

Evaluating PM_{2.5} ionic components and source apportionment in Jinan, China from 2004 to 2008 using trajectory statistical methods

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The mass concentrations and major chemical components of PM_{2.5} in Jinan, Shandong Province, China from Dec. 2004 to Oct. 2008 were analyzed using backward trajectory cluster analysis in conjunction with the potential source contribution function (PSCF) model. The aim of this work was to study the inter-annual variations of mass concentrations and major chemical components of PM_{2.5}, evaluate the air mass flow patterns and identify the potential local and regional source areas that contributed to secondary sulfate and nitrate in PM_{2.5} in Jinan. The annual mean concentrations of PM_{2.5}, sulfate and nitrate in 2004–2008 were almost the highest in the world. The most significant air parcels contributing to the highest mean concentrations of mass and secondary ions in PM_{2.5} originated from the industrialized areas of Shandong Province. Clusters with a lower ratio of NO₃⁻/SO₄²⁻ in PM_{2.5} originated from the Yellow Sea, while a higher ratio was observed in the clusters passing through Beijing and Tianjin. PSCF modeling indicated that the provinces of Shandong, Henan, Jiangsu, Anhui and the Yellow Sea were the major potential source regions for sulfate, in agreement with the cluster analysis results. Regional and long-range transport of NH₄NO₃ played an important role in the nitrate concentration of Jinan. By comparing the distributions of secondary sulfate and nitrate over three years, enhanced emission control management before and during the 29th Olympic Games led to a discernible decrease in source contributions from Beijing and its environs in 2007–2008.

1. Introduction

The rapid economic development that has occurred in China over the past two decades is demonstrated not only in the large growth of gross domestic product (GDP) (30.3 trillion RMB in 2008, almost two times that in 2004), but also in the dramatically increasing consumption of energy, mainly in the form of fossil fuels.¹ As a result, a remarkable increase in emissions of major

trace gases and particulate matter, and subsequent severe air pollution at local and national scales has been observed.² In recent years, under various laws, regulations and standards, the emissions of SO₂ and dust have been reduced, which leads to PM₁₀ as the primary air pollutant in China.³ More attention has been paid to the hazards of fine particulate matter (PM). Fine PM has significant influences on atmospheric visibility, climate change and human health. Fine PM can penetrate into human lungs, leading to about 2.4 million premature deaths worldwide each year, mainly in developing countries in Asia and the Pacific area.⁴ Various studies show that the mass concentration of PM_{2.5} in China significantly exceeds the U.S. National Ambient Air Quality Standards (NAAQS) and the annual ambient Air Quality Guidelines of the World Health Organization (WHO).

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Environmental impact

Located on the northeast coast of China and adjacent to Korea and Japan, Shandong Province is one of the areas with the highest emission intensity of SO₂, NO_x and PM in the world. This paper provided a thorough introduction to the general state of PM_{2.5} pollution over recent years in Jinan, the capital of Shandong Province. Cluster analysis and PSCF modeling were applied to study the transport patterns and identify the potential local and regional source areas contributing to secondary ions in PM_{2.5}. The results are helpful to the determination of the overall PM_{2.5} pollution level in China, as well as the study on the influence of air pollutant transport on the PM_{2.5} pollution in Northeast Asia, which are essential in making the PM_{2.5} standard and control measures in China.

Therefore, PM_{2.5} has been proposed as a critical pollutant for regulation in China. Meanwhile, the study of PM_{2.5} concentration and its major chemical components, as well as its potential source regions is essential to develop and introduce strategies for PM_{2.5} control in China.

Shandong Province, located on the northeast coast of China and adjacent to Korea and Japan across the Bohai Sea, contributes the largest amount of SO₂, NO_x and PM emissions in China.⁵ High emissions of air pollutants arise mainly from coal combustion, coupled with the complex terrain and anti-cyclone system below an altitude of 600 m in Shandong Province, which results in a serious impact on urban and rural air quality. Jinan, the capital of Shandong Province, has a population of 6.62 million and is located less than 500 km south of Beijing. Mountain Tai (1540 m a.s.l.) is the highest mountain in the North China Plain, and stands at the central area of Shandong Province. In the World Bank list of twenty most polluted cities exposed to highest concentrations of PM in 2004, Jinan ranked twelfth (The World Bank). Furthermore, fine PM dominated the components of PM₁₀ in Jinan with a large ratio of PM_{2.5}/PM₁₀ (between 0.24 and 0.92),⁶ which was generally ascribed to secondary particle formation of species such as sulfate and nitrate. Therefore, the special geographical situation and serious air pollution of Jinan make it a crucial location in the study of air pollutant transport in Northeast Asia.

To identify the air mass flow patterns, as well as potential local and national source regions that contributed to secondary ion concentrations, a long-term observation of PM_{2.5} was conducted from December 2004 to October 2008 in Jinan. In advance of the 29th Beijing Olympic Games, a series of emission control regulations enforced in Beijing and its environs^{8,9} led to the emissions of PM₁₀, CO and NO_x being cut by about 50% during the abatement period. As a consequence, the concentrations of PM₁₀, CO and NO₂ decreased by 12.30% to 28.00% in Beijing. A special evaluation of the emission control effects on the contributions of potential source areas to the air quality in Jinan during the Olympic Games is also presented in this study.

Backward trajectory cluster analysis is a valuable tool to investigate origins of air pollutants observed at receptor sites, depending on transport speed and direction simultaneously.¹⁰ Moody and Galloway¹¹ (1988) were the first people to consider trajectory coordinates as clustering variables. Cluster analysis has been used in many research fields such as source of aerosol,¹² precipitation¹⁰ and gas.¹³ In order to predict accurately one-day atmospheric flow based on the observations of PM_{2.5} and minimize the uncertainty in this study, four trajectories were used to simulate a 24-h sampling day. Cluster analysis can be used to identify the origins of air pollutants, but cannot provide any information on the potential source areas. The potential source contribution function (PSCF), originally developed by Ashbaugh *et al.*¹⁴ (1985), was used to obtain the information through linking the residence time at the receptor site with high concentrations of air pollutants. The method was able to get good angular resolution but poor radial resolution.¹⁵ A better estimation of potential source area can be obtained by PSCF using large datasets with higher concentrations.¹⁶ Lupu and Maenhaut¹⁷ (2002) compared PSCF with other trajectory statistics methods and found that they agreed well. The PSCF method had been used to identify the source areas of particle matter in

a number of recent studies.^{18–22} The combination of backward trajectory cluster analysis and PSCF method enhanced the evaluation of the origins and conditional probability fields of PM_{2.5} and its major components.

2. Methodology

2.1 Sampling site and chemical analysis

Samples of PM_{2.5} were collected daily from Dec. 2004 to Oct. 2008 at Shandong University, Jinan, Shandong Province. The sampling site was set on the roof of the teaching building at the “New” campus location (Fig. 1). From Dec. 2004 to Sep. 2005, PM_{2.5} was sampled by a high-flow rate sampler (77.5 L min⁻¹, Dike Electronic Equipment, Ltd. China). A Multiple Reference Ambient Air Sampler (16.7 L min⁻¹, RAAS 2.5-400 Thermo Electron Corporation, USA) was used to collect PM_{2.5} samples from Feb. 2006 to Feb. 2007 and from Dec. 2007 to Oct. 2008. Before sample collections, a parallel experiment was conducted and the results showed that the two samplers had significant correlations ($R \geq 0.98$) at a 99% confidence level with a bias less than 6.5%, which implied that the parallel relationship between the two different samplers was good. Each sample was collected for 24 h. In the case of a severe air pollution day, samples were taken every 12 or 8 h. The detailed description of chemical analysis can be found in Yang *et al.*⁷ (2007). After further data analysis and correction, a total of 264 samples were used in this study.

2.2 Trajectories calculation and cluster analysis

The latest HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory, PC version 4.9) model was used to calculate the backward trajectories with reanalysis data from National Centers for Environmental Prediction (NCEP) global data assimilation system (GDAS). Three-day backward trajectories at 50 m above ground level, approximately equal to the height of the sampling site,⁷ for every 6 h at 00:00, 06:00, 12:00 and 18:00 from Dec. 2004 to Oct. 2008 were computed using the HYSPLIT model for each sample. A total of 960 backward trajectories and 72 hourly trajectory endpoints per sample were used for further analysis.

Trajectory cluster analysis splits the dataset into clusters of similar trajectory using the trajectory coordinates as clustering variables¹¹ and minimizes the differences inside the same trajectory group while maximizes the differences between clusters. A K-means procedure²³ was used to classify the trajectories into several clusters. The suitable cluster numbers obtained were 7, 6, and 8 for Dec. 2004 to Sep. 2005, Feb. 2006 to Feb. 2007, and Dec. 2007 to Oct. 2008, respectively based on the previous study.⁷

2.3 Potential source contribution function (PSCF)

The potential source contribution function (PSCF) is the probability of an air parcel with pollutant concentrations above a certain criterion arriving at the receptor site. The geophysical region, encompassed by the trajectories ranged from 15° N to 65° N, and from 80° E to 130° E, was divided into 2500 grid cells of 1° by 1°. Assuming that the air parcel emitted from a grid cell is transported to the receptor site without any loss from atmospheric diffusion, chemical transformation, or scavenging, the

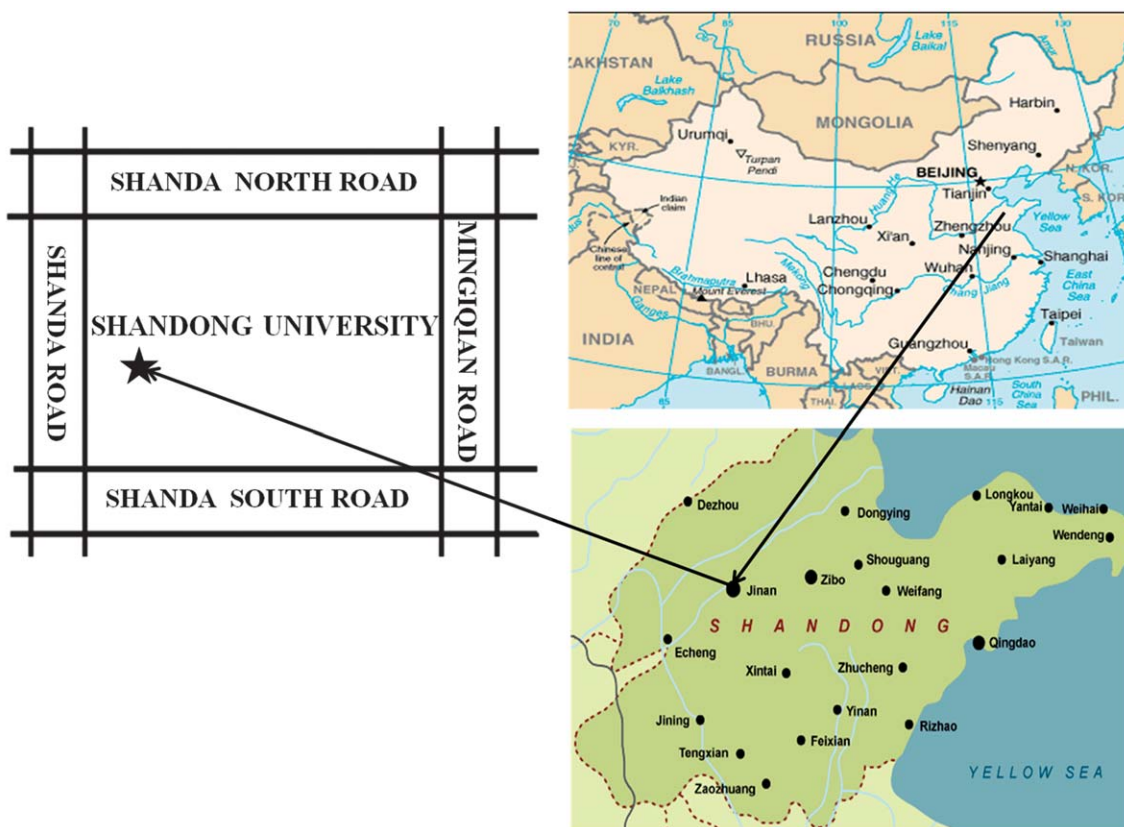


Fig. 1 Location of the sampling site in Jinan, Shandong Province, China.

PSCF of grid cell (i, j) is defined by the following procedure. If $n(i, j)$ is the number of trajectory segment endpoints falling in the grid cell (i, j) and $m(i, j)$ is the number of trajectory segment endpoints that the concentrations of air pollutants at the receptor site are higher than a criterion value when passing through the same cell grid, then the PSCF is defined as a conditional probability, $PSCF(i, j) = m(i, j)/n(i, j)$. Hence, cells related to high PSCF values were likely to produce higher concentrations at the receptor site and assumed to be possible source areas.

In order to reduce the effect of high PSCF values resulting from low n_{ij} , PSCF (i, j) is weighted by a factor W_{ij} , depending on the average trajectory endpoint in each grid cell.²² When the total number of trajectory endpoints in cell (i, j) was less than three times the average value, the factor W_{ij} was calculated as follows:

$$w_{ij} = \begin{cases} 1.0 & 18 < n_{ij} \\ 0.8 & 14 < n_{ij} \leq 18 \\ 0.6 & 10 < n_{ij} \leq 14 \\ 0.4 & 6 < n_{ij} \leq 10 \\ 0.2 & 2 < n_{ij} \leq 6 \\ 0.1 & 0 < n_{ij} \leq 2 \end{cases} \quad (1)$$

$$w_{ij} = \begin{cases} 1.0 & 45 < n_{ij} \\ 0.8 & 36 < n_{ij} \leq 45 \\ 0.6 & 27 < n_{ij} \leq 36 \\ 0.4 & 18 < n_{ij} \leq 27 \\ 0.2 & 9 < n_{ij} \leq 18 \\ 0.1 & 0 < n_{ij} \leq 9 \end{cases} \quad (2)$$

Eqn (1) indicates the PSCF weighted functions used in Dec. 2004–Sep. 2005 and Feb. 2006–Feb. 2007, while eqn (2) was applied in Dec. 2007–Oct. 2008.

3. Results and discussion

3.1 Concentration level of $PM_{2.5}$ and water-soluble ionic components

In order to evaluate the impacts of environmental pollution control measures put forward by Jinan municipal government every year on the inter-annual variations of $PM_{2.5}$ pollution, the whole samples were divided into three periods: Dec. 2004 to Sep. 2005 (55 samples), Feb. 2006 to Feb. 2007 (52 samples), and Dec. 2007 to Oct. 2008 (157 samples). The annual mean concentrations of $PM_{2.5}$ during Dec. 2004 to Sep. 2005, Feb. 2006 to Feb. 2007, and Dec. 2007 to Oct. 2008 were 124.39, 148.71 and 156.25 $\mu\text{g m}^{-3}$, which were 8.29, 9.91 and 10.42 times annual US NAAQS (15.00 $\mu\text{g m}^{-3}$) of $PM_{2.5}$, respectively (Fig. 2). In the three years, 100%, 98.1%, and 97.5% of daily $PM_{2.5}$ concentrations, respectively, were higher than 35.00 $\mu\text{g m}^{-3}$, the daily US NAAQS for $PM_{2.5}$. The $PM_{2.5}$ concentration in Jinan was similar to that of other northern inland cities in China, such as Beijing and Xi'an, about 1–3 times that in coastal cities such as Shanghai, Qingdao, Hong Kong and Taiwan and about 4–7 times that in East Asia, USA and Europe (Table 1). From Dec. 2004 to Oct. 2008, the concentrations of $PM_{2.5}$ in Jinan showed an increasing trend, indicating that the impacts of the environmental pollution control measures taken in Jinan every year and Beijing, Tianjin, Qingdao and other cities for the 29th Olympic

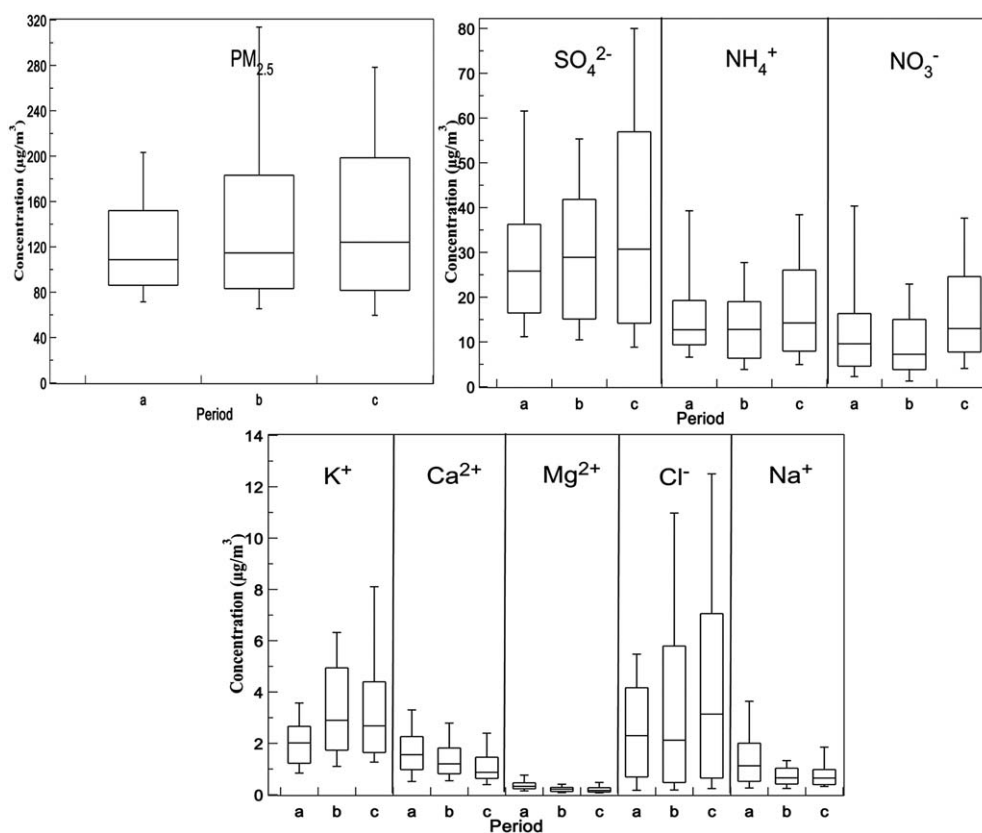


Fig. 2 Inter-annual concentrations of $\text{PM}_{2.5}$ and water-soluble ions from Dec. 2004 to Oct. 2008. a: Dec. 2004–Sep. 2005; b: Feb. 2006–Feb. 2007; c: Dec. 2007–Oct. 2008. The horizontal bar is the median while the bottom and top edges of the box represent the 25th and 75th percentiles and the whiskers show the 10th and 90th percentiles.

Table 1 Mass concentration of $\text{PM}_{2.5}$ and the major chemical components in Jinan and other cities over the world

Site	Type	Period	Mass concentrations ($\mu\text{g m}^{-3}$)				References
			$\text{PM}_{2.5}$	SO_4^{2-}	NH_4^+	NO_3^-	
Jinan, China	Urban	Dec. 2004–Sep. 2005	124.39	29.03	17.08	14.50	This study
Jinan, China	Urban	Feb. 2006–Feb. 2007	148.71	30.92	13.99	10.58	This study
Jinan, China	Urban	Dec. 2007–Oct. 2008	156.25	39.84	19.22	18.00	This study
Beijing, China	Urban	2001–2003	154.26	17.07	8.72	11.52	Wang <i>et al.</i> , 2005 ²⁶
Shanghai, China	Urban	Sep. 2003–Jan. 2005	94.64	10.39	3.78	6.23	Wang <i>et al.</i> , 2006 ³²
Qingdao, China	Coastal	1997–2000	43.60	11.94	5.79	3.40	Hu <i>et al.</i> , 2002 ³³
Xi'an, China	Urban	Oct. 2006–Sep. 2007	130.00	27.90	7.60	12.00	Shen <i>et al.</i> , 2009 ³⁴
Linan, China	Rural	Oct–Nov. 1999	90.00	21.20	8.60	7.70	Xu <i>et al.</i> , 2002 ³⁵
Mong Kok, Hong Kong	Urban	Nov. 2000–Feb. 2001	69.15	10.32	3.84	2.65	Louie <i>et al.</i> , 2005 ³⁶
Taiwan	Urban	2001–2003	59.80	9.45	4.49	1.93	Fang <i>et al.</i> , 2002 ³⁷
Seoul, Korea	Urban	Mar. 2003–Feb. 2005	42.80	7.50	5.50	7.10	Kim <i>et al.</i> , 2007 ³⁸
Tokyo, Japan	Urban	Sep. 2007–Aug. 2008	20.58	3.80	2.27	0.96	Khan <i>et al.</i> , 2010 ³⁹
New York, US	Urban	2002–2003	13.16	4.29	1.93	2.04	Qin <i>et al.</i> , 2006 ⁴⁰
St. Louis, US	Urban	2000–2003	16.40	4.23	1.94	2.48	Lee <i>et al.</i> , 2006 ³¹
Kerbside, Switzerland	Urban	Apr. 1998–Mar. 1999	24.60	2.80	1.60	3.00	Hueglin <i>et al.</i> , 2005 ⁴¹
Huelva, Spain	Urban	1999–2005	19.00	3.60	1.40	0.50	Querol <i>et al.</i> , 2008 ⁴²

Games in 2008 on the $\text{PM}_{2.5}$ pollution was relatively small, while the sharp increase in energy consumption and the number of motor vehicles due to the rapid increase in GDP led to the deterioration of the $\text{PM}_{2.5}$ pollution in Jinan.

In this study, SO_4^{2-} , NO_3^- and NH_4^+ accounted for 46.81% of $\text{PM}_{2.5}$ mass concentrations on average, while the sum of F^- , Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} accounted for only 7.88%. It could be clearly seen that the concentration of SO_4^{2-} in Jinan was about

10 times that in the USA and Europe, which could be due to the high emission of SO_2 in Shandong Province (Table 1). The emission of SO_2 in Shandong Province not only ranks first in China, but also the highest in the world.⁵

SO_4^{2-} , NO_3^- and NH_4^+ , are expected to arise mainly from secondary sources. The reaction between H_2SO_4 and NH_3 precedes the reaction between HNO_3 and NH_3 to form NH_4NO_3 ,²⁴ so NO_3^- will appear in the presence of excess NH_3 .

The slope of NH_4^+ vs. SO_4^{2-} was 3.43, 2.40 and 2.33 in 2004–2005, 2006–2007 and 2007–2008 respectively, which indicated that H_2SO_4 was completely neutralized by NH_3 .²⁴ Moreover, NH_4^+ showed stronger correlation with the combination of SO_4^{2-} and NO_3^- than with either individually in the three study periods, which indicated that NO_3^- , SO_4^{2-} and NH_4^+ coexisted in the aerosol system. Chu²⁵ (2004) described the ammonium availability index $\left(J = \frac{[\text{NH}_4^+]}{2[\text{SO}_4^{2-}] + [\text{NO}_3^-]} \times 100(\%) \right)$ which could be used to identify the extent of ammonia enrichment. The average value of J in 2004–2005, 2006–2007, and 2007–2008 was 1.18, 0.93, and 0.94, respectively, indicating that almost a neutralized system existed in Jinan

3.2 Backward trajectory cluster analysis

Through K-means cluster analysis, clusters with similar transport direction and speed were identified. Every cluster was expressed as a cluster-mean backward trajectory and represented a different transport pattern. Fig. 3 shows the cluster-mean trajectories, the average heights and the corresponding cluster-mean concentrations of $\text{PM}_{2.5}$ and major chemical components in 2004–2005, 2006–2007, and 2007–2008, respectively. The average mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ and concentrations of major water-soluble ions in each cluster from Dec. 2004 to Oct. 2008 are shown in Table 2. All the clusters in the three years can be classified into four groups based on the direction and speed of all the calculated trajectories: (1) a local transport or shortest

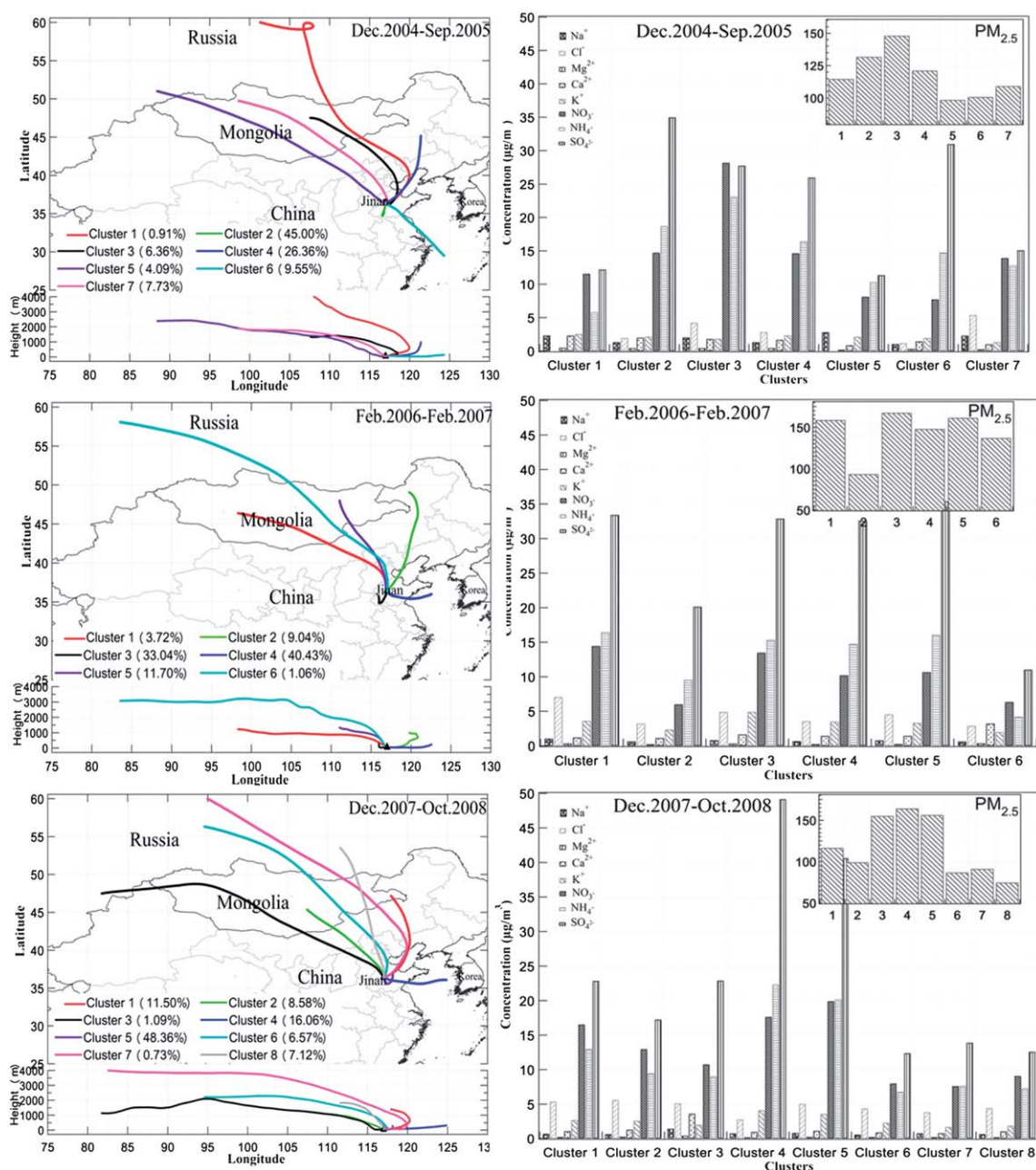


Fig. 3 The left panels show trajectory centers from Dec. 2004–Oct. 2008 resulting from cluster analysis with percentage of trajectories in each cluster. The corresponding mean concentrations of mass and major chemical components in $\text{PM}_{2.5}$ are shown in the right panels.

Table 2 Mean mass ratios of N/S ($\text{NO}_3^-/\text{SO}_4^{2-}$) and major water-soluble ions in each cluster from Dec. 2004 to Oct. 2008

		Cluster1	Cluster2	Cluster3	Cluster4	Cluster5	Cluster6	Cluster7	Cluster8
Dec. 2004–Sep. 2005	N/S	0.95	0.42	1.02	0.56	0.71	0.25	0.92	
	SO_4^{2-}	12.17	34.97	27.72	25.94	11.34	30.97	15.05	
	NH_4^+	5.80	18.69	23.10	16.42	10.32	14.74	12.78	
	NO_3^-	11.52	14.69	28.16	14.61	8.10	7.71	13.89	
	K^+	2.52	2.12	1.79	2.32	2.11	1.92	1.32	
	Ca^{2+}	2.28	1.97	1.77	1.63	0.82	1.42	0.98	
	Mg^{2+}	0.47	0.42	0.40	0.41	0.17	0.29	0.24	
	Cl^-	1.44	1.94	4.20	2.81	2.95	1.15	5.37	
	Na^+	2.30	1.31	2.02	1.32	2.78	1.01	2.27	
Feb. 2006–Feb. 2007	N/S	0.43	0.30	0.41	0.31	0.30	0.57		
	SO_4^{2-}	33.40	20.12	32.87	32.57	35.39	10.98		
	NH_4^+	16.42	9.53	15.32	14.73	16.04	4.20		
	NO_3^-	14.41	5.98	13.45	10.19	10.65	6.32		
	K^+	3.59	2.31	4.88	3.48	3.30	1.97		
	Ca^{2+}	1.17	1.11	1.63	1.40	1.41	3.20		
	Mg^{2+}	0.31	0.18	0.29	0.22	0.24	0.34		
	Cl^-	7.03	3.21	4.88	3.53	4.53	2.87		
	Na^+	1.01	0.62	0.78	0.64	0.75	0.60		
Dec. 2007–Sep. 2008	N/S	0.72	0.75	0.47	0.36	0.49	0.65	0.55	0.72
	SO_4^{2-}	22.83	17.23	22.87	49.13	40.61	12.36	13.87	12.57
	NH_4^+	12.99	9.46	9.01	22.32	20.15	6.76	7.62	7.28
	NO_3^-	16.51	12.94	10.74	17.62	19.89	7.98	7.60	9.07
	K^+	2.68	2.59	2.02	4.11	3.57	2.28	1.68	1.86
	Ca^{2+}	1.09	1.28	3.60	0.98	1.13	0.88	0.79	1.03
	Mg^{2+}	0.18	0.26	0.39	0.15	0.22	0.20	0.17	0.16
	Cl^-	5.35	5.61	5.11	2.75	5.02	4.37	3.81	4.40
	Na^+	0.68	0.64	1.42	0.76	0.82	0.58	0.76	0.63

transport pattern, (2) a flow pattern originating from the Yellow Sea, (3) a northeast flow pattern, and (4) a long-range transport from the northwest of China.

The identified cluster-mean trajectories in 2004–2005, 2006–2007, and 2007–2008 were similar. Group 1 (cluster 2 in 2004–2005, cluster 3 in 2006–2007, cluster 5 in 2007–2008) was associated with trajectories having the shortest transport patterns, indicating that they moved very slowly at the altitude between 500 m and 1000 m and air pollutants were influenced by local and upwind polluted regions. Group 1 was the dominant group and accounted for 45.00%, 33.04%, 48.36% of the total trajectories in 2004–2005, 2006–2007, and 2007–2008, respectively. The highest or second highest concentrations of $\text{PM}_{2.5}$, SO_4^{2-} , NO_3^- and NH_4^+ were observed. The mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ has been used as an indicator of the relative importance of mobile *versus* stationary sources of sulfur and nitrogen in the atmosphere to identify the origin of air masses.²⁶ A lower average mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ (0.44) (Table 2) in group 1 was found, indicating that stationary source emissions were more important than mobile source emissions.

There were two reasons for the high pollution level of $\text{PM}_{2.5}$ in group 1. First, the air parcel had a long residence time over the industrialized regions. Compared to 2007–2008, the travel routes of the trajectory in 2004–2005 and 2006–2007 were similar, originating from the southwest of Shandong Province, including the cities of Jining and Zaozhuang, then flowing over Xuzhou before arriving at Jinan. Jining, the major energy base for Shandong Province, where 48 power plants are situated, accounts for 16.7% of the total power plants in Shandong Province.²⁷ Zaozhuang is the cement production base in Shandong Province with particle emissions of 6.00×10^5 tons per

year.²⁸ The emissions of SO_2 , NO_x and PM_{10} in these regions rank first in Shandong Province. However, in 2007–2008, the air mass came from the middle of Shandong Province, moved southerly and finally turned westerly to Jinan. The center of Shandong Province is also highly industrialized, with a large petrochemical plant located in Zibo. Fig. 4 shows the anthropogenic emissions of PM, SO_2 and NO_x in China in 2006. The distribution of air pollutants is consistent with the distribution of industrial activities in Shandong Province. The second reason for high $\text{PM}_{2.5}$ is the presence of an anticyclone existing from the surface to a height of 600 m in Shandong Province, which is detrimental to the diffusion of air pollutants. The long residence time over industrialized areas and atmospheric anticyclone system led to the high mass and secondary ion concentrations in $\text{PM}_{2.5}$.

Much higher concentrations of $\text{PM}_{2.5}$, SO_4^{2-} , and a lower average ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ (0.32) was observed in group 2 (cluster 6 in 2004–2005, cluster 4 in 2006–2007, cluster 4 in 2007–2008), which originated from the Yellow Sea with a moderate speed at a lower altitude (under 1000 m). In total, 9.55%, 40.43%, 16.06% of the total trajectories in 2004–2005, 2006–2007, and 2007–2008, respectively were included. Compared with those in 2004–2005, trajectories in 2006–2007 and 2007–2008 typically followed a similar flow pattern originating from the Yellow Sea, and passing over the Jiaodong Peninsula before arriving at Jinan. However, in 2004–2005 the air parcels also originated in the Yellow Sea, flowed to the east of Shanghai and Jiangsu Province before arriving at Jinan. There were three reasons for the high sulfate concentrations. First, the contribution of sulfate derived from sea salt and dimethyl sulfide (DMS) oxidation. Second, large emissions of SO_2 and NO_x from commercial ships in the

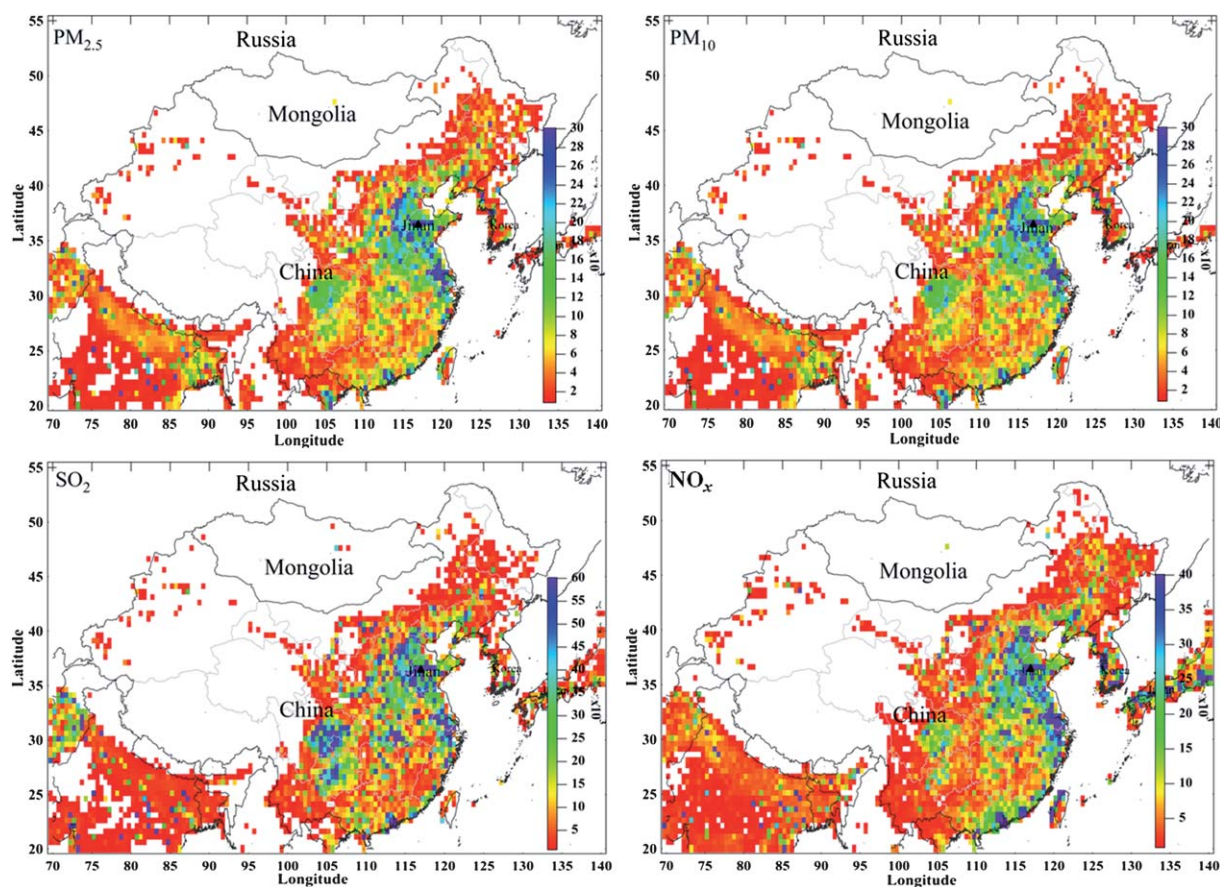


Fig. 4 Geographical distribution of particle matter, SO_2 , and NO_x anthropogenic emissions over China in 2006. Data downloaded from: http://www.cgrer.uiowa.edu/EMISSION_DATA_new/index_16.html.

Yellow Sea, which accounted for 5–8% SO_2 and 15–30% NO_x in the world. Many ships are equipped with older engines and their fuel contains high levels of sulfur and Polycyclic Aromatic Hydrocarbons (PAHS). Incompletely combusted fuel emits large amounts of primary pollutants that may be transported to continental land.¹² Third, the increasing emissions of primary pollutants can be attributed to the rapid industrialization of cities on the east coast of China. The northerly trend of the Pacific subtropical high belt also promotes the formation of secondary sulfate in the highly polluted regions of Shanghai, Jiangsu and Shandong Provinces. Although group 2 originated from the Yellow Sea, the concentrations of Na^+ and Cl^- were not as high as expected. Chloride is a major element for briquettes used in the process of the coal burning in many Chinese cities and sodium is one of the main elements of dust in north China.^{43,44} The high concentrations of Na^+ and Cl^- could be observed in group 4, which passed through the major coal consumption areas including Outer Mongolia, Inner Mongolia, Shanxi Province, Hebei Province and Beijing and these zones were also located in the important pathway that could bring dust storms to north China, indicating that the contributions of coal burning to the concentrations of Cl^- and dust to the concentrations of Na^+ in Jinan were more significant than those from the Yellow Sea.

Lower concentrations of $\text{PM}_{2.5}$ and secondary ions were found in group 3 (cluster 4 in 2004–2005, cluster 2 in 2006–2007, and cluster 1 in 2007–2008) where trajectories followed similar

patterns in the three years. This group originated in northern Inner Mongolia and was transported over western Liaoning Province and the Bohai Sea at a higher altitude. Compared to the total trajectories, 26.36%, 9.04%, and 11.50% of the air mass in 2004–2005, 2006–2007, and 2007–2008, respectively, were included in this group. Lower concentrations of $\text{PM}_{2.5}$ and secondary ions could be attributed to the flowing of the air parcel over areas with low emissions of primary pollutants. This indicated that the air quality of Jinan was less influenced by this air flow pattern.

Group 4 arrived from the northwest, including Russia, Mongolia and northern China, and contained the longest trajectories and highest altitudes in this study. The air parcel moved very fast compared to other groups. High concentrations of $\text{PM}_{2.5}$, NH_4^+ , NO_3^- , Na^+ , Cl^- , Ca^{2+} , K^+ and Mg^{2+} were observed in the clusters (cluster 3 in 2004–2005, clusters 1, 5 in 2006–2007, and cluster 2 in 2007–2008). Group 4 originated from Outer Mongolia, travelled southeast over Inner Mongolia, Hebei Province and Beijing. Hebei Province is a region with high primary emissions and Beijing possesses the highest populations of motor vehicles in China. A higher average ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ (0.58) was found which could be attributed to the large amount of motor vehicle exhaust emissions in Beijing and Tianjin. This flow pattern accounted for 6.36%, 15.42% and 8.58% of total trajectories in 2004–2005, 2006–2007 and 2007–2008, respectively, and had more influence on the air quality of Jinan than other long-range

northwest clusters. Cluster 2 in 2007–2008 travelled almost the same route as cluster 3 in 2004–2005 and clusters 1, 5 in 2006–2007, but the concentrations of $\text{PM}_{2.5}$ and NO_3^- , as well as the average ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ in 2007–2008 were much lower. This may be related to the enhanced mitigation of emissions for the Olympic Games to provide better air quality. Emission control efforts included alternating travel days for private vehicles, shutting down polluting factories, and curbing power-plant emissions in Beijing, Tianjin, and Hebei Province. The much higher concentrations of Ca^{2+} , Na^+ , K^+ and Mg^{2+} were related with these transport pathways where the surface was bare and the weather was dry.

3.3 PSCF results for secondary sulfate and nitrate

A PSCF model with 75% higher concentrations of secondary sulfate and nitrate employed as the criterion was used in this study, and the results for 2004–2005, 2006–2007 and 2007–2008 are shown in Fig. 5.

The PSCF plots of secondary sulfate showed that the province of Shandong, Henan, Anhui, Jiangsu, the south of Hebei and Liaoning, as well as eastern Inner Mongolia, Beijing, Tianjin, and the Yellow Sea were the potential source areas contributing to sulfate in $\text{PM}_{2.5}$ in Jinan. The most significant source areas were Shandong, Henan, Jiangsu, and Anhui Provinces, as well as

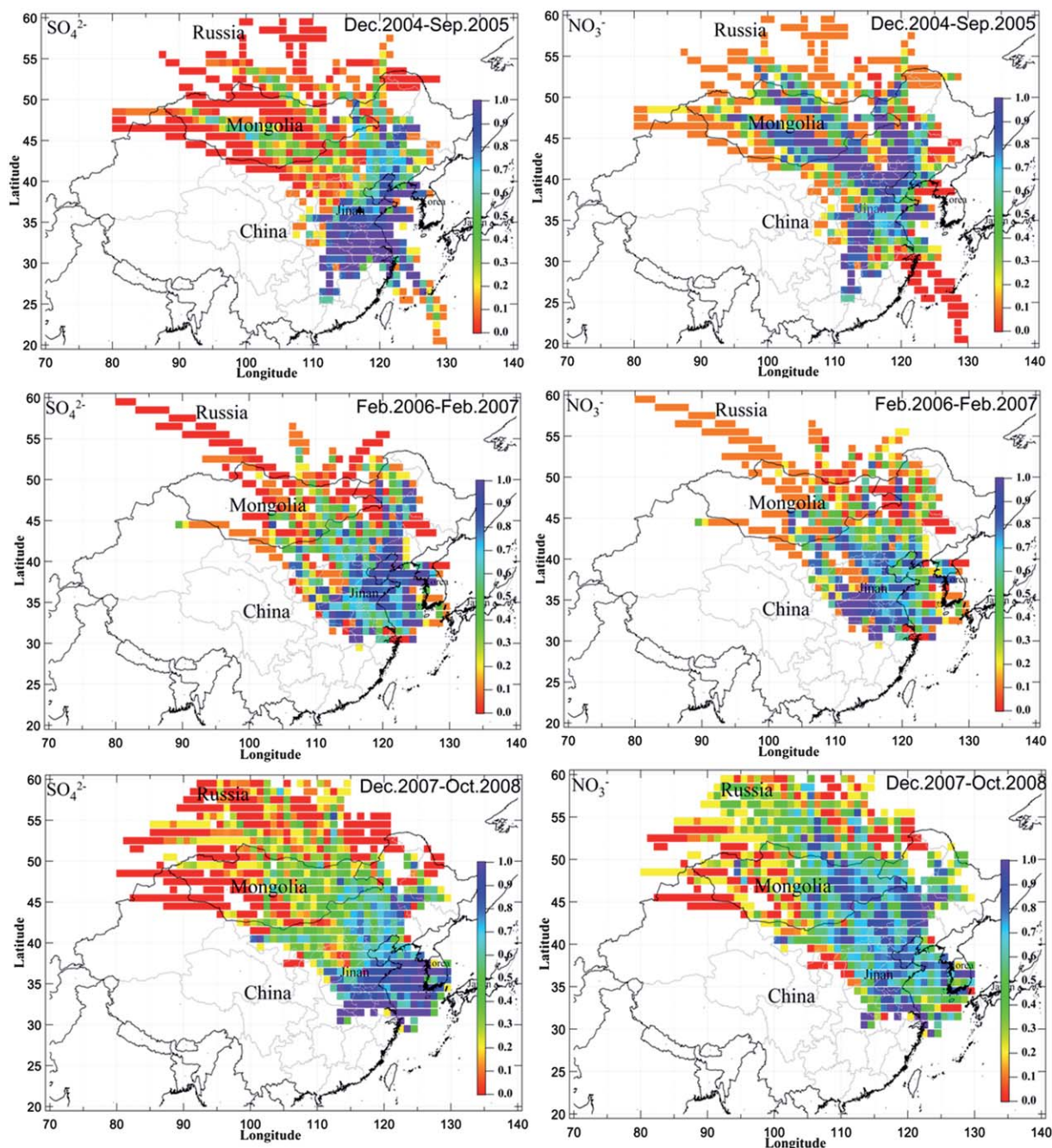


Fig. 5 Likely source areas for secondary sulfate and nitrate in Jinan, China from Dec. 2004–Oct. 2008 by PSCF.

the Yellow Sea which had higher emissions of SO₂, especially Shandong Province.⁵ Wu *et al.*²⁹ (2009) found that the trajectory originating in Shandong Province contributed the most (53%) to PM₁₀ and contained higher concentrations of secondary ions in Beijing using backward trajectory cluster analysis and the PSCF model. A study of PM_{2.5} source areas in three Korean cities, Seoul, Ulsan and Chuncheon,²² indicated that Shandong Province was a main source area that influenced the concentrations of PM_{2.5} in these three cities. Thus, Shandong Province is not only a significant local source but also influences the concentration of PM in Northeast Asia through long-range transport.

High PSCF values for secondary nitrate were found in Henan Province, Hebei Province, Liaoning Province, Inner Mongolia, and Outer Mongolia, which were the major agricultural and livestock farming areas in China. The emissions of NO_x in these areas have rapidly increased in recent years, *e.g.* a 55% increase of NO_x from 2001 to 2006.⁵ These source areas of nitrate were the highest ammonium nitrate (NH₄NO₃) forming areas in East Asia³⁰ and consistent with the distribution of NO_x emissions in 2006 illustrated in Fig. 4, which indicated that the regional transport of NH₄NO₃ was more likely to be the dominant contributor to secondary nitrate than local emissions. This phenomenon was also observed in the study on the source apportionment of PM_{2.5} in St. Louis, Missouri.³¹

The PSCF value of secondary nitrate in Shandong Province in this study was lower, in contrast to the PSCF value of sulfate, while in Outer Mongolia, Inner Mongolia and Liaoning Province was higher. This suggested that besides the regional transport of nitrate from Henan and Hebei Province, the long-range transported nitrate formed over the high emission source regions also played a significant role in the observed concentrations of nitrate in Jinan. Finally, in 2007–2008, the PSCF values of sulfate and nitrate in Beijing and Hebei Province were much lower than those in 2004–2005 and 2006–2007. This can be attributed to the measures employed to reduce emissions of atmospheric pollutants in Beijing and its environs in 2008 in anticipation of hosting the Olympic Games.

4. Summary

A study involving mass concentrations and major chemical compounds in PM_{2.5}, the long-range transport of air masses and potential source areas of secondary sulfate and nitrate were conducted in Jinan, Shandong Province, China from Dec. 2004 to Oct. 2008. The annual mean concentrations of PM_{2.5} during the study period were about 1–7 times that in East Asia, the USA and Europe. Sulfate, nitrate, and ammonium were the major water-soluble ions in PM_{2.5}, accounting for 24.18%, 11.97% and 10.67% of PM_{2.5} mass concentrations, respectively, and mainly existed as (NH₄)₂SO₄ and NH₄NO₃. The concentrations of sulfate and nitrate in PM_{2.5} were the highest in the world.

Four major atmospheric pathways that influenced PM_{2.5} loadings in Jinan were identified using the NOAA HYSPLIT model together with K-means cluster analysis. Among all the trajectories, the largest group (group 1) originated from Shandong Province, comprising 45.00%, 33.04%, and 48.36% of the PM_{2.5} in 2004–2005, 2006–2007 and 2007–2008, respectively. Trajectories in this group had the shortest transport distance and the highest concentrations of PM_{2.5} and secondary ions. The

highest concentration of sulfate was observed in group 2 with a medium length and maritime source. High concentrations of nitrate and a higher ratio of NO₃⁻/SO₄²⁻ was found in group 4, originating in Mongolia, flowing over Hebei Province and Beijing, and containing the longest trajectories with highest altitude. A trajectory with a northeasterly direction in group 3 contained low concentrations of secondary ions.

The PSCF results showed that the largest contributors of sulfate were the Provinces of Shandong, Henan, Jiangsu, Anhui, as well as the Yellow Sea, which was consistent with the cluster results and the inventory of SO₂ emissions in China. However, the high contribution of secondary nitrate observed in Jinan was more likely caused by NH₄NO₃ formed in the large agricultural region including Henan Province, Hebei Province, Liaoning Province, and Mongolia, which suggested that the regional and long-range transport from the northwest could play an important role in nitrate concentrations in Jinan. By comparing the distributions of secondary ions concentrations in three years, the lower contributions from Beijing and its surrounding areas to the concentrations of secondary sulfate and nitrate in 2007–2008 in Jinan were obtained, which could be due to the enhanced emission controls during the 29th Olympic Games.

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Notes and references

- 1 China Statistical Yearbook, National Bureau of Statistics of China, China Statistics Press, Beijing, 2009 (in Chinese).
- 2 C. K. Chan and X. Yao, *Atmos. Environ.*, 2008, **42**, 1–42.
- 3 H. Yi, J. Hao and X. Tang, *Energy Policy*, 2007, **35**, 907–915.
- 4 WHO, *The World Health Report. Fuel of life: household energy and health*. World Health Organization, Geneva, 2006.
- 5 Q. Zhang, D. Streets, G. Carmichael, K. He, H. Huo, A. Kannari, Z. Klimont, I. Park, S. Reddy and J. Fu, *Atmos. Chem. Phys.*, 2009, **9**, 5131–5153.
- 6 M.-T. Hao, W.-g. Hou, X.-H. Zhou and Z. Wang, *J. Shandong Univ. (Eng Sci.)*, 2006, **36**(3), 108–111 (in Chinese).
- 7 L.-x. Yang, D.-c. Wang, S.-h. Cheng, Z. Wang, Y. Zhou, X.-h. Zhou and W.-x. Wang, *Sci. Total Environ.*, 2007, **383**, 164–173.
- 8 T. Wang and S. Xie, *Atmos. Environ.*, 2009, **43**, 5682–5690.
- 9 Y. Zhou, Y. Wu, L. Yang, L. Fu, K. He, S. Wang, J. Hao, J. Chen and C. Li, *Atmos. Environ.*, 2010, **44**, 285–293.
- 10 S. Dorling, T. Davies and C. Pierce, *Atmos. Environ., Part A*, 1992, **26**, 2583–2602.
- 11 J. Moody and J. Galloway, *Tellus, Ser. B*, 1988, **40B**, 463–479.
- 12 P. Salvador, B. Artñano, C. Pio, J. Afonso, M. Legrand, H. Puxbaum and S. Hammer, *Atmos. Environ.*, 2010, **44**, 2316–2329.
- 13 J. A. Baker, *Atmos. Environ.*, 2010, **44**, 563–571.
- 14 L. Ashbaugh, W. Malm and W. Sadeh, *Atmos. Environ.*, 1985, **19**, 1263–1270.
- 15 L. Vasconcelos, J. Kahl, D. Liu, E. Macias and W. White, *J. Geophys. Res.*, 1996, **101**, 19337.
- 16 M. Cheng and C. Lin, *J. Geophys. Res.*, 2001, **106**, 22871.
- 17 A. Lupu and W. Maenhaut, *Atmos. Environ.*, 2002, **36**, 5607–5618.
- 18 L. Zhou, P. Hopke and W. Liu, *Atmos. Environ.*, 2004, **38**, 1955–1963.
- 19 N. Pekney, C. Davidson, L. Zhou and P. Hopke, *Aerosol Sci. Technol.*, 2006, **40**, 952–961.

- 20 Y. Wang, X. Zhang and R. Arimoto, *Sci. Total Environ.*, 2006, **368**, 875–883.
- 21 M. Kim, S. Deshpande and K. Crist, *Atmos. Environ.*, 2007, **41**, 9231–9243.
- 22 Y.-J. Han, T.-S. Kim and H. Kim, *Atmos. Environ.*, 2008, **42**, 4735–4746.
- 23 J. MacQueen, *Proc. Fifth Berkeley Symp. on Math. Statist. And Prob.*, Univ. of Calif. Press, 1967, **1**, 281–297.
- 24 J. H. Seinfeld, *Atmospheric chemistry and physics: from air pollution to climate change*, Wiley, New York, NY, 1986.
- 25 S.-H. Chu, *Atmos. Environ.*, 2004, **38**, 5237–5246.
- 26 Y. Wang, G. Zhuang, A. Tang, H. Yuan, Y. Sun, S. Chen and A. Zheng, *Atmos. Environ.*, 2005, **39**, 3771–3784.
- 27 Liu. Xinling. *Master Thesis*, Shandong University, 2008 (in Chinese).
- 28 *Shandong Statistical Yearbook*, Shandong Provincial Statistics Bureau, China Statistics Press, Beijing, 2009 (in Chinese).
- 29 Z. Wu, M. Hu, K. Shao and J. Slanina, *Chemosphere*, 2009, **76**, 1028–1035.
- 30 J. Heo, P. Hopke and S. Yi, *Atmos. Chem. Phys.*, 2009, **9**, 4957–4971.
- 31 J. H. Lee and P. K. Hopke, *Atmos. Environ.*, 2006, **40**, 360–377.
- 32 Y. Wang, G. Zhuang, X. Zhang, K. Huang, C. Xu, A. Tang, J. Chen and Z. An, *Atmos. Environ.*, 2006, **40**, 2935–2952.
- 33 M. Hu, L.-Y. He, Y.-H. Zhang, M. Wang, Y. Pyo Kim and K. C. Moon, *Atmos. Environ.*, 2002, **36**, 5853–5859.
- 34 Z. Shen, J. Cao, R. Arimoto, Z. Han, R. Zhang, Y. Han, S. Liu, T. Okuda, S. Nakao and S. Tanaka, *Atmos. Environ.*, 2009, **43**, 2911–2918.
- 35 J. Xu, M. H. Bergin, X. Yu, G. Liu, J. Zhao, C. M. Carrico and K. Baumann, *Atmos. Environ.*, 2002, **36**, 161–173.
- 36 P. K. K. Louie, J. G. Watson, J. C. Chow, A. Chen, D. W. M. Sin and A. K. H. Lau, *Atmos. Environ.*, 2005, **39**, 1695–1710.
- 37 G.-C. Fang, C.-N. Chang, Y.-S. Wu, P. P.-C. Fu, C.-J. Yang, C.-D. Chen and S.-C. Chang, *Atmos. Environ.*, 2002, **36**, 1921–1928.
- 38 H. Kim, J. Huh, P. Hopke, T. Holsen and S. Yi, *Atmos. Environ.*, 2007, **41**, 6762–6770.
- 39 M. F. Khan, Y. Shirasuna, K. Hirano and S. Masunaga, *Atmos. Res.*, 2010, **96**, 159–172.
- 40 Y. Qin, E. Kim and P. K. Hopke, *Atmos. Environ.*, 2006, **40**, 312–332.
- 41 C. Hueglin, R. Gehrig, U. Baltensperger, M. Gysel, C. Monn and H. Vonmont, *Atmos. Environ.*, 2005, **39**, 637–651.
- 42 X. Querol, A. Alastuey, T. Moreno, M. M. Viana, S. Castillo, J. Pey, S. Rodríguez, B. Artiñano, P. Salvador, M. Sánchez, S. Garcia Dos Santos, M. D. Herce Garraleta, R. Fernandez-Patier, S. Moreno-Grau, L. Negral, M. C. Minguillón, E. Monfort, M. J. Sanz, R. Palomo-Marín, E. Pinilla-Gil, E. Cuevas, J. de la Rosa and A. Sánchez de la Campa, *Atmos. Environ.*, 2008, **42**, 3964–3979.
- 43 T. Bond, P. Quinn, T. Bates, *The Sixth International Aerosol Conference*, Taipei, Taiwan, September 9–13, 2002.
- 44 Jie Xuan, *Atmos. Environ.*, 2005, **39**, 813–821.