



Stable isotopic compositions of elemental carbon in PM_{1.1} in north suburb of Nanjing Region, China



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ABSTRACT

Stable isotopic compositions ($\delta^{13}\text{C}$) of elemental carbon (EC) in PM_{1.1} in north suburb of Nanjing region were determined in order to quantitatively evaluate the carbon sources of atmospheric fine particles during different seasons. Besides, $\delta^{13}\text{C}$ values from potential sources such as coal combustion, vehicle exhaust, biomass burning, and dust were synchronously measured. The results showed that the average $\delta^{13}\text{C}$ values of EC in PM_{1.1} in winter and summer were $-23.89 \pm 1.6\%$ and $-24.76 \pm 0.9\%$, respectively. Comparing with $\delta^{13}\text{C}$ values from potential sources, we concluded that the main sources of EC in PM_{1.1} were from the emission of coal combustion and vehicle exhaust. The higher $\delta^{13}\text{C}$ values in winter than those in summer were chiefly attributed to the more coal consumption. Combining with the concentrations of SO_4^{2-} and K^+ in PM_{1.1}, the high $\delta^{13}\text{C}$ values of EC on 24 December and 27 December 2013 were ascribed to extra input of corn straw burning in addition to coal combustion and vehicle exhaust.

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1. Introduction

PM_{2.5} is an important atmospheric pollutant, which possesses an extremely complex composition. PM_{1.1} (aerodynamic diameter $\leq 1.1 \mu\text{m}$) is a major component of PM_{2.5}, accounting for 70% of its total mass. PM_{1.1} contains large amounts of toxic and hazardous substances, thereby resulting in a more impact on human health and the quality of atmospheric environment compared to those of PM_{2.5}. Therefore, the investigations about PM_{1.1} are attracting more and more attentions.

Carbon is an important ingredient in PM_{1.1} (Cong et al., 2015; Wan et al., 2015), which can be divided into organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) according to their existing forms. EC is mainly present in the submicron particles, and the sizes of EC particles are predominantly between 0.05 μm and 1 μm with a lifetime varying from 2 to 11 days in the atmosphere (Schulz et al., 2006; Vodicka et al., 2015). The presence of EC in PM_{1.1} is favorable for absorbing visible light and infrared light, thereby resulting in a decrease of atmospheric visibility (Cong et al., 2013). Yu et al (2010) observed that EC-containing particles in the suburban/rural locations had a significant contribution to light extinction budget. In addition, PM_{1.1} might be easily inhaled into the lungs and reach the alveolar of human body, which inevitably affects normal function of the lungs and causes respiratory disease such as asthma and throat irritation. At present, the sources of

EC in the atmosphere are usually identified based on the ratio of OC and EC (Hou et al., 2011; Huang et al., 2006; Querol et al., 2004). However, this method has encountered some limitations for the increasing diversities and complexities of atmospheric carbon source in PM_{1.1} (Mazzoleni et al., 2007; Pavuluria et al., 2015).

Recently, stable isotopes have been used to trace and characterize the sources of the pollutants in the atmosphere due to that isotopic compositions are not generally same in different sources (Guo et al., 2010; Guo et al., 2014; Ma et al., 2010; Masalaite et al., 2015). Therefore, the studies on stable carbon isotope (^{13}C) of EC in PM_{1.1} have a potential to seek for carbon sources in the atmosphere (Song et al., 2008; Wang et al., 2012).

Ho et al (2006) found that there was no notable difference for seasonal distribution of carbon isotopic composition in Hong Kong aerosol and concluded that motor vehicle emission was the main source due to the consistency of $\delta^{13}\text{C}$ values. Wang et al. (2005) determined isotopic compositions of carbonate of surface soil samples from northern China and dust aerosol samples collected at different sites. The results showed that $\delta^{13}\text{C}$ value in the aerosol was lower than those in local surface soils. At Aksu and Dunhuang, dust aerosol showed a higher $\delta^{13}\text{C}$ value compared with those at Yulin. Pavuluria et al (2011) studied the sources and photochemical process of organic aerosols by determining $\delta^{13}\text{C}$ values of total carbon, dicarboxylic acid, and glyoxylic acid in the tropical Indian aerosols. Guo et al (2013) used carbon isotopic approach to identify the anthropogenic input of organic carbon into the soil and trace soil carbon turnover in Beijing. Gao et al (2014) measured the

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isotopic ratios of carbon and nitrogen in suspended matters to make clear the seasonal and spatial dynamics along Yangtze River transport pathway. Carme et al (2014) reported the sources and optical properties of EC and water-soluble organic carbon (WSOC) with a carbon isotopic approach, and found $\delta^{13}\text{C}$ value of MCOH-WSOC ($-20.8 \pm 0.7\%$, MCOH was a long-term receptor station for the South Asian outflow) was higher compared to those of MCOH-EC ($-25.8 \pm 0.3\%$) and mega-city Delhi-WSOC ($-24.1 \pm 0.9\%$). This indicates that WSOC was more inclined to be affected than EC in aerosol aging process during long-range transport from South Asian to Indian Ocean.

Nanjing is one of the central cities in Yangtze River Delta region. With the aggravation of industrialization process, EC and $\text{PM}_{1,1}$ pollution in Nanjing is getting worse. In order to quantitatively clarify $\text{PM}_{1,1}$ pollution and EC sources in Nanjing region during different seasons, we systemically measured $\delta^{13}\text{C}$ values of EC as well as the chemical compositions in $\text{PM}_{1,1}$ from north suburb of Nanjing region. In addition, $\delta^{13}\text{C}$ values from potential polluted sources such as vehicle exhaust, coal combustion, biomass burning, and dust were synchronously determined in order to accurately evaluate carbon sources of EC in $\text{PM}_{1,1}$.

2. Materials and methods

2.1. Sampling site

The sampling site of $\text{PM}_{1,1}$ was located on training building roof of Nanjing University of Information Science & Technology (NUIST,

32.1°N , 118.5°E) in Nanjing, China, as shown in Fig. 1. The sampling site is close to National Road and many industrial enterprises including thermal plants, petrochemical companies, and steel plants. The production of industrial enterprises mainly used coal as fuel, which inevitably resulted in the emission of a large amount of EC and atmospheric particles.

2.2. Samples collection

$\text{PM}_{1,1}$ samples were acquired by using a low-volume FA-3 Aerosol Particle Size Distribution Sampler (cut size: $9.0\text{--}10.0\ \mu\text{m}$, $5.8\text{--}9.0\ \mu\text{m}$, $4.7\text{--}5.8\ \mu\text{m}$, $3.3\text{--}4.7\ \mu\text{m}$, $2.1\text{--}3.3\ \mu\text{m}$, $1.1\text{--}2.1\ \mu\text{m}$, $0.65\text{--}1.1\ \mu\text{m}$, $0.43\text{--}0.65\ \mu\text{m}$, and $<0.43\ \mu\text{m}$) with a flow rate of $28.3\ \text{L} \cdot \text{min}^{-1}$ at the top of the training building in NUIST. $\text{PM}_{1,1}$ sampling were continuously conducted during the winter from 24 December 2013 to 10 January 2014, and the summer from 3 July to 21 July 2014. Thus, thirty $\text{PM}_{1,1}$ samples were obtained in the study based on one sample per day. Before $\text{PM}_{1,1}$ sampling, the glass fiber filters were incinerated in a muffle furnace at 450°C for at least 4 h to prevent the contamination of moisture and organic matters, and then placed in a desiccator to achieve humidity equilibrium for 24 h at room temperature. The sampled filters were immediately brought to the laboratory and reserved in a refrigerator for ion concentrations and carbon isotopic analysis.

In order to accurately trace the carbon sources of EC in $\text{PM}_{1,1}$, coal combustion, vehicle exhaust, biomass burning, and dust were selected for potential sources of $\text{PM}_{1,1}$ in Nanjing region. The soot from coal

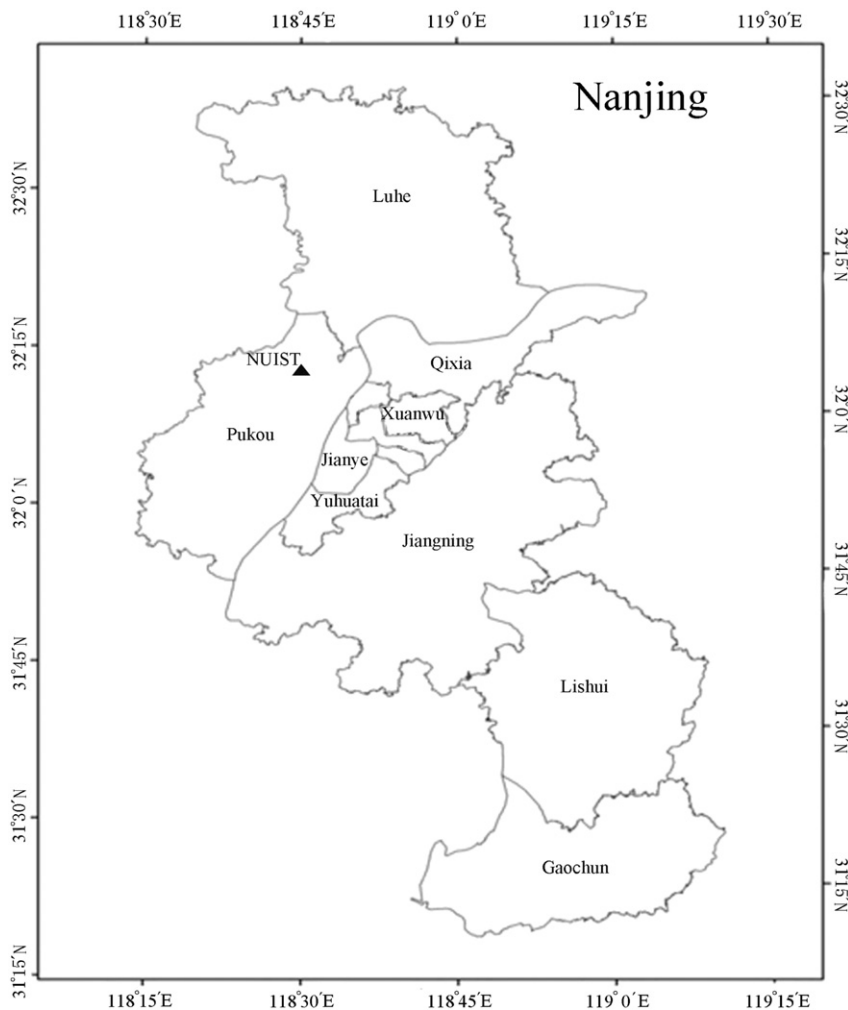


Fig. 1. Sampling site at NUIST in Nanjing, China.

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