 2012), but were unable to probe seasonal variations of carbonaceous aerosols.

The objective of this study is to better characterize the seasonal and diurnal patterns of OC and EC in the PRD region through a year of time resolved measurements. In a recent numerical study, we demonstrated that the minimum R squared method (MRS) can minimize the arbitrariness in SOC estimation. In this study, application of MRS on ambient samples is demonstrated to provide a better estimation of SOC in this region.

5.2 Experimental

5.2.1 Sampling Site

One year of measurements were conducted at the Nancun (NC, 23° 0'11.82"N, 113° 21'18.04"E) site (Figure 5.1) in the Panyu district of the city of Guangzhou from Feb 1, 2012 to Jan 31, 2013. The field carbon analyzer was installed in an air-conditioned room on the third floor of a three story building. NC is a suburban site 17 km away from downtown Guangzhou, and located in a mixed industrial –residential area. A unique feature of the NC station is that it is situated on top of the highest peak (141 m ASL) in Guangzhou’s Panyu district, making the site less impacted by ground-level local emissions. It’s also worth noting that NC is located at the geographic center of the city clusters in the PRD, making it a good location for representing the average atmospheric conditions over the urbanized portion of the PRD region.
5.2.2 Sampling

5.2.2.1 OC and EC measurement

A semi-continuous thermal-optical transmittance (TOT) carbon analyzer (Model RT-4, Sunset Laboratory Inc., Tigard, Oregon, USA) was deployed at the NC site for hourly PM$_{2.5}$ organic carbon (OC) and elemental carbon (EC) measurements. Characterization of the Sunset field carbon analyzer can be found elsewhere (Bae et al., 2004; Bauer et al., 2009). Briefly, ambient air is first drawn into a PM$_{2.5}$ sharp-cut cyclone (BGI, Waltham, Massachusetts, USA) at a flow rate of 8 L min$^{-1}$, then passed through a parallel plated carbon denuder (Sunset Laboratory, Inc., Tigard, Oregon, USA) to remove gaseous OC, and finally collected onto two back-to-back 16 mm diameter quartz filters (Pallflex, Tissuquartz, 2500-QAT-UP, Putnam,
Massachusetts, USA). The back-to-back filter configuration is to prevent filters from breaking during sampling. A stainless steel (SS) pipe, pre-cleaned by acid, is used to connect the cyclone and denuder to the carbon analyzer. To avoid condensation of water in the sampling tubing during summer due to air-conditioned indoor air, a temperature control system was introduced. This system includes two temperature probes (sensor A measuring the outdoor ambient temperature while sensor B monitors the indoor SS tubing temperature) and a tubing heater. If temperature $B < A$, the heater is turned on, while $B \geq A$ the heater is off. As a result the indoor tubing temperature tracks the outdoor temperature during summer to avoid condensation. In the case where temperature $B$ (sampling line temp) is higher than 40 °C, the heater will be turned off for safety reasons.

After 45 min of sampling, the particle laden filter is subjected to analysis in the subsequent 15 min. In thermal-optical analysis, OC is volatized first by programmed temperature steps in an oxygen-free atmosphere with helium as a carrier gas, while in the second stage oxygen is introduced for the combustion of EC. Evolved OC is converted to carbon dioxide (CO$_2$) by a manganese dioxide catalyst. Determination of CO$_2$ from oxidized OC and EC is quantified by a non-dispersive infrared (NDIR) detector. The NDIR detector provides comparable performance to the flame-induced detectors (FID) in previous models of the semi-continuous carbon analyzer (Bae et al., 2004; Bauer et al., 2009). The Sunset RT-4 carbon analyzer has an added advantage of having eliminated the use of compressed air and hydrogen thereby greatly expanding the deployability of the analyzer for field studies. During the Helium stage (OC volatilization) a fraction of OC is pyrolyzed at high temperature and leads to formation of pyrolyzed carbon (PC), resulting in a darkened filter. To minimize this analytical artifact, a tunable red diode laser (660 nm) is used for monitoring the transmittance signal through the filter. Formation of PC in the He stage decreases the laser signal while combustion of PC and EC in the O$_2$ stage results in recovery of the laser signal. When the laser signal in the O$_2$ stage returns to the initial level, the carbon fraction before this point in the O$_2$ stage is quantified as PC, achieving the differentiation of PC and native EC. Therefore, all carbon fractions volatized before all the PC has combusted (known as the OC/EC split) are regarded as OC (OC evolved in He + PC combusted in O$_2$) and after as EC. It should be noted that this correction relies on the assumption that 1) PC combusts before native EC, and 2) PC and native EC have the same light absorption cross-section. Previous studies have shown that neither of these two assumptions are true (Yang and Yu, 2002; Chow et al., 2004), so the laser correction remains a source of uncertainty in the thermal-optical analysis. At the end of each analysis, a
known amount of methane (5% CH₄ in He) is injected automatically as the internal calibration. After analysis, the oven is cooled to the ambient temperature for the next sampling cycle. Table 5.2 shows the detailed temperature steps of the protocol used in this study. This protocol is a simplified version of the NIOSH 5040 protocol (National Institute for Occupational Safety and Health) that is optimized for high time resolution field studies with shortened temperature steps and durations. Implementation of the short NIOSH protocol and conventional NIOSH protocol on a semi-continuous ECOC analyzer has been compared by Bae et al. (2007). Comparison of the short NIOSH protocol implemented on a semi-continuous ECOC analyzer versus a conventional NIOSH protocol on a bench-top ECOC analyzer has been investigated by Hu et al. (2008). These studies have suggested OC and EC reported by the short protocol are comparable with the conventional NIOSH protocol (OC: slope=1.03; R²=0.97. EC: slope=0.88; R²=0.82).

High purity gases (Air Products and Chemicals, Inc., Shenzhen, China) were used in this study. He gas was purified by an O₂ trap (Model 1000, Sigma-Aldrich, St. Louis, MO, USA) before use to remove any trace oxygen.

Table 5.1  Temperature protocol (also known as "rtquartz.par" configuration file in the analyzer software) implemented on semi-continues carbon analyzer

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Temperature(°C)</th>
<th>Duration (Sec)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>Ambient</td>
<td>10</td>
<td>Purging</td>
</tr>
<tr>
<td>He</td>
<td>600</td>
<td>95</td>
<td>Heating</td>
</tr>
<tr>
<td>He</td>
<td>840</td>
<td>85</td>
<td>Heating</td>
</tr>
<tr>
<td>He</td>
<td>550</td>
<td>38</td>
<td>Cool down</td>
</tr>
<tr>
<td>He/O₂</td>
<td>550</td>
<td>35</td>
<td>Heating</td>
</tr>
<tr>
<td>He/O₂</td>
<td>650</td>
<td>45</td>
<td>Heating</td>
</tr>
<tr>
<td>He/O₂</td>
<td>870</td>
<td>90</td>
<td>Heating</td>
</tr>
<tr>
<td>He/CH₄</td>
<td>Back to ambient</td>
<td>135</td>
<td>calibration</td>
</tr>
</tbody>
</table>

5.2.2.2 Observation of PM₂.₅ mass, water soluble ions and gases

Relevant observations including PM₂.₅, water soluble ions and gaseous pollutants are also conducted in NC site. Hourly PM₂.₅ mass concentrations were determined by a Grimm monitor (Model 180, GRIMM Technologies, Inc.). The Grimm monitor utilizes a light scattering technique for aerosol determination, which can provide similar performance
compared with FDMS TEOM (filter dynamic measurement system, tapered element oscillating microbalance) (Hansen et al., 2010; Grimm and Eatough, 2009) and BAM (beta attenuation Mass Monitor) (Grimm et al., 2006). Major water soluble ions like SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and K$^+$ were measured by a MARGA (Monitor for AeRosols and GAses, Model ADI 2080, Metrohm Applikon B.V., Schiedam, The Netherlands) on an hourly basis. Gas pollutant data was obtained during this study, including: ozone (EC9810, Ecotech pty Ltd.), CO (EC9830, Ecotech pty Ltd.), NOx (EC9841, Ecotech pty Ltd.) and SO$_2$ (EC9850, Ecotech pty Ltd.).

5.2.3 QA/QC

Several measures were taken to ensure the data quality of the carbon analyzer, as summarized in Table 5.2. During the one year sampling period (1 Feb 2012- 31 Jan 2013), valid data obtained by the field carbon analyzer covered 85% of the time, while the remaining time was used for regular maintenance (filter change, dynamic blank test and sucrose calibration, etc.) or downtime due to instrument failure (filter blowout, heating coil burnout and computer hang-up, etc.)

Instrument blank (IB) checks were performed daily (00:00 – 00:15 LT) by conducting an analysis without sampling. The campaign average IB was 0.22 ± 0.10 and 0.003 ± 0.002 µgC for OC and EC respectively. As the removal efficiency of the denuder cannot achieve 100% (Subramanian et al., 2004; Arhami et al., 2006), dynamic blanks (DB) were examined every month to determine the influence of residual VOC (positive artifacts) after the denuder. To perform the DB check, two 47mm quartz filters (Pallflex, Tissuquartz, 2500-QAT-UP, Putnam, Massachusetts, USA) were placed in tandem upstream of the denuder to remove any particles. Particle-free ambient air was then sampled and analyzed. This quantifies the OC breakthrough of the whole system. The average DB was 0.63 ± 0.44 µgm$^{-3}$ (mean ± 1σ), which accounts for 8.96% of observed average OC, which is similar to those reported in previous studies (Lin et al., 2009; Polidori et al., 2006). Positive artifact correction is applied to all samples in this study by subtracting the average DB. Negative artifacts due to volatilization of the collected particle were not quantified in this study. Previous studies suggest the upper limit of negative artifacts is ~10% (Subramanian et al., 2004; Polidori et al., 2006). The adsorption capacity of the denuder was also examined by performing a DB check before and after a carbon-impregnated filter (CIF) replacement in the denuder. No discernible DB level change was observed after CIF replacement, indicating the denuder capacity reduction in a month was negligible. The method detection limit (MDL) was 1.32 µgm$^{-3}$ for OC calculated as three times the DB standard
deviation (3 σ). As no EC was observed in the DB samples, the MDL for EC was calculated by 3 σ of the instrument blank EC, which is 0.005 µgC (~0.01 µgCm⁻³).

Table 5.2 Quality control (QC) measures during one year’s measurement at NC

<table>
<thead>
<tr>
<th>QC activity</th>
<th>Frequency</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument blank (IB)</td>
<td>Daily</td>
<td>OC 0.22 ± 0.10 µgC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC 0.003 ± 0.002 µgC</td>
</tr>
<tr>
<td>Dynamic blank (DB)</td>
<td>Monthly</td>
<td>0.63 ± 0.44 µgm⁻³</td>
</tr>
<tr>
<td>method detection limit (MDL)</td>
<td></td>
<td>OC 1.32 µgm⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC 0.005 µgC (~0.01 µgCm⁻³)</td>
</tr>
<tr>
<td>Carrier gas sensor auto zero</td>
<td>Weekly</td>
<td></td>
</tr>
<tr>
<td>6 points sucrose calibration</td>
<td>Monthly</td>
<td></td>
</tr>
<tr>
<td>Filter change</td>
<td>Weekly</td>
<td></td>
</tr>
<tr>
<td>Denuder change</td>
<td>Monthly</td>
<td></td>
</tr>
<tr>
<td>Cyclone clean</td>
<td>Monthly</td>
<td></td>
</tr>
</tbody>
</table>

External calibrations were performed monthly using a sucrose solution. A six point calibration was adopted covering the range of 0 ~ 50 µgC. For each point 2 µl of sucrose solution was spiked onto the pre-baked filter. Minimizing each solution injection volume to 2 µl reduced the interference of water vapor on NDIR. After injection the filter was purged in He for 10 min before the analysis began to dry the filter, which can further reduce the interference of water vapor.

Filters were changed on a weekly basis to minimize the interference of accumulated refractory metal oxide in the TOT analysis. The carrier gas sensor was auto-zeroed weekly. The sharp-cut cyclone was cleaned monthly.

5.3 Results

Annual mean OC, EC and TC concentrations (±1sd) at the NC site are 7.20±5.68, 2.64±2.28 and 9.60±7.90 µgCm⁻³ respectively (Figure 5.1). As shown in Figure 5.1, a notable feature of OC, EC and OC/EC frequency distributions is that they all follow lognormal distributions rather than Gaussian distributions. For comparison, OC and EC measurements by other Sunset semi-continuous carbon analyzers reported in literature are summarized in Table 5.3. OC and EC concentrations observed in this study are comparable to other studies in the
PRD region. But OC and EC at NC are much higher compared to US urban areas (Polidori et al., 2006; Rattigan et al., 2010), highlighting the severe air pollution situation of the PRD region. Annual average contributions (±1sd) of OC, EC, and TC to PM$_{2.5}$ mass are 14.60±9.35%, 5.32±5.14%, and 19.54±14.18%, respectively. OC/PM$_{2.5}$ and EC/PM$_{2.5}$ are lower at the NC site compared with those observed at the Mong Kok roadside monitoring site in Hong Kong (OC/PM$_{2.5}$: 21%, EC/PM$_{2.5}$: 13% Huang et al., 2014b).

Monthly variations of OC and EC at NC are shown in Figure 5.2, which are low in summer and high in winter. Lower concentrations of OC and EC observed in summer are associated with the following factors: a) the large scale wind direction in summer is governed by the Southeast Asia monsoon system as illustrated for primary pollutant levels (e.g. Black Carbon) in a PRD multi-site study (Wu et al., 2013), b) wet removal of OC and EC is more pronounced due to more frequent and heavier precipitation events in summer in the PRD (see Sec. 5.4.5 for more information on rainfall scavenging effects), and c) lower emission of OC and EC in summer in the summer has been suggested by a recent inventory study (He et al., 2011).
Table 5.3 Summary of time-resolved OC and EC measurement around the world

<table>
<thead>
<tr>
<th>Location</th>
<th>Site Type</th>
<th>Sampling Period</th>
<th>Time resolution</th>
<th>OC±1sd</th>
<th>EC±1sd</th>
<th>OC/EC</th>
<th>SOC estimation method</th>
<th>SOC/OC (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hong Kong, PRD, China</td>
<td>Urban</td>
<td>May 2011 – Apr 2012</td>
<td>1 hr</td>
<td>7.82</td>
<td>4.36</td>
<td></td>
<td>/</td>
<td>/</td>
<td>(Huang et al., 2014b)</td>
</tr>
<tr>
<td>Hong Kong, PRD, China</td>
<td>Suburban</td>
<td>Aug 2011</td>
<td>1 hr</td>
<td>3.66</td>
<td>1.55</td>
<td>3.02</td>
<td>EC tracer</td>
<td>33% ~ 43%</td>
<td>(Zhou et al., 2014)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nov 2011</td>
<td></td>
<td>3.76</td>
<td>2.40</td>
<td>1.59</td>
<td></td>
<td>33% ~ 41%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feb 2012</td>
<td></td>
<td>2.94</td>
<td>2.08</td>
<td>1.44</td>
<td></td>
<td>49% ~ 51%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>May 2012</td>
<td></td>
<td>1.62</td>
<td>1.26</td>
<td>1.61</td>
<td></td>
<td>58% ~ 62%</td>
<td></td>
</tr>
<tr>
<td>Guangzhou, PRD, China</td>
<td>Rural</td>
<td>July 2006</td>
<td>1 hr</td>
<td>5.7</td>
<td>3.3</td>
<td></td>
<td>EC tracer</td>
<td>47%</td>
<td>(Hu et al., 2012)</td>
</tr>
<tr>
<td>Guangzhou, PRD, China</td>
<td>Urban</td>
<td>July 2006</td>
<td>1 hr</td>
<td>8.9</td>
<td>4.7</td>
<td></td>
<td>/</td>
<td>/</td>
<td>(Verma et al., 2010)</td>
</tr>
<tr>
<td>Guangzhou, PRD, China</td>
<td>Suburban</td>
<td>Feb 2012 – Jan 2013</td>
<td>1 hr</td>
<td>5.7±5.68</td>
<td>2.64±2.28</td>
<td>2.96±0.96</td>
<td>EC tracer</td>
<td>41%</td>
<td>This study</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Urban</td>
<td>Winter 2005</td>
<td>1 hr</td>
<td>20±19</td>
<td>6.7</td>
<td>3.3±0.8</td>
<td>EC tracer</td>
<td>19%</td>
<td>(Lin et al., 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spring 2006</td>
<td></td>
<td>12±7</td>
<td>6.2</td>
<td>2.6±1.1</td>
<td></td>
<td>27%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Summer 2006</td>
<td></td>
<td>10±5</td>
<td>6.4</td>
<td>2.2±1.1</td>
<td></td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fall 2006</td>
<td></td>
<td>18±11</td>
<td>8.8</td>
<td>2.2±1.1</td>
<td></td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spring 2006</td>
<td></td>
<td>2.75</td>
<td>0.89</td>
<td></td>
<td>EC tracer</td>
<td>38%</td>
<td>(Polidori et al., 2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>March - April 2007</td>
<td></td>
<td>6.07</td>
<td>1.77</td>
<td></td>
<td></td>
<td>60%</td>
<td>(Wang et al., 2012)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>June – July 2007</td>
<td></td>
<td>5.05</td>
<td>0.99</td>
<td></td>
<td></td>
<td>73%</td>
<td></td>
</tr>
<tr>
<td>Jeju Island, Korea</td>
<td>Rural</td>
<td>May – June 2009</td>
<td>1 hr</td>
<td>4.07±2.60</td>
<td>1.35±0.71</td>
<td></td>
<td>EC tracer</td>
<td>31%</td>
<td>(Batmunkh et al., 2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aug – Sep 2009</td>
<td></td>
<td>2.4±0.9</td>
<td>0.7±0.4</td>
<td></td>
<td></td>
<td>18%</td>
<td></td>
</tr>
<tr>
<td>Bangkok, Thailand</td>
<td>Suburban</td>
<td>May-Oct 2007</td>
<td>1 hr</td>
<td>5.3±2.0</td>
<td>3.0±1.2</td>
<td>2</td>
<td>/</td>
<td>/</td>
<td>(Sahu et al., 2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nov 2007 – Feb 2008</td>
<td></td>
<td>13.1±5.8</td>
<td>4.3±1.3</td>
<td>2.95</td>
<td>/</td>
<td>/</td>
<td>(Sahu et al., 2011)</td>
</tr>
<tr>
<td>New York, US</td>
<td>Urban</td>
<td>2006-2008</td>
<td>1 hr</td>
<td>0.5~1.4*</td>
<td>1.0~4.1*</td>
<td>2~4*</td>
<td>EC tracer</td>
<td>40%~73%</td>
<td>(Rattigan et al., 2010)</td>
</tr>
<tr>
<td>Prague, Czech</td>
<td>Suburban</td>
<td>Sep 2009 - Aug 2010</td>
<td>2 hr</td>
<td>5.56±0.24</td>
<td>1.71±1.54</td>
<td>3.16</td>
<td>/</td>
<td>/</td>
<td>(Vodička et al., 2013)</td>
</tr>
<tr>
<td>Taranto, Italy</td>
<td>Coastal</td>
<td>May – Jun 2010</td>
<td>2 hr</td>
<td>1.69±0.73</td>
<td>0.44±0.30</td>
<td></td>
<td>/</td>
<td>/</td>
<td>(Malaguti et al., 2013)</td>
</tr>
</tbody>
</table>

* monthly average
TC/PM$_{2.5}$, OC/PM$_{2.5}$ and EC/PM$_{2.5}$ exhibit similar monthly patterns that are also low in summer and high in winter (Figure 5.3). In winter, the prevailing wind is northeasterly placing NC downwind of downtown Guangzhou. Since the contribution of carbonaceous aerosols to PM$_{2.5}$ mass is much higher near the emission source (e.g. at road site, TC/PM$_{2.5}$ ~40%) (2014b), the elevated OC/PM$_{2.5}$ and EC/PM$_{2.5}$ observed in winter is likely due to the influence from downtown Guangzhou. During the summertime, TC/PM$_{2.5}$ observed at the NC site (13.2%) is comparable with a previous study reported at a rural site in this region (TC/PM$_{2.5}$ 13.6%)(Hu et al., 2012).
Figure 5.3 Annual average contribution to PM$_{2.5}$ mass
(a) Total Carbon (b) Organic Carbon and (c) Elemental Carbon. Grey areas are the frequency distribution histograms. Blue lines represent Gaussian distribution fitting curves. Red lines represent Log-normal distribution fitting curves. Monthly average contribution to PM$_{2.5}$ mass (d) Total Carbon (e) Organic Carbon and (f) Elemental Carbon. Red circles represent monthly average concentrations. The line inside the box indicates the median. Upper and lower boundaries of the box represent the 75th and the 25th percentile; the whiskers above and below each box represent the 95th and 5th percentile.
5.4 Discussion

5.4.1 Estimation of \((\text{OC/EC})_{\text{pri}}\)

Secondary organic carbon (SOC) can be estimated using EC as the tracer for primarily emitted OC (Turpin and Huntzicker, 1995):

\[
\text{OC}_{\text{pri}} = (\text{OC/EC})_{\text{pri}} \times \text{EC} + \text{OC}_{\text{non}} \tag{5.1}
\]

where \((\text{OC/EC})_{\text{pri}}\) is the OC/EC ratio of aerosols from the primary emission source, and \(\text{OC}_{\text{non}}\) is the non-combustion primary OC. SOC concentration can then be estimated by Eq.(5.2):

\[
\text{SOC} = \text{OC}_{\text{total}} - \text{OC}_{\text{pri}} \tag{5.2}
\]

Combing Eq. 5.1&5.2:

\[
\text{SOC} = \text{OC}_{\text{total}} - (\text{OC/EC})_{\text{pri}} \times \text{EC} - \text{OC}_{\text{non}} \tag{5.3}
\]

\((\text{OC/EC})_{\text{pri}}\) is the key parameter in the SOC calculation using the EC tracer method. In our previous work, different approaches for \((\text{OC/EC})_{\text{pri}}\) determination are examined by numerical studies and the results show that the Minimum R Squared method (MRS) exhibits superior SOC estimation performance over the minimum OC/EC and percentile OC/EC methods (Wu and Yu, 2014). The idea behind MRS can be found in examining the correlation \((R^2)\) between measured EC and estimated SOC (from Eq. 5.3) as a function of a series of assumed \((\text{OC/EC})_{\text{pri}}\). OC/EC at the minimum \(R^2\) of the SOC vs EC relationship represents the authentic primary OC/EC ratio (Millet et al., 2005). Application of MRS on the whole year’s data (Figure 5.4) yields a \((\text{OC/EC})_{\text{pri}}\) of 2.26 (corresponding to a OC/EC percentile 24.77%). \((\text{OC/EC})_{\text{pri}}\) by the percentile method is also examined using the entire year’s data. For a fixed percentile of the lowest OC/EC subset, a value of 10% is often used (Lim and Turpin, 2002), but application of the 5% and 20% percentile subsets have also been reported (Lin et al., 2009; Yuan et al., 2006). Application of the 10% and 20% subsets in our samples yield a \((\text{OC/EC})_{\text{pri}}\) of 1.67 and 1.85 by linear regression (Figure 5.5). Weighted orthogonal distance regression (WODR), which account for errors in both x and y variables, is employed for determining slope and intercept. Obviously, the drawback of the percentile method is that it lacks quantitative criteria. Since the process of percentile selection can be arbitrary, introduction of considerable uncertainty for SOC estimation is expected. It’s worth noting that the intercept term in the OC vs EC WODR, which reflects \(\text{OC}_{\text{non}}\) (see Eq. 5.1), is small (-0.07~0.08) throughout the percentile range, (Figure 5.6). This is also confirmed by good agreement in the slope with intercept and slope without intercept comparison. Since this term is negligible, \(\text{OC}_{\text{non}}\) is zeroed for SOC estimation in this study.
Figure 5.4  Annual (OC/EC)$_{pri}$ value determined by the Minimum R Squared method (MRS). The red curve represents the R$^2$ of EC and SOC at corresponding (OC/EC)$_{pri}$ values (x-axis). The black line represents the frequency distribution of measured OC/EC ratios for the entire year’s dataset. The highlighted area in yellow represents the cumulative distribution percentile of the measured OC/EC ratio.

Figure 5.5  Weighted orthogonal distance regressions (WODR) of percentile subsets: (a) 10% subset; (b) 20% subset. The red line represents WODR through the origin. The purple circles represent the selected subset. The blue line represents WODR with intercept.
To account for variations of (OC/EC)$_{pri}$ throughout the year, monthly subsets of the data are used to perform MRS method as illustrated in Figure 5.7 (plots for individual months are shown in Figure 5.8). Three peaks are observed in spring, summer and fall respectively, indicating the variations in primary emission sources. Several factors might be responsible for the elevation of (OC/EC)$_{pri}$ in these specific periods. For example, the OC/EC ratio of vehicular emission has been shown to have a temperature dependence (Zielinska et al., 2004). (OC/EC)$_{pri}$ by diesel emission will increase when ambient temperature drops. Meanwhile, biomass burning events, which have a much higher (OC/EC)$_{pri}$ than local vehicular emission, will alter the ambient average OC/EC ratio. In Southeast Asia, the biomass burning emission intensity peaks in Spring and Fall (Streets et al., 2003b), which coincides with the (OC/EC)$_{pri}$ peaks observed in this study.
Figure 5.7 Monthly variations determined by the Minimum R Squared (MRS) method. The red curve represents the $(OC/EC)_{pri}$ determined by MRS in the corresponding months. The highlighted area in grey represents the cumulative frequency percentile of the OC/EC isolated as $(OC/EC)_{pri}$ as determined by MRS in that particular month.
Figure 5.8 Monthly variations in the (OC/EC)$_{pri}$ determination based on the Minimum R Squared (MRS) method. January = M1
To further examine the characteristics of primary OC/EC ratio, \((\text{OC/EC})_{\text{pri}}\) determined by MRS \(((\text{OC/EC})_{\text{pri}} \text{ MRS})\) is calculated for individual hours after compiling all of the year’s data and is shown in Figure 5.9. The \(R^2\) curve shows a very clear diurnal dependence. Diurnal variations of \((\text{OC/EC})_{\text{pri}}\) MRS are demonstrated in Figure 5.10. For midnight samples (00:00-5:00 LT), the \((\text{OC/EC})_{\text{pri}}\) MRS appears in the range of 2.0-2.3. For morning samples (6:00-10:00 LT), the \((\text{OC/EC})_{\text{pri}}\) MRS fall in the range of 1.8-2.0, with a daily minimum at 9:00. Afternoon (12:00-17:00) and evening samples (18:00-23:00) exhibit much higher \((\text{OC/EC})_{\text{pri}}\) MRS (2.37~3.03). Two possibilities are considered for the elevated \((\text{OC/EC})_{\text{pri}}\) MRS: (a) The dominant emission source in the afternoon is distinctive from the dominant emission sources from around midnight through morning, (b) an SOC interference by EC co-emitted precursors (Grieshop et al., 2009). A recent radio carbon (\(^{14}\text{C}\)) study (Huang et al., 2014a) revealed significant contribution of SOC from fossil sources in mega cites of China. A study by Xie et al. (2003) reported a dual-peak characteristic of traffic volume hourly variations in downtown Guangzhou. The morning peak and afternoon peaks were comparable although influenced by different type of vehicles. As a result, a change of emission type is not likely the dominating factor for elevated \((\text{OC/EC})_{\text{pri}}\) observed in late afternoon. SOC calculated by \((\text{OC/EC})_{\text{pri}}\) at the 5\(^{th}\) and 25\(^{th}\) percentiles can provide upper and lower limits of SOC estimation as shown in Figure 5.10. The diurnal pattern of SOC is not very sensitive to the selection of \((\text{OC/EC})_{\text{pri}}\) from a particular percentile subset. The diurnal variation of \((\text{OC/EC})_{\text{pri}}\) is consistent with trends of SOC, implying that the interference of SOC from EC co-emitted precursors \((\text{SOC}_{\text{coEC}})\) is likely the dominating factor responsible for the increased \((\text{OC/EC})_{\text{pri}}\) observed in the late afternoon. Hence, to minimize the effect of \((\text{SOC}_{\text{coEC}})\), we propose to adopt the diurnal minimum \((\text{OC/EC})_{\text{pri}}\) MRS as the effective \((\text{OC/EC})_{\text{pri}}\) for the SOC calculation. The diurnal minimum \((\text{OC/EC})_{\text{pri}}\) MRS in different months is adopted in this study to account for both the primary ratio variation and the \((\text{SOC}_{\text{coEC}})\) interference (Figure 5.11). It should be noted that the monthly pattern in Figure 5.11 didn’t change much from Figure 5.7, implying that taking the precursor interference into account will not affect the trend of \((\text{OC/EC})_{\text{pri}}\) monthly variations. To facilitate the application of MRS, a handy tool is developed which is called “Primary OC/EC ratio calculator (POERC)”. POERC is written in Igor Pro (WaveMetrics, Inc. Lake Oswego, OR, USA) to provide an easy-to-use graphical user interface. POERC is designed to perform OC and EC data analysis from time resolved observations, with a particular focus on determining \((\text{OC/EC})_{\text{pri}}\) using MRS. Details of POERC are provided in the supplemental materials.
Figure 5.9  (OC/EC)$_{pri}$ determined by Minimum R Squared method (MRS) by hour of day. 
(a) 0:00 – 5:00 (b) 6:00 – 11:00 (c) 12:00 – 17:00 (d) 18:00 – 23:00
Figure 5.10  Hourly variations of (OC/EC)<sub>pri</sub> MRS. The red line is (OC/EC)<sub>pri</sub> MRS at each corresponding hour after compiling all of the year’s data. The upper green line represents SOC calculated by (OC/EC)<sub>pri</sub> from the 5th percentile, which can be considered the upper limit of SOC estimation. The lower green line represents SOC calculated by (OC/EC)<sub>pri</sub> from the 25th percentile, which can be considered the lower limit of SOC estimation. The highlighted area in grey represents the percentile of the (OC/EC)<sub>pri</sub> MRS in that particular hour.

Figure 5.11  Diurnal minimum (OC/EC)<sub>pri</sub> MRS in different months.
5.4.2 Secondary organic carbon (SOC)

The annual average SOC concentration determined using the Diurnal minimum (OC/EC)_{pri} MRS described above is 2.96±2.55 µgCm⁻³, accounting for 41.67±16.47% of the OC mass. This ratio agrees well with previous studies in the PRD (47% in July) (Hu et al., 2012), and is in the range of other studies (20% to 70%) (Table 5.3). Monthly variations of SOC show a pattern that is low in summer and high in winter (Figure 5.2). Besides absolute values, the SOC/OC ratio can provide a more relevant perspective to look at SOC formation activity (Figure 5.12). It is very clear that SOC/OC is high in summer and fall and low in spring and winter, implying that SOC formation is more active in summer and fall. The pronounced SOC production in summer is also evidenced by a strong correlation between SOC and Ozone as shown in Figure 5.13a&b. The daytime R² during summer is around 0.6, significantly higher than winter (~0.2). A similar pattern between SO₄²⁻ and SOC is also observed as illustrated in Figure 5.13d, where SO₄²⁻ and SOC are well correlated in July (R²=0.73), which is much higher than winter (R² ~0.2). Good correlation between SOC and SO₄²⁻ in summer was also observed in Beijing (R² = 0.61) (Lin et al., 2009). In contrast, correlations between SOC and NO₃⁻ are also inspected (Figure 5.13f), showing a reversed seasonal pattern. In winter, SOC is well correlated with NO₃⁻ (R² ~0.6), but in summer the correlation is much weaker (R² ~0.2). Previous studies indicate that secondary organic aerosol (SOA) yields exhibit a dependence on both VOC composition and NOx levels (Kroll and Seinfeld, 2008). For small hydrocarbons (less than 10 carbons), SOA formation will be suppressed in high NOx conditions, while for larger hydrocarbons, high NOx level will increase SOA yield. The combination of VOC composition and NOx abundance may be associated with the distinct monthly variations of SOC and NO₃⁻ correlation observed at NC. A previous study in the PRD found that SO₄²⁻ production has similar large contributions from gas phase oxidation with OH and aqueous phase oxidation with O₃ while NO₃⁻ formation is dominated by NO₂ oxidation by OH in the gas phase (Xue et al., 2014). These results may imply the possible contribution of aqueous reactions in SOC formation during the summer due to the higher correlation with SO₄²⁻ and O₃. Biomass burning could also have potential contributions to SOC in winter, as evidenced by a higher SOC vs. K⁺ correlation in winter than in summer (Figure 5.14). Summertime SOC concentrations are associated with biogenic VOCs. Good correlation is observed at NC between SOC and isoprene as illustrated in Figure 5.15a&b, which peaks at July (R²=0.56). Both Monthly variations and diurnal patterns of isoprene show a clear temperature dependency (Figure 5.15c&d), suggesting that contribution to SOC formation from biogenic VOC is not negligible in summer. Although
the SOC formation mechanism is still not fully understood, the involvement of VOC precursor
gas oxidation by O₃, NO₃⁻ and OH radical is widely accepted.
Figure 5.12 Time series plots showing hourly variations across seasons (x-axis) and diurnal periods (y-axis) of (a) OC; (b) EC; (c) OC/EC ratio; (d) SOC; (e) SOC/OC ratio values (color gradient).
Figure 5.13 Correlation and variations of of SOC vs O₃, SO₄²⁻ and NO₃⁻. (a)(c)(e) show the scatter plots of SOC vs O₃, SO₄ and NO₃ in the month that have highest correlation throughout the year. (b)(d)(f) Demonstrate the monthly variation of SOC vs. O₃, SO₄ and NO₃ respectively with the regression slope (red solid line for regression with intercept, dash line for regression slope without intercept) and R² (purple line). The corresponding intercept is represented by the green line.
Figure 5.14  Correlation of SOC and K⁺.
(a) Scatter plot of SOC vs. K⁺ in February  

(b) Monthly variations of $R^2$ between SOC and K⁺.

Figure 5.15  SOC and isoprene.
(a) Correlation of SOC and isoprene in July during daytime.  
(b) Monthly variations of SOC vs. isoprene daytime correlation.  
(c) Monthly variations of isoprene concentrations.  
(d) Annual average diurnal profile of isoprene.
Two episodic events are discussed to illustrate the different scenarios of SOC variation in summer and winter. For the summer case as shown in Figure 5.16a, estimated SOC concentration reached 8.37 µgCm\(^{-3}\) at 18:00 on 20 July. On 20 July, a tropical depression (TD) was near Philippines, about 1000 km from our sampling site (Figure 5.17a). Subsidence by the TD resulted in calm weather with very weak wind (1 m\(s^{-1}\)) between 19 – 21 July. The stable and sunny weather favors primary pollutant buildup and secondary formation. The trend of O\(_3\) and SOC match quite well throughout the episodic event, implying the contribution of photochemical reactions to SOC production. The SOC/OC varies from 20% to 70%, with a clear diurnal pattern that is high in daytime and low at night. NO concentrations are low during this episode (average: 4.5 ppb). When the TD grew closer to the PRD, as shown in the weather chart (Figure 5.17b) and evidenced by decreased pressure and increased wind speed (Figure 5.16a), the SOC concentration dropped to 2 µgCm\(^{-3}\) on 23 July due to the favorable mixing conditions. A typical winter episode is illustrated in Figure 5.16b. Metrological conditions are one of the essential factors that influence the development of the winter episode. On 18 – 19 February, the wind speed is high (3~4 m\(s^{-1}\)) and the air parcel mainly comes from the north (Figure 5.16b & Figure 5.18a). The air parcel from the north transports primary pollutants to NC sites. A CO peak (~2200 ppb) during the early morning of 19 Feb demonstrates a similar kind of plume passing by. As the north wind is becoming weak on 20 February, primary pollutants start to build up. The ΔEC/ΔCO is a useful indicator for vehicular emission (details are discussed in section 5.4.6). During this winter episode, ΔEC/ΔCO (5.2 ngm\(^{-3}\)ppb\(^{-1}\)) is higher than the summer case (3.6 ngm\(^{-3}\)ppb\(^{-1}\)), indicating the accumulation of primary pollutants, which is also evidenced by high NO concentrations (peak ~123 ppb). Ground level O\(_3\) concentrations during the winter are lower compared to the summer episode, probably due to titration by NO. As shown in the Figure 5.16b, solar radiation in the winter case is much weaker than the summer time. VOC volatilization is less in winter, and isoprene is 10 times lower than summer at NC site (Figure 5.15c). High NO\(_x\) and low VOC along with weak solar radiation may contribute to the limited ozone and SOC formation activity in the winter case. As a result, SOC/OC ratio in the winter case is also lower than the summer case, implying the lower activity of SOC formation. But due to an accumulation effect, the SOC concentrations in the winter episode are twice higher than the summer case. Starting from the evening of 21 February, the wind direction changed from north to south (Figure 5.18 c~d) and wind speeds increased (Figure 5.16b). Air parcel from the ocean brought cleaner background air parcels, resulting in significant reduction of OC and EC concentrations.
Figure 5.16 SOC episodic events.
(a) Summer high SOC episode (b) Winter high SOC episode
Figure 5.17 Weather chart for the summer SOC episode showing the influence of a tropical depression (TD).
(a) TD 1000 km away from PRD (b) TD 500 km away from PRD
5.4.3 SOC contribution resolved by organic carbon fractions of different volatility

In thermal optical analysis (TOA), carbon fractions evolve at different temperatures based on their volatility. Since the shortened NIOSH protocol (two plateaus in the helium stage, Table 5.1) is applied in our sample analysis, two OC fractions are identified in our samples, low temperature OC (OC<sub>lo</sub>), which vaporized in helium under 600 °C, and high temperature OC (OC<sub>hi</sub>), which evolved between 600 to 840 °C in helium. We apply the MRS method to calculate individual (OC/EC)<sub>pri</sub> by inputting OC<sub>lo</sub> and OC<sub>hi</sub> instead of OC. As a
result, POC and SOC in each carbon fraction can be estimated separately, namely POC\textsubscript{lo}, POC\textsubscript{hi}, SOC\textsubscript{lo} and SOC\textsubscript{hi}. To verify the performance of this approach, we compared the sum of fraction resolved POC\textsubscript{cf} = (POC\textsubscript{lo} + POC\textsubscript{hi}), SOC\textsubscript{cf} = (SOC\textsubscript{lo} + SOC\textsubscript{hi}) and the previously determined POC and SOC. As shown in Figure 5.19, the POC and SOC calculated by the two approaches agree very well (Slope = 0.99 R\textsuperscript{2} = 1), confirming that MRS is reliable in SOC estimation. Absolute and relative contributions of POC and SOC on OC\textsubscript{lo} and OC\textsubscript{hi} are illustrated in Figure 5.20a\&b. Annual average concentrations of OC\textsubscript{lo} and OC\textsubscript{hi} are 6.55 and 0.66 µgCm\textsuperscript{-3} respectively. For OC\textsubscript{lo}, 38\% come from SOC\textsubscript{lo} (2.48 µgCm\textsuperscript{-3}) while for OC\textsubscript{hi}, 78\% are secondarily formed. This result suggests that the more thermally stable OC mainly results from SOC, which is expected to be more oxidized than POC. Previous studies (Huffman et al., 2009) using thermal denuder coupling with AMS also found that more oxygenated organic aerosols are typically less volatile. The monthly variations of the SOC\textsubscript{lo}/OC\textsubscript{lo} ratio are shown in Figure 5.20c by their regression slope in each month. A clear seasonal pattern is observed, which is higher in summer and fall (~0.5) and lower in winter and spring (~0.3). These results imply that SOC formation has more contribution on OC\textsubscript{lo} mass in summer. For the high temperature OC, the SOC\textsubscript{hi}/OC\textsubscript{hi} regression slope varies between 0.82 and 0.95 (Figure 5.20d), without a clear seasonal pattern.

Figure 5.19  POC and SOC determinations by MRS using different OC values either split into carbon fractions (y-axis) or not (x-axis).
(a) POC  (b) SOC
5.4.4 Seasonal and diurnal variations of OC, EC and SOC

The annual average diurnal patterns of OC, EC, SOC and the OC/EC ratio are illustrated in Figure 5.21. The OC diurnal pattern is relatively flat, but is lower in the morning and higher in the afternoon. By examining the OC diurnal profile in different seasons (Figure 5.22), a clear seasonal dependence is observed. In spring, the evening peak is more pronounced and the corresponding 95th percentile whiskers of the box plot are much higher than other seasons, implying that more frequent OC episodic events occur between 16:00 – 20:00 LT in spring. The OC diurnal profile in summer is generally lower in concentration but exhibits a peak in the afternoon that is associated with SOC formation. The OC diurnal pattern in fall and winter is similar, but the evening peak is more pronounced in winter. For EC, nighttime concentrations
are higher than daytime. After the morning rush hour (7:00 – 9:00 LT), EC started to decrease and the lowest concentration appeared in the afternoon. The shape of the EC profile doesn’t show a strong seasonal dependence (Figure 5.23), but its level is much lower in summer. In winter time EC concentration is highest among four seasons, and the morning peak is also broader than other seasons.

Figure 5.21 Annual average diurnal variations of OC EC SOC and OC/EC ratio.
Figure 5.22  Diurnal variations of OC in different seasons.

Figure 5.23  Diurnal variations of EC in different seasons.
Estimated SOC exhibits a diurnal pattern that is lower from midnight through morning and high in the afternoon. The highest SOC concentration appears at 16:00, 14:00, 1:00 and 20:00 for spring, summer fall and winter respectively (Figure 5.24). The afternoon peak in spring, fall and winter didn’t decrease until 22:00, lasting much longer than in summer. The time lag between summer and other seasons may be related to the transport of SOC, since the presence of high SOC loading after sunset is unlikely from local formation. The NC site is south of the urban area of Guangzhou. In winter, NC is downwind of urban Guangzhou, likely one of reasons that causes the SOC peak lag compared to summer. Diurnal patterns of OC/EC and SOC/OC ratio in different seasons are shown in Figure 5.25 and Figure 5.26. Both OC/EC and SOC/OC have similar profiles that exhibit amplitudes with a seasonal dependence. In summer and fall the SOC/OC ratio can reach 0.6 between 14:00-17:00 while in spring and winter the ratio in the same period is less than 0.5. SOC/OC is lowest in the morning due to the primary emission during rush hour (spring – fall: 8:00; winter: 9:00). The 1 hour lag of lowest SOC/OC ratio in winter also confirms that these pollutants observed at NC are likely transported from the north (downtown of Guangzhou).
Figure 5.25  Diurnal variations of OC/EC ratio in different seasons.

Figure 5.26  Diurnal variations of SOC/OC ratio in different seasons.
5.4.5 Rainfall scavenging of OC, EC and SOC

Precipitation during the yearlong study period amounted to 1754 mm. Monthly accumulated rainfall is shown in Figure 5.27. 49 individual rain events are identified to examine the effect of wet removal on OC, EC, POC and SOC. Wet removal effects are investigated by scatter plots shown in Figure 5.28. The regression slopes, which represent rain event concentrations versus pre-rain concentrations, are 0.53±0.03, 0.51±0.03, 0.54±0.03 and 0.52±0.04 for OC, EC, POC and SOC respectively. These results show that around 50% of carbonaceous aerosols are removed through the wet deposition process. The removal rate of EC is comparable to an aircraft campaign at Yellow Sea (BC removal rate: 47% Oshima et al., 2012). A previous study in the PRD during summer found water soluble organic carbon (WSOC) contributed a substantial fraction (47%) to OC mass (Hu et al., 2012), which is consistent with the OC removal rate by rain in our study (47%, annual average), implying the linkage between WSOC/OC ratio and wet removal rate of OC. Generally, soot particles have a relatively low wet removal rate due to its hydrophobic nature (Noone et al., 1992). However, in our study the wet removal rate didn’t show dependence on different species, as evidenced by similar slopes (~0.5) of OC, EC, POC and SOC before and during rain (Figure 5.28). The regression slope (0.92, Figure 5.28e) of the OC/EC ratio before and during rain also supports the similar OC and EC reduction rate by rain. Similarity of wet removal rates suggest that substantial POC, SOC and EC are internally mixed in our study. Freshly emitted EC particles from anthropogenic sources are usually bare (Sakurai et al., 2003), but they can gradually become more hygroscopic during the atmospheric aging process accreting a coating of hygroscopic materials (Chung and Seinfeld, 2002; Moteki et al., 2007), typically in less than 24 hrs (Park et al., 2005a). Previous studies of the EC mixing state in the PRD region show that 40~80% of EC containing particles are internally mixed (Huang et al., 2011a; Huang et al., 2012). EC in PRD is found internally mixed with sulfate, nitrate, ammonium using a single particle aerosol mass spectrometer (SPAMS)(Zhang et al., 2014). Since aged EC becomes more hygroscopic, their lifetime in the atmosphere is expected to be lower than externally mixed EC particles. In addition to the aging process, EC particles emitted from biomass burning (BB) were found to be thickly coated with organic materials (Kondo et al., 2011). A previous study in the PRD (Rose et al., 2010) found that 87% of biomass burning (BB) particles can be activated as Cloud condensation nuclei (CCN) at high supersaturation conditions (S=1.27%). The K+/K ratio in the PRD is close to 1, which is very similar to the K+/K ratio observed in BB source profiles (Watson et al., 2001),
implying that potassium observed in this region is dominated by BB. A moderate correlation between the BB tracer K⁺ and EC was observed in our one year study, with monthly R² values ranging from 0.40–0.71 and an annual R² of 0.53 (Figure 5.29), indicating the substantial contribution of EC from BB emission. Monthly R² variation of EC and K⁺ are examined here in Figure 5.29b, showing a higher correlation in wintertime, which agrees with previous studies that find BB is more active in winter (He et al., 2011). As a result, both the aging process and the influence of BB are important factors contributing to the wet removal rate of EC in this region. As a sub-tropical area, summer accounts for 52% of the annual rainfall. The hygroscopic properties of OC and coated EC particles increases their wet removal favorability, particularly in summer when rain events are more frequent and intense and lower OC and EC levels are observed.

Figure 5.27  Monthly precipitation at the NC sampling site from February 2012 to January 2013.
Figure 5.28  OC, EC, POC and SOC concentrations and OC/EC ratio before and during rain events.

Fitting line in red represents linear regression through the origin. Blue line represents linear fitting with intercept. The color of the circles represent precipitation intensity of individual rain events.
Figure 5.29 Correlation of potassium ion (K\(^+\)) and EC.
(a) Scatter plot for annual data, the color scale represents the month of year. (b) Monthly variations of regression slope, intercept and \(R^2\) of K\(^+\) and EC. The solid red line represents the regression slope that considers an intercept, the dashed red line represents a regression slope through the origin. The green line represents the intercept and the purple line is for \(R^2\). The error bars stand for confidence interval of slopes and intercepts estimation.
5.4.6 Correlation of EC and CO

Both EC and carbon monoxide (CO) are produced by incomplete combustion. An inventory study in Guangzhou for the year 2000 indicated that 20.4 Gg BC and 3477.2 Gg CO were emitted into the atmosphere, with emission sources dominated by industry and the transportation sector (Streets et al., 2003a). Monthly variations of CO are shown in Figure 5.30, which exhibit similar trends to EC. Since EC and CO are co-emitted from combustion sources, good correlation of EC and CO is expected (Chen et al., 2001), especially in urban areas like Tokyo (Kondo et al., 2006), Mexico (Subramanian et al., 2010), Beijing (Han et al., 2009) and Guangzhou (Verma et al., 2010). The slope of the EC and CO correlation (ΔEC/ΔCO) varies by different emission sources; for example, ΔEC/ΔCO by diesel vehicles are much higher than gasoline vehicles (Han et al., 2009). Since both EC and CO are relatively inert in the atmosphere, ΔEC/ΔCO is considered to be an indicator to reflect the contribution of changing emission sources in urban areas (Kondo et al., 2006). To minimize ΔEC/ΔCO outliers due to occasional removal events (rain; cold front passing by), only data under weak wind conditions (wind speed ≤ 2 ms\(^{-1}\)) without precipitation are selected for discussion. The annual ΔEC/ΔCO is 7.1 ngm\(^{-3}\)ppb\(^{-1}\) (Figure 5.30a), comparable to previous studies in Guangzhou during summer (5.4ngm\(^{-3}\)ppb\(^{-1}\), Verma et al., 2010), winter (7.9ngm\(^{-3}\)ppb\(^{-1}\), Andreae et al., 2008) and other urban locations around the world (}
Table 5.4). Monthly variations of ΔEC/ΔCO are observed, ranging from 5.8 to 14.3 ngm⁻³ppb⁻¹ (Figure 5.30b). The ΔEC/ΔCO ratio is relatively lower in the summer because of the clean air from the South China Sea and elevated in winter time due to the regional transport of pollutants from Eastern China by the northeast monsoon. Lee et al. (2013) report higher correlation between CO and EC and higher ΔEC/ΔCO in biomass burning episodes in Hong Kong. Han et al. (2009) found that temperature plays an important role in low ΔEC/ΔCO ratios observed in Beijing during winter, due to the temperature dependence of EC and CO emission factors from vehicles. We examine the temperature dependence of ΔEC/ΔCO in our samples (Figure 5.31), but the correlation is quite weak. The possible reason that a pronounced temperature dependence wasn’t observed at the NC site may relate to the subtropical climate of this region. The lowest temperature in Guangzhou throughout the year was around 9 °C, making the cold-start effect less significant compared to Beijing, where winter temperature is as low as -10°C. A distinct diurnal pattern of ΔEC/ΔCO is shown in Figure 5.30d with higher ratios from 00:00 to 12:00 and lower ratios from 12:00 to 24:00. The increased ΔEC/ΔCO during 00:00 to 12:00 is associated with boundary layer height as well as truck regulations in Guangzhou. During night time, due to the shallow boundary layer depth, convection is weak, resulting in accumulation of local primary pollutants. Furthermore, since 2010 October, heavy trucks have been banned from 7:00 ~ 22:00 in Guangzhou (Figure 5.32), making heavy trucks more active at night. Since ΔEC/ΔCO from diesel trucks is higher than other emission sources, and combined with the trapping effect due to the shallow boundary layer, ΔEC/ΔCO is elevated during the nighttime. The highest ΔEC/ΔCO appear at morning rush hour (8:00~10:00), suggesting that traffic activities are one of the major driver of ΔEC/ΔCO variations. This distinct ΔEC/ΔCO diurnal pattern implies that the higher EC concentration observed during 00:00 to 12:00 is not only due to the low mixing height at midnight, but also associated with the high-emitting diesel trucks and morning rush hour.
Figure 5.30 EC and CO correlations.
The regression slope represents $\Delta EC/\Delta CO$. (a) Annual results of EC and CO regression, the color of the dots represent months. (b) Monthly regression slope, intercept and $R^2$ of EC vs. CO (c) Same as (a) but with a color coding of hour (d) Hourly regression slope.
Figure 5.31  dependence of ΔEC/ΔCO on temperature.
The color scale represents the month of each data point.

Y=aX+b
a=-0.0001 ± 0.0000
b=0.0054 ± 0.0001
R^2 =0.0744
N=3829
Figure 5.32  Comparison of truck regulation implementation in the Guangzhou urban area for 2002, 2007 and 2010. The blue area represents time slots available for trucks, while the grey area represent time slots that trucks are banned. The definitions of local/non-local light trucks were changed in 2010 as summarized in the attached table.
Table 5.4 Comparisons of EC concentrations and $\Delta$EC/$\Delta$CO around the world.

<table>
<thead>
<tr>
<th>Location and Time</th>
<th>EC $\mu$g m$^{-3}$</th>
<th>$\Delta$EC/$\Delta$CO ng m$^{-3}$ppb$^{-1}$</th>
<th>EC determination</th>
<th>Reference</th>
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<tr>
<td>Guangzhou, China (Feb 2012-Jan 2013)</td>
<td>2.64</td>
<td>7.1</td>
<td>TOT</td>
<td>this study</td>
</tr>
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<td>Guangzhou, China (Jul 2006)</td>
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<td>5.4</td>
<td>TOT</td>
<td>(Verma et al., 2010)</td>
</tr>
<tr>
<td>Guangzhou, China (Jul 2006)</td>
<td>3.3</td>
<td>7.9</td>
<td>TOT</td>
<td>(Hu et al., 2012)</td>
</tr>
<tr>
<td>Guangzhou, China (Oct-Nov 2004)</td>
<td>7.1</td>
<td>7.9</td>
<td>TOT</td>
<td>(Andreae et al., 2008)</td>
</tr>
<tr>
<td>Beijing, China (2005-2006)</td>
<td>6.9</td>
<td>3.5-5.8</td>
<td>TOT</td>
<td>(Han et al., 2009)</td>
</tr>
<tr>
<td>Tokyo, Japan (2003-2005)</td>
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<td>5.7</td>
<td>TOT</td>
<td>(Kondo et al., 2006)</td>
</tr>
<tr>
<td>Gwanju, South Korea (Mar-May 2001)</td>
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<td>6</td>
<td>TOT</td>
<td>(Park et al., 2005c)</td>
</tr>
<tr>
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<td>3.2</td>
<td>TOT</td>
<td>(Lim and Turpin, 2002)</td>
</tr>
<tr>
<td>Bangkok, Thailand (Apr 2007 – Apr 2008)</td>
<td>2.8-5.6</td>
<td>7.9-9.8</td>
<td>TOT</td>
<td>(Sahu et al., 2011)</td>
</tr>
</tbody>
</table>
5.5 Conclusions

One year of time resolved OC and EC measurements were conducted at a site (NC) located in the heart of the PRD’s city clusters. Annual mean OC, EC and TC concentrations (±1sd) at the NC site are 7.20±5.68, 2.64±2.28 and 9.84±7.80 µgCm⁻³ respectively. Application of MRS for (OC/EC)ₚᵣᵢ estimation shows that (OC/EC)ₚᵣᵢ could be overestimated in the afternoon due to the interference of EC co-emitted SOC precursors. To minimize this artifact, this study adopted the diurnal minimum (OC/EC)ₚᵣᵢ by MRS as the effective (OC/EC)ₚᵣᵢ. In addition, to account for seasonal variation of (OC/EC)ₚᵣᵢ (e.g. elevated (OC/EC)ₚᵣᵢ in the biomass burning season), (OC/EC)ₚᵣᵢ is calculated for individual months. The annual average estimated SOC is 2.96±2.55 µgCm⁻³, accounting for 41% of the OC mass. SOC exhibits a higher abundance in winter, but its formation activity is higher in summer as evidenced by elevated SOC/OC ratios in summer. Good correlations between SOC and O₃ and SO₄²⁻ were observed in summer, while for SOC and NO₃⁻, higher correlation appeared in winter. OC determination with different carbon fractions is used for SOC estimation. Sum of SOC from the individual carbon fractions agrees very well with SOC estimated by total OC. SOC contribute 38% to low temperature OC (evolved <600 °C) and 78% to high temperature OC (evolved between 600 °C and 840°C), implying that most of the high temperature OC (probably more oxygenated) is secondarily formed. A study of 49 individual rain events during the year-long study shows that carbonaceous particle mass is reduced by ~50% during a rain event. The removal rate is similar for POC, SOC and EC, suggesting the mixing state of carbonaceous particles is probably dominated by internal mixing. Higher EC/CO ratios were observed from midnight to morning, and are found to be associated with shallow mixing depths as well as a higher traffic volume of diesel trucks at night and enhanced traffic activities at morning rush hour.
Chapter 6

6. Optical properties of black carbon aerosols in the Pearl River Delta (PRD) region: implications for light absorption enhancement

Chapter summary

Black carbon (BC) aerosol is a crucial component in the atmosphere contributing to the air pollutant PM$_{2.5}$ and impacting climate as a radiative forcer with its ability to absorb light. Light absorption by BC particles is sensitive to the mixing state which varies during the aerosol aging process. Aged BC particles can absorb more light when coated by non-absorbing or weakly absorbing materials. However, light absorption enhancement studies are limited in the Pearl River Delta (PRD) region. In this study core-shell Mie simulation is performed to investigate the probable range of the light absorption enhancement factor ($E_{abs}$). Considering the typical size distribution of BC particles in the PRD, an upper limit of $E_{abs}$ ~2 is estimated. Annual average mass absorption efficiency (MAE) at a PRD suburban site Nancun (NC) is 19.75±8.9 m$^2$g$^{-1}$. Applications of Minimum R Squared (MRS) method and linear regression are conducted to investigate primary MAE (MAE$_{pri}$). The annual average MAE$_{pri}$ estimated by MRS and linear regression is 12.7 and 13.16 m$^2$g$^{-1}$ respectively, implying an annual average $E_{abs}$ of 1.50~1.55. Seasonal variations of MAE are observed, which are much higher in summer. A multiple regression analysis (MRA) shows that from April to September the absorption enhancement is mainly associated with SO$_4^{2-}$ and NO$_3^{-}$, while from October to March, SOC, SO$_4^{2-}$ and NO$_3^{-}$ are responsible for the increased MAE. BC concentrations from an aethalometer and EC from a RT-ECOC analyzer are compared and causes of discrepancy are discussed. Retrieval of the light absorption coefficient ($\sigma_{abs}$) from the RT-ECOC analyzer is demonstrated and exhibits consistent performance with the aethalometer.
6.1 Introduction

Optical properties of black carbon (BC) aerosols can be predicted by knowing their mass concentration, mixing state and size distribution. These factors serve as the cornerstone for modeling the climate effect of BC. In modeling studies faced with a limitation in computational resources, a conversion factor of mass absorption efficiency (MAE) or mass absorption cross-section (MAC) is used to convert black carbon mass to light absorption coefficient ($\sigma_{abs}$). MAE is a quantity to describe the light absorption ability per unit BC mass:

$$\text{MAE} (m^2 g^{-1}) = \frac{\text{absorption coefficient } \sigma_{abs} (Mm^{-1})}{\text{BC mass concentration (\mu gm^{-3})}}$$  

As a fundamental input parameter, MAE has a critical impact on BC’s radiative forcing estimation in climate modeling studies. Mixing state is one of the governing factors affecting MAE. Light absorption of soot particles is enhanced when coated with non-absorbing materials (Fuller et al., 1999) or weak absorbing materials (Lack and Cappa, 2010). The coating materials can focus more light onto the soot core through the lensing effect. Previous studies suggest that absorption of aged soot particles can be 1.5 times greater than fresh soot (Bond et al., 2006; Fuller et al., 1999). Absorption enhancement of soot particles has been found by coating with SOA (Schnaiter et al., 2005), sulfuric acid (Zhang et al., 2008a; Khalizov et al., 2009) and organic materials (Shiraiwa et al., 2010; Saathoff et al., 2003). Besides coating after emission, BC can be internally mixed with organic matter (OM) when emitted from certain sources like biomass burning (Roden et al., 2006). In this study, yearlong MAE measurements at a PRD suburban site are reported, and potential factors that affect the variability of observed MAE are discussed.
6.2 Mie simulation

In addition to using ambient soot particle optical property data, it can be informative to model a single soot particle using Mie theory (Bohren and Huffman, 1983) and understand the theoretical range and variability of soot particle MAE. Three types mixing state are currently available for parameterization: internal mixing, external mixing and core-shell. To better represent the real situation (coating due to the aging process), a core-shell model is considered in Mie the calculation (Figure 6.1), which is more realistic than a volume mixture model (Bond et al., 2006). An aerosol optical closure study in the North China Plain (NCP) found that the core-shell model can provide better performance than assuming purely internal mixing and external mixing (Ma et al., 2012). It should be noted that the core-shell model assumption has its own limitations. Using a single particle soot photometer (SP2), Sedlacek et al. (2012) reported a negative lag time between the scattering and incandescence signals in samples influenced by biomass burning, implying fragmentation of soot and non-absorbing materials, which was thought to be at a near surface location of soot. Recently, near surface type mixing of soot has been observed in Tokyo, which account for 10% of total mixed soot containing particles (Moteki et al., 2014). As a result, considering the domination of core-shell type particles in ambient environment, the core-shell assumption in our optical model was sufficient to approximate the real situation. As shown in Figure 6.1, fresh emitted soot particles are chain-like aggregates of small spheres (30–50nm). After the aging process, soot particles are coated with organic and inorganic materials. Sufficient evidence has shown that the coating not only results in particle size growth, but also makes the soot core become more compact due to its collapse (Alexander et al., 2008; Lewis et al., 2009; Zhang et al., 2008a). Since the spherical like core and shell favor Mie simulation, both core and shell are considered as spheres in the Mie calculation. As suggested by Bond and Bergstrom (2006), a refractive index (RI) of 1.85 – 0.71i and 1.55 are adopted for soot core and non-absorbing coating respectively in the Mie calculation. Simulation work by Bond et al. (2006) indicates that absorption amplification is not sensitive to the RI, thus the result below is not expected to be sensitive to the RI variability. 1.9 gcm$^{-3}$ is chosen as the density of soot following the recommendation of Bond and Bergstrom (2006) while for coating materials the density is set to 1 gcm$^{-3}$. It should be noted that the core-shell type mixing state of particles is still difficult to implement in some atmospheric modals like WRF-Chem (Nordmann et al., 2014).
Variations of MAE and mass scattering efficiency (MSE) of bare soot particles as a function of their size at a wavelength of 550 nm are illustrated in Figure 6.2. MSE is low for particles smaller than 100 nm and peaks at around 217 nm (MSE=5.01 m²g⁻¹) before gradually decreasing. MAE increases from 7 to 9.2 m²g⁻¹ in the range of 10 to 150 nm. Soot particles larger than 150 nm exhibit a decreasing trend in MAE as function of diameter. For a particle of 4 µm, the MAE is 0.3 m²g⁻¹. These results confirm that MSE and MAE are strongly dependent on the Mie size parameter, \( x=\pi d/\lambda \), where \( d \) is the diameter of the particle and \( \lambda \) is the wavelength of incident light. For wavelengths shorter than 550 nm, the maximum MAE occurs at a smaller particle size, while at wavelengths larger than 550 nm, the maximum MAE occurs at the larger particle size.

Correlations between MAE and the number fraction of coated particles have been reported in urban areas in China like Shenzhen (Lan et al., 2013) and Xi’an (Wang et al., 2014a), implying that the elevated MAE observed at these locations was mainly due to the coating of soot particles rather than shift of primary soot size distribution. Therefore, to investigate the effect of coating on MAE variability, a core-shell Mie model study has been conducted and shown in Figure 6.3.
Figure 6.2 Mass absorption efficiency (MAE) and mass scattering efficiency (MSE) of a bare soot particle as a function of diameter at a wavelength of 550 nm. Refractive index is $1.85 - 0.71i$ and density is $1.9 \text{ g cm}^{-3}$.

Figure 6.3 Mass absorption efficiency (MAE) of soot particles at wavelength 550 nm. (a) Combination of different shell (y axis) and core diameters (x axis). The color code represents the MAE of a particle with specific core and shell size; (b) Cross-sections views of (a). The line in blue shows the variations of MAE of bare soot particles at different diameters. The green, purple and red lines illustrate the MAE changes during soot particle growth, demonstrated with core diameters of 60 nm, 100 nm and 150 nm respectively as a function of shell diameters (x axis).
In Figure 6.3a the x- and y-axes represent the core diameter of the soot particle and the shell diameter after coating. So the y=x line is representative of a bare soot particle and data points above y=x line indicate different degrees of coating thickness. The color coding represents the MAE at corresponding core and shell diameter combinations. Figure 6.3 demonstrates that coating characteristics can enhance single particle MAE and the degree of enhancement dependence on both core diameter and coating thickness. Figure 6.3b provides a cross-sectional view of Figure 6.3a to look at the variability of MAE at selected particle sizes. For a 60 nm soot particle, MAE can increase from 7.5 m²g⁻¹ to 39 m²g⁻¹ if it grows to the size of 480 nm. MAE of a 100 nm soot particle can increase from 8.5 m²g⁻¹ to 31 m²g⁻¹ when it grows to the size of 480 nm. For a bare soot particle of 150 nm, its MAE can increase from 9.2 m²g⁻¹ to 20.9 m²g⁻¹ (growth to 480 nm). These results imply that the enhancement due to coating has a limit when coating reach certain thickness. In addition, for the same coating thickness, the elevation of MAE is more significant on particles with a smaller core.

In the EC tracer method, OC is divided into two parts: primary OC, which is co-emitted with EC, and secondary OC (SOC), which forms during the aging process after emission. Similarly, observed $\sigma_{abs}$ can be separated into two parts: $\sigma_{abs\text{-}pri}$ due to uncoated soot particles and extra absorption ($\sigma_{abs\text{-}coat}$) due to the coating.

$$\sigma_{abs\text{-}total} = \sigma_{abs\text{-}pri} + \sigma_{abs\text{-}coat}$$  \hspace{1cm} (6.2)

Here we propose to use MAE$_{pri}$ to represent the ratio of $\sigma_{abs\text{-}pri}/EC$ for uncoated soot particles, similar to the concept of the primary OC/EC ratio in the EC tracer method:

$$MAE_{pri} = \frac{\sigma_{abs\text{-}pri}}{EC}$$  \hspace{1cm} (6.3)

And the overall MAE due to the coating can be defined as:

$$MAE_{total} = \frac{\sigma_{abs\text{-}total}}{EC}$$  \hspace{1cm} (6.4)

Thus the absorption enhancement of a soot particle can be estimated either by MAE or $\sigma_{abs}$ with the following equation.

$$E_{abs} = \frac{MAE}{MAE_{pri}} = \frac{\sigma_{abs\text{-}total}}{\sigma_{abs\text{-}pri}}$$  \hspace{1cm} (6.5)

Thus, the maximum enhancement for a soot particles with core diameters of 60, 100 and 150 nm is 2.3, 3.6 and 5.2 respectively. An artificial coating experiment by Shiraiwa et al. (2010) found an $E_{abs}$ of 2 for graphite particles growing from 185 to 370 nm. Aircraft measurements over Costa Rica observed an enhancement of 1.3 in the lower-troposphere (Schwarz et al., 2008).
Photo-Acoustic Extinctiometer (PAX) coupled with a Single Particle Soot Photometer (SP2) at Xi’an of China measured found an $E_{abs}$ of 1.8 at 870 nm (Wang et al., 2014a). Lan et al. (2013) reported an $E_{abs}$ of 1.3 in Urban Shenzhen of China using SP2 incorporated with a Photoacoustic Soot Spectrometer (PASS3). Both primary soot size distribution and coating thickness can affect the absorption enhancement of ambient BC particles. Soot particles measured in the PRD using laser-induced incandescence (LII) found BC number concentrations peaking at 110 nm and BC mass concentration peaking at 220 nm (Huang et al., 2011b). Considering that the LII technique is specific for BC mass determination which is independent of BC mixing state, the size distribution reported by LII can represent the size distribution of the BC core. A study using a Micro Orifice Uniform Deposit Impactor (MOUDI) found a BC mass size distribution in the PRD exhibiting three modes peaking at ~300, ~900 and ~5000 nm (Yu et al., 2010), implying a substantial coating of BC particles. From this MOUDI measurement, soot particle growth resulted in a diameter amplification of 3. Considering the BC core number concentration measured by SP2 (110 nm) and the MAE growth calculation (Figure 6.3b), the upper limit of $E_{abs}$ in PRD is roughly estimated as ~2.
6.3 MAE estimation from ambient data

Sampling was conducted from Feb 2012 to Jan 2013 at the suburban Nancun (NC) site. Optical measurements was performed by a 7-λ aethalometer (AE-31, Magee Scientific Company, Berkeley, CA, USA) and the EC mass concentrations determined by a real time ECOC analyzer (Model RT-4, Sunset Laboratory Inc., Tigard, Oregon, USA). Details of the instrumental setup and site characteristics have been discussed in chapter 5.

The frequency distribution (log-normal) of $\sigma_{abs}$ is shown in Figure 6.4a, with an annual average ($\pm 1\text{sd}$) of $41.55\pm 29.41\ \text{Mm}^{-1}$. A log-normal distribution is also found in the EC mass concentration (Figure 6.4b), with an annual average of $2.57\pm 2.22\ \mu\text{gm}^3$. Figure 6.4c demonstrates the yearlong frequency distribution of MAE (550 nm) at the NC site. The annual average MAE is $19.75\pm 8.95\ \text{m}^2\text{g}^{-1}$ and peaks ($\pm \sigma$) of the normal and lognormal fits are $16.18\pm 3.28$ and $15.71\pm 0.22\ \text{m}^2\text{g}^{-1}$ respectively. A good correlation is observed between light absorption and EC mass ($R^2=0.91$) as shown in Figure 6.4d.

Linear regression is extensively employed when using the EC tracer method for estimating the primary OC/EC ratio. Similarly, here we apply a weighted orthogonal distance regression (WODR) to account for measurement errors in both the x and y dimensions (Zwolak et al., 2007) when estimating $\text{MAE}_{pri}$ as shown in Figure 6.4d. The slope of the regression line in the scatter plot represents $\text{MAE}_{pri}$ in the NC samples. It should be noted that a clear discrepancy can be found between the slope with intercept (13.16) and without intercept (17.99). Since a fit line of WODR represents the maximum likelihood between $\sigma_{abs}$ and EC, the slope accounts for the correlated part of $\sigma_{abs}$, while the uncorrelated part of absorption is attributed to the intercept. Thus the slope with intercept represents an average $\text{MAE}_{pri}$ of soot particles without coating and the slope without intercept represents average MAE with coating. As a result, the slope (17.99) without intercept is closer to the arithmetic mean of observed MAE (19.75). The annual average $E_{abs}$ for bulk BC following Eq. 6.5 is estimated to be $19.75/13.16=1.50$. The uncertainty of $E_{abs}$ estimation depends on uncertainty propagation from MAE uncertainty, which can be calculated from (Harris, 2010):

$$\text{Unc}_{MAE} = MAE \times \sqrt{\left(\frac{\text{Unc}_{\sigma_{abs}}}{\sigma_{abs}}\right)^2 + \left(\frac{\text{Unc}_{EC}}{EC}\right)^2}$$  

$$\text{Unc}_{E_{abs}} = E_{abs} \times \sqrt{\left(\frac{\text{Unc}_{MAE}}{MAE}\right)^2 + \left(\frac{\text{Unc}_{\text{MAE}_{pri}}}{\text{MAE}_{pri}}\right)^2}$$

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Considering a measurement uncertainty of 5% for Aethalometer (Hansen, 2005) and 24% for RT-ECOC analyzer (Bauer et al., 2009), the propagated relative uncertainty of \( \varepsilon_{\text{abs}} \) is 35%. It should be noted that the \( \varepsilon_{\text{abs}} \) uncertainty is mainly attributed to the measurement uncertainty of RT-ECOC analyzer. Since the measurement uncertainty of RT-ECOC analyzer estimated by Bauer et al. (2009) is obtained from field measurement at an environment (EC below 1 µgCm\(^{-3}\)) that EC is much lower than the present study, so the \( \text{Unc}_{\varepsilon_{\text{abs}}} \) of 35% is only the upper limit for \( \varepsilon_{\text{abs}} \) uncertainty estimation for present study.

Besides linear regression, the Minimum R squared method (MRS) has proved to be a useful tool for estimating \((\text{OC/EC})_{\text{pri}}\), the primary OC/EC ratio (see Chapter 5). As shown in Figure 6.5, the annual average MAE\(_{\text{pri}}\) estimated by MRS is 12.7 m\(^2\)g\(^{-1}\), which is comparable to the MAE\(_{\text{pri}}\) estimated by linear regression (13.16 m\(^2\)g\(^{-1}\)). The annual average \( \varepsilon_{\text{abs}} \) for bulk BC by MRS following Eq. 6.5 is estimated to be 19.75/12.7=1.55, which is comparable to the \( \varepsilon_{\text{abs}} \) reported for a single particle measurement (1.31) by Schwarz et al. (2008). The magnitude of the \( \varepsilon_{\text{abs}} \) estimation using two independent approaches (linear regression and MRS) indicates that the light absorption amplification of soot particles is substantial at the NC site.
Figure 6.4 Frequency distribution of $\sigma_{abs}$, EC and MAE.

(a) Annual frequency distribution of light absorption at 550 nm. (b) Annual frequency distribution of EC mass concentration. (c) Frequency distribution of Mass absorption efficiency (MAE) at 550 nm. (d) Scatter plot of light absorption (550 nm) and EC mass. The slope represents MAE.
Figure 6.5 Minimum R squared (MRS) plot of MAE. The red curve are the correlation results between $\sigma_{\text{abs-coat}} (\sigma_{\text{abs}} - EC \times MAE_{\text{prl}})$ and EC mass. The black line represents the frequency distribution of observed MAE. The area in yellow is the cumulative distribution of observed MAE.
Table 6.1 summarizes previous MAE studies at various locations. Since a range of wavelengths are used in the different studies, equivalent MAE at 550 nm is calculated following equations given by Moosmuller et al. (2011) for comparison purposes. During this conversion, the angstrom absorption exponent (AAE) of BC is assumed to be 1. Many quantities are available to interpret observed MAE, including arithmetic mean, mode (Gaussian fitting) and median. Besides, $\text{MAE}_{\text{pri}}$ can be estimated from the slope of non-zero-intercept linear regression or MRS as demonstrated above. In terms of arithmetic mean, annual average observed MAE at NC (19.75 m$^2$g$^{-1}$) is higher than most studies listed in Table 6.1, like Shenzhen (6.29 m$^2$g$^{-1}$) (Lan et al., 2013), Beijing (Yang et al., 2009) and Mexico city (Doran et al., 2007). The estimated $\text{MAE}_{\text{pri}}$ (linear regression) is higher than other studies like Guangzhou (7.44 m$^2$g$^{-1}$) (Andreae et al., 2008), but comparable to Xi’an (11.34 m$^2$g$^{-1}$) (Wang et al., 2014a), Toronto (9.53~12.57 m$^2$g$^{-1}$) (Knox et al., 2009) and a rural Mediterranean site (12.04 m$^2$g$^{-1}$) (Pandolfi et al., 2011). Two major uncertainties associated with the $\sigma_{\text{abs}}$ and EC determination techniques should be taken into account when comparing MAE across different studies. For the $\sigma_{\text{abs}}$ determination technique, photo-acoustic spectroscopy (PAS) is known as the most reliable in-situ technique but its application is limited by its high cost. The filter based optical transmittance method (e.g., aethalometer, Multi Angle Absorption Photometer, MAAP) is the most widely used technique around the world, but data correction is needed to minimize the bias from artifacts due to the loading effect, matrix effect and scattering effect (Coen et al., 2010). In our study, careful corrective measures are conducted for the Aethalometer $\sigma_{\text{abs}}$ data treatment to minimize the artifact. But we are aware that such artifacts still cannot be fully eliminated. For the EC determination method, different analysis protocols can impact the measurement variability and thus MAE. As shown in Table 6.1, MAE at Fresno varies from 6.1 to 9.3 m$^2$g$^{-1}$, depends on which EC analysis protocol is applied (Chow et al., 2009). A study in the PRD found that discrepancies in measured EC by different analysis protocols could be as large as a factor of 5 (Wu et al., 2012), which adds to the uncertainty for the MAE estimation. In addition, EC by TOA is also different from refractory BC (rBC) reported by the laser induced incandescence (LII) technique. For example, two studies in Toronto (Knox et al., 2009; Chan et al., 2011) both used the PAS for $\sigma_{\text{abs}}$ measurement but different techniques for EC mass determination, resulting in very different MAE results. LII instruments (e.g. single particle soot photometer, SP2) are usually calibrated with a commercially available surrogate (e.g. fullerene) since direct calibration with ambient soot is not easy to achieve. Laborde et al. (2012) indicates that the incandescence response of SP2 exhibits a dependency on soot type (15% between fullerene and denuded diesel soot particles; 14% between biomass burning and denuded diesel
soot particles). All these uncertainties, including the uncertainty of rBC mass determination by SP2, uncertainty of NIOSH EC in thermal-optical analysis, the discrepancy between SP2 rBC and NIOSH EC and the discrepancy of $\sigma_{abs}$ between filter transmission and photo-acoustic methods, will contribute to the differences in MAE estimation listed in Table 6.1.
Table 6.1 Comparison of Mass absorption efficiency (MAE) at various locations. For literature MAE values at different wavelengths rather than 550nm, an estimated MAE at 550nm is given in the brackets.

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Sampling Duration</th>
<th>Inlet</th>
<th>λ (nm)</th>
<th>σabs Instrument</th>
<th>EC determination protocol</th>
<th>σabs ±1sd (Mm⁻¹)</th>
<th>EC mass (µgm⁻³)</th>
<th>estimated MAPtot (µgm⁻²)</th>
<th>observed MAE (µgm⁻²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guangzhou, China</td>
<td>Suburban</td>
<td>2012.2-2013.1</td>
<td>PM₂.₅</td>
<td>550</td>
<td>AE</td>
<td>NIOSH_TOT</td>
<td>41.5±29.41</td>
<td>2.57±2.22</td>
<td>13.16/12.7**</td>
<td>19.75±8.95</td>
<td>This study</td>
</tr>
<tr>
<td>Shenzhen, China</td>
<td>Urban</td>
<td>2011.8-9</td>
<td>PM₂.₅</td>
<td>532</td>
<td>PAS</td>
<td>LII</td>
<td>25.4±19.0</td>
<td>4.0±3.1</td>
<td>/</td>
<td>6.5±0.5[6.29±0.48]</td>
<td>(Lan et al., 2013)</td>
</tr>
<tr>
<td>Xi’an, China</td>
<td>Urban</td>
<td>2012.12-2013.1</td>
<td>PM₂.₅</td>
<td>870</td>
<td>PAS</td>
<td>LII</td>
<td>/</td>
<td>8.8±7.3</td>
<td>7.17[11.34]</td>
<td>/</td>
<td>(Wang et al., 2014a)</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>Urban</td>
<td>2004.10</td>
<td>PM₂.₅</td>
<td>532</td>
<td>PAS</td>
<td>NIOSH_TOT</td>
<td>91±60</td>
<td>7.1</td>
<td>7.7[7.44]</td>
<td>/</td>
<td>(Andreae et al., 2008)</td>
</tr>
<tr>
<td>Fresno, USA</td>
<td>Urban</td>
<td>2005.8-9</td>
<td>PM₂.₅</td>
<td>532</td>
<td>PAS</td>
<td>IMPROVE_A_TOR</td>
<td>5.06</td>
<td>1.01</td>
<td>/</td>
<td>6.1±2.5[5.9±2.42]</td>
<td>(Chow et al., 2009)</td>
</tr>
<tr>
<td>T1, Mexico city, Mexico</td>
<td>Suburban</td>
<td>2006.3</td>
<td>PM₂.₅</td>
<td>870</td>
<td>PAS</td>
<td>NIOSH_TOT</td>
<td>/</td>
<td>/</td>
<td>9.2–9.7***[14.55–15.34]</td>
<td>/</td>
<td>(Doran et al., 2007)</td>
</tr>
<tr>
<td>Pasadena, USA</td>
<td>Urban</td>
<td>2010.5-6</td>
<td>PM₂.₅</td>
<td>532</td>
<td>AM</td>
<td>NIOSH_TOT</td>
<td>3.8±3.4</td>
<td>0.6–0.7</td>
<td>5.7[5.51]</td>
<td>/</td>
<td>(Thompson et al., 2012)</td>
</tr>
<tr>
<td>Toronto, Canada</td>
<td>Suburban</td>
<td>2007.8</td>
<td>PM₂.₅</td>
<td>781</td>
<td>PAS</td>
<td>LII</td>
<td>4.4±2.9</td>
<td>0.27±0.23</td>
<td>/</td>
<td>16±1[22.72±1.42]</td>
<td>(Chan et al., 2011)</td>
</tr>
<tr>
<td>Ottawa, Canada</td>
<td>Urban</td>
<td>2005.3</td>
<td>26±17</td>
<td>1.7±0.9</td>
<td></td>
<td>/</td>
<td>15±3[21.3±4.26]</td>
<td>9.5</td>
<td>11.3</td>
<td>/</td>
<td>(Yang et al., 2009)</td>
</tr>
<tr>
<td>Montseny, Spain</td>
<td>Rural (Mediterranean)</td>
<td>2009.11-2010.10</td>
<td>PM₁₀</td>
<td>637</td>
<td>MAAP</td>
<td>NIOSH_TOT</td>
<td>2.8±2.2</td>
<td>/</td>
<td>10.4[12.04]</td>
<td>/</td>
<td>(Pandolfi et al., 2011)</td>
</tr>
<tr>
<td>Jungfraujoch, Switzerland</td>
<td>Rural (high alpine)</td>
<td>2007.2-3</td>
<td>637</td>
<td>MAAP</td>
<td>LII</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>10.2±3.2[11.81±3.71]</td>
<td>/</td>
<td>(Liu et al., 2010)</td>
</tr>
<tr>
<td>Lin’an, China</td>
<td>Rural</td>
<td>1999.11</td>
<td>PM₂.₅</td>
<td>550</td>
<td>PSAP</td>
<td>NIOSH_TOT</td>
<td>23±14</td>
<td>3.4±1.7</td>
<td>/</td>
<td>8.6±0.7</td>
<td>(Xu et al., 2002)</td>
</tr>
<tr>
<td>Jeju Island, Korea</td>
<td>Coastal Rural, (East China Sea)</td>
<td>2001.4</td>
<td>PM₁₀</td>
<td>550</td>
<td>PSAP</td>
<td>NIOSH_TOT</td>
<td>/</td>
<td>/</td>
<td>12.6±2.6</td>
<td>/</td>
<td>(Chuang et al., 2003)</td>
</tr>
<tr>
<td>Maldives</td>
<td>Oceanic rural</td>
<td>1999.2-3</td>
<td>PM₁₀</td>
<td>550</td>
<td>PSAP</td>
<td>EGA</td>
<td>62±34</td>
<td>2.5±1.4</td>
<td>6.6</td>
<td>8.1</td>
<td>(Mayol-Bracero et al., 2002)</td>
</tr>
</tbody>
</table>

* Determined by linear regression; ** Determined by Minimum R Squared method; *** Median values;
AE: Aethalometer; PAS: photo acoustic spectrometer; MAAP: Multi Angle Absorption Photometer; PSAP: particle soot absorption photometer; AM: albedo meter; LII: Laser induced incandescence
Monthly variations of MAE from the NC site are shown in Figure 6.6a, with a distinct pattern that is high in summer and low in winter. MAE_{pri} calculated by MRS are comparable to regression slope with intercept, while MAE by regression slope without intercept agrees well with the arithmetic mean MAE. Monthly E_{abs} is calculated by Eq. 6.5 using MRS for MAE_{pri} estimation (Figure 6.6b). E_{abs} show clear seasonal variations, which is higher than 1.5 from April to August and relatively lower from September to March. The highest enhancement is found in August (~2). The variation of E_{abs} is expected to associate with mixing stage of the aerosols, where a thicker coating is likely to lead to a higher E_{abs}. 
Figure 6.6 Monthly variations of MAE and $E_{\text{abs}}$
(a) Monthly variations of Mass absorption efficiency (MAE) at 550 nm. Red circles represent monthly average MAE. The line inside the box indicate monthly median MAE. Upper and lower boundaries of the box represent the 75th and the 25th percentile; the whiskers above and below each box represent the 95th and 5th percentile. The green line represents MAE calculated by a linear regression slope with intercept while the red line is without intercept. The black line represents $MAE_{\text{pri}}$ estimated by MRS.
(b) Monthly variations of light absorption enhancement ($E_{\text{abs}}$)
As predicted by Mie theory in Figure 6.3b, MAE enhancement is positively correlated to coating thickness. Since coating thickness is proportional to cube root of coating volume (associated with non-EC PM$_{2.5}$ mass), here an arbitrary quantity “Thick$\text{indicator}$” is defined as

\[
\text{Thick}_{\text{indicator}} = (\text{non-EC PM}_{2.5} \text{ mass})^{1/3}.
\]

Liquid water content (LWC) is major component of PM$_{2.5}$ mass due to high relative humidity (RH) in PRD. Since LWC is difficult to measure directly, E-AIM (model 2) thermodynamic model (Clegg et al., 1998) is employed to estimate LWC mass. As shown in Figure 6.7a, LWC averagely account for significant fraction (44%) of non-EC PM$_{2.5}$ mass. As examined by scatter plot in Figure 6.7b, MAE$_{\text{total}}$ exhibit a positive dependency on Thick$\text{indicator}$ as well as on cube root of LWC mass (color coding). This measurement result confirm the Mie theory predicted MAE enhancement due to the lensing effect of coating materials. The effect of hygroscopic growth is also evidenced by examining the empirical f(RH) of MAE as shown in Figure 6.8.

Attribution of MAE$_{\text{pri}}$ to bare EC and extra MAE due to coating of different chemical compositions are investigated through a multiple regression analysis (MRA). $\sigma_{\text{abs}}$ is regressed against EC, SOC, SO$_4^{2-}$ and NO$_3^-$ in the MRA for a monthly calculation. The slope obtained for EC represent MAE$_{\text{pri}}$ and the slopes of SOC, SO$_4^{2-}$ and NO$_3^-$ represent their contribution to MAE$_{\text{coat}}$ (enhancement). Attribution of MAE to different chemical components are shown in Figure 6.9. The monthly MAE$_{\text{pri}}$ determined by MRS and MRA are in good agreement as shown in Figure 6.9a. The variations in MAE$_{\text{pri}}$ may be associated with variability in the bare soot particle size distribution.

Results from MRA can partially explain MAE$_{\text{coat}}$ (Figure 6.9b). The dominant contributing chemical components of MAE$_{\text{coat}}$ exhibit a clear seasonal dependency. From April to September, the enhancement is mainly due to SO$_4^{2-}$ and NO$_3^-$, which can explain 3.5 ~ 7.4 m$^2$g$^{-1}$ of the MAE enhancement. From October to March, enhanced MAE is associated with SOC, SO$_4^{2-}$ and NO$_3^-$, which contributes 2 ~ 3.5 m$^2$g$^{-1}$ to the MAE enhancement. It should be noted that the MAE$_{\text{coat}}$ by the coating materials is a quantity much smaller compare to the MAE$_{\text{pri}}$ by EC, therefore the MAE$_{\text{coat}}$ estimation have much larger uncertainties than the MAE$_{\text{pri}}$. In addition, another uncertainty contributor to MAE$_{\text{coat}}$ is the measurement uncertainties of the water soluble ions measured by MARGA (The instrument for Measuring AeRosols and GAses)(ten Brink et al., 2007). Considering the measurement uncertainties, the actual uncertainties are higher than the uncertainties due to regression alone. Another challenge in
differentiating $\text{MAE}_{\text{coat}}$ contribution from individual component is that the reflective index of water, SOC, $\text{SO}_4^{2-}$, and $\text{NO}_3^-$ are very close. Considering the limitations as mentioned above, the interpretation of results shown in Figure 6.9 should be focus on the general trends, e.g. the $\text{MAE}_{\text{coat}}$ contribution of $\text{SO}_4^{2-}$, and $\text{NO}_3^-$ are more important in summer. In winter the SOC also contribute to $\text{MAE}_{\text{coat}}$. The value of individual components at each month exist higher uncertainty and cannot be over interpreted. Although current results are estimated from bulk aerosols, these results agree very well with single particle studies from this region (Zhang et al., 2013; Zhang et al., 2014). In a single particle study in Guangzhou, EC was found internally mixed with sulfate. During a single particle study at a PRD receptor site (Zhang et al., 2014), EC was found internally mixed (by number fraction) with sulfate (97.4%), nitrate (89.5%) and oxidized organics (69.6%).
Figure 6.7 Dependence of $\text{MAE}_{\text{total}}$ on non-EC PM$_{2.5}$ and liquid water content (LWC) mass

(a) Distribution of LWC/non-EC PM$_{2.5}$ fraction. 

(b) Scatter plot of $\text{MAE}_{\text{total}}$ vs. (non-EC PM$_{2.5}$)$^{1/3}$. The color coding represents (LWC)$^{1/3}$

$Y = aX + b$

$a = 21.69 \pm 0.13$

$b = -55.71 \pm 0.40$

$R^2 = 0.30$

$N = 6948$

WODR
Figure 6.8 Hygroscopic growth factor ($f$($\text{RH}$)) of EC MAE determined from one year’s sampling data at NC site.

$$y = 4E-05x^2 - 0.0015x + 1.01$$
Figure 6.9 Attribution of MAE to different chemical components.

(a) MAE_{pri} and MAE_{coat} (b) Absolute apportionment of MAE_{coat} due to SOC, SO_{4}^{2-} and NO_{3}^{-}. The error bar represent the confidence interval of each regressed slope (c) Relative contribution of MAE_{coat}.
6.4 Understand Aethalometer BC versus TOT EC comparison

BC data by aethalometer is often carelessly compared with EC in various studies, thus a proper interpretation requires understanding the origin of these two quantities. An aethalometer measures light attenuation (ATN) of particle laden filter tape (Hansen et al., 1984). ATN can be used for $\sigma_{abs}$ and soot mass concentration estimation. Therefore, BC mass concentration is not directly measured, but rather reported as a derivative of the ATN measurement. An empirical conversion factor for BC estimation from ATN can be obtained by linear regression of ATN (aethalometer) and EC mass by the Evolve Gas Analysis (EGA) technique (Gundel et al., 1984). EGA is quite different from the currently widely used TOA protocols (e.g. NIOSH and IMPROVE). In TOA, an inert gas (helium) is used to evolve OC in the first stage and EC is combusted after introduction of Oxygen in the second stage (Birch and Cary, 1996). In EGA, oxygen is used throughout and OC and EC are evolved and combusted at the same time (Novakov, 1981). Since EC itself is operationally defined, and standard materials for EC are still not available (Baumgardner et al., 2012), both factors introduce potential discrepancies in EC determination. As a result, EC reported by different protocols are well correlated but the slopes are often different (Wu et al., 2012). To illustrate the discrepancies, direct comparison of aethalometer BC and NIOSH EC are shown in Figure 6.10.

![Figure 6.10 BC and EC comparison.](image)

(a) BC mass (880 nm) and NIOSH EC comparison for yearlong data, the color coding represents the corresponding OC/EC of each data point; (b) Monthly variations of slope and intercept. The solid red line represents slope with intercept and the dashed red line represents the regression slope without intercept. The error bars represent the confidence interval for the slope and intercept estimation.
A slope of 1.64 (regression including intercept) is obtained in comparison of the yearlong BC and EC datasets. Since the BC estimation is linked to light absorption through ATN, the intercept is associated with the absorption enhancement due to the BC coating (similar to the intercept observed in Figure 6.4d). Several factors may affect the BC/EC discrepancy, including the EC analysis protocol differences, MAE variations and the filter method artifact (e.g. loading effect). As shown in Figure 6.10b, the BC/EC slopes vary monthly (1.5~2). Such variation is likely due to the MAE variations as shown in Figure 6.6a. Considering the monthly BC/EC variation range (1.5~2), BC is consistently higher than EC. Thus, additional discrepancy is can be explained by protocol discrepancy between EGA and NIOSH EC. Previous comparison studies show that EGA EC is higher than NIOSH EC (Soto-Garcia et al., 2011). Similar discrepancies are also reported between MAAP BC and NIOSH EC with a slope of 1.54 (Kanaya et al., 2008) since MAAP is calibrated with VDI 2465-1 protocol (Petzold and Schonlinner, 2004), which has a different temperature profile than NIOSH. The use of BC reported from optical measurements depends on the specific research purpose. To make the BC data comparable with results from other aethalometer datasets around the world, adhering to the manufacturer’s specific attenuation cross section (SACS) is recommended (e.g. 16.68 m²g⁻¹ @ 880nm). To maintain consistency between EC from a filter based sampling network and BC by aethalometer, seasonal SACS determined by a parallel measurement is appropriate for each individual sampling site.

6.5 Light absorption determination by means of RT-ECOC analyzer

The semi-continuous ECOC analyzer was developed in the 1980s at Oregon Graduate Center (Turpin et al., 1990). The analysis principle is identical to the bench-top offline analyzer but the semi-continuous ECOC is coupled with sampling capability. An automated analyzer was commercialized by Sunset Laboratory (Forest Grove, OR) in the 2000s (Bae et al., 2004). To better explain the difference between semi-continuous ECOC and bench top ECOC, the configuration of the oven, sample placement and laser configuration are illustrated in Figure 6.11.
The basic idea of converting an off-line analyzer into an online version is to change the orientation of the quartz filter, making the oven and filter serve as a sampler. In semi-continuous ECOC, the filter is placed at the cross-section of oven, allowing collection of particles that are then ready for analysis. During the sampling mode, the oven fills with a sampling flow for aerosol collection. After sampling, the analyzer shifts to analysis mode by switching the sampling flow to a carrier gas. Then the analysis is conducted identically to the offline analyzer. One unique feature of the semi-continuous ECOC analyzer is its capability of performing optical filter transmittance measurements during sampling. Filter transmittance also serves as the observation principle of light absorption measurement instruments like aethalometer. It should be noted that in RT-ECOC, the laser illuminates the back side of the particle laden filter, which is reversed compared to the filter orientation in an aethalometer and bench-top ECOC analyzer. Two stacked quartz filters are used in the RT-ECOC to avoid filter avulsion during sampling. Conny (2007) reported absorption with two stacked filters is larger than the sum of two individual filters. This potential factor may affect the optical measurement by RT-ECOC.
Some existing studies have already explored the optical information during offline ECOC analysis (Yang and Yu, 2002; Ram and Sarin, 2009; Cheng et al., 2011a; Shen et al., 2013), but the application on a semi-continuous ECOC analyzer has not been reported before. The manufacturer uses an empirical formula to convert light transmittance signal into estimated EC mass concentration, so it is necessary to develop a calibration scheme for the semi-continuous ECOC analyzer to report measurements of the light absorption coefficient at 650nm.

The change of transmittance signal intensities ($I$) between each measurement cycle (1 hr for RT-ECOC analyzer in this study) is recorded for each attenuation (ATN) calculation, which is defined as follows (Beer–Lambert law):

$$ATN = 100 \cdot \ln \frac{I_0}{I}$$

where the $I_0$ and $I$ are the intensities of the transmitted light through the filter without and with aerosol collected, respectively. The light absorption coefficient of aerosols on the filter can be derived from ATN via the following equation:

$$\sigma_{ATN} = ATN \cdot \frac{A}{V}$$

where $\sigma_{ATN}$ is the light absorption coefficient of aerosols on the filter, $A$ is the spot area of the aerosol deposit, and $V$ is the volume of air passing through the filter in each measurement cycle. Data acquired from filter-based measurements such as the aethalometer need careful correction due to measurement artifacts (Weingartner et al., 2003; Virkkula et al., 2007; Schmid et al., 2006; Arnott et al., 2005). Since RT-ECOC shares a similar optical measurement principle with the aethalometer, similar artifacts are expected for the $\sigma_{abs}$ measurement on RT-ECOC analyzer, including those from the loading effect, matrix effect and scattering effect (Coen et al., 2010). The loading effect depends on the amount of soot accumulated on the filter, resulting in a nonlinear relationship between $\sigma_{abs}$ and ATN. The matrix effect is due to the multi-scattering of the filter matrix, resulting in absorption enhancement of particles on the filter compared to particles suspended in the air. A recent study suggests that the degree of enhancement is associated with the type of filter material (Presser et al., 2014). The correction algorithm proposed by Weingartner et al. (2003) was applied in this study for data correction:

$$\sigma_{abs} = \frac{\sigma_{ATN}}{C_{ref} \cdot R(\text{ATN})}$$
where \( C_{\text{ref}} \) is the constant representing the correction for enhancement due to the matrix effect, \( R(\text{ATN}) \) is a function of ATN to correct for nonlinearity due to the loading effect, which is shown in Eq. 6.12.

\[
R(\text{ATN}) = \left(1 - \frac{1}{f}\right) \frac{\ln(\text{ATN}\%)}{\ln(10\%)} - \ln(50\%) - \ln(10\%) + 1
\]

The underlying idea is to first correct all \( \sigma_{\text{ATN}} \) to \( \sigma_{10\%} \), which then can be corrected into \( \sigma_{\text{abs}} \) values through the calibration factor \( C_{\text{ref}} \).

In the aethalometer measurement, when the attenuation of a sample spot on the filter reaches the threshold value (100 by default) at 370 nm after several cycles of measurements, the filter tape will be advanced to a new position for continual measurement. As a result, the duration of each cycle in aethalometer varies to limit ATN below 100. In RT-ECOC, EC is removed during analysis in each analysis cycle, which has a fixed duration (45 min). Since Eq. 6.9 is designed for the aethalometer with ATN ranging from 0 to 100, it is necessary to verify whether the ATN measurement by RT-ECOC analyzer falls in a similar range. As shown in Figure 6.12, 98.4% of ATN measured by RT-ECOC were less than 100, with an average of 32.93 and peak of 18.55 by log-normal fitting. Therefore, application of Eq. 6.9 to RT-ECOC ATN data correction is reasonable. The \( f \) value in Eq. 6.9 depends on aerosol types and their mixing state, which is determined through chamber studies (Weingartner et al., 2003). Considering the substantial absorption enhancement at NC site discussed in the previous section, \( f=1.45 \) is adopted to represent the mixing state in this area.

As shown in Figure 6.13, \( 1/R(\text{ATN}) \) considers ATN=10 as unity, then assigns weighting of other ATN data points to correct for the nonlinearity of ATN. By adjusting \( C_{\text{ref}} \), the unity regression line between Aethalometer corrected \( \sigma_{\text{abs}} \) and RT-ECOC corrected \( \sigma_{\text{abs}} \) can be achieved. As a result, \( C_{\text{ref}} = 4.37 \) was obtained for the yearlong NC data. Comparison of RT-ECOC analyzer \( \sigma_{\text{abs}} \) and aethalometer corrected \( \sigma_{\text{abs}} \) is shown in Figure 6.14, suggesting the RT-ECOC analyzer can provide \( \sigma_{\text{abs}} \) consistent with aethalometer data if careful corrections are performed.
Figure 6.12  Frequency distribution of ATN measured by RT-ECOC analyzer (2012.2-2013.1). The red and blue line are log-normal and normal fitting curves respectively for the distribution. The dashed line in green represents the cumulative distribution of ATN.

Figure 6.13  Curve of $1/R(\text{ATN})$ for loading effect correction.
Figure 6.14 Comparison of RT-ECOC analyzer $\sigma_{\text{abs}}$ and aethalometer $\sigma_{\text{abs}}$. 

$Y = ax + b$

- $a = 1.00 \pm 0.00$
- $a = 1.05 \pm 0.00$
- $b = -2.84 \pm 0.14$

$R^2 = 0.94$

$N = 6945$
6.6 Conclusions

In this study, core-shell Mie simulations are performed to investigate the dependency of soot particle MAE on coating thickness. The results show that MAE is positively correlated with coating thickness. Considering the typical soot size distribution and coating thickness in the PRD, the enhancement \( E_{abs} \) of MAE is expected to be within a factor of 2. The annual average MAE at the suburban PRD site, NC, is 19.75 m\(^2\)g\(^{-1}\). Application of the Minimum R Squared (MRS) method is conducted to investigate primary MAE (MAE\(_{pri}\)) at NC. The annual average MAE\(_{pri}\) estimated by linear regression and MRS is 13.16 and 12.7 m\(^2\)g\(^{-1}\) respectively, suggesting an annual average enhancement factor of 1.50~1.55. Both MAE\(_{pri}\) and \( E_{abs} \) show seasonal variations, implying the complexity of soot particle mixing state variations in this region. The enhancement is more pronounced in summer. Attribution of light absorption enhancement to different chemical compositions is explored with a multiple regression analysis. The results show that during the rainy season the enhancement is mainly associated with SO\(_4\) and NO\(_3\), while in the dry season SOC, SO\(_4\), NO\(_3\) and NH\(_4\) are responsible for the enhancement.

BC reported by Aethalometer and EC obtained from a RT-ECOC analyzer are compared, resulting in a slope of 1.64. The discrepancy from unity is mainly due to the difference in EC analysis protocol, where the Aethalometer is calibrated against evolve gas analysis (EGA) while the RT-ECOC analyzer uses the NIOSH TOT protocol. Monthly variations of BC/EC are also observed corresponding to MAE variations. Retrieval of \( \sigma_{abs} \) from the ATN measurement in RT-ECOC sampling is demonstrated by applying the correction scheme from Weingartner et al. (2003). The result shows that the RT-ECOC analyzer is capable of reporting \( \sigma_{abs} \) consistent with aethalometer \( \sigma_{abs} \) if the careful data correction is performed. \( \sigma_{abs} \) estimation demonstrated here expands the application of the RT-ECOC analyzer from reporting only OC and EC concentrations to be capable of exploring optical properties of soot particles including MAE. The \( E_{abs} \) is expected to be varied by different locations, which depends on the coating thickness and size distribution of the aerosols. Since after undergo atmospheric aging, the \( E_{abs} \) is expected to increase from emission source to rural areas. As discussed in section 6.3, the major uncertainties of MAE estimation is associated with EC mass measurement. For future research, EC mass determination by LII technique is recommended, which is more promising in reducing the measurement uncertainties.
Chapter 7

7. Conclusions and future works

7.1 Conclusions

Characteristics of elemental carbon and black carbon in PRD are investigated in several perspective. Multiple analytical techniques are employed to study the analytical uncertainties, temporal and spatial distributions, as well as optical properties. Major conclusions are summarized herein:

(1) Inter-instrument comparison of OC and EC determination are performed for the first time. The two most widely used carbon analyzers consist with each other very well for reporting OC and EC. Inter-protocol comparison on PRD samples exhibit larger discrepancy between the two most widely used analysis protocols, which is much larger than US samples. Temperature ramping parameters and laser correction method are found to be the dominated contributors of the large discrepancy. Charring, which is associated with temperature parameters, is positively correlated with EC discrepancy.

(2) Observation of light absorption coefficients ($\sigma_{abs}$) and BC concentrations by Aethalometer were conducted at five sites in the Pearl River Delta (PRD) region, South China in two periods: 16 May-20 June 2008 in rainy season and 12 December 2008- 8 January 2009 in dry season. Little difference in BC level was found at a rural site in PRD between the two sampling periods (2.88 and 2.62 μg m$^{-3}$). At the PRD urban sites, the daily average concentration of BC ranged from 1.56 to 37.9 μg m$^{-3}$, higher in the dry season sampling period (12.31 μg m$^{-3}$) and lower in the rainy season sampling period (6.17 μg m$^{-3}$). The observed average $\sigma_{abs}$ values in rainy vs. dry season sampling period are 119 vs. 62 Mm$^{-1}$ at the PRD urban sites, 29 vs. 26 Mm$^{-1}$ at the PRD background site, and 8.4 vs. 7.2 Mm$^{-1}$ at the marine site. At urban/suburban PRD sites, BC was observed to have a diurnal pattern of higher concentrations at night and at the urban sites a small peak in the early morning rush hour.

(3) A pseudo data generation scheme for simulating EC as well as primary and secondary OC is proposed. A systematic evaluation of EC tracer method performance by different (OC/EC)$_{pri}$ calculation approaches, including minimum OC/EC method, percentile (10%) OC/EC method and minimum R squared (MRS) method, is performed through a numerical study. Different scenarios are considered, including single primary source scenario, two independent primary
sources scenario and two correlated primary sources scenario. The results show among the three \((OC/EC)_{pri}\) methods, the MRS method consistently produces SOC estimates of the best accuracy. The two independent primary sources scenario is more challenging for EC tracer method even MRS is employed. If EC can be pre-separated by each sources, MRS can provide unbiased SOC estimation.

(4) One year observation of organic carbon (OC) and elemental carbon (EC) was conducted hourly from 1 February 2012 to 31 January 2013 by using a semi-continues thermal-optical transmittance (TOT) carbon analyzer at suburban site Nancun (NC) of city Guangzhou. Annual average OC, EC and TC concentrations (±1sd) at NC site are 7.20±5.68, 2.64±2.28 and 9.84±7.80 \(\mu\)gCm\(^{-3}\) respectively. Minimum R squared method (MRS) is applied for primary OC/EC ratio estimation. Results shown that interference of EC co-emitted SOC precursor can cause \((OC/EC)_{pri}\) overestimated in the afternoon, alternatively diurnal minimum MRS \((OC/EC)_{pri}\) is adopted to minimized this artifact. In addition, seasonal variations of \((OC/EC)_{pri}\) are observed (e.g. elevated \((OC/EC)_{pri}\) in biomass burning season), therefore \((OC/EC)_{pri}\) is calculated for individual months to account for such variations. The annual average of estimated SOC is 2.96±2.55 \(\mu\)gCm\(^{-3}\), accounting for 41% of OC mass. SOC by resolved carbon fractions are investigated. SOC contribution 38% of low temperature OC (evolved <600 °C) and 78% of high temperature OC (evolved between 600 °C and 840°C), implying that most of the high temperature OC (probably more oxygenated) are secondarily formed. Result from 49 individual rain events shown that carbonaceous particle mass reduced 50% averagely due to wet removal. The removal rate is uniform for POC, SOC and EC, suggesting that mixing state of carbonaceous particles are probably predominated by internal mixing at the sampling site. Higher EC/CO ratio was observed at night time, suggesting the high EC at night is associated with shallow mixing depth as well as higher intensity of primary emission from diesel trucks, which diurnal pattern associated with traffic regulations of city Guangzhou.

(5) Core-shell Mie simulation is performed to investigate the possible range of light absorption enhancement factor (E\(_{abs}\)). Maximum E\(_{abs}\) highly depends on core and shell diameter combination. Considering the typical size distribution of BC particles in PRD, upper limit of E\(_{abs}\) is estimated at ~2. Annual average MAE at NC is 19.75±8.95 m\(^2\)g\(^{-1}\). Primary MAE (MAE\(_{pri}\)) is proposed to represent the MAE if coating is removed. The annual average MAE\(_{pri}\) estimated by linear regression and MRS is 13.16 and 12.7 m\(^2\)g\(^{-1}\) respectively, implying an annual average enhancement factor of 1.50~1.55. Seasonal variations of MAE is found, which is much higher in summer. Enhancement apportionment shown that in rainy season the enhancement is mainly
associated with $\text{SO}_4^{2-}$ and $\text{NO}_3^-$, while in dry season SOC, $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ are response for the enhancement. BC from aethalometer and EC from RT-ECOC analyzer is compared and causes of discrepancy are discussed. Retrieval of light absorption coefficient ($\sigma_{abs}$) from RT-ECOC analyzer is demonstrated, which exhibit consisted performance with aethalometer.

7.2 Recommendation for future works

Systematic comparison of RT-ECOC analyzer and offline analyzer is needed. In PRD offline samples, the OC4 fraction in NIOSH is the major cause of NIOSH and IMPROVE OC/EC split discrepancy. In RT-ECOC results, the OC4 faction in NIOSH is not detectable for most samples. This online/offline discrepancy needs to be investigated. Several potentials factors are worth to explore. (a) By far the 24hr filter sampling in PRD is without organic vapor denuder while the RT-ECOC analyzer come with a denuder. Is the OC4 discrepancy the major contributor of the online/offline discrepancy? (b) The surface loading is quite different between SASS and RT-ECOC analyzer. The surface loading of SASS is a few times higher than RT-ECOC analyzer. If a Hi-vol filter is used, the loading is even higher than the online instrument. It is still unknown whether loading effect will contribute the online/offline discrepancy, since charring may sensitive to the loading on the filter. (c) The optical design is quite different between offline and online instrument. In offline analyzer, laser is illuminated from the particle laden side. In online analyzer, laser is illuminated from the back side of the filter. In addition, single filter is used in offline analysis while stack of two filters are employed in online measurement. The stack of two filters will definitely change the optical behavior but such effect has never been investigated.

Large uncertainties still exist in thermal optical analysis. Since OC and EC are operational defined and reference materials for OC and EC are still unavailable (Baumgardner et al., 2012), direct OC and EC determination accuracy assessment on different protocols is difficult. Alternatively, some quantitative criteria can be established for such assessment. For example, soot reference materials for SP2 have been identified (Laborde et al., 2012). Identifying a soot reference materials for SP2 is easier than thermal optical analysis, because SP2 measurement on EC is independent on mixing state, while TOA can be affected by mixing state. Thus calibrated SP2 can serve as a reference instrument for EC measurement. Assessment of different TOA protocols can be achieved by performing side by side ambient measurement with a SP2 and a RT-ECOC analyzer. The results could site dependent that associated with EC mixing state at that site, e.g., protocol A may have better performance at site C while protocol
B may exhibit better performance at site D. Even OCEC reference material exist, a sharp split between OC and EC is still challenging in ambient samples due to the presence of metal oxidants. Metal oxidant in samples will cause EC loss in helium stage. When certain fractions of OC and EC evolved in helium at the same temperature happens, clear split for these specific OC and EC fraction are impossible in TOA. If laser induced incandescence is proved a better technique for EC determination, OC can estimated by the difference of TC and EC.

Light absorption enhancement has been quantified in bulk aerosols as demonstrated in this thesis. In-depth understanding of this enhancement is needed by single particle measurement like SP2. Recent study suggest non-core-shell structure of soot containing particles in ambient environment, the abundance of soot particles with this type of mixing state is still unknown in PRD region. If the abundance of non-core-shell particle is not negligible, the existing core-shell assumption in modals needs to be revised.

Long-term observation results in PRD shown a decreasing trend of BC, it is interesting to find out the major contributor of this decline. This a good opportunity to evaluate the effectiveness of government policy on BC reduction.
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