Chapter 1

Introduction
Chapter 1

The thesis focuses on characterization and source apportionment of carbonaceous aerosol and its sub-fractions with a special focus on the situation and sources of China. In the introduction I will therefore explain the carbonaceous aerosol from different perspectives that are related to the scope of this thesis, including carbonaceous aerosol’s definition, physical and chemical properties, light-absorbing properties, sources and formation pathway, as well as the approach to identify and characterize carbonaceous aerosol and, the method to apportion its sources. Then the current state of air pollution in China is briefly overviewed. Finally, the aims of the work presented in this thesis are stated.

1.1 Aerosol

Aerosols are defined as suspensions of solid and liquid particles in a gas (Seinfeld and Pandis, 2006) Thus, the term “aerosol” includes both the aerosol particles and the gas phase, in which the particles are suspended. However, in atmospheric studies, “aerosol” usually refers to the particles (or condensed phase, particulate matter). When the gas-particle interactions (e.g., gas-particle partitioning) are considered, it is necessary to make a clear distinction between “particle component” (or “particulate component”, “condensed phase component”) and “gas phase component” (or “gaseous component”).

Aerosols are produced from natural sources, such as wind-borne dust, sea spray, volcanic debris, plant debris and pollens, and from anthropogenic sources, such as coal combustion, liquid fossil fuel combustion (i.e, traffic), biofuel burning. Emitted directly into the atmosphere as primary aerosols or formed in the atmosphere through gas-to-particle conversion processes as secondary aerosols, aerosols are considered to be the particles with size ranging from a few nanometers (nm) to tens of micrometers (μm) in diameter (Pöschl, 2005). While in the atmosphere, particles undergo various physical and chemical processes like condensation of vapor species, evaporation, coagulation with other particles, humidification, gas-particle reaction etc., which change their size and composition. Particles usually have lifetimes from a few days to a few weeks and are removed from the atmosphere by deposition at the Earth’s surface (dry deposition) and incorporation into cloud droplets during the formation of precipitation or scavenged by falling rain drops (wet deposition) (Fig. 1.1).
Aerosols can significantly affect the climate through their interaction with radiation and clouds in complex ways (Pöschl, 2005). On the one hand, aerosols modify the Earth’s radiative balance by scattering and absorbing solar radiation (direct effects). Aerosols that mainly scatter solar radiation have a cooling effect, by enhancing the total reflected solar radiation from the Earth. Strongly absorbing aerosols have the opposite effect and tend to warm the climate system. In the atmosphere, there is a mixture of scattering and absorbing aerosols, and their net effect on climate depends on aerosol properties and environmental conditions. On the other hand, acting as cloud condensation nuclei and ice nuclei, aerosols are involved in the formation of clouds and precipitation (indirect effects). Radiative forcing (RF) is often used to quantify and compare the
potential climate impact of the various aerosol effects. RF is defined as a change in the Earth's radiation balance, induced by anthropogenic or natural changes in atmospheric composition, Earth surface properties, or solar activity. The current RF of the total aerosol effect in the atmosphere relative to that in 1750 (i.e., preindustrial times) is estimated to be $-0.9$ ($-1.9$ to $-0.1$) W m$^{-2}$, as opposed to the RF of greenhouse gases of $3.00$ ($2.22$ to $3.78$) W m$^{-2}$ (IPCC, 2013). However, quantifying these effects accurately is still challenging, due to limited knowledge of aerosol sources, composition, properties and atmospheric processes.

Of aerosol particles with different sizes, fine particles (i.e., particles with diameter of 2.5 μm or less; PM$_{2.5}$) have large impacts on human health (Bell et al., 2007; Pui et al., 2014; Pope et al., 1995). Due to its minute size, PM$_{2.5}$ can bypass the nose and mouth and penetrate deep into the lungs, inducing oxidative stress and respiratory diseases. Epidemiological studies have found significant associations between PM$_{2.5}$ and daily mortality (Cao et al., 2012a; Kan et al., 2007; Ma et al., 2011).

### 1.2 Carbonaceous aerosols

PM$_{2.5}$ contains sulfate (SO$_{4}^{2-}$), ammonium (NH$_4^+$), nitrate (NO$_3^-$), sodium (Na$^+$), chloride (Cl$^-$), trace metals, carbonaceous material and elements (Chow et al., 2015; Tao et al., 2017; Li et al., 2017). The carbonaceous fraction of the aerosols (shortly carbonaceous aerosols) is an important component of PM$_{2.5}$ in almost all environments. Carbonaceous aerosols contribute typically 20–50 % to PM$_{2.5}$ mass in many urban areas in China (Huang et al., 2014; Tao et al., 2017; Cao et al., 2012b) and 30–60 % to PM$_{2.5}$ mass in Europe (e.g., Fuzzi et al., 2015; Pöschl, 2005)). High concentrations of carbonaceous aerosols have been observed in severe air pollution events in China (Huang et al., 2014; Elser et al., 2016; Liu et al., 2016).

Carbonaceous aerosols are often quantified in terms of their carbon content, i.e. by reporting the only mass concentration of carbon atoms contained in the carbonaceous material. The total carbon (TC) content of aerosols is defined as the sum of all carbon contained in aerosols, except the inorganic carbonate. To determine TC, thermochemical analysis is usually applied to aerosols. Thermochemical analysis heats aerosol samples in a stream of gas, so that all the carbon can be volatilized, combusted and oxidized to CO$_2$, which is then transferred to a detector and either measured directly or after conversion to CH$_4$. The TC content of an aerosol sample is quantified from the integration of CO$_2$ emitted over entire temperature range, while the organic carbon (OC) fraction is
defined as the amount of CO$_2$ released up to a certain threshold temperature in an inert atmosphere, and the elemental carbon (EC) fraction is defined as the carbon fraction burned above this threshold temperature in an oxidized atmosphere ($TC = OC + EC$). Usually a correction is necessary for OC that pyrolyzes during the thermal analysis and is released in the oxidized atmosphere together with EC. This can be accomplished by monitoring the light absorption of the filter sample during analysis, resulting in the commonly used thermo-optical methods (e.g., Birch and Cary, 1996; Chow et al., 1993, 2007; Watson et al., 2005; Cavalli et al., 2010). OC includes individual organic compounds, such as polycyclic aromatic hydrocarbons and other components with possible mutagenic and carcinogenic effects. Whereas OC only refers to the sum of the carbon atoms contained in this organic material, the organic fraction of carbonaceous aerosol (organic aerosol, OA) refers to the total organic material in the particles. The mass of OA is therefore the sum of the OC mass and the mass of its associated hydrogens and heteroatoms (Louvaris et al., 2017), which is rather variable. The mass of OA usually estimated by multiplying the OC mass with a factor of about 1.5–2, varying with the molecular composition (Xing et al., 2013; Aiken et al., 2008). EC includes tars, chars, amorphous-like carbon consisting of randomly oriented poly-aromatic layers and carbon nanospheres formed from incomplete combusted carbon-based fuels (Pöschl, 2005). EC is emitted as primary aerosols from incomplete combustion of biomass (e.g., wood, crop residues, and grass) and fossil fuels (e.g., coal, gasoline, and diesel). Besides combustion sources, OC also has other non-combustion sources, for example, biogenic emissions, cooking, etc. Unlike EC that exclusively emitted as primary aerosols, OC includes both primary and secondary OC (SOC), where SOC is formed in the atmosphere by chemical reaction and gas-to-particle conversion of volatile organic compounds from non-fossil (e.g., biomass burning, biogenic emissions, and cooking) and fossil sources (Hallquist et al., 2009; Jacobson et al., 2000; Kanakidou et al., 2005).

In the literature, EC and black carbon (BC) have been used interchangeably, and are generally based on thermochemical and optical techniques, respectively (Pezold et al., 2013). BC is characterized by its strong absorption of visible light and by its resistance to chemical transformation, while EC is differentiated from OC based on thermal reactivity properties. It should be noticed that no clear separation between EC (or BC) and OC exists, but a continuous increase of thermal reactivity from OC to EC, and of optical light absorption from colorless OC to BC (Fig. 1.2). BC can significantly absorb incoming solar radiation and is the most important light-absorbing aerosol component (Bond et
It absorbs solar radiation over a broad spectral range, from the ultraviolet (UV) all the way into the infra-red (IR). On the other hand, OC mainly scatters light, but there is also OC found to be light absorbing with a steep increase of light absorption ultraviolet (UV) and short visible wavelengths with strong wavelength dependence, referred to as brown carbon (BrC) (Bond and Bergstrom, 2006; Laskin et al., 2015).

1.3 Light absorption of brown carbon

BrC is a complex mixture encompassing a large group of organic compounds (e.g., nitrophenols, aromatic carbonyls) with various optical absorptivity. Atmospheric BrC has both primary and secondary origins. Major sources of primary BrC are biomass burning, incomplete combustion of fossil fuels (e.g., coal combustion). Humic substances from soils, plant debris, and bioaerosol (e.g., fungi) may also contribute to BrC. Once in the atmosphere, a variety of chemical reactions and aging processes take place forming secondary OA, which can also contain some light-absorbing molecules (Laskin et al. (2015) and reference therein). So far, most global climate models assume OC to be scattering aerosols, reflecting light only (Chung and Seinfeld, 2002), even though BrC has been observed in particles originating from both primary emissions (Xie et al., 2018; Xie et al., 2017; Sun et al., 2017; Chen and Bond, 2010) and secondary formation in the atmosphere (Zhang et al., 2011; Forrister et al., 2015). This suggests that the cooling effect of OA can be overestimated by ignoring the light absorption of BrC. For example, light absorption by BrC may potentially shift the global radiative forcing of organic carbonaceous aerosols from net cooling to net...
warm ing at the top of the atm osphere (Feng et al., 2013). BrC was estim ated to account for 15–50 % of total light absorption of aerosols in the atm osphere (Chung et al., 2012; Kirchstetter and Thatcher, 2012; Bond et al., 2013; Wang et al., 2018).

Due to the limited understanding of the optical properties and atm ospheric transformation of BrC from different sources, recent modeling studies (Feng et al., 2013; Wang et al., 2014) obtained the optical properties of BrC from laboratory biomass burning experiments (Chen and Bond, 2010) or ambient measurements (Liu et al., 2013; Zhang et al., 2013). However, a growing amount of field studies have identified residential coal combustion as an important contributor to BrC light absorption in the atm osphere (Yan et al., 2017). For example, Lei et al. (2018) investigated the light absorption of OC in northern China at wintertime with significant influence of coal combustion, and attributed an average of 37 % of bulk light absorption to residential coal combustion. Our knowledge of light absorption of BrC from residential coal combustion and how the atm ospheric processing modifies the optical properties of BrC is still rare, and the contribution of coal combustion to BrC absorption are being ignored in modeling studies.

Although the term BrC has been widely used to refer generally to light-absorbing organic substances in atm ospheric aerosol, it is still lacking a formal analytical definition (Laskin et al., 2015). It is difficult to identify BrC using aerosol optical instrum ents, which can not m easure BrC independently of BC. Aerosol optical instrum ents usually determ ine BrC based on differences between observed absorption at short wavelengths (where both BrC and BC absorb light), from the expected light absorption by BC alone. However, this m ethod is lim ited by the influence of organic coatings on BC absorption. For instance, earlier studies found that mixing BC with non-absorbing material can lead to substantial increase in light absorption relative to pure BC, m aking it difficult to attribute the enhanced light absorption at low wavelength to BC mixing state or BrC (Lack and Langridge, 2013). A more definitive approach to identify BrC is possible by liquid extraction of organic com pounds from the aerosol (e.g., in water, m ethanol and/or acetone) followed by absorption measurement using a UV-Visible spectrophotom eter (e.g., Zhang et al., 2013; Zhang et al., 2011; Chen and Bond, 2010). This technique allows measurement of BrC absorption without any interference from other light absorbers (e.g., BC, dust), as these insoluble particles are removed from the extracts. UV-visible spectrometers are used to measure the absorbance of ultra violet or visible light by a sample in solution. As shown in Fig. 1.3, the light source provides the visible and near ultraviolet
radiation covering a wide wavelength range. The output from the light source is focused onto diffraction grating which splits the incoming light into its component colors of different wavelengths, like a prism but more efficiently. For liquid extracts, the sample is held in an optically flat, transparent container called a cuvette. The reference cuvette contains the solvent in which the sample is dissolved and this is commonly referred to as the blank. For each wavelength \( \lambda \) the intensity of light passing through both a reference cuvette \( (I_0) \) and the sample cuvette \( (I) \) is measured. The absorbance of the sample is related to \( I \) and \( I_0 \), according to the following equation:

\[
A = \log_{10} \frac{I_0}{I}
\]  

(1.1)

The concentration of a species in a solution directly affects the absorbance of the solution, this relationship is known as Beer’s Law:

\[
A_\lambda = l \times C \times \varepsilon = l \times \sum_i (C_i \times \varepsilon_i) = l \times b_{abs-sol}
\]  

(1.2)

where the measured absorbance \( A \) at certain wavelength \( \lambda \) \( (A_\lambda) \) is dependent on the concentration of light absorbers in solution \( (C) \), their mass absorption efficiency \( (\varepsilon) \) and absorbing path length \( (l) \). For solutions containing all the light absorbers, the light absorption coefficient \( (b_{abs-sol}, \text{ where “sol” denotes sample in solution}) \) is the sum of all the light absorbers’ concentrations times their mass absorption efficiency over all species \( i \). To convert the absorption coefficient due to light absorbers in the solution to ambient aerosol concentrations of the light absorbers:

\[
b_{abs} (\lambda) = A_\lambda \times \frac{V_{solution}}{V_{air} \times l} \times \ln10
\]  

(1.3)

where \( V_{solution} \) (mL) is the solution volume that the filter punch is extracted into. \( V_{air} \) (m³) is the air volume sampled through the filter pieces. The resulting absorption coefficient at a given wavelength \( (b_{abs} (\lambda) \text{ in units of m}^{-1}) \) is converted from common logarithm to natural logarithm, the form in which atmospheric measurements are typically reported.

The UV-visible spectrometer can provide high resolution (i.e., 1 nm wavelength resolution) over wide wavelength ranges (200–900 nm). Further, using organic solvents and water to extract OC provides understanding of the nature of organic carbon, including its water-solubility. Earlier UV-visible absorbance measurements of water and methanol extracted OC found that a large fraction of light absorption in the near-UV and visible range is caused by OC insoluble in water (e.g., Liu et al., 2013). Most of OC can be extracted by
methanol (e.g., Chen and Bond, 2010; Cheng et al., 2016), while OC from coal combustion and vehicle emissions are largely water-insoluble with extraction efficiency of 13% (Yan et al., 2017) and 8% (Dai et al., 2015), respectively. Due to the high extractable fraction, absorption by methanol extracts are usually considered to represent the behavior of total OC.

The bulk mass absorption coefficient of the solubilized OA faction (bulk MAC) is a key parameter which gives the optical absorption per unit mass of OA ($C_{OA}$). Higher bulk MAC means greater light absorption ability of BrC (Laskin et al., 2015):

$$bulk \ MAC(\lambda) = \frac{b_{abs}(\lambda)}{C_{OA}}$$  \hspace{1cm} (1.4)

where bulk $b_{abs}(\lambda)$ the absorption coefficient of bulk solutions (in Mm$^{-1}$) at a certain wavelength ($\lambda$). Here, the solution bulk MAC is different from the widely known term “mass absorption cross-section (MAC)”, which refers to particles in the air. The light absorption of OA in the homogeneous bulk solution differs from the light absorption that would result from the same OA present in ambient aerosols, considering the effect of the aerosol size distribution and aerosol morphology on light absorption of ambient OA. The “bulk” emphasizes the fact that the measured quantity is the absorbance of a bulk OA extracted from a filter, to differentiate the direct measurements on aerosols.

1.4 Volatility and aging of organic aerosols (OA)

Volatility is an important physical property as it determines the partitioning between gas and particulate phases of organic aerosols (OA). The organic compounds observed in the atmosphere range from very low volatility compounds, which are in the aerosol phase, to highly volatile compounds, which are mainly in the gas phase. Of intermediate volatility are the semi-volatile
organic compounds (SVOCs), which actively partition between the particle phase and the gas phase. A typical OA particle consists of a mixture of 1000’s individual compounds. The vapor pressure of a specific semi-volatile organic compound $i$ directly above a mixed organic particle is roughly proportional to the mass fraction of the compound $i$ in the organic mixture. In the atmosphere, the mass fraction of $i$ in the particle equilibrates so that the vapor pressure of $i$ directly above the particle surface equals the partial pressure of compound $i$ in the gas phase. As a consequence, the total fraction of each semi-volatile compound found in the gas versus the particle phase depends on parameters like temperature, the vapor pressure of the compound and the total OA mass (Donahue et al., 2006).

Since it is not feasible to describe 1000’s of individual compounds, the partitioning can be parametrized using a “volatility basis set” (VBS), a volatility distribution model proposed in Donahue et al. (2006). The VBS bins the organic aerosol (OA) compounds according to the effective saturation concentrations ($C^*$). $C^*$ is a quantity that is proportional to the saturation vapor pressure of a certain compound and relates the mass fraction of the compound in the particle phase to the total organic aerosol concentration $C_{OA}$. For example, if $C_{k}^*$ of the $k$-th bin ($C_{k}^*$) is equal to $C_{OA}$, then 50% of the OA mass in the $k$-th bin will be in the particle phase. If $C_{k}^* = 4 \times C_{OA}$, then the OA is more volatile, and only 20% OA mass in the separated $k$-th bin will be in the particle phase. SVOCs are assumed to distribute with log-spaced $C^*$ ranging from 0.01 μg m$^{-3}$ to 100 000 μg m$^{-3}$. If we project concentrations of organic aerosol ($C_{OA}$) onto the basis set of saturation concentrations, we can estimate the volatility distribution of the organic material.

Earlier studies found that ambient OA with different volatility has different sources and formation mechanisms (Presto et al., 2014; Holzinger et al., 2013). Combustion sources emit a complex mixture of organics with a wide range of volatility (Lipsky and Robinson, 2006; Robinson et al., 2007; Shrivastava et al., 2006; Grieshop et al., 2009a; Grieshop et al., 2009b). A large fraction of the primary OA will evaporate when the emissions are diluted by ambient air, which drives the SVOCs to the gas phase. At the same time, the emissions undergo rapid cooling while diluted by ambient air, and the cooling results in a reduction of the saturation vapor pressures of the organic species, driving the SVOCs into the particle phase. The impacts of dilution and cooling on the gas-particle partitioning are anti-correlated and Fig. 1.4 shows an example how the gas-particle partitioning of emissions would change with dilution and cooling when mixed with ambient air.
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Previous studies investigated several combustion sources of OA, and found that primary OA from fossil fuel emissions is more volatile than that from biomass burning. For example, Grieshop et al. (2009b) found that primary OA from diesel exhaust is more volatile than that from wood burning. And this is consistent with atmospheric observations of Masalaite et al. (2017, 2018) that vehicle exhausts are associated with more volatile fraction of OA, while biomass burning contributes more strongly to less volatile fractions of OA. After the primary organics (both the particle and gas) are emitted into the atmosphere, they undergo oxidation reactions, which are generally called “aging”. During the course of aging, the OA volatility will decrease by heterogeneous oxidation and/or the condensation of low-volatility products in the form of SOA. It is likely that each volatility bin in the volatility basis set has different source contributions. However, it is difficult to trace sources through the complex atmospheric transformations.

1.5 Source apportionment of carbonaceous aerosols

Source apportionment is the identification of emission sources and the quantification of the contribution from each source to pollution levels. In aerosol
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source apportionment, radiocarbon ($^{14}$C) is a very powerful tool to apportion sources of carbonaceous aerosols, by quantifying the relative contributions from fossil and non-fossil sources of aerosol carbon unambiguously (Heal et al., 2004 and references therein). Radiocarbon source apportionment exploits the fact that carbonaceous aerosol emitted from fossil sources (e.g., coal combustion, vehicle emissions) does not contain $^{14}$C, whereas carbonaceous aerosol released from non-fossil (or “contemporary”) sources, such as biomass burning or biogenic emissions, has a typical contemporary $^{14}$C signature. The $^{14}$C/$^{12}$C ratios of an aerosol sample are usually reported against a reference material, and expressed as fraction modern ($F^{14}$C) (Reimer et al., 2004; Mook and Van Der Plicht, 1999):

$$F^{14}C = \frac{(^{14}C/^{12}C)_{\text{sample}}}{(^{14}C/^{12}C)_{1950}}$$

where $F^{14}$C of carbon from fossil sources is 0, and carbon from non-fossil sources (or “contemporary” sources) should have $F^{14}$C of 1. But the extensive release of $^{14}$C from nuclear bomb tests in the late 1950s and early 1960s and $^{14}$C-free CO$_2$ from fossil fuel combustion has perturbed the atmospheric $F^{14}$C values significantly. The former increased the $F^{14}$C in the atmosphere by up to a factor of 2 in the northern hemisphere in the 1960s (Fig. 1.5). The nuclear tests have been banned in the atmosphere, outer space and under water since 1963. Since then, the atmospheric $F^{14}$C has been slowly decreasing, as $^{14}$C is mainly taken up by the oceans and terrestrial biosphere and diluted by $^{14}$C-free CO$_2$ (Levin et al., 2010; Hua and Barbetti, 2004). Currently, the $F^{14}$C of the atmospheric CO$_2$ is now approximately 1.04 (Levin et al., 2010).

Performing $^{14}$C measurements of OC and EC separately allows separation of the relative contribution from non-fossil and fossil sources to carbonaceous aerosols. Figure 1.6 illustrates a “top-down” apportionment of total aerosol carbon into broad categories, first into EC and OC, which are further divided according to non-fossil and fossil sources by $^{14}$C measurements (Heal (2014) and references therein) (Table 1.1):

1) EC is directly apportioned into EC from biomass burning (EC$_{bb}$) and EC from fossil fuel combustion (EC$_{fossil}$), as biomass burning is the only non-fossil sources of EC.

2) OC is apportioned between non-fossil sources (OC$_{nf}$) and fossil sources (OC$_{fossil}$). Whereas EC is only emitted as primary aerosol, OC has both primary and secondary origins. OC$_{nf}$ includes OC from all non-fossil sources, including primary and secondary biomass burning (POC$_{bb}$ and SOC$_{bb}$, respectively), primary and secondary biogenic OC, as well
as cooking emissions. In most cases, contributions of primary biogenic OC to PM$_{2.5}$ are small. OC$_{\text{fossil}}$ includes primary and secondary OC from fossil sources (POC$_{\text{fossil}}$ and SOC$_{\text{fossil}}$, respectively), for example, coal combustion, vehicle emissions etc.

Figure 1.5. Fraction modern ($^{14}$C) of atmospheric CO$_2$ and oceans representative for the northern hemisphere ($^{14}$C is ~1 before the nuclear weapon tests in the 1960s; the 2010 values of $^{14}$C is approximately 1.04). (Source: Lång et al., 2016).

Figure 1.6. A ‘top-down’ apportionment of aerosol carbon into broad categories, first into elemental carbon (EC) and organic carbon (OC), with further subdivision into fossil (EC$_{\text{fossil}}$, OC$_{\text{fossil}}$) or non-fossil sources (EC$_{\text{bb}}$, OC$_{\text{nf}}$) by $^{14}$C measurement.
More detailed source apportionment of OC and EC can be achieved by combining $^{14}$C-apportioned OC and EC with characteristic primary OC/EC ratios for each source: biomass burning usually has higher OC/EC ratios ($r_{bb} = 3–10$) than those for coal combustion ($r_{coal} = 1.6–3$) and vehicle exhausts ($r_{vehicle} = 0.5–1.3$) (Ni et al. (2017) and references therein) (Table 1.1).

OC$_{nf}$ can be subdivided into primary biomass-burning OC (POC$_{bb}$) and all the other non-fossil sources (OC$_{o,nf}$):

$$OC_{nf} = POC_{bb} + OC_{o,nf} \tag{1.6}$$

where OC$_{o,nf}$ includes OC from all non-fossil sources other than primary biomass burning, thus mainly consists of primary and secondary biogenic OC, secondary OC from biomass burning, as well as cooking emissions. In most cases, contributions of primary biogenic OC to PM$_{2.5}$ are likely small. POC$_{bb}$ can be estimated by multiplying EC$_{bb}$ with $r_{bb}$:

$$POC_{bb} = EC_{bb} \times r_{bb} \tag{1.7}$$

OC$_{fossil}$ includes both primary and secondary fossil OC from fossil sources (POC$_{fossil}$ and SOC$_{fossil}$, respectively):

$$OC_{fossil} = POC_{fossil} + SOC_{fossil}, \tag{1.8}$$

where POC$_{fossil}$ can be estimated from EC$_{fossil}$ and primary OC/EC ratio of fossil fuel combustion ($r_{fossil}$):

$$POC_{fossil} = EC_{fossil} \times r_{fossil}. \tag{1.9}$$

Fossil sources in China are almost exclusively from coal combustion and vehicle emissions, thus $r_{fossil}$ can be estimated as

$$r_{fossil} = r_{coal} \times p + r_{vehicle} \times (1 - p), \tag{1.10}$$

where $p$ is the relative contribution of coal combustion to fossil EC (i.e., $p = EC_{coal}/EC_{fossil}$).

This is a relatively crude estimation and limited by the uncertainties regarding the knowledge of OC/EC ratio for each source, since OC/EC emission ratios are variable with combustion condition and even measurement methods (Han et al., 2016; Chow et al., 2001; Wu et al., 2016). Moreover, this method requires an effective physical isolation of the OC and EC fractions, which are operationally defined quantities (Petzold et al., 2013). Indeed, the analytical separation of OC from EC using thermal protocols is ambiguous because part of the OC can pyrolyze (or char) to form an EC-like material (charred OC), especially in an oxygen-poor atmosphere, and some of this charred OC and
native EC can both evolve simultaneously in the presence of oxygen (Watson et al., 2005). However, it is still very useful to get a first estimate of contributions from primary combustion sources vs secondary sources.

Another limitation is that \(^{14}\text{C}\) measurement alone cannot distinguish coal combustion and vehicle emissions, since they do not contain \(^{14}\text{C}\). However, coal burning emissions are usually enriched in the stable carbon isotope \(^{13}\text{C}\) compared to vehicle emissions and therefore measurement of the \(^{13}\text{C}/^{12}\text{C}\) ratio can help to distinguish these two sources (Andersson et al., 2015). Using the radiocarbon and stable isotope \(^{13}\text{C}\) of EC and assuming isotope mass balance, it is possible to differentiate the three main sources of EC: biomass burning, vehicle emissions and coal combustion:

\[
\begin{bmatrix}
F^{14}\text{C}_{\text{EC}} \\
\delta^{13}\text{C}_{\text{EC}} \\
1
\end{bmatrix}
= 
\begin{bmatrix}
F^{14}\text{C}_{\text{bb}} \\
\delta^{13}\text{C}_{\text{bb}} \\
1
\end{bmatrix}
\begin{bmatrix}
F^{14}\text{C}_{\text{vehicle}} \\
\delta^{13}\text{C}_{\text{vehicle}} \\
1
\end{bmatrix}
\begin{bmatrix}
F^{14}\text{C}_{\text{coal}} \\
\delta^{13}\text{C}_{\text{coal}} \\
1
\end{bmatrix}
\begin{bmatrix}
f_{\text{bb}} \\
f_{\text{vehicle}} \\
f_{\text{coal}}
\end{bmatrix}
\] (1.11)

where the last row ensures the mass balance; \(f_{\text{bb}}, f_{\text{vehicle}}\) and \(f_{\text{coal}}\) are the relative contribution from biomass burning, vehicle emissions and coal combustion to EC, respectively; \(F^{14}\text{C}_{\text{EC}}\) is the \(F^{14}\text{C}\) of EC in the atmosphere, \(F^{14}\text{C}_{\text{bb}}\) is the \(F^{14}\text{C}\) of biomass burning which can be estimated by tree-ring models (Lewis et al., 2004; Mohn et al., 2008). \(F^{14}\text{C}_{\text{vehicle}}\) and \(F^{14}\text{C}_{\text{coal}}\) are zero due to the long-term decay. \(\delta^{13}\text{C}_{\text{EC}}\) is the stable isotope signature of \(^{13}\text{C}/^{12}\text{C}\) (expressed as \(\delta^{13}\text{C}\)) of EC, \(\delta^{13}\text{C}_{\text{bb}}, \delta^{13}\text{C}_{\text{liq.fossil}}\) and \(\delta^{13}\text{C}_{\text{coal}}\) are the \(\delta^{13}\text{C}\) signature of EC emitted from biomass burning, liquid fossil fuel combustion and coal combustion, respectively. Markov chain Monte Carlo (MCMC) simulations can be employed to perform statistical source apportionment modelling of the \(F^{14}\text{C}\) and \(\delta^{13}\text{C}\) signature of EC (Andersson, 2011) (Fig. 1.7).

The source signature for \(\delta^{13}\text{C}\) (i.e., \(\delta^{13}\text{C}_{\text{bb}}, \delta^{13}\text{C}_{\text{liq.fossil}}\) and \(\delta^{13}\text{C}_{\text{coal}}\)) are less well-constrained than for \(F^{14}\text{C}\), as \(\delta^{13}\text{C}\) varies with fuel types and combustion conditions. The \(\delta^{13}\text{C}\) source signatures for EC can be compiled and established by literature search of the \(\delta^{13}\text{C}\) of EC from each source. However, so far the studies on \(\delta^{13}\text{C}_{\text{bb}}, \delta^{13}\text{C}_{\text{liq.fossil}}\) and \(\delta^{13}\text{C}_{\text{coal}}\) are very limited (Anderssson et al., 2015 and reference therein).

The interpretation of the stable carbon isotope signature for OC source apportionment is more difficult, because OC is chemically reactive and \(\delta^{13}\text{C}\) signatures of OC are not only determined by the source signatures but also influenced by chemical reactions that the organic compounds undergo in the atmosphere (Fig. 1.8; Pavuluri and Kawamura, 2016; Irei et al., 2011).
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Figure 1.7. EC source apportionment scheme based on $^{14}$C and $\delta^{13}$C signature of EC (e.g.,) using the Markov chain Monte Carlo (MCMC) simulations. The relative contribution of biomass burning ($f_{bb}$), coal combustion ($f_{coal}$) and vehicle emissions ($f_{vehicle}$) to EC can be resolved.

Figure 1.8. A simplistic illustration of how different atmospheric processes are expected to affect the $\delta^{13}$C of OC. Secondary OC (SOC) formed from VOCs in the atmosphere is depleted (blue arrow) in $\delta^{13}$C compared to its gaseous precursors, if the precursors are only partially reacted. If the precursors react completely, then there is no change of the $\delta^{13}$C between the produced SOC and the corresponding precursors (*). Photochemical aging of particulate OC leads to enrichment in $\delta^{13}$C of the remaining aged OC because of a faster loss of the lighter carbon isotope $^{12}$C (red arrow). $\delta^{13}$C in fuels and in emission products (e.g., VOCs, primary OC particle) can also be different resulting from incomplete combustion, which varies with fuel types and depends on combustion conditions. But this is not shown in this figure. This overview is based on a literature search (Widory, 2006; Pavuluri and Kawamura, 2016; Fisseha et al., 2009; Irei et al., 2006; Irei et al., 2011; Kirillova et al., 2013).
Table 1.1. Schematic representation of the carbonaceous aerosols derived by combining radiocarbon measurements with characteristic primary OC/EC emission ratios for each source or stable isotope $^{13}$C.

<table>
<thead>
<tr>
<th>Carbonaceous aerosols</th>
<th>Organic/elemental</th>
<th>Non-fossil/fossil sources ($^{14}$C info)</th>
<th>$^{14}$C of OC and EC combined with primary O C/EC ratios</th>
<th>$^{14}$C combined with $^{13}$C of OC and EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total carbon (TC)</td>
<td>Elemental carbon (EC)</td>
<td>EC from biomass burning (EC$_{bb}$)</td>
<td>primary OC (POC) from biomass burning (POC) (POC$<em>{bb}$=EC$</em>{bb}$× r$_{bb}$; Eq. 1.7)</td>
<td>EC from biomass burning (EC$_{bb}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC from fossil sources (EC$_{fossil}$) (i.e., EC from coal combustion and vehicle emissions)</td>
<td>O C from other non-fossil sources except PO C$<em>{bb}$ (O C$</em>{o,nf}$) (OC$<em>{o,nf}$=OC$</em>{nf}$-POC$_{bb}$; Eq. 1.6) (i.e., secondary OC from biomass burning, primary and secondary OC from biogenic sources as well as cooking emissions)</td>
<td>EC from coal combustion (EC$_{coal}$; Eq. 1.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EC from vehicle emissions (EC$_{vehicle}$; Eq. 1.11)</td>
</tr>
<tr>
<td>Organic carbon (OC)</td>
<td></td>
<td>O C from non-fossil sources (O G$_{nf}$) (i.e., primary and secondary OC from biomass burning, biogenic emissions, cooking etc.)</td>
<td>fossil fuel combustion (POC$<em>{fossil}$) (POC$</em>{fossil}$=EC$<em>{fossil}$× r$</em>{fossil}$, where r$<em>{fossil}$=EC$</em>{coal}$/EC$<em>{fossil}$×(1-p) and p is the EC$</em>{coal}$/EC$_{fossil}$ ratio; for regions with negligible coal combustion, p can be assigned as 0; Eq. 1.9-1.10)</td>
<td>PO C from coal combustion (POC$<em>{coal}$) (POC$</em>{coal}$= EC$<em>{coal}$× r$</em>{coal}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O C from fossil sources (O G$_{fossil}$) (i.e., primary and secondary OC from coal combustion, vehicle emissions)</td>
<td>fossil fuel combustion (SO C$<em>{fossil}$) (SO C$</em>{fossil}$=OC$<em>{fossil}$-POC$</em>{fossil}$, or PO C$<em>{fossil}$=OC$</em>{fossil}$-POC$<em>{coal}$-POC$</em>{vehicle}$; Eq. 1.8) (i.e., secondary OC from fossil sources including coal combustion and vehicle emissions)</td>
<td>PO C from vehicle emissions (POC$<em>{vehicle}$) (POC$</em>{vehicle}$=EC$<em>{vehicle}$× r$</em>{vehicle}$)</td>
</tr>
</tbody>
</table>

* Carbonaceous aerosols of primary or secondary origins are color coded: primary (blue), secondary (orange), a mixture of primary and secondary (pink)
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1.6 Ambient PM$_{2.5}$ pollution in China

China experiences severe and extensive air pollution, mainly due to the rapid growth of the economy and increasing urbanization in the recent years. Major contributors to China’s widespread air pollution include tremendous fossil fuel (e.g., coal, liquid fossil fuel) and biofuel consumption, extensive agricultural burning, and natural reasons which include the city’s surrounding topography and meteorological conditions. Haze or smog episodes characterized by high concentrations of PM$_{2.5}$ and reduced visibility have frequently been reported in Chinese cities, especially in the most developed and high-populated cities, such as Beijing (Fig. 1.9), Xi’anz and Shanghai (Guo et al., 2014; Huang et al., 2014; Mao et al., 2018; Chan and Yao, 2008). The concentration of PM$_{2.5}$ is measured and regulated in China since 2016 due to its role in adverse health effects (Cao et al., 2013). The regulation states that the annual average PM$_{2.5}$ mass concentration in Chinese cities should not exceed 35 μg m$^{-3}$ and a daily average of 75 μg m$^{-3}$ should not be exceeded (MEP and AQISQ, 2012). For the European Union these limits are 25 μg m$^{-3}$ per calendar year (European Parliament and the Council, 2008). The World Health Organization (WHO) is recommending to make limits stricter. The safe level of PM$_{2.5}$ mass concentrations recommended by the WHO is below 10 μg m$^{-3}$ per year, and 25 μg m$^{-3}$ per 24 hr average (WHO 2005).

Figure 1.9. (a) Haze is seen stretching across the skyline during a heavily polluted day (16 January 2014) in Beijing, China. (b) A clean day (12 January 2014) in Beijing, China.

China is one of the most polluted regions with the highest PM$_{2.5}$ concentrations in the world. During the year of 2014/2015, only 25 out of 190 Chinese cities, where hourly PM$_{2.5}$ concentrations were released to the public, could meet the National Ambient Air Quality Standards of China (35 μg m$^{-3}$), and all the urban population in China lives in cities with higher PM$_{2.5}$
concentrations than the WHO Air Quality Guideline (10 μg m\(^{-3}\) per year) (Fig. 1.10; Zhang and Cao, 2015).

Figure 1.10. Averaged PM\(_{2.5}\) concentrations of the 190 cities in China, during the year of 2014/2015 (a) and in the spring (b), summer (c), autumn (d), and winter (e). (Source: Zhang and Cao, 2015).
Heavy haze episodes happen more frequently in winter than in other seasons, due to the enhanced emissions from fossil fuel combustion and biomass burning and unfavorable meteorological conditions (Cao et al., 2017). For example, in January of 2013, China experienced extremely heavy and persistent haze pollution, affecting ~1.3 million km$^2$ and ~800 million people. In megacities such as Beijing, Shanghai, Guangzhou and Xi’an, located respectively in the northern, eastern, southern and western regions of China, daily average PM$_{2.5}$ concentrations were ~3–14 times higher than the WHO recommended safe level of 25 μg m$^{-3}$. The daily average PM$_{2.5}$ concentrations were in the order of Xi’an (345 μg m$^{-3}$) > Beijing (159 μg m$^{-3}$) > Shanghai (91 μg m$^{-3}$) > Guangzhou (69 μg m$^{-3}$) (Huang et al., 2014). Huang et al. (2014) investigated the sources of haze pollution in the four Chinese megacities and found out that in addition to the accumulation of primary emissions, secondary aerosol formation was responsible for 30–77% of PM$_{2.5}$ and 44–71% of organic aerosol, respectively. Furthermore, high contribution of coal combustion to PM$_{2.5}$ mass (interquartile range: 9–21%) was found in Beijing and Xi’an, associated with residential coal combustion for heating in northern and western China. During the same haze event, Andersson et al. (2015) quantified the relative source strengths from different incomplete combustion processes (i.e., biomass burning, vehicle emissions and coal combustion) using the radiocarbon and stable isotope signature of EC, and found out that coal combustion contributed 66% (median; 46–74%; 95% Credible Intervals) to EC concentrations in Beijing.

Coal combustion has long been of great concern due to the large contribution of coal emissions to PM$_{2.5}$ (Zhang et al., 2017; Ma et al., 2017; Liu et al., 2017; Cheng et al., 2017) and to light-absorbing carbon including BrC and BC (or EC) (Sun et al., 2017; Yan et al., 2017; Bond and Bergstrom, 2006). As the most abundant and relatively cheap fossil fuel, coal has played dominant role in the energy supply in China. For example, 93 Tg (teragram, 1×10$^{12}$ kg) of coal was burned in the residential sector in 2013 (NBSC, 2014), emitting respectively 592 Gg (gigagram, 1×10$^{6}$ kg) BrC and 482 Gg BC estimated from measured emissions factors of BrC and BC (Sun et al., 2017). In response, Chinese authorities attempted to ban coal-heating and promoted the use of natural gas instead (“coal ban”) in 28 cities in northern China since October 2017. The coal ban resulted in a rush to switch to natural gas, which led to a shortage of natural gas and a surge in price to record highs since the start of the winter heating season last year (mid-November, 2017). However, due to delays in setting up pipelines and the gas shortage letting people have no heating at freezing temperature, the coal ban was lifted on 4 December, 2017. Therefore, if the stable supplies of the
natural gas can not be ensured, significant amount of coal will be still in use in the near future.

1.7 Motivation and thesis outline

Overall, China has been suffering from severe haze episodes characterized by high PM$_{2.5}$ mass concentrations. From the overview in the previous sections, carbonaceous aerosols (OC + EC) are known as an important component of PM$_{2.5}$ and have adverse impact on air quality, human health and climate. Knowledge of the sources is required for mitigation of PM$_{2.5}$ pollution and improving our understanding of carbonaceous aerosols’ role in climate radiative forcing. One of the aims of this thesis is to quantify the contribution of different sources to carbonaceous aerosols in China, with a special focus on coal combustion, which contributes substantially the haze pollutions in China.

In chapter 2, seasonal changes in sources of organic carbon (OC) and elemental carbon (EC) in Xi’an, China were investigated based on measurements of radiocarbon and the stable isotope $^{13}$C. By combining radiocarbon and stable carbon signature, the relative contribution from biomass burning, vehicle emissions and coal combustion to EC can be quantified. Based on apportioned EC and the characteristic primary OC/EC ratios for each source, concentrations and sources of primary OC were estimated and compared to the total OC, to get insight into the importance of secondary formation and other chemical processes for OC concentrations.

Recently emitted primary OC and newly formed SOC are usually more volatile than OC that has undergone extensive photochemical processing in the atmosphere (aged OC). Chapter 3 focuses on investigating sources of more and less volatile OC as well as EC in winter in six Chinese megacities (i.e., Xi’an, Beijing, Taiyuan, Shanghai, Chongqing and Guangzhou) by radiocarbon measurements. This is the first time that the more volatile OC (m vOC) is isolated using a custom-made aerosol combustion system for $^{14}$C analysis. This new isolation method (i.e., desorbing OC from the filter samples in He at 200 °C) was first evaluated for its reproducibility and representativeness of isolated m vOC both in terms of the isolated amount and F$^{14}$C data. The variability of fossil and non-fossil contribution to m vOC, OC and EC in different Chinese cities is investigated based on $^{14}$C measurements. Further, based on the $^{14}$C-apportioned OC and EC, concentrations and sources of SOC were estimated and then compared to m vOC to further explore sources and formation mechanism of m vOC and SOC.
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Among the major sources of PM, coal combustion is of great concern in China. Apart from the adverse impact of coal combustion emissions on air quality, coal combustion is also an important source of light-absorbing OC (referred to as brown carbon, BrC), affecting the Earth’s radiative forcing. To date, relatively few measurements have been conducted to examine BrC from residential coal combustion and even fewer measurements have examined absorption properties of aged BrC. Accordingly, another aim of this thesis is to understand light absorption of BrC from coal combustion emissions as a function of aging. In chapter 4, we conducted 12 individual burns in a traditional Chinese stove in the residential sector, using five different coals collected from major coal producing areas in China. This is the first time that the variability in measured light absorption of BrC is linked to burning condition and photochemical aging, based on controlled smog chamber experiments. The results of this study can be applied to climate models and can be extrapolated to other regions with ubiquitous coal-derived aerosols, such as Poland, Ireland and India. Chapter 5 summarizes the major conclusions of this study, and outlines the scope for future measurements and studies.
Introduction

References


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Introduction

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