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Atmospheric Chemistry and Physics Discussions

Measurement Report: Chemical components and ^{13}C and ^{15}N isotope ratios of fine aerosols over Tianjin, North China: Year-round observations

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Abstract. To better understand the origins, atmospheric processes and seasonality of atmospheric aerosols in North China, we collected fine aerosols ($PM_{2.5}$) at an urban (Nankai District, ND) and a suburban (Haihe Education Park, HEP) sites in Tianjin from July 2018 to July 2019. The $PM_{2.5}$ studied for carbonaceous, nitrogenous and ionic components and stable carbon and nitrogen isotope ratios of total carbon ($\delta^{13}C_{TC}$) and nitrogen ($\delta^{15}N_{TN}$). On average, mass concentration of $PM_{2.5}$, organic carbon (OC), elemental carbon (EC) and water-soluble OC (WSOC found to be higher in winter than that in summer at both ND and HEP. SO_4^{2-}, NO_3^- and NH_4^+ were dominant ions and accounted for 89% and 87% of the total ionic mass at ND and HEP respectively. NO_3^- and NH_4^+ peaked in winter and minimized in summer, whereas SO_4^{2-} was higher in summer at both the sites. $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ were −26.5−(−)21.9‰ and +1.01−(+)22.8‰, respectively, at ND and −25.5−(−)22.8‰ and +4.91−(+)18.6‰, respectively, at HEP. Based on seasonal variations in the measured parameters, we found that coal and biomass combustion emissions are dominant sources of $PM_{2.5}$ in autumn and winter, while biological and/or marine emissions are important in spring and summer in the Tianjin region, North China. In addition, our results implied that the secondary formation pathways of secondary organic aerosols in autumn/winter were different from that in spring/summer, i.e., they were mainly driven by NO_3 radicals in the former period.

1 Introduction

Atmospheric aerosols are mainly composed of carbonaceous and inorganic components such as elemental carbon (EC), organic matter (OM), sulfate, nitrate, ammonium, sea salt and minerals, usually, each accounting for about 10−30% of the aerosol mass load that generally range 1−100 μg m^{-3} (Poeschl, 2006;Pavuluri et al., 2015b). They have severe impacts on the Earth's climate system, air quality, visibility (Laden et al., 2000;Samet et al., 2000;Chow et al., 2002) and human health (Wessels et al., 2010).

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Aerosols can affect the climate directly by absorbing and scattering solar radiation and indirectly by acting as cloud condensation nuclei (CNN), and thus hydrological cycle, at local, regional and global scales (Menon et al., 2002;Chow et al., 2006;Ramanathan et al., 2001). It has been recognized that ambient aerosol pollution is one of the major reasons for cancer (Wang et al., 2016b) and other diseases in humans. According to the global burden of disease (GBD) 2010 comparative risk assessment, it has been estimated that fine aerosol ($PM_{2.5}$) pollution causing a death of about 3 million people worldwide per year (Lim et al., 2012), and the total number of daily deaths are increased by ~1.5% for every 10 μg m^{-3} increase in the average $PM_{2.5}$ loading over two days (Schwartz et al., 1996).

Carbonaceous components: EC and organic carbon (OC, i.e., (OM)), account for 20−50% of $PM_{2.5}$ mass (Cui et al., 2015;Sillanpää et al., 2005). EC directly emits from incomplete combustion of fossil fuels and biomass burning (Robinson et al., 2007;Larson and Cass, 1989). While OC can be directly emitted into the atmosphere from combustion sources, soil dust and biota (primary OC, POC) and also produced from volatile organic compounds (VOCs) by photochemical reactions in the atmosphere (secondary OC, SOC) (Robinson et al., 2007). It has been estimated that OC and EC emissions have been increased (2127 and 1356 Gg, respectively) from 2000 to 2012 (2749 and 1857 Gg, respectively) by 29% and 37%, respectively, in China (Jimenez et al., 2009;Cui et al., 2015). Previous studies have reported very high loadings of OC and EC at large cities in China, particularly the Beijing-Tianjin-Hebei (Yang et al., 2011;Duan et al., 2005;Zhao et al., 2013;Dan et al., 2004), the Yangtze River Delta (Huang et al., 2013;Feng et al., 2006;Feng et al., 2009;Wang et al., 2010) and the Pearl River Delta (Huang et al., 2012) regions, which are densely populated and economically developed.

Since industrialization, the annual production of reactive nitrogen (Nr) has more than doubled due to combustion of fossil fuels and production of nitrogen fertilizers and other industrial products (Gu et al., 2013). Global Nr has dramatically increased from 15 Tg N yr^{-1} in 1860 to 156 Tg N yr^{-1} in 1995 and then to 192 Tg N yr^{-1} in 2008, significantly exceeding the annual natural production from terrestrial ecosystems (40−100 Tg N yr^{-1}) (Gu et al., 2013). The consumption of Haber-Bosch N fixatives (HBNF) is high (35 Tg) for agricultural and industrial applications in China, which account for about 30% of the world's total HBNF consumption (Gu et al., 2015;Galloway et al., 2008). The Nr species such as nitrogen oxides (NO_x: NO_2 and NO) and ammonia (NH_3) participate in a series of physical and chemical transformations and 60−80% of them convert to nitrogen-containing aerosols, affecting a variety of chemical reactions in the atmosphere (Fajardie et al., 1998). The photochemical cycle of NO_x provides an important precursor for the formation of ozone. Also, the NO_x can oxidize hydrocarbons resulting secondary pollutants such as aldehydes, ketones, acids, peroxyacetyl nitrate (PAN), leading to the formation of photochemical smog, that impact the environment and cause serious harm to human health (Wolfe, 2002). On the other hand, NH_3 is an important alkaline gas in the atmosphere and affects the optical properties, pH and CCN activity of aerosols and thus, can influence the energy balance of the Earth's atmosphere (Bencs et al., 2010). It has also been established that secondary inorganic ions (SNA: $SO_4^{2-} + NO_3^{-} + NH_4^{+}$) are the main water-soluble inorganic ionic substances, which can directly affect the acidity of atmospheric precipitation, causing serious impacts on the ecological environment (Andreae et al.,

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2008), in addition to the impacts on the Earth's climate system.

However, the long-term measurements and seasonal characterization of carbonaceous and nitrogenous components and water-soluble inorganic ions that are important to better understand the source and characteristics of the $PM_{2.5}$ are scarce, although they have been well studied for short-periods at different locale over the world. Furthermore, most studies have been focused on inorganic ions and carbonaceous components (Cao et al., 2007;Dentener et al., 2006;Pavuluri et al., 2015b), but not on organic N (ON), which represent a significant fraction (up to 80 %) of total aerosol N and may play a critical role in biogeochemical cycles (Pavuluri et al., 2015a;Cape et al., 2011). In fact, the aerosol OC and both inorganic N (IN) and ON that are produced in the atmosphere by several processes (Ottley and Harrison, 1992; Utsunomiya and Wakamatsu, 1996) from VOCs and gaseous N species, respectively, emitted from different sources. Therefore, it is difficult to understand the origins of aerosols C and N from only the measurement of their species and/or specific markers.

It is well known that the stable C ($\delta^{13}C_{TC}$) and N ($\delta^{15}N_{TN}$) isotope ratios of total C (TC) and nitrogen (TN) depend on theier sources (Freyer, 1978; Moore, 1977). It has been reported that the particles emitted by sea-spray are highly enriched with ^{13}C and ^{15}N (Chesselet et al., 1981; Cachier et al., 1986; Miyazaki et al., 2011) and differ from that of continental origins such as burning of C_3 plants, C_4 plants, coal combustion and vehicular emissions (Cachier et al., 1986; Turekian et al., 1998; Martinelli et al., 2002; Widory, 2006; Cao et al., 2011). On the other hand, they are modified by several chemical and physical processes in the atmosphere such as oxidation and secondary aerosol formation and/or transformations. Therefore, the $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ of $PM_{2.5}$ would provide insights on their origins, and also secondary formation/transformations during atmospheric transport, if the removal processes including physical transformation (particle-to-gas phase), are significant and thus, useful for better constraining the relative significance of such factors (Bikkina et al., 2017;Pavuluri et al., 2010;Jickells et al., 2003;Martinelli et al., 2002). The application of $\delta^{13}C$ and $\delta^{15}N$ as potential tracers to investigate the origin and atmospheric processing (aging) of C and N species is well documented and has been applied in several studies in last two decades (Kundu et al., 2010;Martinelli et al., 2002;Pavuluri et al., 2015c;Rudolph, 2002). However, it should be noted that the influence of isotopic fractionation by the aging on $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ values of $PM_{2.5}$ become insignificant when the local fresh air masses are mixed with the aged air masses that transported from distant source regions and/or the aerosol removal processes are insignificant, despite fact that the isotopic fraction must be significant at molecular level.

Because of rapid economic growth, the aerosol loading is commonly observed to be high in China, particularly the Beijing-Tianjin-Hebei region. According to the data analysis of the "2 + 26" list of urban industrial sources in 2018, primary emissions of $PM_{2.5}$, SO_2, NOx and VOCs from industrial sources account for 60%, 46%, 23% and 49% of the total regional emissions, respectively. Moreover, Tianjin is surrounded by the areas largely covered with agricultural fields and forests that emit large amounts of VOCs and bioaerosols. On the other hand, the East Asian monsoon climate prevailing over the region brings the long-range transported air masses to Tianjin and their origins vary with the season (Wang et al., 2018). Hence,

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Tianjin represents an ideal location to collect the air masses derived from Eurasia passing over the Siberian forest and northern parts of China and the surrounding oceans and mixed with the local industrial and domestic pollutant emissions in North China. However, the studies on Tianjin aerosols are limited, which mostly focused on the short-term measurements of mass concentrations of $PM_{2.5}$, EC and OC and/or inorganic ions (Kong et al., 2010;Li et al., 2009;Li et al., 2012;Li et al., 2017). Therefore, the comprehensive study of various chemical components and $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ of $PM_{2.5}$ in Tianjin is highly needed in order to better understand their origins and even aging for some extent over the region.

Here, we present the characteristics and seasonality of carbonaceous and nitrogenous components, inorganic ions and $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in $PM_{2.5}$ collected over a one-year period at an urban and a suburban sites in Tianjin, North China. Based on the chemical compositions, $\delta^{15}N_{TN}$ and $\delta^{13}C_{TC}$ and their seasonal changes, we discuss the origins and possible aging of $PM_{2.5}$ over the Tianjin region.

2 Materials and methods

2.1 Aerosol sampling and measurement of its mass

$PM_{2.5}$ sampling was performed at an urban site: Nankai District (ND), located in the central part at 39.11°N, 117.18°E and a suburban (background) site: Haihe Education Park (HEP), located at 39.00°N, 117.32°E, 23 km away from the ND, in Tianjin, a coastal metropolis located on the lower reaches of Haihe river and Bohai sea in Beijing-Tianjin-Hebei urban economic circle in the northern part of the China mainland, with a population of ~16 million (https://wiki.hk.wjbk.site). The $PM_{2.5}$ sampling was conducted on the rooftop of a 7-storey teaching building of Tianjin University Weijin road campus in ND for about 72 h (3-consecutive days) each sample continuously from 5 July 2018 to 4 July 2019 using precombusted (450℃, 6h) quartz membrane (Pallflex 2500QAT-UP) and high-volume air sampler (Tisch Environmental, TE-6070DX) (n = 121). Simultaneously, the $PM_{2.5}$ sampling was conducted on the rooftop of a 6-storey teaching building of Tianjin University Peiyangyuan campus in HEP with the same sample frequency (72 h each) for 1 month period in each season: from 5 July-4 August in summer, 30 September-30 October in autumn 2018 and 1 January-1 February in winter and 2 April-2 May in spring 2019. Prior to analysis, the filter samples were placed in a precombusted glass jar with a Teflon-lined cap and stored in dark at −20°C. A blank filter sample was also collected in each season, following the same procedure without turning on the sampler pump and placing the filter in filter hood for 10 minutes.

Each filter was dehumidified in a desiccator for 48 hours before and after sampling and the mass concentration of $PM_{2.5}$ was determined by gravimetric analysis.

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2.2 Chemical analyses

2.2.1 Measurements of carbonaceous components

OC and EC were measured using OC/EC analyzer (USA, Sunset Laboratory Inc.), based on thermal light transmission following the IMPROVE protocol of the protective visual environment (Wan et al., 2017;Wan et al., 2015;Chow et al., 2007) and assuming the carbonate carbon was negligible (Pavuluri et al., 2011;Wang et al., 2019)· Briefly, an aliquot of filter (1.5 cm^2) of each sample was punched and placed in a quartz boat in the thermal desorption chamber of the analyzer, and then the carbon content of each sample was measured by a two-step heating procedure. The analytical principle of the instrument has been described in detail in the literature (Cao et al., 2007;Watson et al., 2005). During the experiment, sucrose solution with known carbon content (36.1 ± 1.8 μg C^{-1}) was used as standard reference for the measurement of OC and EC. The analytical errors in duplicate analyses were within 2% for OC and 5% for EC.

The total organic carbon (TOC) analyzer (model: OI, 1030W + 1088) was used to measure the content of water-soluble OC (WSOC). Total inorganic carbon (TIC, acidizing) and TOC (wet oxidation) can be measured simultaneously with the same sample by oxidizing the sample at 100℃ for analysis, ensuring the highest detection accuracy and reliability of the data. An aliquot of filter sample (one disc of 14 mm and 22 mm in diameter for # 1-65 and # 66-172 filters, respectively) were extracted into 20 ml and 30 ml organic-free Milli Q water, respectively, under ultrasonication for 20 minutes (Wang et al., 2019). The extracts were filtered through a 0.22 μm PTFE syringe filter, and then the content of WSOC was measured using TOC analyzer. The analytical uncertainty in measurements was generally less than 5%. The concentrations of OC, EC and WSOC were corrected for field blanks.

The sum of OC and EC was considered as TC, and the difference between OC and WSOC was considered as the water-insoluble OC (WIOC) (Wang et al., 2018).

Due to a lack of analytical methods to directly measure secondary OC (SOC) (Turpin and Huntzicker, 1995), the SOC was estimated using the OC/EC tracer-based method proposed by Turpin et al. (Ji et al., 2014). The formula for its calculation is as follows:

$$SOC = OC - EC \times (OC/EC)_{pri}$$

where $(OC/EC)_{pri}$ is the mass concentration ratio between OC and EC generated by primary emission, which is generally the minimum value among the measured OC/EC. Because the OC/EC is highly influenced by meteorological conditions, emission sources and other factors, and thus the estimation of SOC using the minimum value results a large deviation, we used the average value of three minimum values in the OC/EC ratios as the $(OC/EC)_{pri}$, which was 6.71 at ND and 4.62 at HEP.

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2.2.2 Measurements of inorganic ions

Inorganic ions were measured using ion chromatography (ICS-5000 System, China, Dai An). An aliquot of filter sample (one disc with 22 mm in diameter) was extracted into 30 ml Milli Q water under ultrasonication for 30 min and filtered with a PTFE syringe filter (0.22 μm) and then injected into an ion chromatography. A mixture of $NaHCO_3$ and Na_2CO_3 and NaOH (50% NaOH solution) eluent and IonPac AG11-HC/AS11-HC column and 30 mM KOH suppresser with a flow rate of 1.2 ml min^{-1} were used for anion measurement. For cationic measurement, methyl sulfonic acid and IonPac CS12A and CG12A column at a flow rate of 1.0 ml min^{-1} with 20 mM mesylate suppressor were used. The analytical error in duplicate analyses was generally less than 5%. Concentrations of all the ions were corrected for field blanks.

2.2.3 Determination of nitrogenous components

Water-soluble total nitrogen (WSTN) was determined using a continuous flow analyzer (CFA, Skalar, the Netherlands, San++), following the standard procedure. Briefly, an aliquot of filter (3.80 cm^2) sample extracted into 10 ml Milli Q water under ultrasonication for 10 min each for three times and then the extracts were filtered through 0.22 μm size Teflon syringe filters to remove filter debris. The filter extracts mixed with excess potassium persulfate and then digested in the UV digester to convert all N to nitrate and passed through a reduction column equipped with granular copper and cadmium column to reduce nitrate to nitrite. The produced nitrite is reacted with aminobenzene sulfonic acid to result in high molecular weight nitrogen compounds (azo dye) and then the absorbance of total N was measured at 540 nm. The average analysis error of the repeated analysis was 167.1%. Such a large analytical error can be attributed to the slightly lower instrument reproducibility and the uneven distribution of particles in the sampling filter. with the detection limit of 0.01−5mg L^{-1}.

The N contents of NO_2^-, NO_3^- and NH_4^+ were calculated from their concentrations. The sum of those contents was considered as total inorganic nitrogen (IN). The difference between the concentrations of WSTN and IN were considered as WSON (Matsumoto et al., 2018):

$$\text{WSON} = \text{WSTN} - \text{IN}$$

However, it should be noted that the analytical uncertainties associated with the measurements of WSTN and NO_2^-, NO_3^- and NH_4^+ must result huge error in the estimation of WSON. The propagating error in WSON estimation from duplicate analysis of the samples for NO_3^-, NH_4^+ and WSTN with an uncertainty of 0.78%, 1.82% and 16.1%, respectively, was 0.83. However, we consider such errors do not influence the conclusions drawn from this study.

2.2.4 Determination of stable carbon and nitrogen isotope ratios of TC ($\delta^{13}C_{TC}$) and TN ($\delta^{15}N_{TN}$)

$\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ were determined using an elemental analyzer (EA, Flash 2000HT) coupled with stable isotope ratio mass

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spectrometer (IrMS, 253 Plus). Briefly, an aliquot of filter subjected for acid steaming by placing it in a dry dish containing concentrated HNO_3 for 12 h to remove any inorganic carbon ($CaCO_3$) content, which affect the result of the $\delta^{13}C_{TC}$, and then dried out in the oven for 24 h and packed in a tin cup, was introduced into EA. The derived gases: CO_2 and N_2, were transferred into IrMS through ConFlo-II to measure the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ in TC and TN, respectively.

The isotope ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ are expressed as delta (δ) values ($\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$, respectively) after the normalization with those of the reference standards in parts per million (Duarte et al., 2019). The $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ were calculated using the following formula, respectively (Fu et al., 2012;Pavuluri et al., 2010):

$$\delta^{13}C_{TC} = [(^{13}C\ /\ ^{12}C)_{sample}/(^{13}C\ /\ ^{12}C)_{standard} - 1] \times 1000.$$

$$\delta^{15}N_{TN} = [(^{15}N\ /\ ^{14}N)_{sample}/(^{15}N\ /\ ^{14}N)_{standard} - 1] \times 1000.$$

3 Results and discussion

3.1 Meteorology and backward air mass trajectories

The meteorology data at Tianjin was collected from mobile weather station (Gill MetPak, UK) installed at the sampling site during the campaign. Temporal variations in the averages of the data for each sample period are depicted in Fig. 1. The ambient temperature, relative humidity (RH) and wind speed showed a clear seasonal pattern (Fig. 1). On average, the temperature was higher (27.3℃) in summer and lower (1.28℃) in winter. The annual average of RH was 39.2%. It was relatively higher in summer and autumn than that in winter and spring. The average wind speed in autumn (2.03 m s^{-1}) was almost similar to that in spring (2.06 m s^{-1}), but lower in summer (1.64 m s^{-1}) and winter (1.58 m s^{-1}).

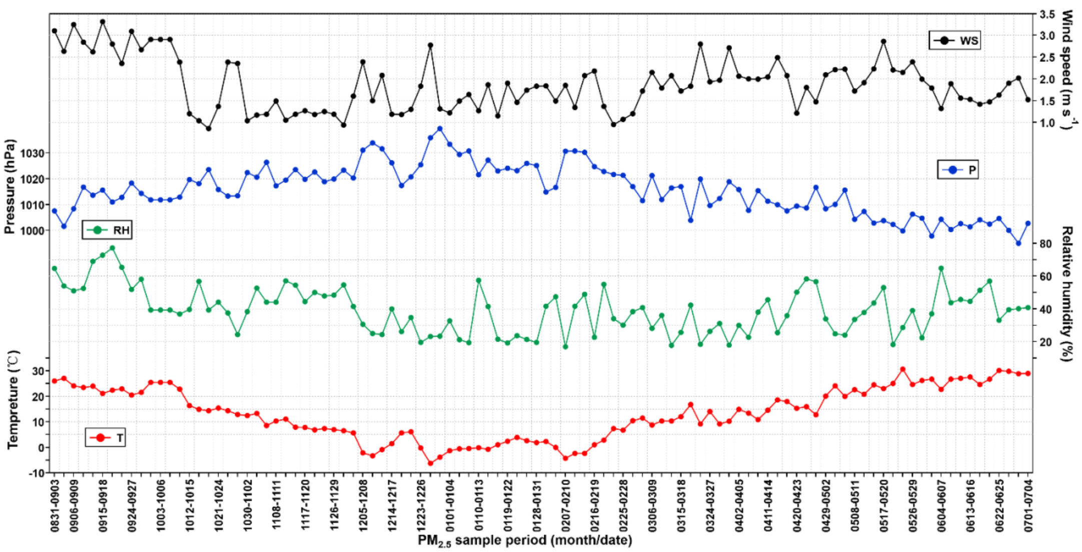

Figure 1. Temporal variations of ambient temperature (T), atmospheric pressure (P), wind speed (WS) and relative humidity

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(RH) at Tianjin from September 2018 to July 2019.

5-Day backward air mass trajectory clustering analysis was conducted using the NOAA HYLSPLIT modeling system (https://www.ready.noaa.gov/HYSPLIT.php) for every month to identify the source regions of the air parcels arrived over Tianjin at 500 m above the ground level during the campaign, and their plots are depicted in Fig. 2. The trajectories showed that most of the air masses arrived in Tianjin were originated from the ocean region in summer (Fig. 2). In particular, 50% of the air masses were originated from the East Sea in July 2018, while a small portion of the air masses were originated from northeast China and Siberia. Whereas in autumn, winter and spring, they were mostly originated from Siberia and Mongolia as well as from inland China (Fig. 2). It is noteworthy that 33% and 28% of the air masses arrived in Tianjin during September and October, respectively, were originated from northern parts of China. Therefore, the chemical composition and characteristics of $PM_{2.5}$ in Tianjin should have been significantly influenced by the long-range transported air masses and varied according to seasonal changes, in addition to the local emissions.

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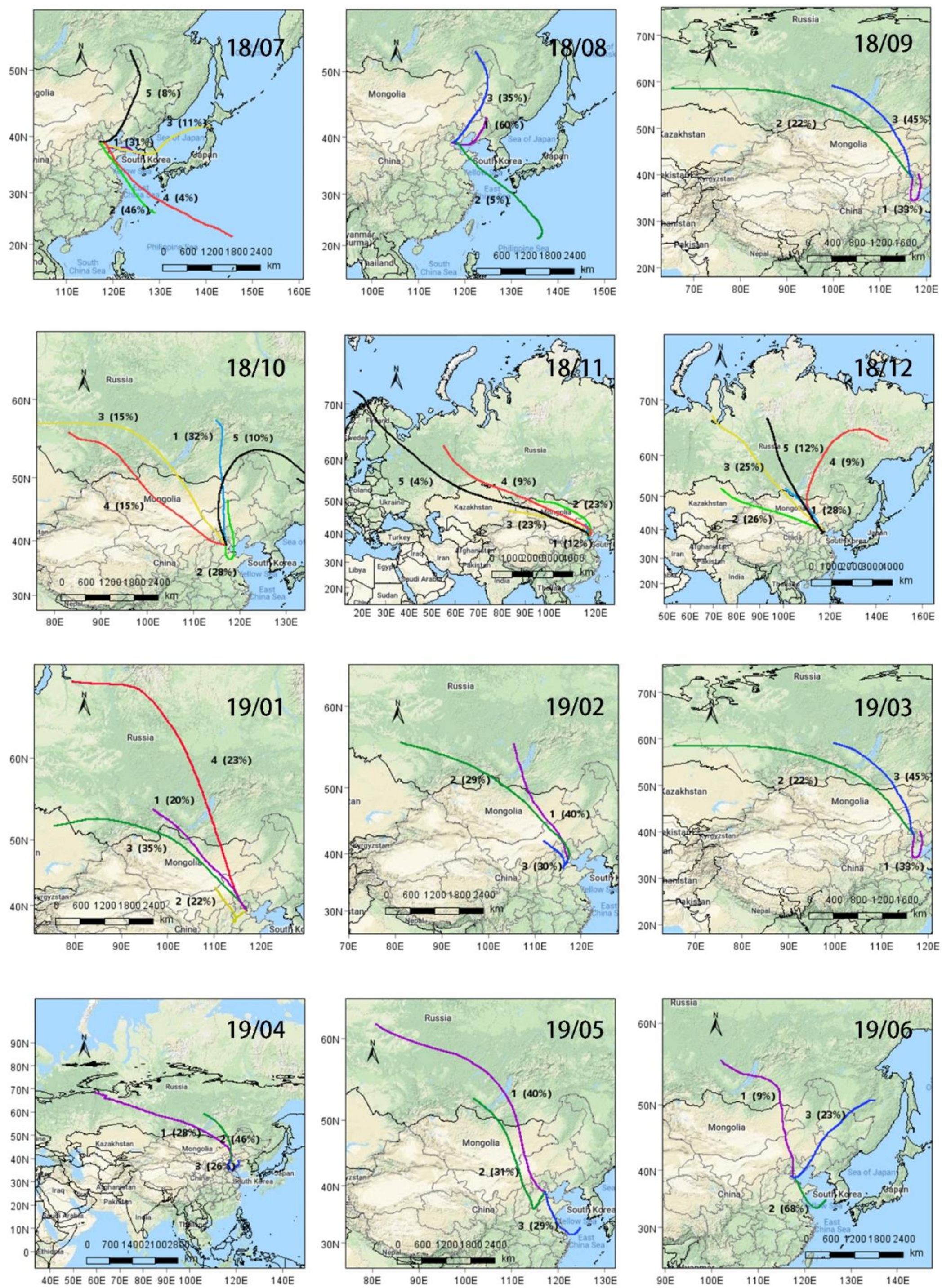

Figure 2. Monthly cluster analysis plots of 5-day backward air mass trajectories arriving over Tianjin at 500 m above the ground level during the campaign period. (The maps were generated by the MeteoInfo software using the © Google Maps)

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3.2 Characteristics of $PM_{2.5}$

Concentrations of $PM_{2.5}$ and its carbonaceous components: EC, OC, SOC, WSOC, WIOC and TC, nitrogenous components: WSTN, IN and WSON, and inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}), as well as $\delta^{13}C_{TC}$ and $\delta^{15}C_{TN}$ in each season and during the whole campaign (annual) at ND and HEP in Tianjin, North China are summarized in Table 1. Temporal variations in $PM_{2.5}$ mass and its carbonaceous and nitrogenous components and $\delta^{13}C_{TC}$ and $\delta^{15}C_{TN}$ are depicted in Fig. 3, and those of inorganic ions are showed in Fig. 4.

Averages of $PM_{2.5}$ in spring, summer, autumn and winter at ND were 28.4 ± 14.5 μg m^{-3}, 13.9 ± 6.24 μg m^{-3}, 39.4 ± 33.0 μg m^{-3}, and 55.1 ± 34.9 μg m^{-3}, respectively, and 34.9 ± 29.8 μg m^{-3} during the whole campaign period. While at HEP, they were 49.8 ± 17.8 μg m^{-3}, 20.3 ± 9.73 μg m^{-3}, 41.6 ± 21.7 μg m^{-3} and 62.2 ± 23.2 μg m^{-3} and 43.5 ± 23.8 μg m^{-3}, respectively. On average, the concentrations of $PM_{2.5}$ at ND and HEP in winter were 4 and 3 times, respectively, higher than that in summer (Table 1). According to China ambient air quality standard (GB3095-2012), the average $PM_{2.5}$ concentration limit in the ambient environment is 75 μg m^{-3} for 24 h and 35 μg m^{-3} for annum. Although the annual average concentration of $PM_{2.5}$ in Tianjin did not exceed the national $PM_{2.5}$ limit, it is about 3 times higher to that of the global limit (10 μg m^{-3}) stipulated by world health organization. Furthermore, the average concentration of $PM_{2.5}$ found to be higher in spring than in autumn (Table 1), probably due to enhanced eruption of dust from open lands, due to gradual increase in wind speed in spring (Fig. 1).

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Table 1. Summary of concentrations of carbonaceous (EC, OC, SOC, WSOC, WIOC and TC), nitrogenous (WSTN, IN and WSON) and inorganic ionic (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) components and stable carbon and nitrogen isotope ratios of total carbon ($\delta^{13}C_{TC}$) and nitrogen ($\delta^{15}C_{TN}$) in fine aerosols together with the $PM_{2.5}$ mass at an urban (ND) and a suburban (HEP) sites in Tianjin, North China during 5 July 2018 and 5 July 2019.

Components	Annual		Summer		Autumn		Winter		Spring	
	Range/Med	Ave±SD	Range/Med	Ave±SD	Range/Med	Ave±SD	Range/Med	Ave±SD	Range/Med	Ave±SD
	ND (n=121) HEP (n=40)		ND (n=30, Jun-Aug) HEP (n=10, Jul)		ND (n=30, Sep-Nov) HEP (n=10, Oct)		ND (n=30, Dec-Feb) HEP (n=10, Jan)		ND (n=31, Mar-May) HEP (n=10, Apr)	
					Carbonaceous components					
EC	0.10–0.56/0.26	0.27±0.11	0.11–0.31/0.18	0.18±0.05	0.21–0.54/0.33	0.36±0.10	0.10–0.56/0.28	0.30±0.10	0.10–0.34/0.25	0.24±0.07
	0.09–0.81/0.40	0.40±0.18	0.09–0.59/0.27	0.28±0.16	0.41–0.81/0.61	0.59±0.13	0.15–0.53/0.39	0.37±0.10	0.18–-0.62/0.32	0.36±0.15
OC	1.37–24.7/3.40	4.93±3.79	1.37–3.26/2.31	2.31±0.52	1.48–12.8/4.44	5.00±2.65	2.49–24.7/7.97	8.79±4.85	1.52–6.58/3.38	3.36±1.12
	0.85–14.7/4.40	5.61±3.55	0.85–4.34/2.25	2.44±1.20	3.01–9.86/4.62	5.28±2.07	7.18–14.7/9.51	10.4±2.98	2.46–5.68/4.39	4.30±1.11
WSOC	0.69–16.0/2.56	3.25±2.18	1.14–3.12/1.74	1.88±0.53	1.16–7.68/3.13	3.45±1.74	1.37–16.0/4.19	5.06±2.99	0.69–4.03/2.44	2.48±0.82
	0.66–9.44/3.52	3.47±2.04	0.66–3.73/1.81	2.16±1.17	1.48–6.11/2.93	3.08±1.41	4.00–9.44/5.50	4.00–9.44	0.95–4.38/2.44	2.70±1.18
WIOC	0.00–8.93/1.01	1.68±1.77	0.00–1.33/0.38	0.43±0.32	0.21–5.07/1.37	1.55±1.04	0.00–8.93/3.33	3.74±2.09	0.23–2.62/0.73	0.88±0.63
	0.00–7.39/1.77	2.14±1.75	0.00–0.67/0.22	0.29±0.21	0.61–3.75/2.26	2.20±0.86	3.02–7.39/3.93	4.48±1.45	0.51–3.15/1.43	1.60±0.70
SOC	0.00–20.9/1.65	3.11±3.43	0.24–1.75/1.13	1.08±0.37	0.00–10.7/2.24	2.59±2.58	1.58–20.9/5.92	6.78±4.35	0.83–4.88/1.51	1.73±0.87
	0.00–12.8/2.86	3.75±3.48	0.00–2.97/0.71	1.18±1.01	0.05–6.73/2.56	2.56±2.15	5.46–12.8/8.48	8.68±2.90	1.04–4.18/2.67	2.63±1.08
WSOC/OC	0.30–1.05/0.72	0.71±0.15	0.54–1.05/0.80	0.82±0.12	0.43–0.92/0.70	0.70±0.10	0.41–1.05/0.57	0.57±0.11	0.30–0.93/0.79	0.75±0.14
	0.30–1.04/0.61	0.66±0.17	0.77–1.04/0.84	0.87±0.09	0.47–0.85/0.57	0.58±0.11	0.46–0.67/0.58	0.57±0.07	0.30–0.82/0.62	0.61±0.17
OC/EC	6.56–48.1/14.4	17.8±9.46	7.64–16.2/13.3	13.1±2.18	6.56–41.7/12.5	14.5±8.39	16.1–48.1/28.1	29.2±9.73	9.37–25.9/13.3	14.1±3.18
	4.01–63.0/12.4	15.7±11.5	4.01–14.9/10.1	9.67±3.62	4.67–14.5/10.3	9.31±3.70	16.1–63.0/29.5	30.4±13.1	6.28–19.7/13.2	13.2±4.70
SOC/OC	0.00–0.86/0.53	0.53±0.20	0.12–0.58/0.49	0.47±0.11	0.00–0.84/0.46	0.41±0.26	0.58–0.86/0.76	0.74±0.08	0.28–0.74/0.49	0.50±0.09
	0.00–0.93/0.63	0.57±0.25	0.00–0.69/0.54	0.46±0.22	0.01–0.68/0.55	0.41±0.26	0.71–0.93/0.84	0.82±0.07	0.27–0.77/0.65	0.60±0.16
					Nitrogenous components					
WSTN	0.32–26.3/3.15	5.45 ± 5.50	0.56–4.57/1.73	1.77±0.86	0.32–24.9/5.47	6.63±6.06	1.52–26.3/5.84	8.51±6.40	0.73–16.1/3.33	4.80±4.03
	1.34–18.4/6.25	7.34 ± 5.13	1.37–6.61/3.93	3.64±1.57	1.57–18.2/5.92	7.23±5.90	4.68–18.4/7.94	9.68±4.20	1.34–17.5/8.57	8.80±5.67
IN	0.00–26.5/3.35	5.21 ± 5.01	0.00–5.67/1.79	1.82±0.96	0.19–21.3/5.32	6.10±5.38	1.86–26.5/5.82	8.23±5.91	1.00–16.0/3.50	4.68±3.55
	1.39–14.8/5.40	6.14 ± 3.90	1.40–5.43/3.54	3.32±1.17	1.39–14.5/6.43	6.45±4.61	4.24–14.2/6.81	7.98±3.08	1.61–14.8/5.97	6.82±4.32
WSON	0.00–3.51/0.72	0.40 ± 0.69	0.00–0.39/0.03	0.07±0.09	0.00–3.51/0.31	0.63±0.83	0.00–2.32/0.01	0.40±0.65	0.00–3.14/0.17	0.50±0.77
	0.00–9.80/0.77	1.29 ± 1.47	0.00–1.18/0.43	0.47±0.36	0.00–3.65/0.10	1.01±1.46	0.44–4.18/1.18	1.70±1.30	0.00–6.03/1.57	2.01±1.90
WSON/WE	0.00–0.40/0.07	0.07 ± 0.08	0.00–0.17/0.02	0.05±0.06	0.00–0.40/0.10	0.12±0.10	0.00–0.17/0.00	0.03 ± 0.04	0.00–0.31/0.06	0.07±0.08
TN	0.00–0.48/0.16	0.14 ± 0.10	0.00–0.18/0.12	0.11±0.07	0.00–0.22/0.05	0.09±0.10	0.09–0.31/0.14	0.16 ± 0.06	0.00–0.48/0.16	0.19±0.12
					Inorganic ions					
Cl^-	0.01–9.22/0.68	1.44±1.80	0.02–0.13/0.06	0.07±0.03	0.01–4.97/1.36	1.46±1.45	0.64–9.22/3.30	3.49±1.94	0.07–2.22/0.57	0.64±0.55
	0.04–6.83/1.25	1.87±1.91	0.04–0.37/0.08	0.14±0.12	0.11–4.05/1.84	1.90±1.07	2.70–6.83/4.08	4.56±1.34	0.20–2.29/0.80	0.87±0.62

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SO_4^{2-}	0.50–21.6/3.73	4.56±3.32	1.79–8.81/4.43	4.42±1.73	0.50–12.8/4.58	4.39±2.91	1.21–21.6/3.26	5.62±5.05	0.99–9.15/3.13	3.55±2.00
	1.00–15.0/5.44	5.93±3.78	3.09–15.0/9.18	9.21±4.63	1.00–8.57/5.44	4.30±2.68	2.29–12.0/3.79	4.93±3.00	2.00–10.9/5.03	5.28±2.77
NO_3^-	0.08–37.7/4.69	7.38±8.16	0.08–8.85/0.33	0.91±1.65	0.13–31.8/8.11	9.90±9.41	2.26–37.7/8.38	11.1±8.29	0.74–21.0/4.91	6.90±5.85
	0.18–27.6/6.35	8.59±7.57	0.18–5.59/1.21	2.06±1.98	1.35–27.6/11.0	11.4±9.63	4.68–18.6/9.82	10.7±4.66	1.91–24.5/7.55	10.2±8.14
Na^+	0.00–0.80/0.11	0.15±0.14	0.00–0.27/0.06	0.09±0.06	0.01–0.38/0.20	0.19±0.11	0.00–0.80/0.22	0.27±0.20	0.00–0.24/0.07	0.08±0.07
	0.01–0.37/0.15	0.16±0.09	0.11–0.22/0.14	0.16±0.04	0.15–0.33/0.23	0.23±0.06	0.02–0.37/0.12	0.15±0.11	0.01–0.25/0.10	0.11±0.08
NH_4^+	0.19–23.2/3.01	4.59±4.12	0.62–4.72/2.17	2.08±0.90	0.19–18.2/4.48	4.97±4.35	1.73–23.2/5.26	6.92±5.05	0.97–14.5/3.10	4.01±2.92
	1.06–13.1/5.02	5.40±3.08	1.42–5.35/3.93	3.67±1.43	1.06–10.6/5.07	4.99±3.46	4.09–13.1/5.93	7.16±2.88	1.52–11.9/5.48	5.79±3.41
K^+	0.03–3.83/0.29	0.48±0.53	0.06–0.23/0.12	0.13±0.05	0.03–1.17/0.45	0.49±0.36	0.16–3.83/0.67	0.96±0.77	0.07–0.56/0.27	0.29±0.14
	0.09–1.27/0.39	0.49±0.31	0.09–0.33/0.24	0.21±0.09	0.24–1.05/0.54	0.55±0.28	0.56–1.27/0.79	0.84±0.24	0.15–0.68/0.32	0.38±0.19
Mg^{2+}	0.00–0.36/0.03	0.03±0.04	0.00–0.06/0.00	0.00±0.01	0.00–0.06/0.00	0.01±0.02	0.02–0.36/0.04	0.06±0.07	0.00–0.06/0.03	0.03±0.02
	0.00–0.15/0.03	0.03±0.04	0.00–0.03/0.03	0.00±0.01	0.00–0.00/0.00	0.00±0.00	0.04–0.15/0.06	0.07±0.03	0.00–0.11/0.03	0.04±0.04
Ca^{2+}	0.00–0.81/0.13	0.11±0.12	0.00–0.30/0.00	0.02±0.06	0.00–0.32/0.01	0.07±0.08	0.05–0.81/0.15	0.20±0.14	0.02–0.47/0.11	0.14±0.11
	0.00–1.08/0.17	0.22±0.23	0.00–0.41/0.05	0.08±0.12	0.04–0.21/0.10	0.11±0.05	0.14–1.08/0.30	0.37±0.26	0.01–0.85/0.29	0.34±0.25
					Isotope ratios					
$\delta^{13}C_{TC}$	-26.5–(-)21.9/-25.2	-25.0±0.70	-26.0–(-)25.1/-25.6	-25.6±0.26	-25.7–(-)21.9/-24.9	-24.7±0.81	-25.9–(-)23.7/-24.5	-24.5±0.48	-26.5–(-)24.4/-25.4	-25.4±0.53
	-25.5–(-)22.8/-24.5	-24.5±0.55	-25.1–(-)24.1/-24.8	-24.7±0.30	-24.5–(-)22.8/-24.0	-23.9±0.60	-25.1–(-)24.1/-24.5	-24.5±0.29	-25.5–(-)24.3/-24.9	-24.9±0.34
$\delta^{15}N_{TN}$	1.01–22.8/10.2	11.4±4.83	13.2–22.8/17.4	17.6±2.52	2.93–20.2/9.90	10.4±4.52	1.01–11.8/8.86	8.21±2.49	5.06–16.1/9.79	9.82±2.72
	4.91–18.6/9.75	10.4±3.43	6.86–18.6/14.8	14.5±3.46	5.61–12.6/9.49	8.78±2.27	4.91–11.9/8.66	8.41±2.12	7.01–12.2/10.0	9.94±1.66
					Aerosol mass					
$PM_{2.5}$	3.38–170/23.6	34.9±29.8	3.38–30.4/13.6	13.9±6.24	5.02–134/33.9	39.4±33.0	14.1–170/42.4	55.1±34.9	9.15–67.5/23.6	28.4±14.5
	7.56–103/38.9	43.5±23.8	7.56–36.6/20.7	20.3±9.73	19.3–80.1/38.3	41.6±21.7	38.9–103/54.2	62.2±23.2	29.2–78.5/48.6	49.8±17.8

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However, the average $PM_{2.5}$ concentration found in this study is significantly lower than that (109.8 μg m^{-3}) reported ten years before in Tianjin (Li et al., 2009). Further it is also lower than that reported in Harbin, northeast China, but similar to that recorded in the southeastern coastal cities in China: Ningbo and Guangzhou (Table 2). Such relatively lower concentration of $PM_{2.5}$ observed in this study compared to that reported from previous studies is likely, because the control measures on air pollutant emissions were implementing in northern China since 2013, and the replacement of coal with natural gas and electricity is strictly implemented starting from 2017 (http://huanbao.bjx.com.cn/news/20170901/847140.shtml). It has been reported that the average concentration of $PM_{2.5}$ has been decreased from 2011 to 2017 in the southwestern city of Chengdu, consistent with the variations trend of $PM_{2.5}$ concentration in most cities in north China (Table 2), which indicate that the government measures on prevention and control of air pollution are fruitful in China. But still the $PM_{2.5}$ loading in the atmosphere over most Chinese cities including Tianjin is much higher than that reported in American cities (Table 2). Such comparisons indicate that the aerosol loading is significantly high in the Tianjin atmosphere and needs to further enforce the control and prevention measures on pollutant emissions from various sources to improve the air quality further in this region.

Table 2. $PM_{2.5}$ mass concentrations in Tianjin and those reported at different other locale in China and over the world.

City/nation	Sampling period	$PM_{2.5}$ (μg m^{-3})	Reference
Tianjin, north China (urban site)	2018-2019	34.9±29.7	This study
Tianjin, north China (suburban petrochemical industrial site)	2018-2019	43.47±23.5	This study
Zibo, north China	2006-2007	164.61 ± 79.14	Luo et al., 2018
Beijing, north China	2009-2010	135.0	Zhang et al.,2013
Beijing, north China	2013	84	Xu et al., 2020
Beijing, north China	2018	50	Xu et al., 2020
Tianjin, north China	2008	109.8	Gu et al.,2010
Harbin, northeast China	2017	59.39 ± 46.9	Chen et al., 2019
Chengdu, southeast China	2017	56.3±28.1	Huang et al., 2018
Chengdu, southeast China	2014-2015	67.0±43.4	Wang et al., 2018
Chengdu, southeast China	2011	119 ± 56	Tao et al., 2014
Ningbo, southeast coastal China	2012-2013	42.4	M. Li et al., 2017
Nanjing, southeast coastal China	2013-2014	129	Li et al., 2016
Guangzhou, south China	2012-2013	44.2	Lai et al., 2016
Shanghai, southeast coastal China	2011-2012	68.4	Zhao et al., 2015
Los Angeles, USA	2005-2006	19.88	Hasheminassab et al., 2014
Atlanta-Yorkville, USA	2001-2005	14.3	Chen et al., 2012

3.3 Carbonaceous components

Concentrations of EC and OC were 0.10−0.56 μg m^{-3} with an average of 0.27 and 1.34−24.7 μg m^{-3} (ave. 4.93 μg m^{-3}), respectively, at ND (n = 121) during the campaign (Table 1). They were 0.09−0.81 μg m^{-3} (0.40 μg m^{-3}) and 0.85−14.7 μg m^{-3} (5.61 μg m^{-3}), respectively, at HEP (n = 40) (Table 1). While WSOC was 0.69−16.0 μg m^{-3} (3.25 μg m^{-3}) at ND and 0.66−9.44 μg m^{-3} (3.47 μg m^{-3}) at HEP. On average, the OC accounted for 17.3% and 13.3% in $PM_{2.5}$ mass at ND and HEP, respectively, in Tianjin. The relative abundance of WSOC in OC was found to be 71.1 ± 14.5% at ND and 65.6 ± 16.8% at HEP. Average concentration of SOC was 3.11 ± 3.42 μg m^{-3} at ND and 3.76 ± 3.44 μg m^{-3} at HEP, accounting for 53.3% and 57.5%, respectively, in OC.

OC, WSOC and SOC showed clear seasonal changes during the campaign (Fig. 3). Normally, $PM_{2.5}$ levels are controlled by emissions, transport, chemical transformation and deposition processes, all of which are influenced by meteorological

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conditions. Temporal trend of $PM_{2.5}$ found to be similar to that of RH and opposite to that of wind speed (Fig. 1). At ND, the average concentrations of $PM_{2.5}$, OC and WSOC were higher in winter than in autumn followed by spring and summer. On average, OC was four times higher in winter than that in summer at both ND and HEP. However, the average concentration of EC in winter was only about 1.7 and 1.3 times compared to that in summer at ND and HEP, respectively. The higher loading of OC compared to that of EC in winter indicates that the OC emission from coal/biomass combustion should be higher rather than EC in winter. In addition, the secondary formation of OC might be significant *via* adsorption and/or NO_3 radical driven oxidation reactions of VOCs. On the other hand, the frequent precipitation events might result the enhanced wet deposition of pollutants including EC in summer. Interestingly, the average concentration of SOC in winter (6.78 µg m^{-3}, ND; 8.68 µg m^{-3}, HEP) found to be 6 times higher than that in summer (1.08 µg m^{-3}, ND; 1.18 µg m^{-3}, HEP), which indicate that the formation of SOC was highly significant in the Tianjin atmosphere during winter. The average WSOC was 0.69-16.0 and 0.66-9.44 µg m^{-3} at ND and HEP, respectively. Such higher level of WSOC at ND compared to that at HEP, indicates its enhanced emission (potentially from biomass burning) and/or secondary formation under high abundance of oxidants at the ND than that at the HEP.

3.3.1 Linear relations and mass ratios of selected components: implications for sources

Generally, EC does not react at ambient temperature and remains relatively stable in the atmosphere, and hence, it is often used as a tracer for primary pollutants. Therefore, the scatter plots between EC and OC and their mass ratios can provide insights in tracing the origins of atmospheric aerosols and the extent of secondary formation in the atmosphere. As shown in Fig. 5, OC showed a moderate correlation with EC in $PM_{2.5}$ at ND in spring ($R^2 = 0.45$), summer ($R^2 = 0.50$) and winter ($R^2 = 0.54$), whereas weak ($R^2 = 0.05$) in autumn. Such linear relations suggest that both OC and EC might have been derived from similar sources in spring, summer and winter at ND, whereas their sources might be different in autumn. The slope value fond to be higher in winter, which indicates that the contribution of OC from primary sources was high in winter than in other seasons. However, at HEP, the correlation between OC and EC in $PM_{2.5}$ in spring, summer, autumn as well as in winter was very poor (Fig 5b), which imply that the sources of OC and EC were significantly different at HEP. Such differences between ND and HEP suggest that possible emission of biogenic VOCs from rich vegetation including agricultural plants and/or biomass burning might be high at HEP and surrounding areas, and those VOCs must be subjected for *in-situ* photochemical oxidation, resulting high loading of OC compared to that of EC.

Generally, OC/EC ratio in the atmosphere is used to identify the emission and transformation characteristics of carbon particles. Chow et al. reported that when the OC/EC is higher than 2.0, it could be considered that the secondary formation of OC in the atmosphere is significant. On the other hand, the OC/EC varies significantly depending on their relative contributions from the emissions of coal combustion (range, 8.1−12.7), vehicle exhaust (0.7−2.4), biomass burning (4.1−14.5), wood combustion (16.8−40,0) and cooking (32.9−81.6) (Watson et al., 2001). The OC/EC 6.56−48.1 and 4.01−63.0 at ND and HEP, respectively, which are close to those reported for the particles emitted from biomass burning, coal combustion, and wood combustion, but not those from diesel and gasoline-driven vehicle exhaust.

Average OC/EC was 17.8 at ND and 15.7 at HEP, which are several times higher than 2.0, indicating the significant secondary formation of OA over the Tianjin region. It has been reported that the ambient OC/EC in aerosols was gradually increasing over a period from 2000 to 2010 in China, confirming the increase of OC that should have been producing by enhanced oxidation in the atmosphere rather than that from primary emissions (Cui et al., 2015). The high OC/EC ratios in the atmosphere of Tianjin once again demonstrated the enhanced emission and/or secondary formation of OC in China. On the other hand, the OC/EC ratio in winter is significantly higher than that in other seasons, especially at HEP, despite the fact that it is a suburban area (Fig. 4). Therefore, the increase of OC/EC in winter can be attributed to the increase in coal consumption for domestic heating, and stagnant weather conditions.

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WSOC is mainly generated by oxidation reactions of VOCs in the atmosphere, in addition to primary emissions from biomass burning and fossil fuel combustion. The mass fraction of WSOC in OC can be regarded as an indicator of aging of aerosols in the atmosphere, when the contribution of WSOC is insignificant from biomass burning (Aggarwal and Kawamura, 2009). Interestingly, WSOC/OC in Tianjin aerosols found to be higher in spring and summer than in winter and autumn at both the sites (Fig. 4). Such high abundance of WSOC indicates the enhanced secondary formation of OC in spring and summer than in autumn and winter, because the biomass/biofuel combustion is significantly lower in spring/summer than that in autumn/winter. It is likely because the emission of VOCs from terrestrial plants including croplands is higher in spring that would be transformed to particulate OC upon subsequent secondary processes in gas and/or aqueous phases. While in summer, being a coastal city, Tianjin receives the marine air masses that are enriched with marine biological emissions due to the occurrence of sea breeze during daytime, which are subjected for subsequent photochemical oxidation in the atmosphere. In addition, the air masses arrived in Tianjin during summer were originated from the Oceanic region (Fig. 2) that were also enriched with marine biological emissions and aged during the long-range atmospheric transport. On the other hand, the range and average WSOC/OC in Tianjin aerosols at ND and HEP (Table 1) are similar to those reported at urban locations: Nanjing, China (0.40−0.51) (Yang et al., 2005) and Chennai, India (0.23−0.61) (Pavuluri et al., 2011) and in largely rural areas of Hungary (range 0.38−0.72, average 0.66) (Kiss et al., 2002), where biomass burning was considered to be the main source of the atmospheric aerosols. In fact, WSOC and OC showed a very good linear relationship at both the sites, which indicate that the contribution of OA from biomass burning emissions were also significant, in addition to the secondary formation and/or transformations in the Tianjin region.

Interestingly, SOC/OC ratios found to be higher in winter followed by spring, summer and autumn (Table 1). The higher loading of SOC in winter might have been occurred due to enhanced absorption/adsorption of VOCs to existing particles. In addition, despite lower temperatures prevailing over the Tianjin region, the secondary formation of OA might be intensive in winter by NO_3 radical reactions. It has been reported that the haze formation in China is mainly driven by the enhanced secondary formation of aerosols by NO_3 radical reactions (Wang et al., 2016a). It is worthy to note that the loading of NO_3^- ion reported to be several times abundant in winter than in summer in Tianjin aerosols (Table 1). Therefore, the oxidation reaction of VOCs by NO_3 radical should have been enhanced and promoted the formation of SOA including organic nitrates, which may not be fully soluble. In fact, the average concentration of WSOC was higher than that of SOC in spring, summer and autumn but the opposite in winter (Table 1). Such differences indicate that the SOC produced in spring, summer and autumn might be mostly water-soluble, whereas in winter, part of the SOC is water-insoluble. In addition, WSOC might have been substantially derived from primary sources (e.g., biomass burning) in spring, summer and autumn than in winter. In fact, WIOC account for 41.8% and 43.2% of OC in winter at ND and HEP, respectively, suggesting that part of SOC (e.g., N-containing organics) might be water-insoluble. However, the temporal trends of WIOC, SOC, and WSOC were similar, which indicate that they should have been originated from the same/similar sources and their formation processes might be similar in each season over the Tianjin region.

Furthermore, SOC showed a strong correlation with WIOC at both ND and HEP ($R^2 = 0.86$ and 0.67, respectively), and their slope values were significantly higher in winter, but not in summer ($R^2 = 0.05$ and 0.00, respectively; Fig. 5). Such differences clearly imply that the secondary formation and/or transformation processes were quite different in winter from that in summer, and most of the SOC generated in winter was water-insoluble. Simulations, field observations, and laboratory studies have shown that the secondary formation of OA in the atmosphere over China is enhanced in winter, and only the aqueous-phase secondary formation has been considered as the prominent pathway (Huang et al., 2014;Wang et al., 2016a). Therefore, the enhanced formation of SOC in Tianjin aerosols, including WIOC, warrants the need of further investigation of the possible formation processes of the WIOC, a subject of further research.

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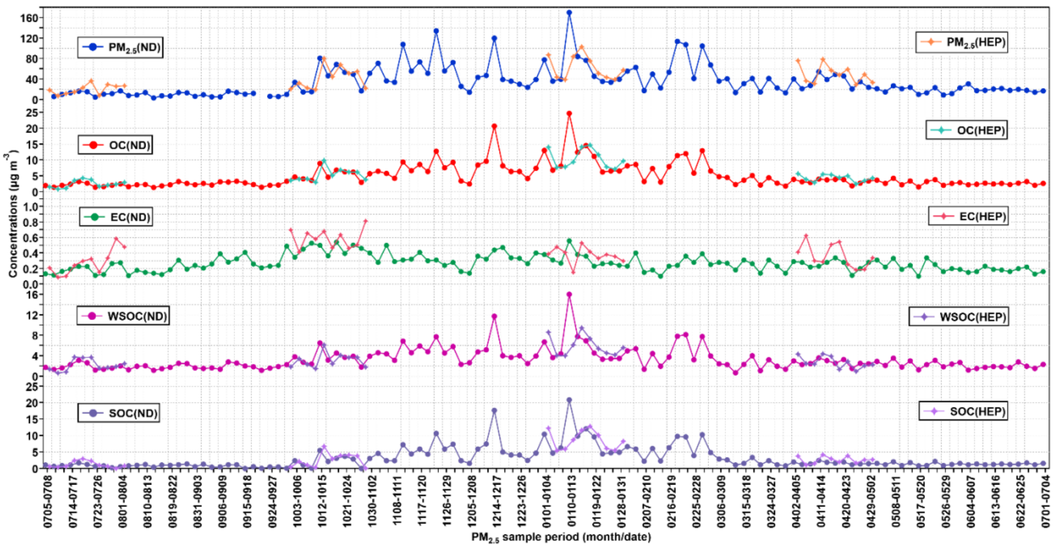

Figure 3. Temporal variations in concentration (μg m^{-3}) of $PM_{2.5}$ and its chemical components: OC, EC, WSOC and SOC, at ND (solid dots) and HEP (solid star shape) in Tianjin during 2018-2019. See text for abbreviations.

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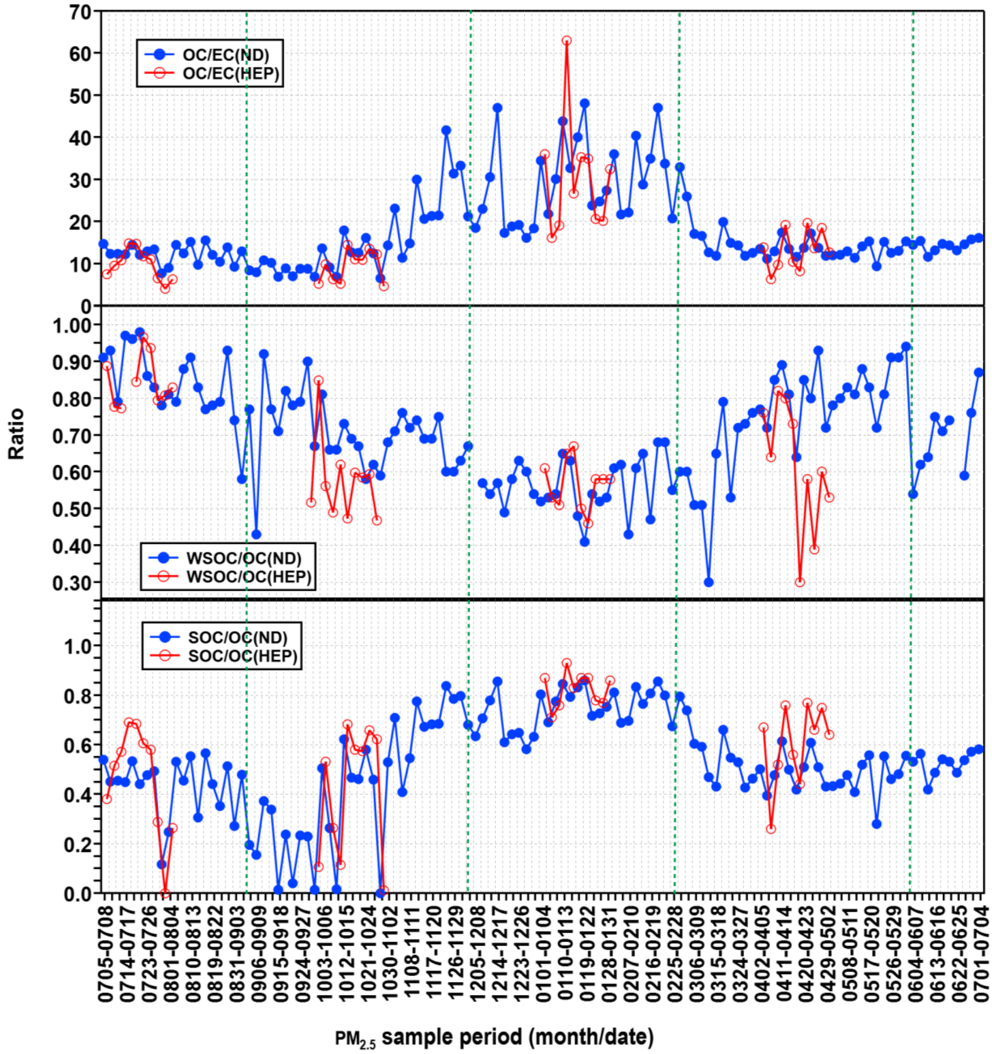

Figure 4. Temporal variations in the ratios of OC/EC, WSOC/OC, and SOC/OC in $PM_{2.5}$ at ND (solid dots) and HEP (hollow small ball) in Tianjin during 2018-2019. See text for abbreviations.

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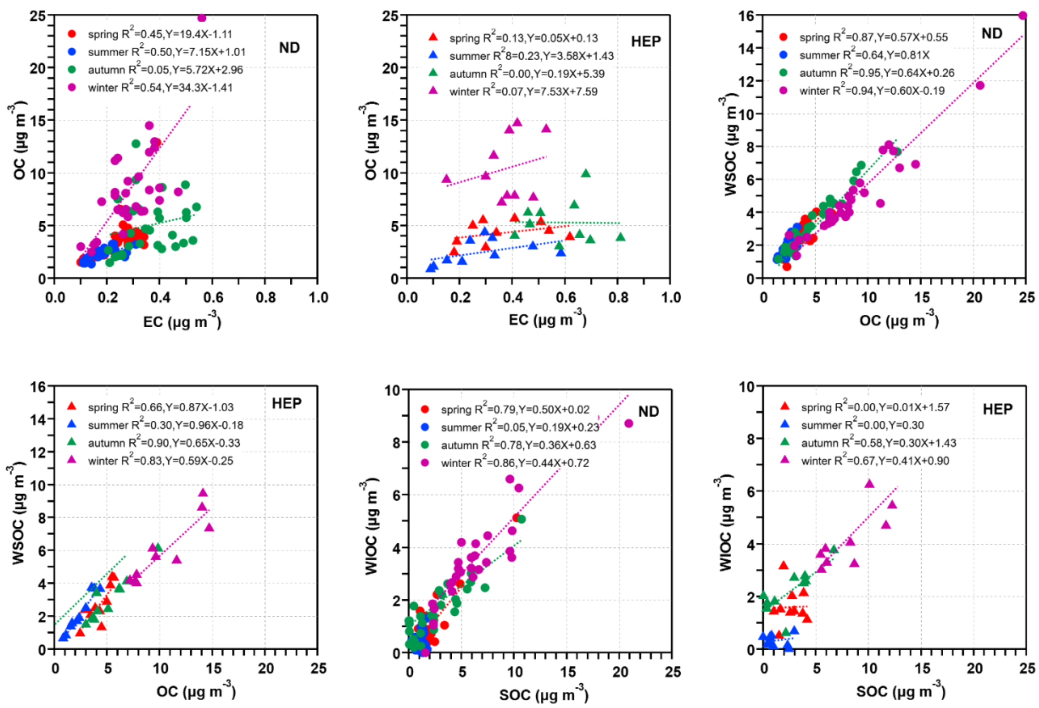

Figure 5. Scatter plots of selected carbonaceous components in $PM_{2.5}$ in Tianjin at ND and HEP.

3.4 Characteristics of inorganic ions

3.4.1 Ionic balance

The pH value of precipitation can be directly affected by the pH of atmospheric aerosols, which is controlled by chemical composition of aerosols. Studies have shown that anions such as NO_3^- and SO_4^{2-} and other strong acids will increase the acidity of atmospheric aerosols, whereas cations of strong bases such as NH_4^+, Na^+ and other will increase the alkalinity of the particles. Although organic acid and base compounds that exist in the atmospheric aerosol material also can influence the acid-base properties of aerosol particles, their concentrations are usually 3 orders of magnitude lower than those of inorganic ions concentration and hence, their influence can be ignored for acid-base balance. Based on the measured ions in this study, the ionic balance is estimated as follows:

$$A = [Cl^-]/37.5 + [NO_3^-]/62 + 2[SO_4^{2-}]/96$$

$$C = [Na^+]/23 + [NH_4^+]/18 + [K^+]/39 + 2[Mg^{2+}]/24 + 2[Ca^{2+}]/40$$

where A is the equivalent concentration of anions in $PM_{2.5}$; C is the equivalent concentration of cations. The units of A, C, and each ion are μg m^{-3}.

During the campaign period, the C/A ratios in Tianjin aerosols found to be mostly above 1.00, which indicate that they were weakly alkaline. It is possibly due to higher levels of NH_4^+ in $PM_{2.5}$ and also the lower levels of NO_3^-. In autumn and winter, the ratio of NH_4^+/C was above 0.80, indicating that NH_4^+ was the main neutralizing alkaline ion in the Tianjin $PM_{2.5}$.

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3.4.2 Concentrations and seasonal variations

Concentrations of the measured water-soluble inorganic ions showed the high abundance of NO_3^- at both the sites followed by NH_4^+ > SO_4^{2-} > Cl^- > K^+ > Na^+ > Ca^{2+} > Mg^{2+} at ND and SO_4^{2-} > NH_4^+ > Cl^- > K^+ > Ca^{2+} > Na^+ > Mg^{2+} at HEP in Tianjin. Averages of the sums of ions were 18.7 ± 16.9 μg m^{-3} and 22.7 ± 13.1 μg m^{-3} (Table 1), accounting for 55% and 56% of the $PM_{2.5}$ mass, at ND and HEP, respectively. SO_4^{2-}, NO_3^- and NH_4^+ were found to be the major ions and their total concentrations accounted for 89% and 87% in the total concentration of the measured ions at ND and HEP, respectively. Among them, SO_4^{2-}, NO_3^- and NH_4^+ are 33%, 31% and 25% respectively, at ND and 29%, 33% and 24%, respectively, at HEP. The concentration of NO_3^- was the highest, accounting for 17% and 18% of the $PM_{2.5}$ mass at ND and HEP, respectively.

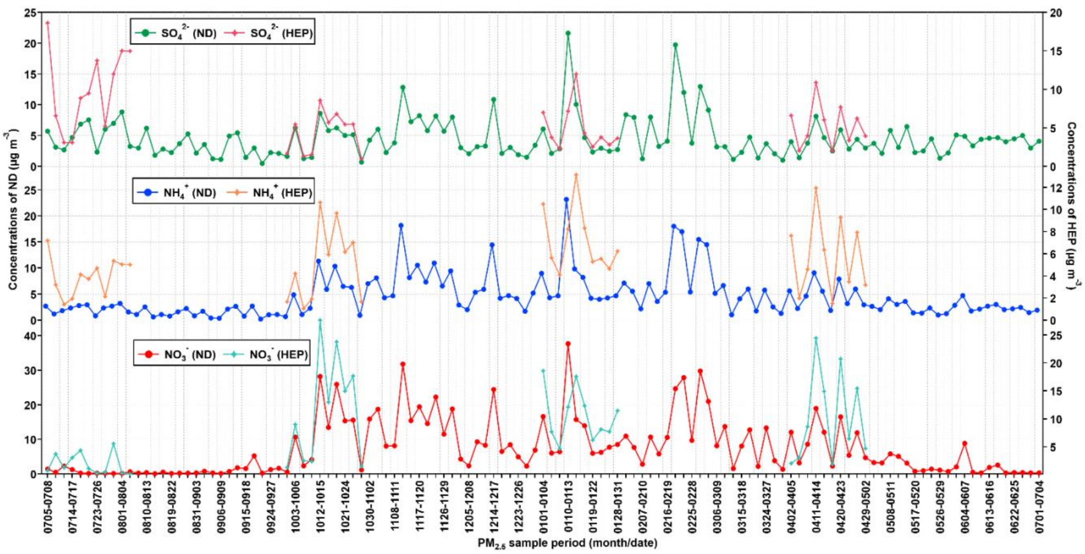

Figure 6. Temporal variations in concentrations (μg m^{-3}) of secondary ionic species in $PM_{2.5}$ at ND and HEP in Tianjin during the campaign period (2018-2019).

As can be seen from Fig. 6, concentration of NO_3^- was peaked in winter and lower in summer. It is likely because the low temperatures in winter promote the partition of NO_3^- from gas to particulate phase, whereas in summer, the higher temperatures enhance the transformation of NH_4NO_3 to HNO_3 and the frequent precipitation causes the wet deposition of the NO_3^-. The highest concentration of SO_4^{2-} occurred in winter and the lowest in spring (Table 1). In winter, SO_2 emission is significantly increased due to high consumption of fossil fuel including coal combustion for heating in northern parts of China. The higher concentration of SO_4^{2-} in summer than in spring might be due to higher temperature, relative humidity and abundant sun light, which provide favorable conditions for the photochemical conversion of SO_2 to SO_4^{2-} through gas and aqueous phase reactions. Interestingly, the seasonal variations of SO_4^{2-} at HEP was quite different from that at ND; highest in summer and the lowest in autumn. In addition, the loading of SO_4^{2-} was always higher at HEP than at ND. In fact, as noted earlier, HEP was much closer to seashore and the aerosol composition must be more influenced by sea breeze during daytime throughout the year. While in summer, the air masses were originated from oceanic region that should have been enriched with marine biogenic emissions including dimethyl sulfide (DMS), which converts to SO_2 and then SO_4^{2-} upon photochemical oxidation. On the other hand, the industries including petrochemical processing units are located near to the seashore and their emissions including SO_2 might have significant impact on the aerosol composition at HEP, whereas at ND, local anthropogenic emissions e.g., automobile exhausts might have greater influence on the composition of $PM_{2.5}$.

The mass ratio of NO_3^- to SO_4^{2-} reflects the relative contribution from local moving sources (motor vehicles) and fixed sources (including coal combustion) to atmospheric aerosols. Generally, if the ratio is ≥1, automobile exhaust is considered as an important source of the particles in the given environment (Ming et al., 2017). The NO_3^-/SO_4^{2-} ratio found to be higher than 1 in all seasons, except for summer (0.21), and the annual average was 1.63 at ND, which indicate that the automobile exhaust was also an important source of the $PM_{2.5}$ in urban area of Tianjin. In summer, the air masses originated from oceanic region should have been enriched with the marine biogenic emissions including DMS and thus the contribution of biogenic SO_4^{2-} might be significant in Tianjin aerosol. The NO_3^-/SO_4^{2-} in Tianjin (ND: 1.63, HEP: 1.35) is similar to that reported at Beijing (1.37) (Xu et al., 2017) and Shanghai (1.05) , where the automobile exhaust has been considered as one of the major sources. Such comparison again supports our finding that the automobile exhaust is an important source of aerosols in Tianjin.

The correlation between SO_4^{2-} and NO_3^- was good in spring, autumn and winter ($R^2 \geqslant 0.55$), but not in summer (R^2 = 0.00 at ND and 0.06 at HEP). Such comparability might appear due to high emissions of NO_x and SO_2 from fossil fuel including coal combustion during the heating period (late autumn to the following early spring) and subsequent secondary formation. Whereas in summer, the emission of SO_2 from coal combustion in industrial sector and marine biogenic emission of DMS might be larger than in other seasons. In addition, the NO_3^- is more susceptible for decomposition at higher temperatures prevailed in summer. The annual average concentration of Cl^- was 1.45 ± 1.79 μg m^{-3}, accounting for 4.15% of the $PM_{2.5}$ mass, at ND with the higher loading in winter than in other seasons. Such high loading again confirms the enhanced consumption of coal in winter for domestic heating, because the emission of Cl^- is abundant from coal combustion (Zhang et al., 2017;He et al., 2001). While K^+ was also found to be higher in winter, followed by autumn, spring and summer (Table 1). The high loading of K^+ in winter might be due to enhanced biomass burning for domestic heating.

3.4.3 Correlation analysis

SO_4^{2-} and NO_3^- showed a good correlation with NH_4^+ at ND and a moderate and good correlation at HEP and weak or no correlation with alkali (Na^+, Ca^{2+} and Mg^{2+}) ions at both the sites (Table 3). Such relations suggest that they were mainly associated with NH_4^+ in the form of $(NH_4)_2SO_4$/NH_4HSO_4 and NH_4NO_3, rather than with alkali metals. Interestingly, the SO_4^{2-}, NO_3^- and NH_4^+ showed a medium correlation with K^+, except for SO_4^{2-} at HEP, which suggest that SO_4^{2-}, NO_3^- and NH_4^+ might be significantly derived from biomass burning emissions. The no correlation between K^+ and SO_4^{2-} indicate that the sources of SO_4^{2-} were significantly different from those of NH_4^+, NO_3^- and K^+ at HEP. As discussed in previous section, the SO_4^{2-} might have been significantly derived from industrial emissions, particularly from petrochemical plants existed near HEP, and/or larger contribution of SO_4^{2-} derived from marine biogenic emissions due to sea breeze. The correlation coefficient between Ca^{2+} and Mg^{2+} was relatively high (Table 3), indicating that they might have been emitted from the same source such as soil dust. Further the mass ratio of Mg^{2+} to Ca^{2+} was 0.27 at ND and 0.14 at HEP, which are comparable to those reported at the point source of coal combustion (Wang et al., 2005), implying that the Ca^{2+} and Mg^{2+} in Tianjin aerosols are not only derived from soil dust but also from coal combustion emissions.

Table 3. Correlation coefficients (R^2) of inorganic ions in $PM_{2.5}$ at ND (right) and HEP (left) in Tianjin, North China.

	$PM_{2.5}$	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
$PM_{2.5}$		0.71	0.63	0.86	0.29	0.90	0.64	0.22	0.26
Cl^-	0.43		0.31	0.56	0.40	0.62	0.67	0.27	0.24
SO_4^{2-}	0.05	0.03		0.54	0.10	0.74	0.46	0.16	0.09
NO_3^-	0.57	0.21	0.03		0.21	0.92	0.49	0.11	0.15

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Na^+	0.17	0.07	0.09	0.13		0.21	0.20	0.05	0.19
NH_4^+	0.80	0.30	0.24	0.71	0.18		0.56	0.15	0.16
K^+	0.64	0.71	0.00	0.47	0.19	0.55		0.66	0.24
Mg^{2+}	0.36	0.30	0.00	0.04	0.02	0.21	0.27		0.45
Ca^{2+}	0.38	0.13	0.01	0.07	0.06	0.25	0.18	0.81	

The molar ratios of NH_4^+/SO_4^{2-}, NH_4^+/NO_3^- and $NH_4^+/(2SO_4^{2-}+NO_3^-)$ can indicate their coexistence forms (Lyu et al., 2015;Behera et al., 2013). Fig. 7 shows the linear relations between NH_4^+ and SO_4^{2-}, NO_3^- and $(2SO_4^{2-}+NO_3^-)$. NH_4^+ showed significant correlations with SO_4^{2-} and NO_3^- except for summer, confirming that sufficient NH_3 was present to neutralize H_2SO_4 and HNO_3 during the measurement period. The relatively high correlation of NH_4^+ with NO_3^- than that with SO_4^{2-} suggests that NH_4NO_3 might be more likely formed than $(NH_4)_2SO_4$, because of better affinity between the two ions at both the sites (Table 3). Furthermore, the slopes and coefficients between the selected ions (Fig. 7) indicated that NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 were the more likely existing forms of secondary inorganic ions at Tianjin in all seasons, except for summer, during which the $(NH_4)_2SO_4$ might coexist due to the loss of HNO_3 and enhancement of NH_3 emissions at high temperatures.

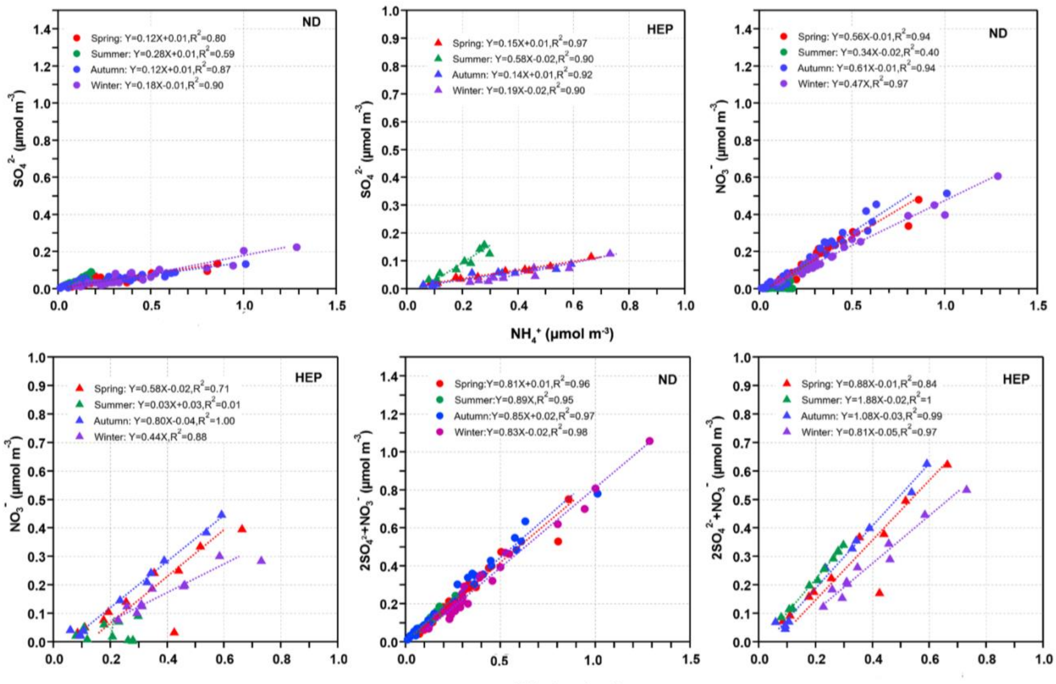

Figure 7. Linear relations between secondary ions in $PM_{2.5}$ at ND (solid dots) and HEP (solid triangles) in Tianjin during the campaign period.

3.5 Water-soluble nitrogenous components

Average concentrations of WSTN, IN and WSON were 5.45 ± 5.48 μg m^{-3}, 5.21 ± 5.01 μg m^{-3} and 0.40 ± 0.69 μg m^{-3}, respectively, at ND (Table 1). Since WSTN is mainly composed of IN (ΣNO_3^-–N+NH_4^+–N), the temporal trend of WSTN

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found to be similar to that of IN (Fig. 8). Average concentrations of WSTN and IN were high from mid-autumn to winter and the IN peaked in mid-winter, whereas WSON peaked in late autumn. In addition, the average concentration of WSON was higher in autumn followed by spring, winter and summer. On average, the mass fraction of WSON in WSTN was 6.74 ± 7.81% (range 0−39.5%). At HEP, average concentrations of WSTN and IN were 7.34 ± 5.13 μg m^{-3} and 6.14 ± 3.90 μg m^{-3}, respectively (Table 1). Their average concentrations showed a seasonal pattern with higher levels in winter followed by spring and autumn, and the WSTN peaked in winter, whereas IN maximized in spring. In addition, the concentration of WSON was higher (2.01 ± 1.80 μg m^{-3}) in growing season than that in winter and autumn.

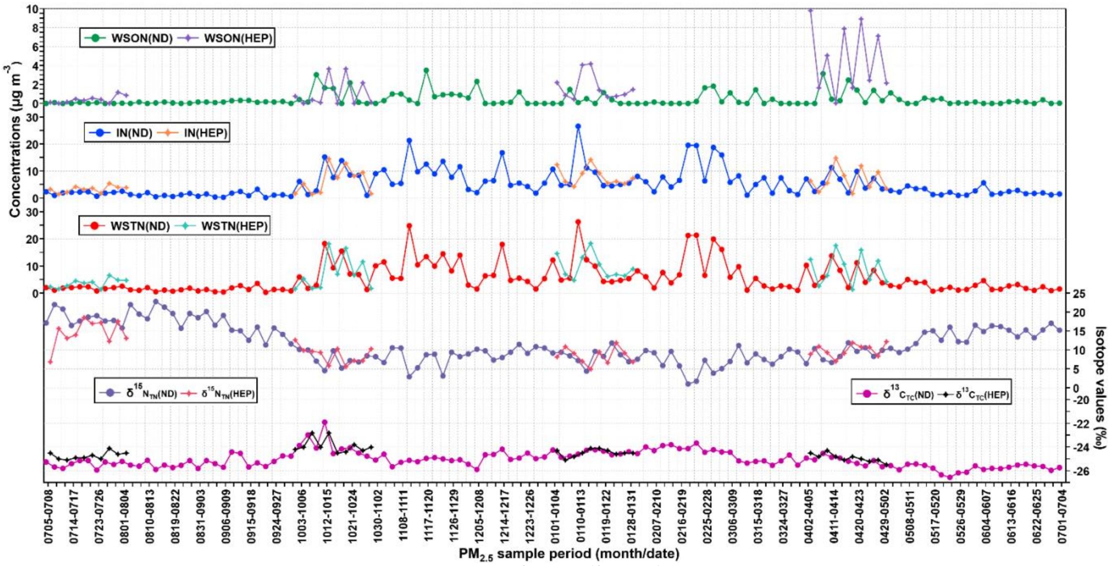

Figure 8. Temporal variations in WSTN, IN, WSON (μg m^{-3}) and $\delta^{13}C_{TC}$, $\delta^{15}N_{TN}$ in $PM_{2.5}$ at ND (solid dots) and HEP (solid stars) in Tianjin during the campaign period (2018-2019).

3.6 Stable carbon isotope ratios of total carbon ($\delta^{13}C_{TC}$)

Fig. 9 shows the box-and-whisker plots of seasons and annual $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in Tianjin aerosols. The $\delta^{13}C_{TC}$ was −6.5 −(−)21.9‰ with an average of −25.0 ± 0.7‰ at ND (Table 1). They showed a temporal trend with a gradual enrichment of ^{13}C in autumn and winter followed by a gradual depletion in the ^{13}C to early summer and remained stable thereafter, except for few cases (Fig. 9). While at HEP, $\delta^{13}C_{TC}$ −25.5 –(−)22.8‰ (average −24.5 ± 0.55‰) during the campaign period, and their seasonal variations were similar to those found at ND, which indicate that the Tianjin aerosols should have been significantly derived from different sources in different seasons. The decreasing trend of $\delta^{13}C_{TC}$ from late winter to early summer through spring confirms the important role of biological emissions, because the VOCs and unsaturated fatty acids emitted from higher plants are depleted in ^{13}C, as evidenced by the $\delta^{13}C_{TC}$ of fatty acids in unburned C_3 vegetation (range: −38.5% −(−)32.4%) (Ballentine et al., 1998). In summer, the stability of $\delta^{13}C_{TC}$ might have been controlled by significant aging of OA under high solar radiation through enhanced photochemical reactions, which simultaneously lead to the enrichment of ^{13}C in reactants and its depletion in product compounds. The increasing trend of $\delta^{13}C_{TC}$ in autumn and winter indicates that the contribution of carbonaceous aerosols from biomass burning and fossil fuel combustion was large. The enrichment of ^{13}C occurred in particles produced by biomass burning, while the $\delta^{13}C$ of aerosol carbon produced by fossil fuel combustion was relatively higher than that of aerosol carbon produced by biological sources. In fact, the consumption of fossil fuels for heating in winter in Tianjin

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is much higher than in other seasons.

Fig. 10 shows the $\delta^{13}C_{TC}$ of the particles emitted from point sources and/or source materials reported in the literature together with those found in Tianjin aerosols at both ND and HEP. The average $\delta^{13}C_{TC}$ at ND was comparable to those reported for total suspended particle (TSP) over the western South China Sea (SCS), which were considered to be significantly influenced by biomass burning emissions especially C_3 plants (Song et al., 2018). They were also comparable to those reported in aerosols (fine mode ($D_P < 2$ mm) and PM_{10}) in Santarem region, and in Mumbai, India, where biomass/biofuel burning emissions were expected as the major sources of carbonaceous aerosols (Cloern et al., 2002;Pavuluri et al., 2015c). Furthermore, the average $\delta^{13}C_{TC}$ in HEP aerosols was similar to that reported in TSP from Mountain Tai in early June, which were considered to be highly influenced by burning activities of crop residues in north China plain (Fu et al., 2012). Pavuluri et al. (2017) reported similar $\delta^{13}C_{TC}$ (−24.8 ± 0.68 ‰) in TSP in Sapporo, which were also strongly influenced by biomass burning and fossil fuel combustion emissions (Pavuluri and Kawamura, 2017). Such comparisons clearly imply that the biomass burning emissions are the major sources of atmospheric aerosols in Tianjin region, although we do not preclude the importance of other sources.

3.6 Isotope ratios of total nitrogen ($\delta^{15}N_{TN}$)

$\delta^{15}N_{TN}$ was 1.10−22.8‰ (11.4 ± 4.8 ‰) at ND and 4.91−18.6‰ (10.4 ± 3.4‰) at HEP during the campaign. Their temporal trends at ND and HEP were highly comparable with each other. The averages of $\delta^{15}N$ varied significantly from season to season with the higher values in summer (17.7 ± 2.51‰ at ND and 14.5 ± 3.3‰ at HEP) and lower value (8.07 ± 2.5‰ at ND and 8.41 ± 2.0‰ at HEP) in winter. Such seasonal changes in $\delta^{15}N_{TN}$ suggest that the aerosol N was significantly influenced by season-specific source(s) and/or the chemical aging of N species.

The range (or average) of $\delta^{15}N$ reported for the particles emitted from point sources as well as those reported in atmospheric aerosols from different locations around the world together with those obtained in Tianjin $PM_{2.5}$ are depicted in Fig. 11. $\delta^{15}N_{TN}$ in Tianjin $PM_{2.5}$ are slightly higher than those (−19.4 to 15.4 ‰) reported for the particles emitted from point sources of fossil fuel combustion and waste incineration burning (Fig. 11). They are also higher than those reported in the marine aerosols over the western North Pacific (4.9 ± 2.8‰), which were considered to be mainly derived from sea-to-air emissions (Miyazaki et al., 2011). However, $\delta^{15}N_{TN}$ in Tianjin $PM_{2.5}$ are comparable to the higher ends of the $\delta^{15}N_{TN}$ reported in atmospheric aerosols from Jeju Island, Korea (Fig. 11), which were attributed to vehicle emissions, coal burning and straw burning (Kundu et al., 2010), and to those reported in urban aerosols from Paris, France, where fossil fuel combustion was expected as a major source (Widory, 2007). Furthermore, the lower ends of $\delta^{15}N_{TN}$ in Tianjin $PM_{2.5}$ are comparable to the lower ends of $\delta^{15}N_{TN}$ reported for the particles emitted from the controlled burning of C_3 plant debris (range, +2.0 to +19.5 ‰), and the higher ends of $\delta^{15}N_{TN}$ in Tianjin $PM_{2.5}$ are comparable to the higher ends of $\delta^{15}N_{TN}$ from C_4 plant debris (+9.8 to +22.7‰) in a laboratory study and to those of atmospheric aerosols from Piracicaba and the Amazon basin, Brazil, where biomass burning is a dominant source (Cloern et al., 2002) (Fig. 11). This is consistent with the fact that wheat and corn are the main crops in Tianjin. Such comparisons again confirm that the biomass burning is a major source of atmospheric aerosols followed by fossil fuel combustion in the Tianjin region.

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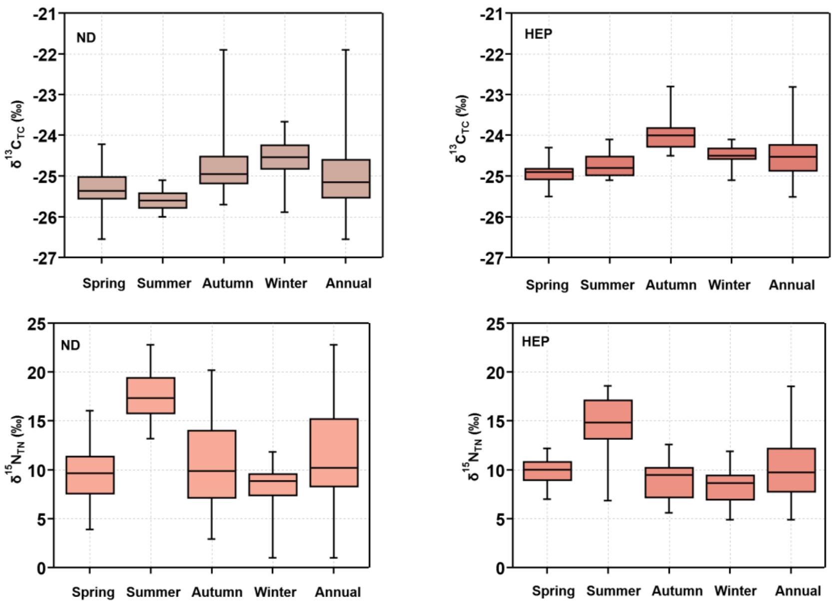

Figure 9. Box-and-whisker plot of seasonal variations in stable carbon isotope ratios of total carbon ($\delta^{13}C_{TC}$) and nitrogen ($\delta^{15}N_{TN}$) in $PM_{2.5}$ at ND and HEP in Tianjin during the campaign. The cross bar in the box and open circles show the median and outliers, respectively.

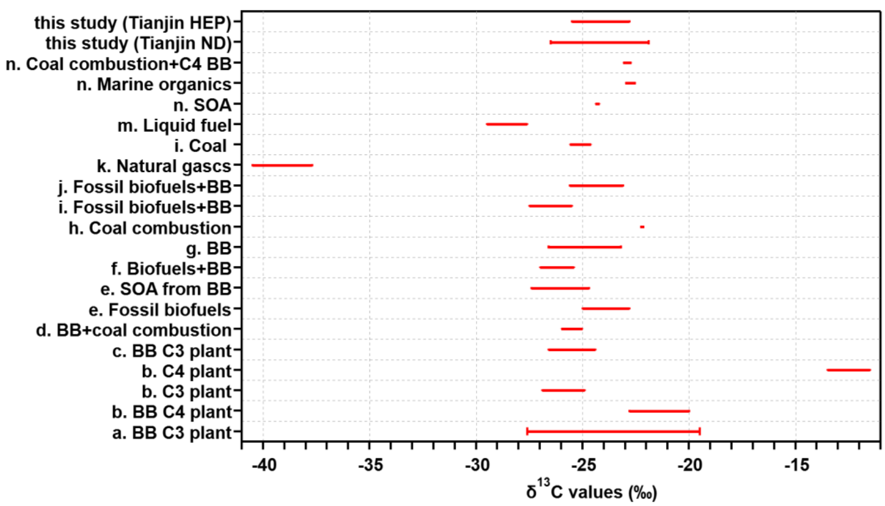

Figure 10. Range or mean $\delta^{13}C_{TC}$ in the particles emitted from point sources, source substance, and atmospheric aerosols from different sites around the world. a Fang Cao et al. (2016); b Martinelli et al. (2002); c Junwei Song et al. (2018); d Garbaras et al. (2015); e Bikkina et al. (2016); f Aggarwal et al. (2013); g Pingqing Fu et al. (2012); h Kunwar et al. (2016); i Cachier et al. (1986); j Pavuluri et al. (2016); k; l; m Widory et al. (2006); n Kundu et al. (2014).

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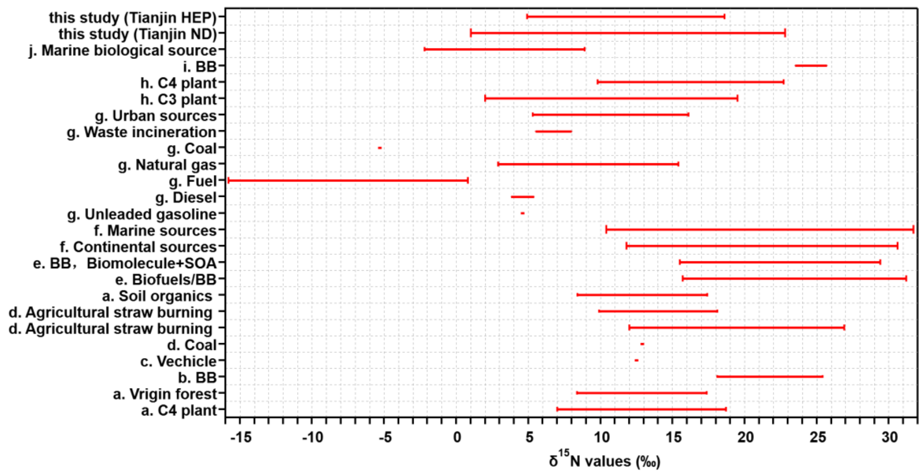

Figure 11. Range or mean $\delta^{15}N_{TN}$ in the particles emitted from point sources, source substance, and atmospheric aerosols from different sites around the world. a Martinelli et al. (2002); b Aggarwal et al. (2013); c Kunwar et al. (2016); d Kundu et al. (2010); e Pavuluri et al. (2010); f Bikkina et al. (2016); g Widory et al. (2007); h Turekian et al. (1998); i Kundu et al. (2010); j Miyazaki et al. (2011).

4 Summary and conclusions

Fine aerosol ($PM_{2.5}$) samples were collected with a frequency of 3 consecutive days each over one-year period from July 2018 to July 2019 at an urban (ND) and a suburban (HEP) sites in the Tianjin atmosphere, North China. The $PM_{2.5}$ were studied for carbonaceous (OC, EC, WSOC, WIOC, SOC and TC), nitrogenous (WSTN, IN and WSON), and inorganic ionic (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) components as well as stable carbon and nitrogen isotope ratios of total carbon ($\delta^{13}C_{TC}$) and nitrogen ($\delta^{15}N_{TN}$). The characteristics of $PM_{2.5}$ and its components showed a clear seasonal pattern with higher concentrations in winter and lower concentrations mostly in summer. The mass ratios of OC/EC, WSOC/OC and SOC/OC suggested that Tianjin aerosols were derived from coal combustion, biomass burning and photochemical reactions of VOCs, and also implied that the Tianjin aerosols were more aged during long-- atmospheric transport in summer. The seasonal variation in ions concentrations highlighted that coal combustion was the main source of aerosol and the automobile exhaust also played an important role in controlling the Tianjin aerosol loading. In addition, the concentration of SO_4^{2-} at HEP was peaked in summer and minimized in autumn, and the overall levels were higher at the HEP than that at ND Tianjin, which suggested that contribution of the marine air masses originated from the oceanic region in summer and sea breeze throughout the year and/or industrial emissions, particularly petrochemical industry located at the sea shore, were larger at the HEP than at the ND. The values of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ were confirmed that biomass and coal combustion are the major sources of aerosols in autumn and winter and dust, biological emissions and the oceanic emissions were major in spring and summer in Tianjin. Moreover, this study has also provided a comprehensive baseline data of carbonaceous and inorganic aerosols as well as their isotope ratios in the Tianjin region, North China.

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Data availability

The data used in this study can be found online at https://zenodo.org/record/5140861#.Ylqa3i0RqgR.

Competing interests

The authors declare that they have no conflict of interest.

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Investigation: Zhichao Dong, Yu Wang, Peisen Li

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Writing – review & editing: Chandra Mouli Pavuluri, Zhanjie Xu, Pingqing Fu, Cong-Qiang Liu

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