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Stable Isotopes Unravel the Sources and Transport of $PM_{2.5}$ in the Yangtze River Delta, China

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Abstract: To understand the sources and migration pattern of $PM_{2.5}$ in the Yangtze River Delta (YRD), China, the total carbon (TC) and total nitrogen (TN) concentrations and the corresponding stable isotope ratios ($\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$) were determined in aerosol samples simultaneously collected from August 2014 to April 2015 at three different locations (Shanghai, Ningbo, Nanjing). Ningbo and Shanghai are geographically closer, the research results precisely divide Nanjing and the other two cities into two categories. Nanjing has a higher proportion of nitrogen in $PM_{2.5}$ (13.2–15.3%) than Shanghai and Ningbo (8.6–12.6%), and the correlation analysis shows that nitrogen components (mainly ammonium nitrogen) might be the main driving force for the formation of $PM_{2.5}$. The isotopes were proven to be sensitive sensors to reflect the impact of special events on $PM_{2.5}$. For example, compared to other seasons, $\delta^{13}C_{TC}$ in autumn in the three cities are relatively depleted, indicating an input from biomass combustion to $PM_{2.5}$ at this time. On New Year's Eve, three cities simultaneously observed enriched $\delta^{13}C_{TC}$ due to the burning of fireworks. During the Qingming Festival, abnormally depleted nitrogen isotope ratios were observed, reflecting the vehicle exhaust pollution caused by people's short travel. Isotopes are also used to trace the transport process of $PM_{2.5}$. Postponing the sampling date in Nanjing by one day increased the linear fit (r^2) of $\delta^{13}C_{TC}$ between Nanjing and Ningbo from 0.03 to 0.75, while that of $\delta^{15}N_{TN}$ improved from 0.16 to 0.63, which means $PM_{2.5}$ might transport from Nanjing to Shanghai and Ningbo, and the transfer time takes one day.

Keywords: $PM_{2.5}$; stable carbon isotope; stable nitrogen isotope; sources and transport

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1. Introduction

With rapid economic development and the associated increase in energy consumption, fine particles ($PM_{2.5}$) are a particular concern regarding air quality in China. Fine particles are released from various sources, including agriculture, combustion of bio-fuels, fossil fuels, and industrial processes [1,2]. These particles not only cause reduced visibility but can also deleteriously affect human health [3]. To efficiently control $PM_{2.5}$ pollution in China, it is necessary to know both the sources of $PM_{2.5}$ and its subsequent transport patterns. Traditional tools, such as measurements of the concentrations and fluxes of certain components, can describe $PM_{2.5}$ pollution to a certain extent but are limited in ability to provenance sources. Factor analytical models (source-unknown models), such as positive matrix factorization (PMF), principle component analysis (PCA), and chemical mass balance (CMB) models [4] have been widely used to estimate source contributions., but these often have prerequisites that must be met and limited in provenancing power.

Stable isotope signatures were previously been used to determine the provenance of a wide range of materials from food to environmental samples, similar to verifying the origin of red wine from different countries [5] or cow milk samples from different provinces in China [6], tracing the transport and transformation of N species in water [7,8], and also been used to study atmospheric particulate matter [9]. In recent years, carbon and nitrogen isotopes in particulate matter were wildly studied to trace the source of pollutants [10–13]. However, research on the simultaneous observation of multiple isotopes in multiple cities is still limited, and few people have paid attention to the significant impact of special human activities such as fireworks or large-scale traffic congestion on $PM_{2.5}$ during holidays.

The overall objective of this study was to investigate the sources and transport of air pollution in the Yangtze River Delta and, if possible, determine the main factors in $PM_{2.5}$ formation in this area. In this study, we present the temporal variations in TC, TN, $\delta^{13}C_{TC,}$ and $\delta^{15}N_{TN}$ in $PM_{2.5}$ measurements collected in Shanghai, Ningbo, and Nanjing from August 2014 to April 2015. All samples were collected as synchronously as possible and covered all four seasons.

2. Methods

2.1. Sampling Sites

We conducted $PM_{2.5}$ collection at three locations in the YRD, Shanghai, Nanjing, and Ningbo. The YRD is one of the largest economic regions in China and is characterized by high population density and well-developed industry. Nanjing is located 308 km northwest of Shanghai and 430 km of Ningbo, Shanghai and Ningbo are relatively closer, with a straight-line distance of 151 km (Figure 1). Sampling sites for the three cities were the Shanghai Academy of Environmental Science, Nanjing University, and the University of Nottingham campus (Ningbo, China), respectively. All the samplers were installed on the rooftops of buildings, with heights of 18–21 m above the ground.

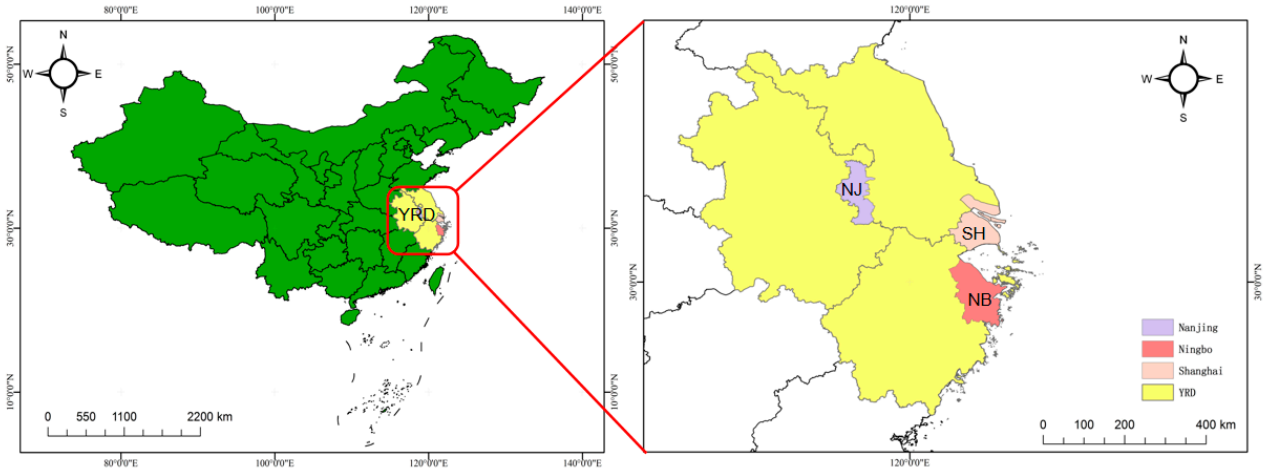

Figure 1. Sampling sites at Yangtze River Delta.

2.2. Sample Collection

Fine particles were collected for 24 h periods simultaneously at the Shanghai, Ningbo, and Nanjing sites during summer (3–26 August 2014), autumn (10 October–21 November 2014), winter (23 December 2014–15 January 2015), and spring (28 March–28 April 2015). Samples were collected on preheated (500 °C, 4 h) quartz filters (8 × 10 inch, Whatman, QM-A, Maidstone, UK) using a high-volume sampler (TH1000H, Wuhan Tianhong Intelligence Instrumentation Facility, Wuhan, China) at a flow rate of 1.05 m^3 min^{-1}. A total of 216 samples were collected. Due to rain or insufficient staff on weekends and holidays, the sampling times were not always perfectly synchronized in the three locations, but samples were taken over the same time period each season at each location. All the samples were covered with aluminum foil and stored at −20 °C until analysis. Field blank was mounted

onto the sampler for a few minutes without sucking the air. The blank samples (24 blank filters) were collected before and after sampling at each site in each season.

2.3. Sample Analysis

The $PM_{2.5}$ dry mass was measured by subtracting the preheated blank filter's weight from the sample filter's weight. Before each weighing with the balance, the filter was put into a constant temperature (25 °C) and humidity box (50%) for 24 h. Total carbon (TC) and total nitrogen (TN) contents in $PM_{2.5}$ samples and the stable isotope ratios of TC ($\delta^{13}C_{TC}$) and TN ($\delta^{15}N_{TN}$) were determined using a Flash HT Series Elemental Analyzer connected via a Conflo IV to a Delta V Advantage Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) following the protocol described elsewhere [12], a 1 × 1 cm piece of each sample filter was cut and wrapped inside a tin cup and loaded on the autosampler for analyses. The C and N contents (as % of dry mass) were calculated based on the area output of the mass spectrometer and the dry mass (mg) analyzed.

For determination of inorganic ions (NH_4^+, NO_3^-, Mg^{2+}, and Ca^{2+}), a 3 × 3 cm piece of the sample filter was cut and extracted with 7.5 mL Milli-Q water using an ultrasonic ice bath (ANPEL Laboratory technologies (Shanghai) Inc., Shanghai, China) for 20 min, and the extract was passed through a 0.45 μm pore size filter (Millex Syringe Filter, Hydrophilic PTEE, Karnataka, India). The extraction was repeated with a second 7.5 mL of Milli-Q water and then combined filtrates. The NH_4^+ and NO_3^- contents of the filtrate were measured by ion chromatography (ICS3000, Dionex, Sunnyvale, CA, USA), The Mg^{2+} and Ca^{2+} were measured by ICP-MS (7500, Agilent, Santa Clara, CA, USA). All the measurements were repeated twice for each sample and the average of the results was taken.

2.4. Quality Control and Quality Assurance

Prior to carbon and stable isotope analyses, instrumental blanks were checked with two pre-cleaned tin cups, USGS40 was used as reference material and quantifying isotope-ratio-scale contraction with USGS41, these two standards were certified for both $\delta^{13}C$ (‰VPDB) (-26.39 ± 0.04‰ for USGS40, 37.63 ± 0.05‰ for USGS41) and $\delta^{15}N$ (‰air) (-4.52 ± 0.06‰ for USGS40, 47.57 ± 0.11‰ forUSGS41). Filter blanks were also analyzed and the analytical signal of samples was corrected for blanks using isotopic mass balance equations. The measured $\delta^{13}C$ and $\delta^{15}N$ values of USGS40 were -25.83 ± 0.06‰ and -4.46 ± 0.12‰. The overall analytical uncertainties in the measurement of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ were 0.2‰ and 0.4‰, respectively. The analytical uncertainties in the measurement of TC and TN were estimated to be within 3%, and the inorganic ions were within 2%. All data were corrected using the field blank.

3. Results and Discussion

3.1. Levels of $PM_{2.5}$, TC, TN and TC/TN Ratio of $PM_{2.5}$ in the YRD

The mass concentration in $PM_{2.5}$ and the average TC, TN, $\delta^{13}C$, and $\delta^{15}N$ values during the sampling periods are summarized in Table S1.

Over the entire year, haze rarely occurs in summer, the average concentration of $PM_{2.5}$ was as low as 59.4 μg/m^3 across the three sites, which was much higher in other seasons, for example, the average concentration of $PM_{2.5}$ reached 121.5 μg/m^3 in Shanghai in spring, 103.1 μg/m^3 and 91.5 μg/m^3 in Ningbo and Nanjing in winter. Over a single 24 h period, the highest $PM_{2.5}$ concentration of 224.0 μg/m^3 was found in Ningbo on New Year's Eve (31 December, Figure S1), other outlying data were also found on this date and will be discussed later.

The currently reported aerosol mass concentration levels are comparable to recent studies in the YRD region; Wang et al. [14] reported mean values of $PM_{2.5}$ during clean days in the range of 48.0 to 70.4 μg/m^3. Dong et al. [15] considered summer the cleanest season due to a high planetary boundary layer height, stronger advection, and a clean parcel of ocean air introduced by the Southeast Asia monsoon during this time. Another possible reason was that the local government of Nanjing made great efforts to limit pollutant

sources emissions during the second Youth Olympic Games (YOG, Nanjing) from 16–28 August 2014 [16].

The average seasonal total carbon concentrations (TC) in $PM_{2.5}$ during the sampling ranged from 6.8 ± 1.6 μg/m^3 to 21.1 ± 10.1 μg/m^3. From Table S1 and Figure 2a, It can be seen that the mean percentage of TC in $PM_{2.5}$ was lower during summer and spring (15.2% and 14.8%) than that in autumn and winter (19.3% and 19.8%), indicating that it is not simply an increase in the concentration of existing carbon pollutants, but rather a possible contribution of new carbon-containing pollutants in autumn and winter.

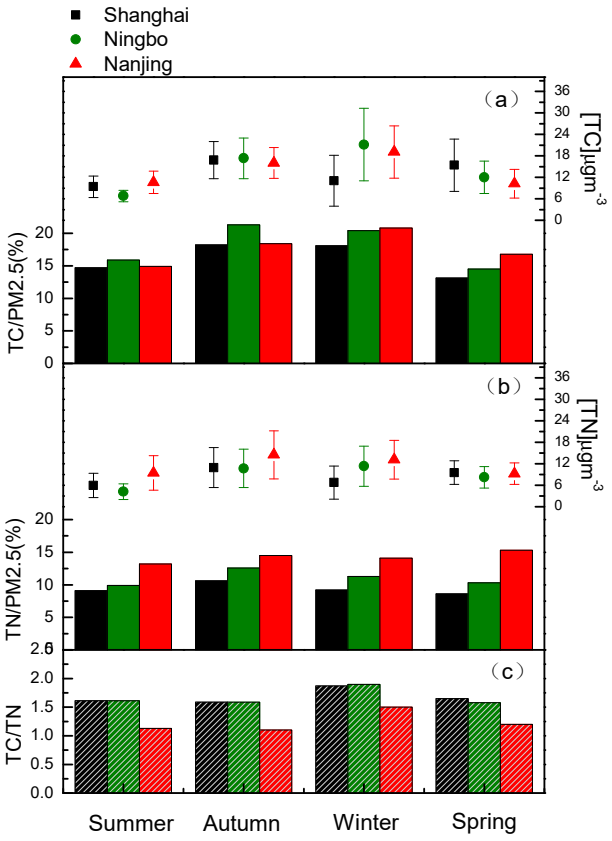

Figure 2. The concentration and percentage of TC (**a**) and TN (**b**) in $PM_{2.5}$. (**c**) The ratio of the concentration of TC to TN.

The average total seasonal nitrogen (TN) concentration in $PM_{2.5}$ ranged from 4.2 ± 2.2 μg/m^3 to 14.9 ± 6.8 μg/m^3 (Table S1 and Figure 2b). No clear seasonal trend for the percentage of TN in $PM_{2.5}$ was observed; however, there were regular differences between cities. Nanjing (13.2–15.3%) had a higher average percentage of TN in $PM_{2.5}$ than Shanghai and Ningbo (8.6–12.6%) (Table S1 and Figure 2b). An analogous result was also observed for TC/TN, with results for Nanjing (1.13–1.49) differing from those for Shanghai and Ningbo (1.58–1.92) (Table S1 and Figure 2c). The possible reason for this result is the relative proximity of Shanghai and Ningbo to each other; the $PM_{2.5}$ in these two cities may have similar sources or be influenced by the same air mass transported from other regions.

The TC/TN ratios reported here (1.13–1.92) are lower than those reported in several other regions. For example, Mkoma et al. (2014) reported values of 6.9–13.9 in $PM_{2.5}$ from Morogoro aerosols in Tanzania, with high values being explained by the contributions of biomass/biofuel burning organics to $PM_{2.5}$. In India, values of 7.2 in summer to 9.2 in winter have been reported in Mumbai [17] and values of 5.9 to 7.8 have been reported in the coastal megacity of Chennai [18]. It is known that TC/TN ratios are useful to distinguish terrestrial versus marine-based sources. Biomass/biofuel burning can produce larger amounts of carbonaceous species, whereas marine biogenic emissions are important

sources of nitrogenous species [19]. In our results, however, this is not the case. Nanjing is an inland city but shows higher nitrogen content, which seems more likely from local sources. To clarify the reason, we studied the composition of nitrogen.

The nitrogen species in $PM_{2.5}$ are predominantly nitrate and ammonium. In the YRD region, total inorganic nitrogen accounted for 66.4% to 100.1% of TN, and ammonium was the major nitrogen species in $PM_{2.5}$, contributing from 38.6 to 76.7% of nitrogen. In contrast, nitrate contributed only between 13.9 and 38.6%. Similar situations have been found in other parts of China. Xing et al. [20] reported that ammonium accounts for 54.5% of total nitrogen in $PM_{2.5}$ in Jiaozhou Bay, while nitrate only accounted for 29.2%. Huang et al. [21] reported that ammonium accounts for 74% of TN in Beijing, 68% in Shanghai, 73% in Guangzhou, and 70% in Xi'an. Geng et al. [22] using national-scale ground-based measurement data collected from 2005 to 2012, calculated that the contribution of ammonium to TN ranged from 52 to 90% with a mean value of 71%. Huang et al. [21] concluded that haze pollution events in China were primarily driven by secondary aerosol formation, both organic (SOA) and inorganic (SIA) in nature. Among SIAs, ammonia (NH_3) plays an important, and currently underestimated, role in aerosol nucleation and growth, causing haze formation during its conversion into ammonium (NH_4^+) [23]. Wu [24] found that emissions of NH_3 are more associated with the spatiotemporal variation in $PM_{2.5}$ levels than emissions of either SO_2 or NO_x and argued that $PM_{2.5}$ pollution in China is substantially affected by ammonia emissions.

3.2. The Characteristics of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ of $PM_{2.5}$

The seasonal average carbon isotope of TC ($\delta^{13}C_{TC}$) and nitrogen isotope of TN ($\delta^{15}N_{TN}$) are presented in Table S1, detailed temporal trends are presented in Figures 3 and 4.

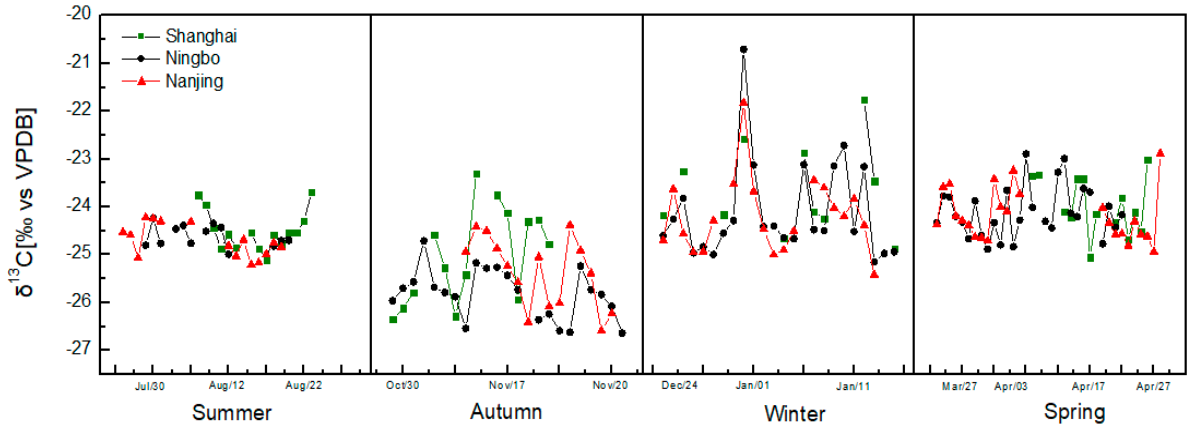

Figure 3. Time-resolved distribution of stable isotope ratio of TC ($\delta^{13}C$) in $PM_{2.5}$ samples.

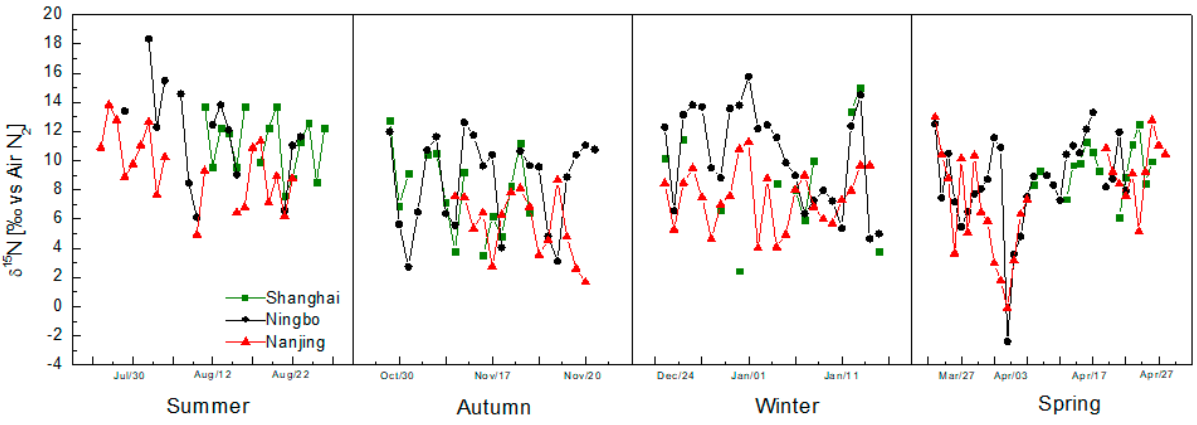

Figure 4. Time-resolved distribution of stable isotope ratio of TN ($\delta^{15}N$) in $PM_{2.5}$ samples.

Throughout the year, $\delta^{13}C_{TC}$ varied from -25.8 ± 0.5‰ to -23.7 ± 0.9‰. As mentioned before, summer is the cleanest season in the YRD, when the average concentration of $PM_{2.5}$ is the lowest. At this time, the $\delta^{13}C_{TC}$ of the three cities also had the lowest variability. The variability in $\delta^{13}C_{TC}$ in other seasons was larger than that in summer, especially in autumn and winter, confirming that not only an increase in the original sources of carbon in $PM_{2.5}$ but also the emergence of new carbon sources during autumn and winter as mentioned before.

Seasonally, the most depleted $\delta^{13}C$ values of $PM_{2.5}$ across the three cities were observed in autumn (−25.4‰), while in summer (−24.6‰), winter (−24.0‰) and spring (−24.1‰), more enriched values were observed (Table S1 and Figure 3). Similar depleted $\delta^{13}C$ values were observed in $PM_{2.5}$ from the Sanjiang Plain area during the autumn harvest season, and the lower $\delta^{13}C$ values were attributed to biomass burning [25]. The YRD contains the most fertile soils in China; 15% of the total rice and 19% of the total wheat production in China occurs in this delta [26]. Agricultural waste from the main crops is always burned in the open air. The highly depleted $\delta^{13}C$ values observed in autumn are consistent with the burning of crop residues of predominantly C3 plants such as rice and wheat in this season. Moreover, Zhang et al. [27] also reported major air pollutants from crop residue burning for the year 2014 in China, the MODIS fire counts clearly shown rice residues burning was the major contributor to the $PM_{2.5}$ in the Yangtze River Delta and reaches its peak in autumn, which further confirmed our speculation. The $\delta^{13}C_{TC}$ values of autumn are also within the range of values produced from the combustion of liquid fossil fuels, including gasoline and diesel (−28‰ to −25‰) [28] (Kirillova et al., 2013). However, the $PM_{2.5}$ collection was at the same locations for all seasons, and daily traffic is not expected to vary much between seasons, except for during special festivals. We, therefore, conclude that the depleted $\delta^{13}C_{TC}$ values in autumn most likely result from biomass burning.

Generally, the variation in $\delta^{15}N_{TN}$ was greater than that in $\delta^{13}C_{TC}$ (Figures 2 and 3). For example, $\delta^{15}N_{TN}$ in Ningbo ranged from 6.1‰ to 18.3‰ during summer and from −2.4‰ to 13.3‰ during spring. Across all sites and seasons, the mean $\delta^{15}N$ varied from 5.5‰ to 11.7‰. Such larger variations in $\delta^{15}N_{TN}$ of $PM_{2.5}$ were mainly due to the source fingerprint of nitrogen varied in a wider range than that of carbon. For example, the $\delta^{15}N_{NH3}$ is from −10.5 to −21.1‰ for vehicle exhaust, from −29.2 to −32.5‰ for landfill, −13.0‰ for power plant NH_3 slip, and for −50.0% for chemical fertilizer. Moreover, larger N isotope effects in the chemical equilibrium also contribute to the variation in $\delta^{15}N_{TN.}$ The fractionation between aqueous NH_3 and NH_4^+ as high as 45‰ [13], the fractionation between NOx and NO^{3-} is about −10‰ for biogenic NOx from bacteria, from −20 to 10‰ for vehicle NOx, and from 5 to 20‰ for power plant NOx [11]. However, the isotopic variation of carbon source is much smaller, similar to the emissions from motor vehicles range from −24.9‰ to −20.3‰, coal combustion range from −24.4‰ to −23.3‰ [10], $\delta^{13}C$ of marine-derived particles ranged between −20‰ and −22‰, The biggest carbon isotope difference may come from C3 and C4 plants, C3 plants have $\delta^{13}C$ values of approximately −28.0‰, whereasC4 plants present the value around at −14.0‰ [12]. Therefore, nitrogen isotope tracing may be more significant than carbon isotope tracing.

The most enriched mean $\delta^{15}N_{TN}$ values were detected in summer (10.9‰), coinciding with the lowest concentrations of TN; otherwise, little seasonal variation was observed. In all seasons, the mean $\delta^{15}N_{TN}$ value in Nanjing was depleted compared with that in Ningbo and Shanghai. This result is consistent with Nanjing differing from the other two cities in other nitrogen-based parameters, such as the TC/TN ratio, proportion of TN in $PM_{2.5}$ (TN/$PM_{2.5}$), and proportion of N_{NH4+} in TN, the research results precisely divide Nanjing and the other two cities into two categories. The higher concentration of NH_4^+ in $PM_{2.5}$ coupled with more depleted $\delta^{15}N_{TN}$ values may indicate that Nanjing has a greater proportion of depleted ammonia in its emissions than either Shanghai or Ningbo. The source of the depleted ammonia is likely to be agricultural in nature. The$\delta^{15}N$ of NH_3 emissions associated with agriculture, such as volatilized livestock waste, range from −56‰ to −38‰, while volatilized fertilizer ranges from −48‰ to −36‰; these values are

considerably more depleted than emissions from fossil fuel (coal combustion −7‰ to 2‰; vehicle emissions −4.6‰ to −2.2‰) [29].

Another explanation for the $\delta^{15}N$ values in aerosols was attributed to the aging of N species during long-range transport [18]. Based on this theory, the relative depletion of $\delta^{15}N_{TN}$ in Nanjing might be explained if it is the source of N emissions in Ningbo and Shanghai. This phenomenon is probably true when northerly winds prevail (autumn and winter), as Nanjing will be located upwind. However, when southerly winds prevail [summer], [30], it is difficult to envisage Nanjing acting as a source of emissions in Shanghai and Ningbo. As we currently observed $\delta^{15}N_{TN}$ depletion in all four seasons in Nanjing compared with Ningbo and Shanghai, we conclude that $\delta^{15}N_{TN}$ in Nanjing is more influenced by local agriculture.

3.3. Relationships between TC, TN, $PM_{2.5}$, $\delta^{13}C$, and $\delta^{15}N$

Strong positive correlations were found between TC, TN and $PM_{2.5}$ aerosol mass at all sites during summer, autumn and winter (r^2 = 0.59–0.96) (Figure S2) except for Shanghai in summer. Although TC accounts for more $PM_{2.5}$ than TN, the correlations between TN and $PM_{2.5}$ were slightly stronger than those between TC and $PM_{2.5}$, confirming that nitrogen species were more important to the formation of $PM_{2.5}$ aerosols.

Moreover, severe haze events occurred in Nanjing during the autumn period on November 10th and 11th, with aerosol masses reaching 149.17 and 175.96 μg/m^3, respectively. During these haze events, TN increased linearly with $PM_{2.5}$ (Figure 5). However, the increase in TC was less than expected from the relationship of TC with $PM_{2.5}$ (Red plots and surrounded with dotted line). Consequently, during haze events, the TC/TN ratios of 0.69 and 0.58 were lower than those normally observed (1.1–1.6 Table S1). We conclude that the increase in nitrogen species is a major factor in haze formation. Analogous results were observed in Shanghai in winter immediately before (29 and 31 December) and after (4 January) the New Year holiday period (Figure S2c). Overall, our current data suggest a dominant role of nitrogen species in $PM_{2.5}$ formation when compared with carbon compounds. We, therefore, suggest that mitigation strategies to reduce $PM_{2.5}$, especially during haze periods, would be better aimed at reducing nitrogenous emissions to the atmosphere than carbon emissions. Reducing industrial emissions, including those from chemical, coal, steel, cement, and other industries, as well as reducing automobile exhaust emissions, the use of agricultural fertilizers, and fuel combustion, can effectively reduce $PM_{2.5}$.

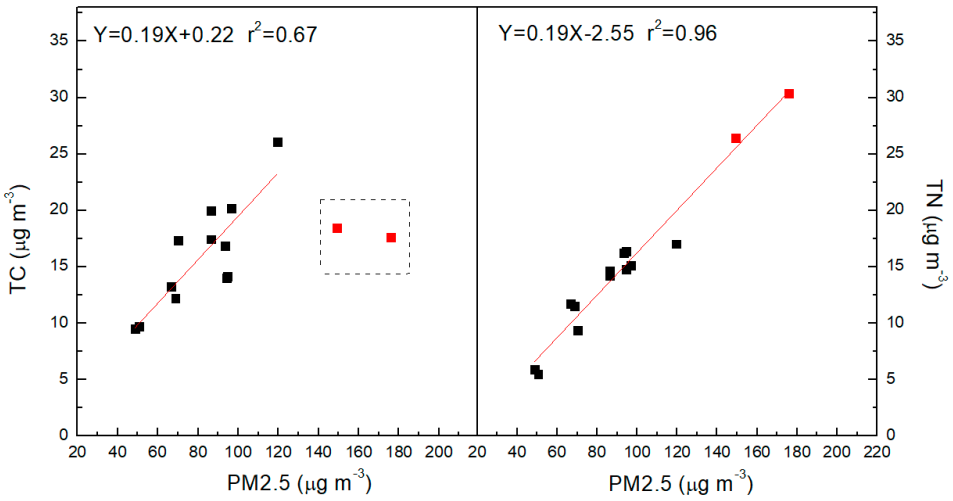

Figure 5. Correlation of TC/TN and $PM_{2.5}$ in Autumn (During these haze events (red sqaures) in Nanjing, TN increased linearly with $PM_{2.5}$ (red squares in **right**), while TC legged behind (**left**, red squares in dashed line in left)).

Unlike other seasons, we found that the correlation between TC and TN with $PM_{2.5}$ in the three cities in spring is relatively weak (Figure S2), which may be due to climatic factors at this time. Using backward trajectory analysis, we [30] determined that a northerly wind prevailed from October to March in the YRD, while southeasterly winds prevailed from May to September. The spring season, therefore, includes a less stable (in terms of wind direction) transition period between two differing prevailing winds. Additionally, in the spring period, we [30] noted that frequent sandstorms can contribute substantially to $PM_{2.5}$. As a result, $PM_{2.5}$ in YRD may have multiple pollution sources in different directions and be affected by uncommon sandstorms during this period.

In autumn, all three cities showed weak negative correlations between $\delta^{13}C$ and TC (r^2 = 0.42 in Nanjing, 0.36 in Ningbo, and 0.23 in Shanghai, Figure S3), suggesting an increased contribution of TC from relatively depleted carbon sources, such as the combustion of C3 plant material. In Brazil [31], a similar negative correlation between $\delta^{13}C$ and TC was previously observed at night during a period of intensive biomass burning, which further confirms our speculation before.

A negative correlation between $\delta^{15}N$ and the TN concentration was observed in most instances, which was explained by the adsorption/condensation of gaseous NH_3 and HNO_3 onto pre-existing particles to form solid-phase NH_4^+ and NO_3, favoring an increase in light ^{14}N in particles [14]. While weak or no correlation between $\delta^{15}N$ and TN was observed in Nanjing in autumn and in Shanghai in winter (Figure S3). These periods were exactly when the increase in $PM_{2.5}$ was matched by the increase in TN, while TC lagged behind, indicating the emergence of new nitrogen sources during these two periods.

3.4. Stable Isotopes Reflect the Impact of Unusual Events on $PM_{2.5}$

Mapping the carbon and nitrogen isotope to distinguish three cities. In the plots of $\delta^{13}C$ versus $\delta^{15}N$, no clear separation of the three cities emerged (Figure 6). However, partial separation can be seen in summer and autumn mainly due to Shanghai having slightly more enriched $\delta^{13}C$ values than the other two cities and Ningbo having slightly more enriched $\delta^{15}N$ values than Nanjing (Figure 6). This partial separation suggests that each city had, at least to some extent, characteristic local pollution sources.

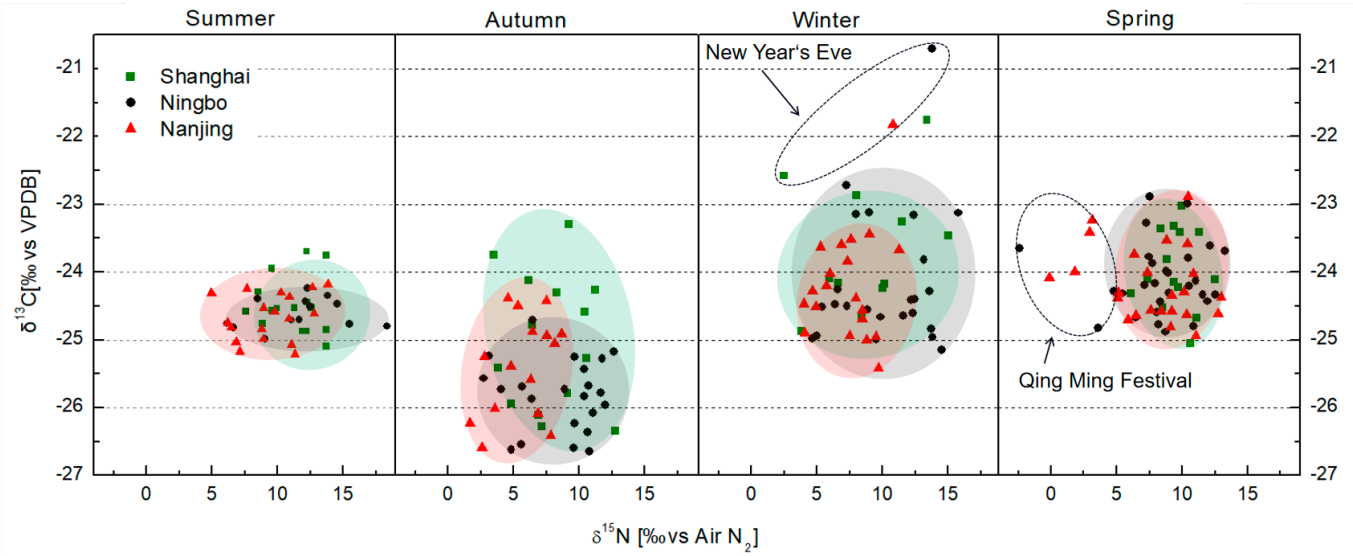

Figure 6. The plot of all isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) values illustrating differences among particular cities of the Yangtze River Delta (The distribution of each city is covered with different color shadows).

However, abnormal carbon and nitrogen isotope values were observed during two holidays during the sampling period. On New Year's Eve, the $PM_{2.5}$ of all three cities

simultaneously experienced abnormal enrichment in carbon isotopes. In China, it is traditional for people to set off fireworks during celebrations. On New Year's Eve, the $PM_{2.5}$ concentration in Ningbo reached 223.9 $\mu g/m^3$ (average winter value = 98.7 $\mu g/m^3$), the highest aerosol mass concentrations observed during the whole sampling year. A statistically higher level of Ca (8.73 $\mu g/m^3$ compared with an average of 1.33 $\mu g/m^3$) and Mg (0.39 $\mu g/m^3$ compared with an average of 0.09 $\mu g/m^3$) was also detected, as found in Baranyai's research on the effect of a fireworks event on the elemental variation of dust collected in Hungary [32]. Although the $\delta^{13}C$ value of fireworks are not available in the literature, it can be assumed that the extremely enriched $\delta^{13}C$ in Ningbo (−20.71‰) New Year's Eve high related with the fireworks burning. Due to the high urbanization of Shanghai and Nanjing, considering the air quality problem, the fireworks were restricted in these two cities, and there is no significant change in $PM_{2.5}$ or elemental concentration on New Year's Eve. While the abnormally enriched $\delta^{13}C$ value in Shanghai (−21.76‰) and Nanjing (−21.83‰) still reveal the influence of fireworks events in surrounding rural areas on the carbonaceous components of $PM_{2.5}$.

Another set of outliers occurred in spring on the distribution of $\delta^{15}N_{TN}$ with some samples having particularly depleted $\delta^{15}N$ values (Figure 6). These outliers were all sampled around the Qing Ming Festival in Nanjing and Ningbo (Unfortunately, no samples were collected in Shanghai over this period). The Qing Ming Festival (4–6 April 2015) is a three-day holiday in spring, family always take a road trip together. The most depleted nitrogen isotope value was observed on 3 April 2015, one day before the Qing Ming Festival, it is the time that residents start to travel and always generate traffic jams. Increases in NO_3^- and NH_4^+ were also found at this time in Ningbo on 3rd and 4th April, where the concentrations of NO_3^- reached 13.5 $\mu g/m^3$ and 20.8 $\mu g/m^3$, respectively (average April [NO_3^-] = 8.1 $\mu g/m^3$), and NH_4^+ reached 9.4 $\mu g/m^3$ and 10.8 $\mu g/m^3$ (average April [NH_4^+] = 5.1 $\mu g/m^3$). It is well known that anthropogenic NOx emissions have surpassed natural NOx since the industrial revolution and vehicle exhaust is the largest source of anthropogenic NOx [33]. The $\delta^{15}N$-NOx values from vehicle emissions range from −19.1‰ to 9.8‰ and are more depleted than^{15}N-NOx values from coal-fired power plants values 17.6 ± 0.4‰ (Selective Catalytic Reducers (SCR)-equipped) and 10.4 ± 0.2‰ (without SCR) [34]. Vehicles equipped with SCR show a negative correlation between NOx concentrations and $\delta^{15}N$-NO_x [33], which means the more NOx released, the more depleted $\delta^{15}N$-NO_x is, especially during the traffic jams, approximately 60−80% of the total NOx emissions occur during the first 200 s cold-start operation, which releases the lowest $\delta^{15}N$-NO_x values. Although no clear increase of NO_3^- and NH_4^+ was found in Nanjing, the similar trend of decrease of $\delta^{15}N$-TN observed during Qingming Festival indicates that a relatively new depleted nitrogen source emerged during this period, probably due to the similar reason that suddenly increased of vehicles on the road for the short trip on the holiday. The isotope composition is more timely and reflects the change of the pollution source than the concentration.

3.5. Stable Isotopes Can Trace Air Mass Transport

Due to logistic reasons, sampling in the three cities was not always perfectly synchronous. Nevertheless, over the period from 6th to 18th October, we could see similarities between the sites in the short-term temporal variability of both carbon (Figure 7a) and nitrogen isotopes in $PM_{2.5}$ (Figure 7b). The pattern and timing of carbon and nitrogen isotope variability were more similar between Ningbo and Shanghai than between either of these cities and Nanjing; this result is not too surprising from the previous analysis. However, we noticed the special connection between those two cities and Nanjing during this period, as shown in Figure 7, postponing the sampling date in Nanjing by one day increased the linear fit (r^2) of $\delta^{13}C_{TC}$ between Nanjing and Ningbo from 0.03 to 0.75 (Figure 7a), while that of $\delta^{15}N_{TN}$ improved from 0.16 to 0.63 (Figure 7b). This means that the pollutants in the air of Nanjing the day before were highly similar to those in Ningbo and Shanghai today, moreover, according to backward trajectory statistics, the dominant wind direction

is northerly between October and March in the YRD [30]. During this period, Nanjing was upwind of Shanghai and Ningbo, these finding strongly suggests that during the period from 6th to 18th October, pollutants and their unique isotope signatures in $PM_{2.5}$ travel with the prevailing winds from Nanjing to Shanghai and Ningbo, and the transmission time takes one day.

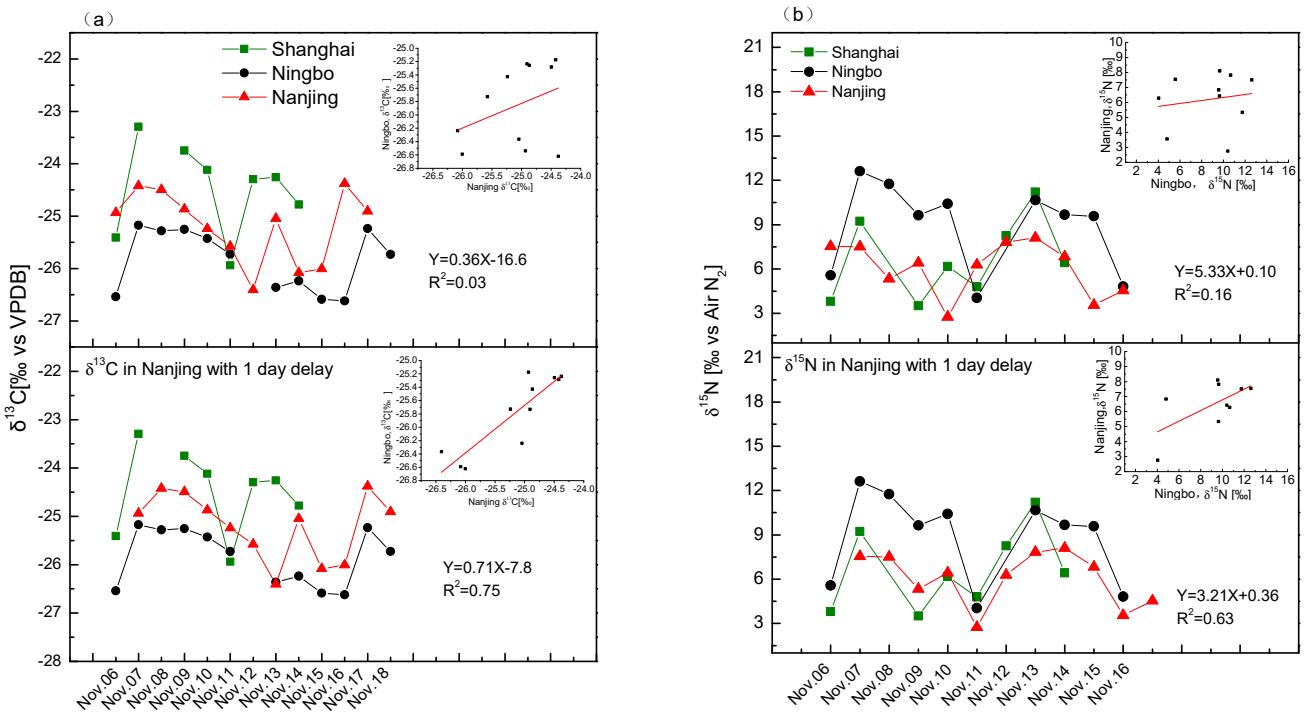

Figure 7. Time-resolved distribution of δ13CTC (**a**), δ15NTN (**b**) from 6 November to 16 November and the correlation between Nanjing and Ningbo.

4. Conclusions

This study investigated the characteristics of $PM_{2.5}$ in different cities within a certain research area at the same time, which proposed a new way to study the sources and transport of $PM_{2.5}$ pollution. The relationship between samples collected from different cities at the same time provided more information than simply studying one city.

The same trend among samples can serve as a common characteristic of the research area. For example, the TC/TN ratios in $PM_{2.5}$ of the three cities during the whole sampling year were lower than that of other countries, considering the $PM_{2.5}$ pollution in this region is also higher than in other countries, indicating that nitrogen-containing pollutants are the main driving force for the $PM_{2.5}$ in YRD region. Furthermore, the same abnormal trend in different cities at a certain time can help to more clearly identify common special pollution sources, such as the abnormal enrichment in carbon isotopes observed in all three cities on New Year's Eve. Reflect the influence of fireworks burning, the depletion of nitrogen isotopes observed during the Qingming festival was attributed to the increased vehicular traffic.

The different trends among samples can well reflect the unique pollution sources of a certain city. For example, $PM_{2.5}$ in Nanjing contained higher percentages of TN with more depleted $\delta^{15}N_{TN}$ values than the other two cities, suggesting a different source of pollution. As a relatively inland city, Nanjing might be more affected by agricultural emissions. The differences in $PM_{2.5}$ characteristics precisely divide Nanjing and the other two cities into two categories, which coincides with their geographical differences. The different trends and the interrelationships among samples can even be used to infer the transmission process of $PM_{2.5}$. The comparison of the temporal variation in stable isotopes and combine

backward trajectory statistics show that during certain period pollution transport from Nanjing to Shanghai and Ningbo takes one day for the journey.

Furthermore, in this study, isotopes have been shown to reflect changes in $PM_{2.5}$ composition more sensitively than concentrations, making them a powerful tool for studying the sources, formation, and transport of atmospheric pollutants. Such information has great potential in diagnosing the influence of fine particle loading on air quality and providing a starting point for developing model simulations as well as controlling strategies in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos14071120/s1, Table S1: Concentration of Aerosol mass ($PM_{2.5}$), total Carbon (TC) and nitrogen (TN) contents and their stable isotope ratios ($\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$), inorganic ions, and their percentages in $PM_{2.5}$ collected from Shanghai, Ningbo and Nanjing in 2014–2015; Figure S1: Time-resolved distribution of $PM_{2.5}$; Figure S2: Correlation of TC/TN and $PM_{2.5}$ in four seasons. (a) Summer (b) Autumn (c) Winter (d) Spring; Figure S3: Correlation of $\delta^{13}C_{TC}$ and TC, $\delta^{15}N_{TN}$ and TN in four seasons. (a) Summer (b) Autumn (c) Winter (d) Spring.

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