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# Source contributions to water-soluble organic carbon and water-insoluble organic carbon in $PM_{2.5}$ during Spring Festival, heating and non-heating seasons

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ABSTRACT

To investigate the influences of anthropogenic activities on carbon aerosols, especially on water-soluble organic carbon (WSOC), $PM_{2.5}$ samples were collected at an urban site in a northern city of China during Spring Festival (SF), heating season (HS), and non-heating season (NHS). Carbonaceous species and ions ($Ca^{2+}$, $SO_4^{2-}$, $NO_3^-$, etc.) were analyzed. Mass concentrations of WSOC and WSIC exhibited higher levels in SF and HS, and high WSOC/OC ratios (67.4%) on average were found. Stronger correlations between WSOC and $K^+$, $Cl^-$ occurred in SF, which might due to contributions of firework emissions. Six major sources of $PM_{2.5}$ were quantified by PMF model, which contributed in aerosol mass differently in different periods: biomass & firework burning exhibited higher contribution (11.2%) in SF; crustal dust accounted for 19.4% during NHS; secondary particles contributed most (41.0%) in HS; during SF and HS, coal combustion devoted more to aerosol mass. Contributions to WSOC were in the order of vehicular exhaust (41.0% of WSOC) > coal combustion (29.3%) > secondary formation (17.0%) > biomass & firework burning (12.7%). The 82.0% of WIOC were from coal combustion and the rest were devoted by vehicular exhaust. Obvious peaks of firework burning contributions to WSOC were observed on SF's Eve and Lantern Festival. Coal combustion contributed to organic carbons highly in SF and HS. Results implied that anthropogenic activities contributions, like firework burning and coal combustion, significantly influenced the levels of $PM_{2.5}$ and WSOC.

## 1. Introduction

Carbonaceous species consist of organic carbon (OC) and elemental carbon (EC), which are rich in particulate matter. Among them, EC is usually exhausted from incomplete combustion (Ram and Sarin, 2009; Cheng et al., 2011a, 2011b; Chen et al., 2014). OC can be produced from many different sources (such as coal combustion, industrial activities, and natural sources), as well as complex atmospheric processes (such as direct emission, homogenous gas-phase oxidation, gas-aerosol partitioning, heterogeneous conversion, etc.) (Xiao et al., 2011; Shen et al., 2012; Verma et al., 2012; Timonen et al., 2013; Ji et al., 2018). OC is a mixture of hundreds of compounds, which can be classified as water-soluble organic carbon compounds (WSOC) and water-insoluble carbon compounds (WIOC) (Zhang et al., 2012; Huo et al., 2016). WSOC plays important roles in visibility, climate change, atmospheric brown cloud formation, and aqueous phase chemistry and is also known for its significant effect on human health and air quality (Asa-Awuku et al., 2009; Cheng et al., 2011a, 2011b; Du et al., 2014; Hecobian et al., 2010; Hegde et al., 2007). Therefore, it is necessary to understand and study WSOC. Previous studies found that WSOC usually accounts for a high fraction of OC (15–80%) (Feng et al., 2006; Zhang et al., 2008; Cho and Park, 2013; Singh et al., 2016; Deshmukh et al., 2016). However, characteristics of WSOC under different anthropogenic activities remain poorly understood, especially the relationship between WSOC and chemical composition (Cheng et al., 2008). Furthermore, this limited knowledge of WSOC ultimately restricts our understanding of the most relevant particle sources.

At present, growing anthropogenic activities linked with fossil fuel combustion, biomass burning, and industrial organic manufacturing have led to high concentration of $PM_{2.5}$ (particulate matter with

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aerodynamic diameter less than 2.5 μm) and carbonaceous compounds in south and south-east Asia (Aggarwal and Kawamura, 2009; Kirpa and Sarin, 2011; Tzompa et al., 2014; Tao et al., 2014; Kong et al., 2015), especially in China (Andreae et al., 2008; Yang et al., 2005). Ambient $PM_{2.5}$ is deemed to be a primary environmental issue resulted from the strong effects on climate change, regional visibility and human health (Megido et al., 2017; Wang et al., 2017). To understanding the physical and chemical characteristics of $PM_{2.5}$ and its chemical compositions remains a complicated subject (Palma et al., 2017). Aerosols are influenced by complex anthropogenic activities such as fossil fuel combustion (industrial production, thermal power plants, and vehicular emission), biomass burning and secondary formation according to former researches (Cheng et al., 2011a, 2011b; Duan et al., 2004; Kawamura et al., 2013; Wonaschutz et al., 2011), along with several other specific sources (e.g., crustal dust, construction dust).

Anthropogenic emissions usually vary within different periods. Spring Festival (CNY, China New Year Day) is a dramatic traditional episodes and the most important folk holiday in China. During Spring Festival, some specific activities such as firework displaying tend to spill over into the preceding and succeeding days, which would greatly change the emission patterns (Huang et al., 2012; Liu et al., 2016), whereas other ordinary activities (such as industrial production and traffic) are decreased (Feng et al., 2012). During the heating season (from November to March, ensuing year) in Northern China, increased coal may be combusted for heating. The changes in anthropogenic emission patterns provide a unique opportunity to study the influence of anthropogenic activities on carbon aerosols and the origins of WSOC.

Receptor models such as Chemical Mass Balance (CMB) and Positive matrix factorization (PMF) were widely used to quantify the contributions from emission sources (Bari and Kindzierski, 2017; Tian et al., 2017). Several studies have used PMF to investigate potential sources and formation mechanisms of WSOCPeople and Places Shaping Food Procurement among Recipients of Supplemental Nutrition Assistance Program (SNAP)yed PMF model to investigate the sources of two WSOC fractions in Gwangju, Korea, indicating that WSOC were affected by sources such as traffic emissions and biomass emissions, etc. Saarikoski et al. (2008) used PMF for water-soluble OC in Helsinki deduced that four sources including biomass combustion, traffic, long-range transport and secondary production closely impact the local ambient $PM_1$. Otherwise, due to the complexity of WSOC, it is challenging to thoroughly study their sources and formation (Robinson et al., 2008; Shakya et al., 2010). There were limited researches to investigate the relationships between WSOC and other species, especially during different anthropogenic events (such as Spring Festival and heating season), would be useful to better understand its origins.

To study the influence of anthropogenic activities on carbon aerosols, especially on WSOC during specific period of China, simultaneous measurements of $PM_{2.5}$ and chemical species (OC, EC, WSOC and inorganic constituents) in $PM_{2.5}$ were conducted in a megacity in northern China (Tianjin) during the Spring Festival (SF), the heating season (HS), and the non-heating season (NHS). We focused on exploring the fluctuation characteristics of WSOC and relevant species in $PM_{2.5}$, as well as the relationships among primary chemical species. Furthermore, quantitative source apportionment for ambient aerosol by PMF, as well as contributions of WSOC to aerosol mass during different sampling periods influenced by various anthropogenic activities were investigated.

## 2. Materials and methods

### 2.1. Sampling

The sampling site, NKU (39° 10' N, 117° 16' E) (Fig. 1), is in the urban area of Tianjin city, China. During the wintertime, Tianjin experienced several severe haze weather events.

Ambient $PM_{2.5}$ samples were collected on pretreated polypropylene and quartz fiber filters by simultaneously operating two medium-volume air samplers (Tianhong, MA, China) at a flow rate of 100 L $min^{-1}$, and each sample was integrated for 24-h to filter ~ 120–140 $m^3$ of ambient air. Samplers were set up approximately 15 m above ground on the building at NKU. In this study, sampling periods were defined as the Spring Festival (SF: Jan 30th, the first day of the Chinese lunar calendar– Feb 14th, the fourteenth day of the Chinese lunar calendar), the heating season (HS: Jan 27th-Jan 29th, Feb 15th–Mar 15th), and the non-heating season (NHS: Mar 18th–Apr 9th). Overall, a total of 45 $PM_{2.5}$ samples were obtained every third day (except SF: continuously collected for 15 days and then occasionally due to instrument maintenance) during the sampling period from January 23rd to April 8th, 2014. Field blank filters were also collected and analyzed for blank correction. Each filter was conserved in a refrigerator (-4 °C) without illumination until further analysis. For detailed information on storage, refer to a previously published study (Ram and Sarin, 2010). In addition, meteorological data were collected synchronously during the sampling periods, which are displayed in the supplementary information section.

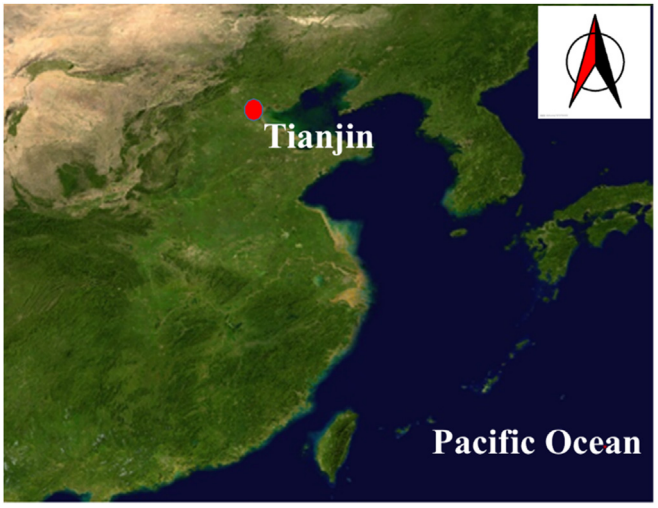


**Fig. 1.** The urban sampling location, Nankai University, in Tianjin.

### 2.2. Chemical analyses

In this study, the ambient filters were analyzed for water-soluble ions, OC, EC, and WSOC. The $PM_{2.5}$ mass was determined using the standard gravimetric method (over one million electronic scales) at 45% RH. For the analysis of water-soluble species, the samples were intercepted from a 1/8 membrane filter and extracted with 5 mL of distilled deionized water (DDW). The liquid extracts were filtered through a 0.45 mm PTFE syringe filter, and then the 5 μl extracts were injected into an ion chromatography (IC) system (Dionex DX-500, CA, USA) for the detection of water-soluble ions (anions: $Cl^-$, $NO_3^-$ and $SO_4^{2-}$; cations: $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) (Wang et al., 2012a; Wang et al., 2012b).

The concentrations of OC and EC were measured on a 0.508 $cm^2$ punch from each filter by thermal optical reflectance (TOR), following the IMPROVE-A protocol on a thermal/optical carbon analyzer (Model 2001A, USA). To calibrate the instrument, parallel analyses of both standard and ambient samples were carried out. The minimum detection limits (MDL) were 0.8 mgC $cm^2$ for OC and 0.4 mgC $cm^2$ for EC, with precision of better than 10% for total carbon (TC) (Feng et al., 2006).

The concentrations of WSOC were measured using a high-sensitivity carbon analyzer (DRI-2001, USA). The filter was extracted into 5 mL of DDW for pretreatment using an ultrasonic bath for 1 h. WSOC was quantified, and the estimated MDL of WSOC was 0.1 mg $m^{-3}$ with an