Summary

Air pollution caused by aerosols — microscopic particles suspended in the air—is a major problem in China. The carbonaceous fraction of the aerosol (carbonaceous aerosols; CAs) is the major component of aerosols, and has adverse impact on air quality, human health and climate. CAs are classified into elemental carbon (EC) and organic carbon (OC). EC can significantly absorb incoming solar radiation. On the other hand, OC mainly scatters light, but there is also OC found with light absorbing properties, referred to as brown carbon (BrC). CAs are believed to contribute large uncertainties in climate radiative forcing by absorbing and scattering light. EC and OC are mainly emitted from incomplete combustion of biomass (e.g., wood, crop residues, and grass) and fossil fuels (e.g., coal, gasoline, and diesel). Biomass burning is the only non-fossil source for EC, but OC also has other sources, for example, biogenic emissions (i.e., emissions from natural sources, such as plants and trees) and cooking. Unlike EC that is directly emitted as primary CAs, OC includes both primary (POC) and secondary OC (SOC). SOC is formed in the atmosphere via atmospheric oxidation of organic gases from both fossil and non-fossil sources (e.g., biomass burning, biogenic emissions, and cooking). Because of the complex formation mechanisms, it remains unclear how much each of these major sources contributes to CAs in China. Better knowledge of the sources of CAs is required to mitigate air pollution and improve our understanding of CAs’ role in climate radiative forcing.

Unfortunately, it is very challenging to estimate the contribution of pollution sources to CAs concentrations. The most direct method to find the main sources of CAs is analysis of radiocarbon (\(^{14}\text{C}\)). Living material is in equilibrium with CO\(_2\) in the atmosphere and contains a known typical abundance of \(^{14}\text{C}\). On death, the \(^{14}\text{C}\) isotope decays with a half-life of 5,730 years. Fossil fuels are much older than this and therefore do not contain \(^{14}\text{C}\). If we succeed in measuring \(^{14}\text{C}\) on
CAs, we can separate at least the two main sources of CAs: fossil sources (e.g., coal combustion, vehicle emissions) that do not contain $^{14}$C, and non-fossil (or contemporary) sources (e.g., biomass burning or biogenic emissions, cooking) that have a typical, relatively constant abundance of $^{14}$C. However, this method is not applied widely in China due to the fact that $^{14}$C analysis is time-consuming, labor-intensive and expensive. This thesis applied $^{14}$C measurement on different fractions of CAs to quantify the source contributions in China, with a special focus on coal combustion, which contributes substantially the polluted air in China.

Source contributions change in different seasons. In chapter 2, seasonal changes in sources of OC and EC in Xi’an, China during 2008/2009 were studied by measuring $^{14}$C on OC and EC separately. We found that EC is dominated by fossil sources, whereas OC is mainly attributed to non-fossil sources (e.g., biomass burning, biogenic emissions, cooking) throughout the year. Both OC and EC have increased contribution from non-fossil sources in winter in contrast to warm period, reflecting the enhanced activities of biomass burning for heating in winter. Using the stable carbon isotope $^{13}$C, fossil sources of EC are further divided into coal combustion and vehicle emissions. This can be achieved because EC from coal combustion is on average more enriched in $^{13}$C compared to vehicle emissions. Coal combustion dominated fossil EC in winter, and vehicle emissions dominated during the warm period. Further, based on the known EC sources, concentrations and sources of primary OC (POC) were estimated and compared to the observed total OC. The differences between observed OC and estimated POC result from SOC that is not included in the estimation of POC. We found that the estimated POC was similar to the observed total OC in terms of absolute concentrations, variability and seasonality, except in winter when the concentrations of observed OC exceed POC. However, the sources of OC and POC were quite different, which can not be reconciled without overestimating the OC mass concentrations. We therefore conclude that both secondary formation and photochemical loss processes influence the final OC concentrations, especially in warm period.

OC is a complex mixture of thousands of different individual organic species covering wide range of volatility. Volatility determines the partitioning of organic compounds between the gas and particle phase. Low volatility organic compounds are mainly observed in the aerosol phase, and highly volatile compounds 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. Primary OC from various sources has different
volatility. After primary OC is emitted into the atmosphere, it undergoes oxidation reactions, which are generally called “aging”. Earlier studies found that recently emitted primary OC and newly formed secondary OC (SOC) are usually more volatile than OC that has undergone extensive photochemical processing in the atmosphere (aged OC). It is therefore important to investigate the sources of OC with different volatilities for better understanding of the atmospheric processes of organic aerosols. Chapter 3 focuses on sources of more and less volatile fraction of OC using $^{14}$C measurement for the first time. We developed and tested a $^{14}$C based approach for investigating sources of more volatile fraction of OC (mvOC). mvOC is isolated by desorbing organic carbon from the filter samples in He at 200 °C in a custom-made aerosol combustion system for $^{14}$C analysis. Evaluation of this new isolation method shows that the isolated mvOC is reproducible both in terms of the amount and $^{14}$C data. We further applied this to aerosol samples collected in 6 Chinese megacities. We found from $^{14}$C results of mvOC and OC that mvOC was influenced more strongly by fossil sources than total OC, regardless of the fact that different cities have quiet different primary combustion sources indicated by $^{14}$C results of EC, ranging from largely biomass burning to largely fossil fuel dominated. This is consistent with source studies indicating that primary emissions from vehicular sources are more volatile than primary emissions from biomass burning. However, the relative contribution of mvOC to OC in the ambient samples is much smaller than that typical for primary emissions, suggesting active processing of the aerosol in atmosphere even during wintertime, when colder temperature and diminished sunlight both slow chemical reactions. Further, based on $^{14}$C-apportioned OC and EC in the six Chinese cities, we estimated the SOC concentrations and found that SOC (an average of $15 \pm 9 \, \mu g \, m^{-3}$) is an important contributor to OC ($30 \pm 14 \, \mu g \, m^{-3}$). Our results suggest that, in addition to reduce primary emissions, reducing the emissions of organic gases that can form secondary aerosols is also important for air pollution control in China.

Among the major sources of air pollution, coal combustion is of great concern in China, especially in the heating season. As the most abundant and relatively cheap fossil fuel, coal will inevitably remain an important indigenous energy resource in China for the foreseeable future. Apart from the adverse impact of coal combustion emissions on air quality, a few recent studies suggest that coal combustion also contributes to BrC, affecting the Earth’s climate radiative forcing by absorbing light. However, our knowledge of light absorption of BrC from residential coal combustion and how the atmospheric processing modifies the light absorption ability of BrC is still poor. This limits climate
models in their capacity to take into consideration of BrC absorption, hindering our understanding of CAs’ role in affecting climate. In Chapter 4, we investigated for the first time the light absorption ability of BrC from both primary and aged coal combustion emissions in China. It shows that the light absorption ability of BrC from primary emissions depends on combustion conditions and decreases after aging. We conclude that coal combustion emissions also play an important role in light absorption of BrC and should be considered in further climate model. The results from this study can be extrapolated to other regions with ubiquitous coal-derived aerosols, such as Poland, Ireland and India.

This thesis showed that through applying radiocarbon measurements on different fractions of CAs, increased knowledge and understanding of sources and atmospheric processing of CAs can be gained. Results from this thesis can contribute to devise better reduction strategies in some most polluted Chinese cities, but also in many regions where similar sources and processes play a role. On the other hand, characterization of primary and aged BrC from coal combustion helps in evaluating the effects of the carbonaceous aerosol on climate. Chapter 5 discusses the factors that limit our knowledge of CAs and outlines the scope for future measurements and studies to better understand the role of CAs regarding source attribution and their effects on air quality and climate.