Investigating the Pollution Characteristics and Primary Components Source Apportionment of PM10 in Nanjing Port

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Investigating the Pollution Characteristics and Primary Components Source Apportionment of PM10 in Nanjing Port

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Abstract. In order to investigate the characteristics and the sources of PM 10, the Nanjing port was selected as the sampling site for atmospheric PM10 samples collections. The sampling was introduced during represent months in summer and winter. Then the elements, ions and OC/ EC chemical components were detected by ICP-MS, ion chromatography and carbon analyzer, respectively. The results showed that the average concentration of atmospheric PM 10 in summer and winter for Nanjing port Was 88.1 ± 31.9 μg/m 3 and 136.9 ± 76.8 μg/m 3, respectively. The concentrations of in organic secondary Components In summer and winter were25.4μg/m 3 and 40.8μg/m 3, accounting for 28.9% and 31.1% of the total PM 10, respectively ; the concentration was highest for NO 3 - in summer and for SO 4 2- in winter. There is obvious difference between the concentration of carbonaceous components in summer and winter, and the concentration of total carbonaceous components was 88.1 ± 31.9 μg/m 3 and 136.9 ± 76.8 μg/m 3, accounting for 24.4% and 39.7% of the total PM 10, respectively; Variation of primary carbonaceous components is the reason Causing the difference s. Source apportionment results indicate d that the soil dust and coal combustion, metallurgy, motor vehicle, ship and sea salt were the main contributors To the PM 10 in Nanjing port. Soil dust contributed most (33%), and the contribution percentages of sea salt and ships were approximately 6.4% and 6.6%, respectively. The contribution s of sea salt and ship emissions in winter were slightly higher in winter than that in summer.

1. Introduction

Atmospheric particulate matter pollution is currently the most prominent atmospheric environmental problem in China [1]. Atmospheric particulate matter, especially aerosols with smaller particle sizes, such as PM $_{10}$, is a complex pollutant. Its composition includes both primary pollutants such as EC, primary organic carbon, heavy metals, etc., which are directly discharged into the atmosphere, as well as secondary groups generated by complex chemical reactions in the atmosphere (such as SO_2, NOx, VOCs, etc.). Points (such as sulfates, nitrates, ammonium salts, secondary organic aerosols, etc.) [2]. Studies have found that long-term exposure to atmospheric particulate matter can have many adverse effects on human health [3–5]. Since the atmospheric particles may absorb or scatter the sunlight, thus reducing atmosphere visibility [6], and the impact of climate change [7]. Studying the chemical composition of atmospheric particulate matter and analyzing its source and contribution can provide an important scientific basis for the formulation ofparticulate pollution prevention and control programs.

At present, Chinese scholars have carried out more research on atmospheric particulate matter, which mainly focuses on urban areas. [8–10], there is less concern and research on the port area, especially the river port area. On the other hand, as China's economic development, but also the rapid

development of the transport ship, the main port throughputincreased from 1.256 billion tons in 2000 to 7.846 billion tons in 2015, a growth rate of over 500% [11, 12]. The rapid development of the shipping industry has brought more emissions of marine pollutants. With the in- depth development of air pollution prevention and control work in China, ship emissions and control have gradually attracted attention. As a land areadirectly affected by ships, the current characteristics of atmospheric particulate matter pollution are still unclear, and the impact of ship discharge on the surroundingatmospheric particulate matter is unclear.

Nanjing Port is one of the largest inland ports in Asia, a main hub port and a port open to the outside world. It is a major port on the coast of China and a hub port for water and land transport and rivers and seas in the Yangtze River Basin. In 2016, the cargo throughput of Nanjing Port exceeded 100 million tons, and the container throughput exceeded 3 million TEUs. This paper selects Nanjing Port as the research area, conducts atmospheric PM_{10} sampling and component analysis, studies the chemical composition andpollution characteristics of atmospheric particulate matter in the port area, analyzes the pollution source of atmospheric particulate matter, and explores the contribution of ship discharge to atmospheric PM_{10} in the port area. Provide scientific basis for air quality improvement and ship emission control in the port area.

2. Research Method

2.1 Experimental Method

2.1.1 Sample Collection. In order to study the air quality of the port area and the environmental impact of ship emissions, the sampling point of this study is located near the Nanjing Port Fourth Company. Sampling port height from the ground is about 10 m. The sampling instrument uses a two-channel atmospheric particulate sampler to collect atmospheric PM_{10} samples using a PM_{10}cutting head with a flow rate of 16.7 L/min. The sampling membrane was selected from quartz membrane and Teflon membrane for simultaneous sampling. It was used for carbon-componentanalysis- OC/EC analysis and elemental and ionic composition analysis. The sampling membrane diameter was 47 mm. Sampling times were selected to carry out summer and winter periods representatives, representatives of the summer period to July 13, 2014 - July 27, representatives of the winter period is January 22, 2015 - 2 May 5.

Before and after the sample collection, the sample film was placed in atmospheric particulates constant temperature and humidity (temperature: 20 ± 5°C, Humidity: 40 ± 2%) cleanprocess chamber 48 hours, to ensure consistency before and after conditions to reduce errors. The sampling membrane was weighed using a precision electronic balance (Model: Sartorius TB-215D, accuracy: 0.01 mg), and the weight of the sampled film was recorded. After the weighing is completed, the sample was placed in a polytetrafluoroethylene atmospheric particles sealed in plastic bags, stored disposed within 4°C refrigerator.

2.1.2 Sample Analysis. Inductively coupled plasma mass spectrometry (ICP-MS, 7500a, Thermo) and inductively coupled plasma atomic emission spectrometry (ICP-AES) were used to analyze As, Se, Cr, Sb, Zn, Sr, Pb, Ni, The contents of elements such as Co, Cd, Fe, Mn, Mg, V, Ca, Cu, Ti, Sc, Eu, Al, Ce, Na, and S were analyzed. The contents of NO_3^-, SO_4^{2-}, NH_4^+, Na^+ions in the samples were analyzed using a Metrohm ion chromatograph (861 Advanced Compact IC). By heat/light carbon analyzer (DRI, Model 2001) of organic carbon (O rganic carbon, OC), elemental carbon (Elemental carbon, EC) for analysis of the concentration. Primary organic carbon (POC), and secondary organic carbon gas (SOC) obtained by estimating OC/ECratio of the minimum value method (Equation (1), (2)) [13]. The organic carbon is further multiplied by a factor of 1.6 to give a concentration of common organic aerosol (POA and SOA),[14]. In order to ensure the accuracy of sampling and analysis results, strict quality control is adopted in the aspects of sample collection, analysis and data processing.

$$POC=EC\times(OC/EC)_{min} \quad (1)$$

$$SOC=OC-POC \quad (2)$$

2.2 Particle Source Analysis Method

Particle analytical methods are Receptor source model method (e.g., n Matrix Factorization PMF, a chemical mass balance CMB, principal component analysis (Principal Component Analysis, PCA)) and numerical simulation method [15-17]. The receptor model model method is often used to analyze the source of primary pollutants in the atmosphere. In the receptor model, CMB needs to obtain the detailed chemical composition of the particulate matter in the atmosphere and the chemical composition of the particulate matter of different pollution sources; PCA is easier to operate than CMB and PMF, and its advantage is that it does not need to know the number and composition of the pollution source in advance, and use the mathematical theory. Statistical means extract relevant information about the type and number of pollution sources from the environmental sample data. In this study, principal component analysis (PCA) was used to analyze the source of PM $_{10}$ in Nanjing Port. The principle is a statistical method, the number of PM $_{10}$ and has a complex relationship of chemical composition of the sample attributed to several factors comprehensive (source), these factors may reflect most of the information of the sample $_{10}$ PM. The number of comprehensive factors reflects the number of sources of pollutants obtained by analysis; for specific factors, the pollution source of the comprehensive factor can be qualitatively judged according to the magnitude of the load of different factors (chemical components). At present, this method has been widely used in the analysis of atmospheric particulate matter [18-19].

3. Results and Discussion

3. 1 PM10 Concentration Characteristics

Table 1 shows the atmospheric PM_{10} concentration in Nanjing Port during the sampling period. Nanjing winter air port during the sampling the PM_{10} were significantly higher than the average mass summer, PM $_{10}$ two seasons mean concentrations were 88. 1 ± 31.9 μg/m^3, 136.9 ± 76.8 μg/m^3, the national standard of 0.59 Double and 0.91 times. This may be caused by the following reasons: from the perspective of diffusion conditions, the atmospheric boundary layer height in summer is higher than that in winter, and the winter inversion temperature and static stability weather occur more frequently than in summer, resulting in weaker vertical diffusion of pollutants in winter, which is easy. The local accumulation of pollutants; the average summer wind speed (2.85m/s) is also slightly higher than the winter (2.50m/s), making the summer pollutants horizontal diffusion ability stronger than the winter; summer rainfall is significantly higher than the winter, making summer The effect of wet deposition is more obvious, which is conducive to the reduction of pollutant concentration to some extent. In addition, the east and southeast winds prevail in winter, and it is easy to transport pollutants from the Yangtze River Delta to Nanjing Port, which will increase air pollution in Nanjing.

The amendments of 2012 "Ambient Air Quality Standard" (GB3095-2012), daily average concentration of PM_{10} two standard limits of 150 μg/m^{3,} Nanjing port during the sampling rate exceeded 6.7% in the summer, winter, the over-standard rate was 42.9 %. Wherein the highest average daily concentration of summer, winter, respectively PM_{10} 159.0 μg/m^3, 281.0μg/m^3, the concentration is two PM_{10} standard limits the daily average 1.1, 1.9 times.

Table 1. The PM $_{10}$ concentration in Nanjing Port during the sampling time

season	concentration	Maximum	Minimum value	Excess rate
	Gg/m ^{3}			
summer	88.1±31.9	159.0	38.0	6.7%
winter	136.9±76.8	281.0	43.0	42.9%

3. 2 Ionic and Carbon Component Composition Characteristics

3.2.1 Secondary Inorganic Ion Composition Characteristics. Secondary inorganic ions (Secondary inorganic aerosol, SIA) include $SO_4^{2-,}$ NO_3^- and $NH_4^{+.}$ Sampling and ion chromatography analysis indicated that the sampling device, summer and winter Nanjing port concentration in atmospheric PM

SIA $_{10}$ are 25.4μg/m^3 and 40.8μg/m^{3,} respectively, accounted for a total of PM$_{10}$ 28.9% With 37.1 %. And causes air pollutionPM $_{10}$ similar, higher concentrations may be more winter SIA and static stability weather, pollutants vertical and horizontal proliferation of weak and partial east/southeast of the dominant wind direction is easy to eastern Jiangsu, Shanghai and other places pollution The transport of substances to Nanjing is related. In addition, the high humidity in winter in southern China also promotes the conversion of secondary ions (sulfate, nitrate) precursors (SO_2, NOx).

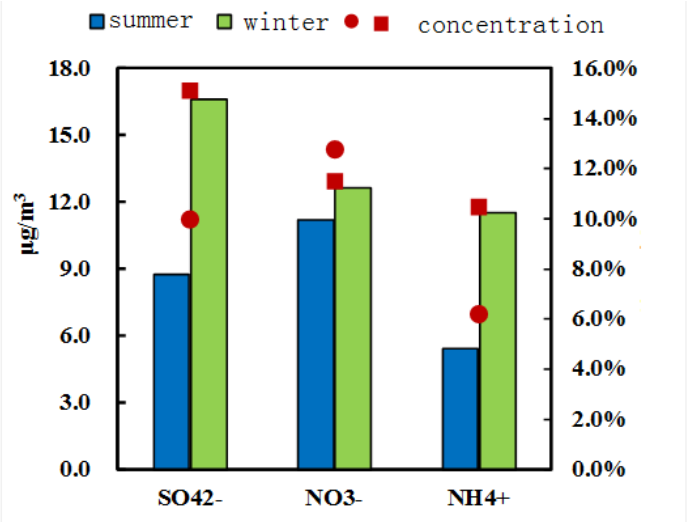

Figure 1. Concentration of secondary inorganic particles in PM $_{10}$ In Nanjing Port

Three kinds of inorganic ions, the summer NO_3^- the highest (11.2 μg/m$^{3),}$ accounting for the PM 12.8% $_{10}$ atmosphere, followed $SO_4^{2-,}$ accounting for 10.0%; winter is SO_4^{2-} The highest (16.6 μg/m^3), accounting for 15.1 %, followed by NO_3^- with a proportion of 11.5 %. The concentration of SO_4^{2-} in winter is higher than that in summer. This may be due to the large demand for electricity in winter heating. The increase in power generation leads to increased consumption of coal and more SO2 emissions, resulting in conversion to SO_4^{2-} increase. In addition, the concentration of NO_3^- in winter is also higher than that in summer, because NO_3^- mainly exists in the form of NH_4 NO_3 in the atmosphere, its thermal stability is poor, and the atmospheric temperature in summer is high, which is not conducive to NO_3^- is stable; the winter relatively low temperature, is conducive to NO_3^- is stable [16, 17].

3.2.2 Carbon Composition Characteristics

The carbonaceous components in atmospheric particulates mainly include elemental carbon (EC), primary organic aerosol (POA) and secondary organic aerosol (SOA). The totalconcentration of the carbonaceous component (EC+POA+SOA) in the summer PM$_{10}$ is Nanjing Port Atmospheric 21.5μg/m^3, compared with the summer, winter carbonaceous component concentrations significantly increased as 43.7 μg/m^3. Summer and winter respectively, of the carbonaceous component accounted for total PM 24.4% $_{10}$ and 39.7%. Further analysis revealed that summer and winter differences carbonaceous component mainly from a carbon-containing component (EC, POA), wherein EC concentrations were 2.9μg/m^3 and 5.1μg/m^3, compared with the summer in winter, the growth rate is 78.3%. POA growth more evident by 10.2μg/m^3 increase in summer as in winter 28.7μg/m^3, an increase of about 1.8 times. The primary carbonaceous component is mainly from the combustion source, and the significant increase in the primary carbonaceous composition in winter is related to the large increase in coal combustion in winter. Compared with primary aerosols, the secondary organic aerosols did not differ much in winter and summer, and slightly higher in summer than in summer, with concentrations of 9.9 μg/m^3 and 8.4 μg/m^{3,} respectively. Can be found, the organic aerosol, the aerosol to a main summer and winter respectively POA accounted for 54.8% and 74.4%, SOA relatively high proportion of summer, winter low as 45.2% and 25.6%, respectively. The proportion of

summer SOA in Nanjing Port Area is close to that of Beijing, but it is significantly lower than that in Beijing (~45%-50%) in winter, indicating that the secondary pollution of summer carbonaceous components in Nanjing Port Area is similar to that in Beijing, but it is lower than Beijing in winter. The source of the carbonaceous component can be roughly determined based on the ratio of POC/EC in the atmospheric particulate matter. Literature survey results show that, vehicle exhaust, coal, wood burning biomass combustion emissions OC/EC ratio in the range of approximately 1.0 to 4.2, 1.0 to 3.5, 16.8 to 40.0, 7.7 [20-21], Nanjing port summer, and winter value POC/EC were 2.2 and 3.5, with emissions and similar coal, carbonaceous components described in the atmospheric PM $_{10}$ by the combined effect of vehicle exhaust gas and coal.

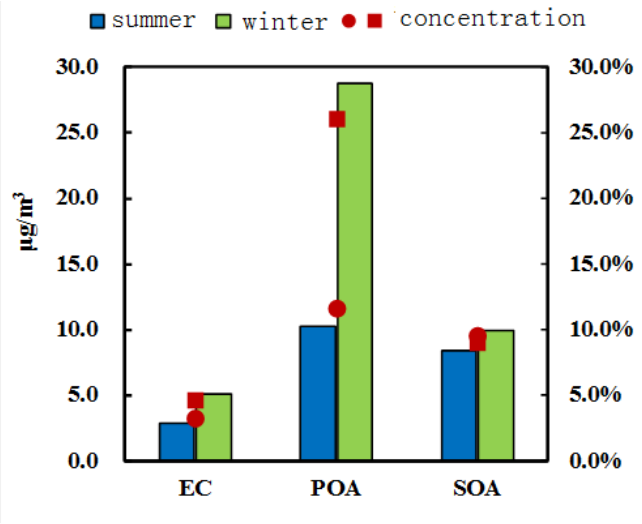

Figure 2. Concentration of carbonaceous components in PM $_{10}$ In Nanjing Port

3.3 One PM10 Source Resolution

To further quantify the effect of different sources of Nanjing port atmospheric particulates, based on atmospheric PM $_{10}$ sampling partial primary components (element part ions)analyzing the data using principal component analysis (PCA) method, respectively in summer and winter time PM $_{10}$ The source has been analyzed and analyzed.

3.3.1 PM10 Source Apportionment Summer Time. Table 2 shows the summer factors and load results of the Nanjing Port Area obtained by PCA analysis. The analysis results show that there are mainly five types of PM $_{10}$ pollutants in the port area of Nanjing in the summer, which explains a total variable of 91.9%. The first factors have higher loadings of Mg, Al, Ca and Ti, which are 0.695, 10656, 0.949 and0.874, respectively. Mg, Al and Ca are crustal elements, which may be derived from soil dust with a contribution rate of 33.4%. The second factors have higher loadings of elements S, Mn, Fe, Cu, Zn and Pb, which are 0.647, 0.962, 0.809, 0.675, 0.624 and 0.902, respectively. S and Pb are characteristic elements of coal combustion, and Mn, Fe, Cu and Zn are characteristic elements of metal smelting, with a contribution rate of 27.5%. The third factor has higher Cr and Ni loads, and Cr and Ni are characteristic elements of automobile exhaust, which are characteristic elements of vehicle emissions, with a contribution rate of 18.9%. In the fourth factor, the element V load is higher, and V is the ship's emission characteristic element [22]. Therefore, it may be derived from the ship with a contribution rate of 6.3%. The fifth factor has a higher Na^+ loading, and Na^+ is a characteristic component of sea salt, so it may be derived from sea salt emissions with a contribution rate of 5.7%. In summary, there are five main sources of atmospheric PM_{10} in the Nanjing Port Area during the summer: soil dust, metallurgy and coal combustion, motor vehicles, ship emissions and sea salt. The contribution rates are 33.4%, 27.5%, 18.9%, 6.3 % and 5.7%, respectively..

Table 2. PCA results for PM_{10} in summer

variable	Factor load				
	1	2	3	4	5
Mg	0.695	0.549	0.303	0.160	-0.131
Al	0.656	0.122	0.671	0.249	-0.142
S	0.409	0.647	0.156	-0.022	-0.163
Ca	0.949	0.615	0.400	0.153	-0.150
Ti	0.874	0.356	0.171	0.000	-0.040
V	-0.163	0.473	0.021	0.719	-0.024
Cr	-0.148	-0.891	0.615	0.233	-0.094
Mn	0.072	0.962	0.206	-0.126	-0.027
Fe	0.392	0.809	0.287	0.046	-0.102
Ni	-0.023	-0.115	0.741	0.283	-0.023
Cu	0.375	0.675	0.515	0.212	0.129
Zn	0.034	0.824	0.477	-0.081	0.011
Pb	-0.003	0.902	0.052	-0.024	-0.052
Na^+	-0.113	-0.101	0.010	-0.024	0.980
Variance contribution	33.4	27.5	18.9	6.3	5.7
Cumulative contribution	33.4	60.9	79.8	86.1	91.9

3.3.2 PM 10 Source Apportionment Winter

Table 3. PCA results for PM_{10} in autumn

variable	Factor load				
	1	2	3	4	5
Mg	0.928	0.169	-0.035	-0.056	0.236
Al	0.951	0.023	-0.076	-0.107	-0.019
S	-0.073	0.904	-0.231	0.019	0.139
Ca	0.911	0.264	-0.069	0.037	0.161
Ti	0.287	-0.245	0.868	-0.092	0.018
V	0.108	0.107	-0.070	0.052	0.971
Cr	0.860	0.031	0.764	-0.045	-0.220
Mn	0.898	0.238	0.259	-0.088	0.123
Fe	0.800	-0.111	0.545	-0.131	0.073
Ni	-0.136	-0.202	0.906	-0.228	-0.145
Cu	0.145	-0.093	0.909	-0.029	-0.036
Zn	0.509	-0.171	0.723	0.328	0.130
Pb	0.555	0.656	-0.208	0.372	0.088
Na^+	-0.232	0.109	-0.260	0.900	0.049
Variance contribution	32.6	22.6	21.6	7.1	6.8
Cumulative contribution	32.6	55.2	76.8	83.9	90.8

The results show that there are five main sources of PM_{10} pollution in the winter in Nanjing Port Area, accounting for 90.8% of the total variables. The first factors have higher loadings of Mg, Al, Ca, Mn and Fe, which are 0.928, 0.951, 0.911, 0.898 and 0.800 respectively. Mg, Al, Ca, Mn and Fe are crust elements, which may be derived from soil dust. Therefore, factor 1 represents the soil dust source with a contribution rate of 32.6%. In the second factor, the elements S and Pb have higher loads, and S and Pb are characteristic components of coal combustion with a contribution rate of 22.6%. The third factor has higher loadings of Cr, Ni, Cu and Zn, which are 0.764, 0.906, 0.909 and 0.723 respectively. Cr andNi are characteristic elements of automobile exhaust and are the characteristic elements of motor vehicle emissions. Cu and Zn are characteristic elements of metal smelting, with a contribution rate of 21.6%. The fourth factor has a higher Na^+ loading, and Na^+ is a characteristic component of

sea salt, which is derived from sea salt emissions with a contribution rate of 7.1%. In the fifth factor, the element V load is high, and V is the characteristic element of the ship's emission. It is derived from the ship and the contribution rate is 6.8%. In summary, there are five main sources of PM_{10} in the winter in Nanjing Port Area: soil dust, coal, motor vehicles and metallurgy. The contribution rates of sea salt and ship emissions are 32.6%, 22.6%, 21.6%, 7.1% and 6.8%.

Comparing the PM_{10} source results in summer and winter, it can be found that soil dust is the main contribution source of PM_{10} in Nanjing Port Area, with an average contribution rate of 33.0%; followed by coal burning; due to the proximity to the East China Sea, sea salt also has a certain contribution. The contribution rate is 6.4%; the ship's emissions contribution is about 6.6%. The contribution of sea salt and ship emissions in winter is slightly higher than that in summer, which may be related to the east and southeast winds in winter, and it is easier to transport coastal ships and sea salt ions to Nanjing.

4. Conclusions

In summary, the study has the following conclusions:

(1) Concentration Nanjing port summer and winter seasons PM sampling period were 88.1 ± 31.9 $\mu g/m^3$, 136.9 ±76.8 $\mu g/m^3$, respectively, and the standard 0.59 times 0.91 times.Winter pollution was more serious than in summer.

(2) Summer and winter Nanjing port concentration in the atmosphere PM_{10} SIA were 25.4$\mu g/m^3$ and 40.8$\mu g/m^3$, accounting for 28.9% and 37.1%, respectively. In summer, NO_3^- highest (11.2 $\mu g/m^3$), and in winter, SO_4^{2-} highest (16.6 $\mu g/m^3$). SIA concentrations whole winter than in summer.

(3) Winter Nanjing port substance significantly higher than the carbon component concentration in summer, concentrations of 43.7$\mu g/m^3$ and 21.5$\mu g/m^3$, accounting for 24.4% and39.7%, respectively. The high concentration in winter is mainly due to the increase of primary carbonaceous components. SOA is significantly higher than winter in summer.

(4) Nanjing Port summer and winter atmosphere similar to a PM_{10} sources, primarily for soil dust, metallurgy, automobile, coal, shipbuilding and sea salt, soil dust up to about33.0%, sea salt and ship contributions were approximately 6.4% and 6.6%. The contribution of sea salt and ship emissions in winter is slightly higher than in summer.

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